Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

50X1-HUM

Page Denied

Next 39 Page(s) In Document Denied

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

EINE DIELEKTRISCHE METHODE ZUM STUDIUM VON KOMPLEXEN DES TRIBUTYLPHOSPHATS IN VERDÜNNTEN ORGANISCHEN LÖSUNGEN

K. Schaarschmidt und G. Mende - Deutsche Demokratische Republik

Die Dielektrizitätskonstante ε von verdünnten Lösungen eines polaren Stoffes B /Molenbruch x_B in der Grössenordnung 10^{-2}/ in einem unpolaren Lösungsmittel ist im allgemeinen linear von x_B abhängig. Der Anstiegswert $a_B = \frac{\Delta\varepsilon}{\Delta x_B}$ ist in dem betreffenden Löser charakteristisch für den Stoff B, er wird auch dann gefunden, wenn man den reinen Löser definiert mit einem polaren Stoff A /x_A ebenfalls in der Grössenordnung 10^{-2}/ versetzt - vorausgesetzt, es treten keine Wechselwirkungen zwischen A und B auf.

Es wird gezeigt, wie im Falle von Komplexbildung zwischen A und B aus DK-Messungen auf das stöchiometrische Reaktionsverhältnis, auf die Vollständigkeit des Reaktionsablaufs und auf das Dipolmoment der gebildeten Komplexe geschlossen werden kann. Eine Isolierung der Reaktionsprodukte ist dabei nicht notwendig.

Die Methode wurde an den Komplexen des Tributylphosphats mit $CoCl_2$, $ZnCl_2$ und HCl erprobt. Die DK-Messungen wurden durch kryoskopische und spektrofotometrische Messungen ergänzt.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

THE DETERMINATION OF DISSOCIATION CONSTANTS OF MONOMOLYBDIC ACID BY THE ELECTROMIGRATION MEASUREMENT

J. Chojnacka - Poland

In spite of very numerous studies the forming of molybdic isopolyacids in the acidified water solutions as well as their structure is at present an insolved problem.

Treating the polymolybdates as the mesodesmic compounds like the silicates, borates or metaphosphorates, the passage from anisodesmic monomolybdate to mesodesmic polymolybdates can have place, when in acidified solutions the protonation of ion $[MoO_4]^{2-}$ is followed by the hydratation :

$$[MoO_4]^{-2} + H^+ \xrightleftharpoons{k_1} \left[Mo\begin{matrix}OH\\O_3\end{matrix}\right]^- \xrightleftharpoons{2H_2O} \left[Mo\begin{matrix}/OH/_5\\O\end{matrix}\right]^-$$

$$[MoO_4]^{2-} + 2H^+ \xrightleftharpoons{k_2} \left[Mo\begin{matrix}/OH/_2\\O_2\end{matrix}\right]^0 \xrightleftharpoons{2H_2O} \left[Mo/OH/_6\right]^0$$

$$[MoO_4]^{-2} + 3H^+ \xrightleftharpoons{k_3} \left[Mo\begin{matrix}/OH/_3\\O\end{matrix}\right]^+ \xrightleftharpoons{2H_2O} \left[Mo\begin{matrix}/OH/_5\\H_2O\end{matrix}\right]^+$$

The partition of several complexes, which are created by protonation of $[MoO_4]^{-2}$, was studied by means of measurements of their mobilities. The mobility of molybdate in extremely diluted solution was determined by the electromigration throungh a stripe of filter paper.

The values of pH in each series of measurements extented from 7,0 to 0,3; the patterns of ions migration in acidified solutions obtained for several amounts of Mo /10^{-5} - 10^{-8} Mo/ allowed to establish the relation between the velocity of migration and pH of solution.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Assumption that in extremely diluted solution the ions appears chiefly in their monomeric forms permits to apply the theory developed for infinite dilution and to calculate the equilibrium constants k_1, k_2, k_3, for the protomation reactions. The partition of protonated monoacids computed from equilibrium constants is a function of pH-value and at different intervals of pH various forms of monomer are predominant.

I range : pH = 5 - 7 predominant form $[MoO_4]^{-2}$, II range : $2,5 < pH < 4,5$ - exist three forms, $[MoO_4]^{-2}$, $[HMoO_4]^{-}$ or $[Mo^{/OH/5}_{O}]^{-}$ and $[H_2MoO_4]^{o}$ or $[Mo/OH/_6]^{o}$. III range: $1 < pH < 2,5$ - predominant form $[Mo/OH/_6]^{o}$ and $[Mo^{/OH/5}_{O}]^{-}$, $[Mo^{/OH/5}_{H_2O}]^{+}$. IV range : $pH < 1$ - the form $[Mo/OH/_6]^{o}$ disappears and cationic forms appear.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Abstract

THE ROLE OF OXYGEN IN COORDINATION COMPOUNDS

B. Jeżowska-Trzebiatowska - Poland

Oxygen in complex compounds plays an essential role, which arises from its ability to form various types of bonds with other atoms, namely: the ion-, covalent-, donor σ and donor π bonds. In the same state oxygen valency changes from +2 to -2. Ability of oxygen for bond formation is a result of its electron-orbital structure, connected with the value of electron affinity and atomic radius. When the difference in the electronegativity of oxygen and its partners is not very great, and when the partner's atom possesses the accessible orbitals d and f then the very strong couplings are formed and a system of molecular orbitals arises. Oxygen thus complexed with metals forms a new chemical species, sometimes passing without change from compound to compound.

Three types of oxygen-metal nuclei appear in the complex compounds of transition elements: type I MeO, type II MeO_2, type III MeOMe. In each case the complex becomes stable owing to oxygen-metal π bonds. It particularly applies to complexes of II and III.

A strong coupling with oxygen often causes a change in the magnetic properties of metal y atoms and gives to the absorption spectrum its characteristic trait.

The electron orbital structure of the complexes will be discussed with the nuclei of all the 3 types mentioned above. It will be demonstrated that the molecular orbital theory may be applied to explain the magnetic and optical properties of oxygen metal nuclei. In the nucleus of type III oxygen acts as a bridge bond between metal atoms.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

ÜBER DIE ROLLE DER METALLKATIONEN BEIM ABBAU DER POLYPHOSPHATE IN WÄSSRIGER LÖSUNG

W. Wieker - Deutsche Demokratische Republik

Durch kinetische Untersuchung des primär zu Trimata- und Monophosphat führenden Polyphosphatabbaus in wässriger Lösung wurde festgestellt, dass diese Reaktion in schwach alkalischem Medium durch Metallsalze katalytisch beschleunigt wird und dass nur die Metallkationen die katalytische Reaktionsbeschleunigung hervorrufen. Abbaureaktionen unter Zusatz von Alkali- und Erdalkali- und Aluminiumchlorid ergaben, dass die katalytische Wirksamkeit innerhalb einer Gruppe des Periodensystems von oben nach unten also mit steigendem Ionenradius abnimmt und mit steigender Ladung des Kations zunimmt. Somit ergibt sich für diese Kationen folgende Reihe ihrer katalytischen Wirksamkeit.

$$K^+ < Na^+ < Li^+ < /H^+/ < Ba^{++} < Sr^{++} < Ca^{++} < Mg^{++} < Al^{+++}$$

einwertig < zweiwertig < dreiwertig

Die Messung der Abbaugeschwindigkeit von Polyphosphaten in Lösungen steigender $MgCl_2$-Konzentration und Versuche, bei denen die zugesetzten Mg-Ionen durch Äthylendiaminotetraessigsäure komplexiert wurden, sowie Reaktionen bei verminderter DK des Lösungsmittels, zeigten, dass nur die mit dem Polyphosphatanion in Lösung assoziierten Kationen die Abbaureaktion katalysieren. Ein Vergleich der Reaktionsgeschwindigkeitskontanten mit den Assoziationskonstanten der Alkalikationen mit den Polyphosphatanionen ergibt ferner, dass beide Werte parallel laufen und vom Kalium zum Lithium ansteigen. Als Ursache der katalytischen Wirkung von Metallkationen auf den Polyphosphatabbau wird eine Positivierung der P-Atome angesehen.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

DAS KOMPLEXCHEMISCHE VERHALTEN DES ADENINS GEGENÜBER KUPFER/II/

R. Weiss - Deutsche Demokratische Republik

Adenin bildet mit Cu^{++} in Abhängigkeit vom p_H-Wert verschiedene Komplexe. Es wird ihre Darstellung beschrieben.
Die Zuordnung der Liganden wird durch tensiometrischen Abbau sowie durch verschiedene Umsetzungen ermittelt.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

COMPLEX HYDRIDES OF IRIDIUM

Lamberto Malatesta - Italia

Following the preparation of the two isomers of IrH_3L_3 / L = triphenylphosphine/, the corresponding compounds have been obtained with triphenylarsine and triphenylstibine. Also the unsaturated IrH_2L_3 has been prepared, which adds easily carbon monoxide, ammonia, pyridine and other ligands.

The coordinatively unsaturated perchlorate $[IrH_2L_3][ClO_4]$, obtained from IrH_3L_3 and $HClO_4$ in ethanol, adds carbon monoxide giving $[IrH_2L_3CO][ClO_4]$, which with alkali forms quantitatively $IrHL_3CO$. The latter was also prepared from $K[Ir(CO)_2I_4]$ with excess of L and sodium borohydride in ethanol, and is obtained in very poor yelds from $[IrH_2L_3][ClO_4]$ in boiling ethanolic potassium hydroxide.

Milano, Instituto di Chimica Generale dell Universita
In partial fulfillment of the grant 62-34 Air Force Office of Scientific Research OAR, thru the European Office, Aerospace Research, United States Air Force.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Abstract

COMPLEXES DU TELLRE ET LEUR UTILISATION

R.Ripan - Romania

On a détermine la constante d´ instabilité des complexes suivants du tellure: $[TeCl_6]\ H_2$ et $[TeBr_6]\ H_2$ sur des resines changeurs d´ions - D.W.E.X 1 sous forme de Cl^- ou Br^-. On a utilisé L´isotope radio-actif Te^{127}.

Les conditions établies ont montré que pour HCl 3N-4N le tellure est entièrement intégré dans le complexe.

Ayant étudié parallelement le comportement du sélénium dans les mêmes conditions, on a constaté que, tandis que le sélénium se réduit très facilement avec différents réducteurs, le tellure est stabilisé par le fait qu´il est cointeressé dans les ions complexes $[TeX_6]^{-2}$

En mettant à profit ces comportements différents pour le sélénium et le tellure, on a institué une methode polarographique d´analyse du système Tellure + Sélénium + Or.

Vu que le tellure en milieu d´acide chlorhydrique forme le complexe $[TeCl_6]\ H_2$, stable à l´action des réducteurs, notamment de la thiosemicarbazide dans ce milieu acide, on a institué aussi une méthode chimique gravimétrique pour la séparation et le dosage du sélénium et du tellure dans un mélange.

Le problème résolu a des contingences directes avec la production, notamment avec l´usinage des minerais non ferreus, étant donné que c´est surtout dans les minerais aurifères que l´on trouve le tellure et le sélénium à côté d l´or.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

ANOMALOUS MOBILITIES OF SOME COMPLEX IONS IN STRONG ELECTRIC FIELDS

T.Kwasik - Poland

Mobilities of some anions of Hg, Cd, Co, Ni and Bi with halogenides or thiocyanates were studied. New types of isoapheretic chambers were designed for this purpose. Chromatographic paper or cotton fiber were used as solid support.

At field strengths above 10 V/cm in most cases a decrease of mobility towards the anode was stated; for some complexes even migration of the metal ion towards the cathode was observed.

The critical value of field strength depends on concentration of complexing anion and the stability of the complex. For very stable complexes /e.g. ferro- and ferricynide ions/ change of mobility was not observed in the range of field strengths used.

The phenomenon was not described in literature. The autor has found analogies with the so called second WIEN effect /increase/ of conductivity for weak electrolytes/. The assumptions has been made, that in both cases high electric fields cause an extremely strong polarisation of molecules or complex ions which leads to additional dissociation.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

ALKYL SULPHOXIDE COMPLEXES OF URANIUM AND OF MINERAL ACIDS IN EXTRACTION SYSTEM

W.Korpak - Poland

Bearing in mind the influence of the radical structure and of substituents on the extraction power of oxygen containing organic compounds as extractants for mineral acides and uranium salts, it was predicted that the alkyl sulphoxides /SO/ ought to be analogous to the alkyl phosphates and phosphine oxides. Measuring the dependency of the extraction coefficient as a function of the acidity and neutral salt concentration the composition of the extracted complexes was found. The sulphoxide complexes of uranium and mineral acids are more stable than those of tributyl phosphate /TBP/, but less so than of trioctyl phosphine oxide /TOPO/. By the extraction of uranyl complexes from sulphate solutions with dioctyl phosphoric /D2EHPA/ and monododecyl phosphoric acids /DDPA/ synergistic and antagonistic behaviour of sulphoxides was observed, respectively. This behaviour and higher stability of the sulphoxide complexes point on a stronger basicity of the sulphoxide oxygen than the oxygen of the P=O group in TBP, but weaker than in TOPO. The extracted complexes were: HNO_3,SO, HCl.SO, $R_2S.Cl_2$, UO_2Cl_2.2SO, $UO_2/NO_3/$. 2SO. Both the uranyl and sulphoxidonium chloride complexes were obtained in crystal form. The IR spectra proved that the coordination is via oxygen of the SO group.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Abstract

WIDMO OSCYLACYJNE I STRUKTURA KOMPLEKSÓW RODANKOWYCH

A. Tramer - Polska

Zbadano widma absorpcji w podczerwieni i rozproszenia ramanowskiego kilkudziesięciu kompleksów rodankowych w roztworach wodnych i acetonowych i w fazie stałej. Wyniki potwierdzają istnienie izomerii: rodanek X - SCN - izorodanek X - NCS związków nieorganicznych.

Wyznaczono charakterystyczne przesunięcia linii związane z powstawaniem wiązań metal - siarka i metal - azot. Oceniono wpływ typu i siły wiązania koordynacyjnego na stałe siłowe wiązań C-S i C-N oraz na natężenie linii widma oscylacyjnego.

Badanie widm oscylacyjnych monokryształów zorientowanych pozwoliło ustalić strukturę geometryczną kompleksów. W szczególności stwierdzono, że układ X -NCS jest liniowy i kompleksy izorodankowe $X/NCS/_4$ i $X/NCS/_6$ posiadają strukturę regularnych tetraedrów i oktaedrów, podczas gdy symetria jonów rodankowych $X/SCN/_4$, w skutek nieliniowości układu X - SCN, nie jest wyższa niż S_4.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Abstract

EXTRACTIONS STUDIES OF THE INTERACTION BETWEEN $GeCl_4$ MOLECULES AND ORGANIC SOLVENTS

S.Siekierski, R.Olszer - Poland

As previous studies have shown the extraction coefficient of complex compounds depends on the thermodynamic activity of an extracting agent and on the activity coefficient of the complex in the organic phase. The activity coefficient of the complex has been found dependent on the solubility parameter $/\delta_x/$ of the diluent used. In order to study directly the influence of the solubility parameter on the extraction of complexes, the extraction of $GeCl_4$ from concentrated HCl solutions into various organic solvents has been investigated. The extraction coefficient has been determined by measurement of the activity of ^{71}Ge. Since in the case of $GeCl_4$ the molecules of diluent do not enter the inner coordination shell of the cation, the extraction coefficient should directly depend on the solubility parameter and should be represented by the following equation: $\log k = A / \delta_{Ge} - \delta_x /^2$. The experiments indicate that the interaction between $GeCl_4$ and the molecules of the solvent can be described only approximately by the value of the solubility parameter. The difference between the theoretically calculated and experimentally determined extraction coefficient depends on the method of calculation of the partial molar entropy of mixing.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

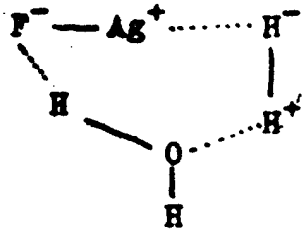
Abstract

THE EFFECT OF FLUORIDE IONS ON THE ACTIVATION OF MOLECULAR HYDROGEN BY SILVER /I/

M.T. Beck - Hungary

The fluoride ions dramatically increase the velocity of the reaction between silver /I/ and H_2. The activation effect of fluoride ions exceeds even that of the most effective polyamines. In comparison with the aquocomplex the velocity of the reaction is ten thousand times larger.

The most probable explanation of the activation effect is that in the heterolytic splitting of H_2 the concerted action of silver /I/ and the coordinated fluoride occurs. Due to steric considerations the following activated complex can be assumed:



$$-\frac{dH_2}{dt} = -\frac{1}{2}\frac{dAg^+}{dt} =$$

$$KF \rightleftharpoons K^+ + F^-$$

$$F^- + Ag^+ \rightleftharpoons AgF$$

$$AgF + H_2 \xrightarrow{k} [A^*]$$

$$k\frac{c_{Ag}\,K[F^-]}{1+K[F^-]}[H_2]$$

$$-\frac{dH_2}{dt} = k[AgF][H_2] = \frac{K[Ag^+][F^-][H_2]}{K+1}$$

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Page Denied

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

BRIEF COMMUNICATIONS

A VOLATILE HIGHER CHLORIDE OF RUTHENIUM

S. A. Shchukarev, N. I. Kolbin and A. N. Ryabov

In the chlorination of metallic ruthenium with chlorine, we observed that above 400° a deposit of amorphous $RuCl_3$ is formed on the cooler parts of the apparatus. This cannot be due simply to evaporation, since the vapour pressure of $RuCl_3$ at 400° is negligibly small.[1] More deposit is formed when $RuCl_3$ is heated in chlorine, suggesting that it reacts with Cl_2 to form a hitherto unknown gaseous higher chloride, which reverts to $RuCl_3$ and Cl_2 when condensed on the cooler surfaces.

The loss of ruthenium from boats containing $RuCl_3$ in a current of Cl_2 and of nitrogen at 484°–756° has been measured by weighing before and after. Simultaneous measurements were made of the gas carrying the $RuCl_3$ vapour and the vapour of a volatile compound probably formed according to the reaction:

$$RuCl_3 + \frac{1}{2} Cl_2 = RuCl_4$$

The vapour pressure of the $RuCl_4$ was determined from the difference in the Ru lost when chlorine and nitrogen were passed; it is plotted against temperature in Fig. 1.

The curves show that the total vapour pressure of $RuCl_3$ and $RuCl_4$ is much greater than that of $RuCl_3$ alone, which confirms the formation of $RuCl_4$. The data are insufficient for thermodynamic calculations, but if it is assumed that the reaction is reversible, the order of magnitude of the enthalpy change can be estimated. Assuming further that ΔH° remains constant between 484° and 756°, its value is approximately 10 kcal; thus the formation of gaseous $RuCl_4$ from solid $RuCl_3$ and Cl_2 is slightly endothermic.

The study of the reaction is being continued.

As far as we are aware there are no published data on a higher gaseous chloride of ruthenium, though Claus[2] reported a yellow smoke, which he believed to be a higher chloride, at the start of the chlorination of metallic ruthenium.

Fig. 1. Vapour pressure of ruthenium chlorides vs. temperature:

1) vapour pressure of pure $RuCl_3$; 2) total vapour pressure of $RuCl_3 + RuCl_4$ in a current of Cl_2.

1. S. A. Shchukarev, N. I. Kolbin, and A. N. Ryabov, Zhur. Neorg. Khim., 5, 1721 (1960).
2. C. C. Claus, Liebigs. Ann. Chem., 59, 234 (1846).

Inorganic Chemistry Dept., Zhdanov State University, Leningrad

Received 23rd February 1960

COMPLEX FORMATION BY THE PENTAVALENT NEPTUNIUM ION

Yu. A. Zolotov and Yu. P. Novikov

Pentavalent neptunium forms the ion NpO_2^+ in solution, which because of its low charge and large size (Np–O distance[1] 1.96 Å), has the least tendency of any neptunium ion to form complexes. Few data are available on complex compounds of Np(V).

The absorption spectrum of Np(V) is the same in 1 M $HClO_4$, HNO_3, HCl, H_2SO_4 and in 0.5 M HNO_3 containing hydrogen peroxide,[2,3] indicating apparently the absence of complex formation. In HCl stronger than 3 M, however, the NpO_2^+ ion appears to form chloro complexes, as indicated by the ready elution of Np(V) from a cation exchange column with HCl[4] and the absorption of the ion by an anion-exchange resin from solutions of HCl stronger than 4 M.[5] The change in the absorption spectrum of Np(V) in the presence of oxalate ions has been assumed to be due to the formation of oxalate complexes,[6] and has been studied spectrophotometrically.[7] Changes in the spectrum of Np(V) have also been observed in the presence of thiocyanate, acetate, citrate and phthalate ions.[7]

The ions UO_2^+, PuO_2^+ and AmO_2^+ are also weak complex-forming species. For Pu(V) the only complexes known are the chloro complex[8] and that with ethylenediaminetetraacetic acid.[9] The UO_2^+ ion has been reported to form unstable complexes with chloride and sulphate ions.[10] There are no data on complex formation by the AmO_2^+ ion.

The present communication reports new data on complex formation in Np(V) solutions containing organic acid ligands. The absorption spectrum of Np(V) changes in solutions containing tartaric, trihydroxyglutaric, citric, salicylic, 2,3-dihydroxyterephthalic, acetic, phthalic and ethylenediaminetetraacetic acids, indicating complex formation.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

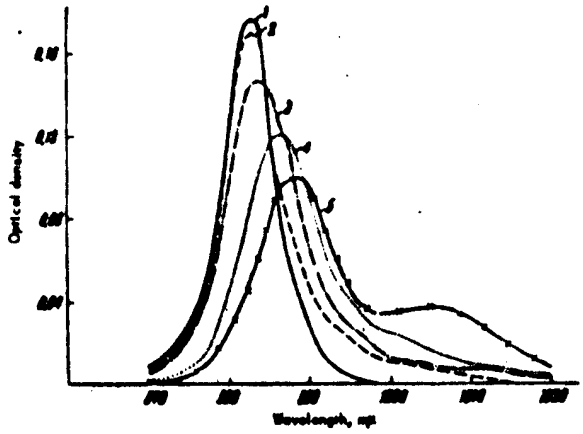


Fig. 1. Absorption spectra of Np(V) solutions containing trihydroxyglutaric acid:

1) pH 0.8; 2) pH 2.2; 3) pH 3.0; 4) pH 3.8; 5) pH 6.0.

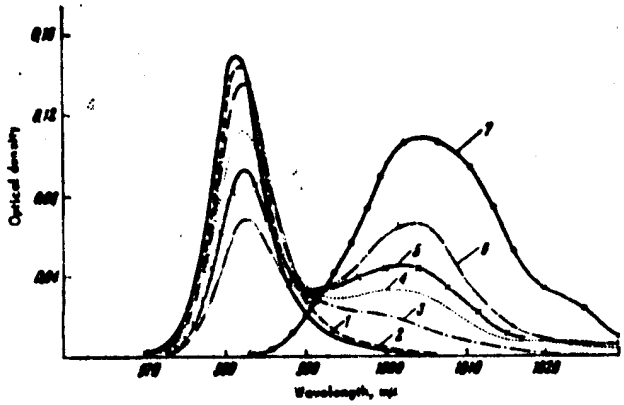


Fig. 2. Absorption spectra of Np(V) solutions containing 2,3-dihydroxyterephthalic acid:

1) pH 2.8; 2) pH 4.2; 3) pH 5.3; 4) pH 5.5; 5) pH 5.7; 6) pH 5.8; 7) pH 6.0.

EXPERIMENTAL

The Np(V) solution was prepared by treating one of Np(V) and Np(VI) with 0.1 M $KBrO_3$ in 1–2 M HNO_3, and extracting the oxidised Np with ether. The Np was reextracted with 0.1 M hydrazine hydrochloride, which reduced the neptunium in the cold to Np(V). Np(V) hydroxide was precipitated with concentrated NaOH, washed with dilute NaOH and water, and dissolved by heating in $HClO_4$ previously purified by distillation. The solution contained 3.6×10^{-3} M Np(V). Np(VI) or Np(IV) could not be detected spectrophotometrically. The organic acid solutions used were 1.0 and 0.5 M.

An SF-4 quartz spectrophotometer with rectangular cells giving an optical path length of 10.03 ± 0.01 mm was used. The slit width was 0.030 mm, this small constant value being necessary for measurements of the sharp absorption bands, such as the Np(V) band lying at 983 mμ for 1 M $HClO_4$, since the spectral bands isolated by the slit are not sufficiently narrow compared with the width of the absorption band. The solutions were prepared in the cells. The pH was determined spectrophotometrically[11] using thymol blue for the pH range 0.7–3.0 and methyl red for the range 3.5–6.5. These indicators have a small salt error[12] and do not absorb in the wavelength range from 965 to 1050 mμ. The measurements with thymol blue were made at 544 mμ and those with methyl red at 530 mμ. Np(V) shows very little absorption in this region. The slit width for these measurements was 0.015 mm, and the pH, adjusted with $HClO_4$ and NaOH, was measured from a calibration curve for each indicator.

Measurement of the changes in the spectrum were made in the region of the most characteristic absorption maximum for Np(V), 983 mμ in 1 M $HClO_4$. No measurements were made in other spectral regions. The molar ratio of complex-forming acid to Np(V) was 100 : 1 in all experiments. The spectra for each complex-forming acid were recorded at various pH values, and always at room temperature.

RESULTS AND DISCUSSION

Tartaric, citric and trihydroxyglutaric acids, aliphatic hydroxyacids with similar complex-forming action, change the spectrum of Np(V) considerably. Fig. 1 gives the absorption spectrum of Np(V) in trihydroxyglutaric acid and shows that as the pH is increased from 0.8 to 6.0 the band is displaced to longer wavelengths (to 988 mμ at pH 6.0) and the maximum becomes smaller. A new maximum is observed at approximately 1005 mμ. Observations with citric and, to a lesser extent, with tartaric acid are similar.

Acetic acid causes only a slight displacement of the band to longer wavelengths, with a reduction in the maximum. Salicylic acid causes a similar change, but phthalic acid shifts the maximum without a decrease in its value. The greatest spectral change is that produced by 2,3-dihydroxyterephthalic acid, whose molecule contains two salicylic acid groups*. Increase in the pH from 2.8 to 6.0 (Fig. 2) markedly lowers the absorption at 983 mμ (the position of this maximum remains unchanged) and produces a new maximum near 1005 mμ. This increase in the absorption at 1005 mμ is proportional to the reduction at 983 mμ (Fig. 3), which suggests the formation of one complex ion only. The change in the spectrum in the presence of ethylenediaminetetraacetic acid (Fig. 4) is of interest, since raising the pH to 4.4 does not change the position of the Np(V) absorption maximum, a further rise shifts the absorption band by 8 mμ to higher wavelengths and increase in pH from 4.9 to 6.2 causes no further change in the position of the maximum. This indicates that all the neptunium is bound in the complex in this pH range, which agrees with the data of Gel'man and Mefod'eva.[13]

Before accepting these changes as proof of complex formation, the behaviour of pure Np(V) in perchlorate solution at different pH values was studied. Raising the pH to 6.0 caused no change in the spectrum, but with pH 6.5 the maximum at 983 mμ was displaced to 1020 mμ and became much

* The authors thank N. N. Basargin who synthesised the acid; he has shown that the acid forms stable complexes with a number of elements of Groups III and IV.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

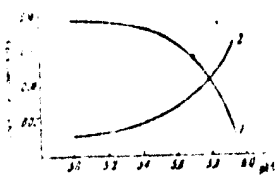


Fig. 3. Optical density of Np(V) solution containing 2,3-dihydroxyterephthalic acid at 983 (1) and 1003 (2) mμ.

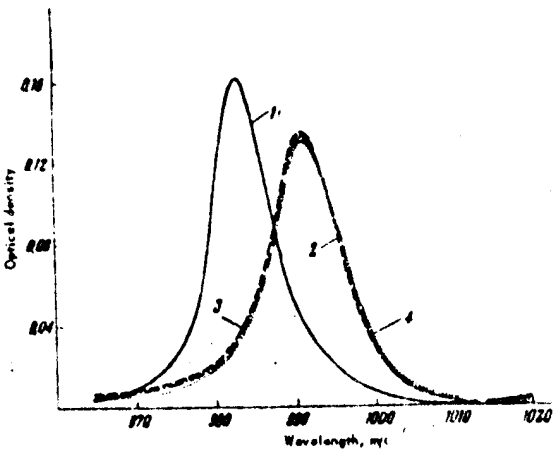


Fig. 4. Absorption spectra of Np(V) solution containing ethylenediaminetetraacetic acid:

1) pH 4.4; 2) pH 4.9; 3) pH 5.5; 4) pH 6.2.

less sharp. These changes are ascribed to hydrolysis of the NpO_2^+ ion.

When applied to the actinides, the spectrophotometric method of studying complex compounds has the disadvantage that complex formation may not produce changes in the absorption spectrum because of the screening of the 5f-electrons.[13] Changes in the spectrum with change in the concentration of complex-forming species or pH do, however, prove that complex formation takes place.

The complex-forming species which we have studied contain the OH group and the data obtained (Fig. 2) show that the reactions with these substances take place for the most part at pH values close to 6. Since hydrolysis of the NpO_2^+ ion also begins here, it may be assumed, in accordance with Kuznetsov's "analogy hypothesis", that other organic reagents containing the OH group should also react with the NpO_2^+ at approximately the same pH.

The authors wish to express their thanks to I.P. Alimarin and P.N. Palei for their interest and useful advice.

SUMMARY

Changes in the absorption spectrum of Np(V) show that the ion NpO_2^+ forms complexes with tartaric, trihydroxyglutaric, citric, salicylic, 2,3-dihydroxyterephthalic, acetic, phthalic and ethylenediaminetetraacetic acids.

1. L. H. Jones and R. A. Penneman, J. Chem. Phys., 21, 542 (1953).
2. J. C. Hindman, L. B. Magnusson, and T. J. La Chapelle, "The Transuranium Elements", Nat. Nucl. En. Ser., Div. IV, 14B, paper 15.2, New York, 1949.
3. R. Sjoblom and J. C. Hindman, J. Amer. Chem. Soc., 73, 1744 (1951).
4. R. M. Diamond, K. Street, and G. T. Seaborg, J. Amer. Chem. Soc., 76, 1461 (1954).
5. E. K. Hyde, "Proceedings of the International Conference on the Peaceful Uses of Atomic Energy. Nuclear Chemistry and the Effects of Radiation", Vol. 7 of the Russian Edition, Geneva, 8-20th August, 1955, p. 366.
6. G. Gibson, D. M. Gruen, and J. J. Katz, J. Amer. Chem. Soc., 74, 2103 (1952).
7. D. M. Gruen and J. J. Katz, J. Amer. Chem. Soc., 75, 3772 (1953).
8. S. W. Rabideau, J. Amer. Chem. Soc., 78, 2705 (1956).
9. A. D. Gel'man, P. I. Artyukhin, and A. I. Moskvin, Zhur. Neorg. Khim., 4, 1332 (1959); [Rus. J. Inorg. Chem., 4, 599 (1959)].
10. G. T. Seaborg and J. J. Katz (Eds.), "The Actinide Elements", paper by H. Hoekstra and J. J. Katz (Translated into Russian), Inostr. Lit., Moscow, 1955, p. 157.
11. W. R. Brode, J. Amer. Chem. Soc., 46, 581 (1924).
12. I. M. Kolthoff and C. Rosenblum, "Acid-base Indicators", New York, 1937, pp. 339, 343.
13. G. T. Seaborg and J. J. Katz (Eds.), "The Actinide Elements", paper by J. C. Hindman (Translated into Russian), Inostr. Lit., Moscow, 1955, p. 277.
14. V. I. Kuznetsov, Zhur. Anal. Khim., 2, 67 (1947).
15. A. D. Gel'man and M. P. Mefod'eva, Dokl. Akad. Nauk SSSR, 124, 815 (1959).

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, the USSR Academy of Sciences

Received 10th July 1958

THE VALENCY STATE OF THE METAL IN CERIUM TETRACARBONATE

D. I. Ryabchikov

Golovnya and Pospelova[1] described the preparation of dark red crystals with the composition $(CN_3H_6)_3 \cdot [Ce(CO_3)_4] \cdot 2H_2O$. It was pointed out to them that the cerium was tetravalent in this compound but they continued to assert that it was trivalent.

Carbonate solutions of lanthanum and cerium were prepared as described by them, but a colour change was observed only with cerium. This difference can only be due to the change Ce(III) → Ce(IV), which occurs more readily in a complex compound.

Two equal weights of the substance were analysed. In the first the cerium was separated as the hydroxide and amounted to 0.0420 g. The second was dissolved in 4 N H_2SO_4 and the yellow solution titrated potentiometrically with 0.05 N ferrous ammonium sulphate. The initial potential, 1.44 V relative to the hydrogen, indicated that the cerium was tetravalent. The titration, carried out by V. A. Zarinskii,

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

ROLE OF THE SOLVENT IN THE EXTRACTION OF ION-PAIR COMPLEXES

A.G. Maddock, A.J. Fench - England

It is well known that solvates are commonly involved in the solvent extraction of the complex halo-acids, such as chloroferric and chlorauric acids, from aqueous solutions. In these systems the metals extract as ion-pair complexes, at least, if the metal concentration is not too low. There are several lines of evidence that in the case of $H^+FeCl_4^-$ the solvent is associated with the cationic, rather than the anionic, part of the extracting ion-pair.

The molecular composition of the extracting complex can be investigated by studying the influence of an inert diluent on the extraction. It is shown that some care is necessary in the choice of suitable conditions for such measurements.

Using this technique it is shown that several complex halo-acids give similar solvates, in keeping with the suggestion that the solvation concerns only the common cation in the ion-pairs. To obtain the number of solvent molecules in the ion-pair it is necessary to measure the activity of the complexing solvent as a function of the composition of the organic phase. When this is done it is found that the composition of the extracting complex may very with the identity of the diluent.

The significance of these results will be discussed.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Abstract

THE ELECTRONIC STRUCTURE OF $Cr/CO/_6$

Miklos I. Ban, Szanieslo Fenyi, Magdolna Hegyhati- Hungary

The molecular orbital energies of $Cr/CO/_6$ were calculated by the LCAO MO method. It was assumed that in the formation of molecular orbitals the five 3d, one 4s and three 4p atomic orbitals of the central Cr-atom, three 2p orbitals of each C-atom and two 2p orbitals of each O-atom took part. Six electrons of Cr-atom and six electrons of each CO-group were taken into consideration. The H_{ii} integrals in the secular equations were estimated by corresponding ionization energies. The "group overlap" integrals were reduced to atomic overlaps. Some of these were taken from tables. To calculate the remaining overlap integrals a new graphic method was elaborated. The results obtained by this method were checked by an interpolation method. The good agreement between the results verified the usefulness of both method and suggested to shelve the approximation method used in previous works for obtaining overlap integrals. By the energy values obtained as solutions of the secular equations the bands occuring in the electronic absorption spectrum could be interpreted.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

THE LIGAND FIELD THEORY AND ITS APPLICATION TO THE STUDY OCTA-CYANIDES OF MOLYBDENUM /IV/ AND TUNGSTEN /IV/

A. Gołębiowski, Kraków, Poland

The work consists of two parts: Part I is concerned with a general theory, part II is its application to the study of octacyanides of molybdenum and of tungsten.

I. Let us assume that the σ-bonds between the central atom and the ligands are built of n orthonormal atomic orbitals $\phi_1 \ldots \phi_n$ of the central atom and k orthonormal ligand orbitals $\phi_1 \ldots \phi_k$. In the theory of directed bonds k hybrids from ϕ_i s are formed, $\psi_1 \ldots \psi_k$, such that the negative sum of resonance integrals /closely related to familiar bond strengths/,

$$-\sum /\phi_i/\hat{H}/\psi_i/, \qquad /1/$$

is a maximum. Recently we have shown that this maximum is equal to $\sum \epsilon/-$, where $\epsilon/-_i$ s are the square roots of eigenvalues of $\mathbf{H}\mathbf{H}^T$, where $\mathbf{H}$ is a matrix with elements $H_{ij} = /\phi_i|\hat{H}|\phi_j/$, and $\mathbf{H}^T$ is $\mathbf{H}$ transposed.

Let us further assume that ϕ_i s are eigenfunctions in the pure ionic approximation, basic in the familiar electrostatic ligand field theory. We have shown in part I that by certain Hückel-type approximations the secular determinant in the m.o. theory can take the form:

$$/a_L-E/^{k-n} \left| \mathbf{H}^T\mathbf{H} - /a_L-E/ \cdot \mathbf{d}/a_i-E/ \right| = 0 \qquad /2/$$

where a_L, a_i s are Coulomb integrals of ligand and various central atom orbitals respectively and $\mathbf{d}/a_i - E/$ is a diagonal matrix with elements equal to a_i-E, $i = 1,2, \ldots k$

Putting $\mathbf{H}^T\mathbf{H} = \mathbf{0}$ in /2/, we obtain the eigenvalues in the electrostatic theory. We generalise this theory considering $\mathbf{H}^T\mathbf{H}$ as a perturbation. If, alternatively, the bonds have predominantly a covalent character, we can put $a_i = a_M$ /constant/.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Then eq. /2/yields n-k non-bonding orbitals with $E_i = a_M$, and k pairs of bonding and anti-bonding orbitals,

$$E_i = \frac{1}{2}(a_L + a_M) \pm \left\{\frac{1}{4}(a_L - a_M)^2 + \epsilon_i^2\right\}^{\frac{1}{2}} \qquad /3/$$

Eq. /3/ is a generalisation of the theory of directed bonds and for $a_L \sim a_M$ it leads to an equillibrium criterium equivalent to eq. /1/.

In p.I the generalisations of the pure ionic and the pure covalent approximations, and also the general formulae necessary, have been discussed in details.

II. The geometry of $/W(CN)_8/^{4-}$ is not known, that of $/Mo(CN)_8/^{4-}$ is not certain; two alternative symmetry groups are proposed, D_{2d} /dodecahedron/ and D_{4d} /antiprism/. This discrepancy makes also the discussion of photoproducts, like $/Mo(CN)_3(N_2H_4)_2/^{4-}$, rather difficult. In part II we make an attempt to solve this problem from a theoretical discussion of the absorption spectrum of octacyanides and their photoproducts. With this purpose we discuss the electronic spectrum theoretically, in the predominantly ionic and the predominantly covalent limits.

The irregular dodecahedron and the antiprism do not differ much; they can be transformed one into the other after relatively small changes of bond angles. The intermediate has the symmetry D_2. We have discussed the expected electronic spectrum in terms of this transformation and the position of N_2H_4 or NH_3 /in the case of photoproducts/.

The limited space does not allow us to discuss the results in details.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

THE EFFECT OF COMPLEX FORMATION ON THE ELECTRON TRANSFER SPECTRA OF DIVALENT TRANSITION METAL IONS

W. Libuś - Poland

Investigation of spectral changes in the region of electrontransfer bands accompanying various types of complex formation and outer-sphere association in solution have been undertaken. The present communication deals with the results obtained for divalent transition metal ions.

As the basis for further investigations ultraviolet absorption spectra of hydrated cations Mn^{++}, Fe^{++}, Co^{++}, Ni^{++} and Cu^{++} have been measured down to 190 mμ. It has been observed that the intensity of the absorption bands corresponding to the process: $Me/II/H_2O + h\nu \longrightarrow Me/III/H_2O^-$ is significantly lower than that of the bands corresponding to: $Me/II/H_2O + h\nu \longrightarrow Me/I/H_2O^+$

Spectral changes in ultraviolet accompanying complex formation have been determined for the following systems in water solutions: 1/ Cu/II/ + en, 2/Cu/II/ + N_3^-, 3/ Cu/II/ + Cl^-, 4/ Co/II/ + Cl^-, 5/ Co/II/ + Br^-, 6/ Co/II/ + NCS^-.

It has been found that the exchange of a water molecule in the aquo complex of Cu/II/ for another ligand of lower electronegativity results in the appearance of a new absorption band at a higher wavelength, its position being only slightly changed on introduction of further groups of the same ligand provided that only equivalent coordination positions are involved.

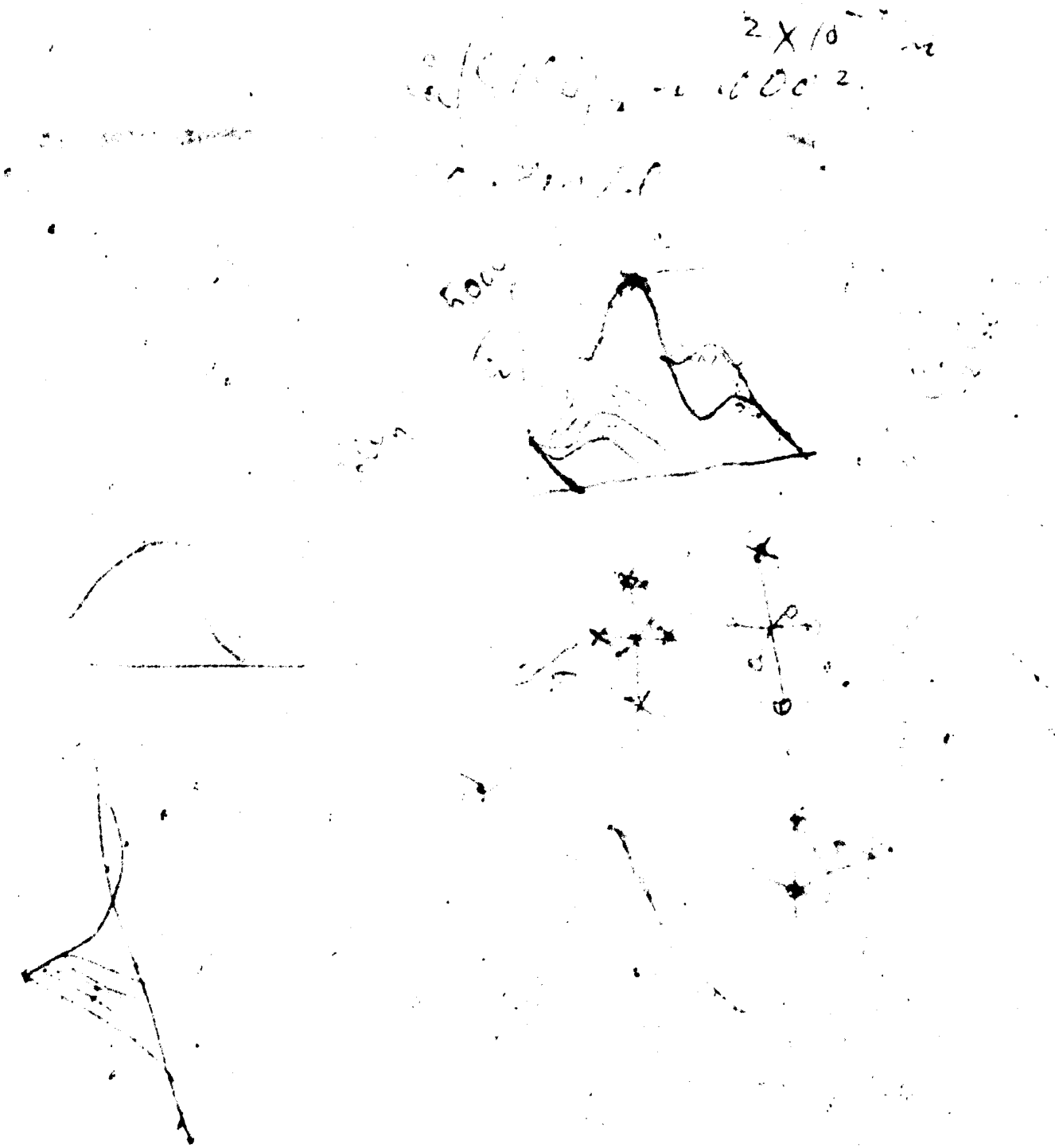
The introduction of Cl^- or Br^- ions into the coordination sphere of Co/II/ does not result in an appearance of new bands above 190 mμ unless tetrahedral complexes are formed. It follows that the positions of electron transfer bands corresponding to the same ligand in the complex are essentially different for tetrahedral and octahedral coordination.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

At the same time ligand exchange involving equivalent coordination positions in tetrahedral complexes does not effect significantly the positions of the corresponding electron-transfer bands.

In water solutions of $Cu/ClO_4/_2$ + LiCl/ or HCl/ complicated complex forming equilibria are established. The structures of the complexes formed are discussed basing on spectral effects observed and the regularities mentioned above.



Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Page Denied

Next 1 Page(s) In Document Denied

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Резюме

НЕКОТОРЫЕ РЕЗУЛЬТАТЫ НОВЫХ РЕНТГЕНОСТРУКТУРНЫХ ИССЛЕДОВАНИЙ КОМПЛЕКСНЫХ СОЕДИНЕНИЙ ПЕРЕХОДНЫХ МЕТАЛЛОВ

М.А.Порай-Кошиц - СССР

Обсуждаются стереохимические результаты структурных исследований комплексных соединений металлов седьмой, восьмой и первой-б групп, выполненных в 1961 году в лабораториях кристаллохимии ИОНХ АН СССР и химического факультета МГУ.

I. Исследования соединений металлов 4-го периода дополняют и уточняют найденные ранее[x/] стереохимические закономерности в ряду Fe, Co, Ni, Cu, Zn.

I/ Двойной роданид меди и ртути $CuHg(SCN)_4$

/Ван Цзин-Лин и М.А.Порай-Кошиц, МГУ/

Так же как и в $CoHg(SCN)_4$ и в $NiHg(SCN)_4 \cdot 2H_2O$ роданидные группы связывают атомы Hg и переходного металла в бесконечной каркас с тетраэдрическими узлами HgS_4. В отличие от кобальтовой соли координация меди не тетраэдрическая, а искаженно-октаэдрическая, в отличие от никелевой - квадратное окружение дополняется до октаэдрического не дополнительными молекулами воды, а атомами серы, образующих удлиненные связи с Cu (Cu-N = 2,I Å, Cu-S = 3,0 Å/

2/ Дихлоро- и дибромодиэтилендиамин-никель $NiEn_2Cl_2$ и $NiEn_2Br_2$

/А.С.Анцышкина, М.А.Порай-Кошиц, ИОНХ/

Вопреки ожиданию и в отличие от $NiEn_2(NCS)_2$ кристаллы построены не из молекулярных мономерных комплексов с транс-расположением кис-

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

лотных остатков, X = Cl или Br, а из димерных катионов $[En_2NiX_2NiEn_2]^{2+}$ с мостиковыми атомами X, находящимися в цис-положении, и анионов X^-. Обсуждается значение этого результата для характеристики реакции обмена и сокристаллизации при получении смешанных соединений $NiEn_2XY$.

II. Исследования соединений металлов 5-го и 6-го периодов демонстрируют отклонение от традиционной квадратной координации характерной для Pd /II/, Pt /II/ и их электронных аналогов и от октаэдрической координации, характерной для Pd /IV/, Pt /IV/, Rh, Ir, Ru, Os, Re в обычных валентностях. Причины отклонений - необычная связь лиганда с металлом или необычная валентность металла.

I/ Аллилхлорид палладия $PdClC_3H_5$

/В.Ф.Ледвик. М.А.Порай-Кошиц, МГУ/

Кристалл построен из димерных молекул $C_3H_5PdCl_2PdC_3H_5$ с мостиковыми атомами хлора. Аллильный радикал присоединяется не как монодентатный лиганд $-CH_2-CH=CH_2$, и не как бидентатный лиганд $-CH_2-\overset{|}{C}H-CH_2-$, а аналогично сендвичевым лигандам типа бензола, пентадиэнила и циклобутадиена. Плоскость радикала почти перпендикулярно оси Pd·····Pd. Соединение является важным промежуточным членом в ряду лигандов, образующих с металлом многоцентровые связи /этилен - 2 атома C, аллил - 3 атома C, циклобутадиен - 4 атома C и т.д./.

2/ Ацетат родия / М.А.Порай-Кошиц, А.С.Анцышкина, ИОНХ/

Структурное исследование доказывает, что соединение является ацетатом двухвалентного родия и имеет состав $Rh^{II}(CH_3COO)_2 \cdot H_2O$. Кристаллы изоструктурны аналогичному соединению меди и построены из димерных молекул с мостиковыми ацетатными группами. Проводится квантово-химический анализ связей Rh-лиганд и Rh-Rh /расстояние Rh-Rh = 2,45 Å/ и обсуждаются причины различия строения ацетатов и формиатов разных переходных металлов.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

3. Кислый тетрахлорореннат пиридиния $HPyHReCl_4$ xx/

/В.Г.Кузнецов, П.А.Козьмин, ИОНХ/

В основе структуры лежат димерные анионы $[Cl_4Re-ReCl_4]^{4-}$ с тетрагонально-пирамидальной координацией атома рения четырьмя атомами хлора и вторым атомом рения. Расстояние Re-Re = 2,22 Å. Исследование доказывает, что рений образует димерные комплексы не только за счет мостиковых лигандов /например в $[Cl_5Re-O-ReCl_5]^{4-}$ /, но и при непосредственной связи Re-Re. На основе квантово-химического анализа предполагается, что связь Re-Re является тройной.

III. Исследования комплексных окси-соединений развивают работы предшетствующих лет xxx/ по анализу структур соединений, содержащих кратные связи металл-лиганд

Тетрагидроксоосмиат калия $K_2[OsO_2(OH)_4]$

/М.А.Порай-Кошиц, Л.О.Атовмян, В.Г.Андреанов, ИОНХ/

Исследование доказало, что из четырех структурных формул, приписывавшихся соединению $K_2[OsO_4]\cdot 2H_2O$, $K_2[OsO_4(H_2O)_2]$, $K_2H_4[OsO_6]$, $K_2[OsO_2(OH)_4]$ - справедлива последняя. Из меди кислородных лигандов два /в транспоположении/ находятся на расстоянии 1,57 Å и четыре - на расстоянии 2,03 Å. Структура родственна $K_2[OsO_2Cl_4]$ /с понижением симметрии вследствие образования водородных связей между гидроксильными группами/. Приводятся предварительные данные структурного исследования $K_2[MoO_2Cl_5]$

---

x/ М.А.Порай-Кошиц. ДАН СССР, 134, 1104/1960/

xx/ Лаборатория рентгеноструктурного анализа

xxx/ Г.Б.Бокий, Л.О.Атовмян, Т.С.Ходашова. ДАН СССР, 128, 78/1959/

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

CRYSTAL STRUCTURE OF THE COPPER DIAMMINE ACETATE

M. Bukowska-Strzyżewska - Poland

Crystals of $Cu/NH_3/_2/CH_3COO/_2$ were obtained by dissolving cuprio acetate in concentrated ammoniacal solution and slow crystalization at 26°- 30°C. Monoclinic intensively coloured-blue crystals slowly decompose in the air. The axial ration determined by goniometric measurements are: a:b:c = 0,528:1:0,724. The unit cell-dimensions are: a = 5,47 ± 0,01 Å; b = 10,27 ± 0,02 Å; c = 7,47 ± 0,02 Å β = 107°20'. The pycnometric density d_{pycn} = 1,78 g/ccm. The unit cell contains two formula weights. The space group is $C_{2h}^5 = P2_1/c$. The general structure outline was found by analysing the Patterson projections along [100] and [001]. Coordinates of the atoms were found by gradually approximating projections of electronic density along [100] [010] and [001]. Coordinates of the atoms were refined introducing Booth correction. Final atomic coordinates are tabulated in table I. The final disagreement indices - R, calculated for all reflections up to sin θ/λ = 0,64 are: R/h0l/ = 0,108; R/0kl/ = 0,131; R/hk0/ = 0,132 ($B_{/h0l/} = B_{/hk0/} = 2,3$; $B_{/0kl/} = 2,7$).

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Table I. Atomic coordinates in the crystal structure of $Cu/NH_3/_2$ $/CH_3COO/_2$

Atoms	X	Y	Z
Cu	0	0	0
O_I	0,335	0,093	0,117
O_{II}	0,082	0,257	0,017
C_I	0,302	0,214	0,061
C_{II}	0,513	0,309	0,133
NH_3	-0,077	0,020	0,243

The probable standart errors of the atomic positions were calculated according Wajnsztejn's formulas:

$\Delta x_o = \Delta y_o = \Delta z_o = \Delta x_N = \Delta z_N = 0,02$ Å

$\Delta x_c = 0,03$ Å ; $\Delta y_c = \Delta z_c = 0,025$ Å

Main interatomic distances are tabulated in table II.

Table II

Interatomic distances and bond angles within atomic groups $Cu/NH_3/_2$ $/CH_3COO/_2$			Intermolecular distances
$Cu - 2O_I = 2,02$ Å		$\angle O_I - Cu - NH_3 = 88°$	$NH_3 - O_{II} = 3,24$ Å
$Cu - 2O_{II} = 2,68$ Å		$\angle O_{II} - Cu - NH_3 = 86°$	$NH_3 - O_{II} = 3,02$ Å
$Cu - 2NH_3 = 2,00$ Å		$\angle O_I - Cu - O_{II} = 53°$	$NH_3 - C_{II} = 3,54$ Å
$C_I - O_I = 1,16$ Å		$\angle O_I - C_I - O_{II} = 122°$	$C_{II} - O_{II} = 3,53$ Å
$C_{II} - O_{II} = 1,24$ Å		$\angle O_I - C_I - C_{II} = 129°$	
$C_{II} - C_I = 1,47$ Å		$\angle O_{II} - C_I - C_{II} = 117°$	

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

The structure consists of complex molecules $Cu/NH_3/_2$ $/CH_3COO/_2$ Two oxygen atoms O_I and two NH_3 groups form a square around the copper atoms. The other two oxygen atoms O_{II} of two different acetate groups approach to the copper atoms at a distance of 2,58 Å. The angle O_I-Cu-NH_3 = 88° differs but slightly from 90°, but the anglo O_I-Cu-O_{II} = 158° whereby the octahedrical coordination typical for copper atoms is completely distorted. This deformation is caused by the structure of the acetate group, in the examinated compound which does not form the typical bridge bond between two complexes. Both its oxygen atoms are coordinated to the same copper atom.

The acetate group is plane /within experimental error/. The intermolecular distances do not suggest the existence of strong hydrogen bonds.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

PREPARATION AND PROPERTIES OF ALKALINE EARTH RHODANOBISMUTHATES /III/

A. Cygański - Poland

Complex rhodanobismuthates /III/ : $Ca_3/Bi(SCN)_6/_2 \cdot 14H_2O$, $Sr_3/Bi(SCN)_6/_2 \cdot 6H_2O$, $Ba_3/Bi(SCN)_6/_2 \cdot 10H_2O$ not recorded in literature were synthesized.

The properties of these compounds have been investigated. Rhodanobismuthates were found to dissolve readily in acid solutions, but they are decomposed by the action of water, alkaline and carbonate solutions. The reaction of hydrolysis is given by the following formula.

$$Me_3/Bi(SCN)_6/_2 + 2H_2O \rightleftharpoons 2BiOSCN + 3Me(SCN)_2 + 4HNCS$$

where

Me = Ca, Sr, Ba ions

The results of solubility investigations in 0,25 m $HClO_4$ show that $Ba_3/Bi(SCN)_6/_2 \cdot 10H_2O$ has the highest solubility and $Ca_3/Bi(SCN)_6/_2 \cdot 14H_2O$ the lowest one.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Abstract

CRYSTAL FIELD EFFECTS AND SURFACE PROCESSES

J. Haber - Poland

In the last few years the ligand field theory has been successfully applied to the interpretation of many properties of crystals as well as complexes. The present study aims at the application of this theory to the interpretation of the mechanism of surface processes.

The influence of light on nickel oxide carrying adsorbed oxygen has been examined, from 200 mμ to 3000 mμ, The activity was confined to the region of 650-800 mμ, where photodesorption has been observed. This region of spectrum corresponds to the absorption bands of NiO, due to the splitting of d-electron levels of Ni^{+2} ions in the octahedral field of $O^{=}$ ligands. As the result of optical excitation the system loses the additional stabilising energy, due to the crystal field effect, and desorption of oxygen takes place.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Abstract

FORMATION OF ION COMPLEXES OF URANIUM /IV/ CHLORIDE IN MOLTEN LiCl-KCl eutectic mixture.

A.Kisza, A.Bogacz and W.Trzebiatowski - Poland

The existence of complex ions in melted LiCl-KCl eutectic mixture containing UCl_4, has been established by EMF measurements of a suitable cell and also by special migration experiments along an electric potential gradient. The following syntetic cell was used:

$$-Pt \;/\; \begin{matrix} UCl_3 & x_1 \\ UCl_4 & x_2 \\ LiCl\text{-}KCl & \end{matrix} \;//\; LiCl\text{-}KCl \;/\; Cl_2,\; C+$$

and the standart red-ox potential $E^{o}_{U^{+3}/U^{+4}}$ was determined in diluted solutions between 400-570°. The thermodynamic properties of UCl_3 in this melt has been prior determined [x]/. Basing on this data, it was possible to disclose that uranium /IV/ chloride exhibit strong negative deviations from the Raoult's rule.

These strong deviations originate from formation of such complex ions as $UCl_6^{=}$ in the melt.

The presence of these complexes was also confirmed directly, by measuring the migration of uranium ions at 450°. In a specially designed apparatus, larger amounts of uranium were found in the anodic than in the cathodic compatment.

[x]/ A.Kisza and W.Trzebiatowski: Bull.Acad.Polon.Sci.ser.chim. 10/1962/ In press.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Abstract

Tc/IV/ COMPLEX FORMATION ON THE Re/IV/ CARRIER.

J.Ziółkowski, M.Bałka, B.Jeżowska- Trzebiatowska

To obtain data for pure technetium complex synthesis the attempt was made to form similar complexes for Tc/IV/on the basis of rhenium carrier as in the syntheses of the well known mono- and bi-nuclear complexes of Re/IV/. $K/ReTcO_4$, $K_2/ReTcCl_6$, $ReTcO_2$ were obtained and from them the following $Re/Tc/^{+4}$ complexes : with the organic acids

$K_2/(ReTc)/OH/_4sal/$ $K_2H_2/(ReTc)_2O/OH/_6citr_2/$

$K_4/(ReTc)_2O/OH/_2ver_2/$ $K_2H_2/(ReTc)_2O/OH/_6vin_2/$

and bi-nuclear complex

$K_4/(ReTc)_2OCl_{10}/$

The radiometric analysis of technet content in the substracts and in the reaction products of complex formation,yields of which would be bigger then the yields of the corresponding reactions for Re/IV/.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Abstract

ÜBER DEN EINFLUSS VON KATIONEN AUF DEN ALKALISCHEN PERMANGANATZERFALL

R. Landsberg und R. Thiele - Deutsche Demokratische Republik

Es wird über weitere Untersuchungen zum alkalischen Permanganatserfall berichtet.
Dabei wurde festgestellt, dass die Katalysatoren, die den zweiten Reaktionsschritt des alkalischen Permanganatserfalls beschleunigen, meist auch in geringerem Masse den ersten Reaktionsschritt beschleunigen. Neben den Übergangsmetallen, von denen vor allem Kupfer und Silber besonders wirksame Katalysatoren sind, konnte ein katalytischer Einfluss auch für Rubidium- und Caesiumionen festgestellt werden. Experimente wurden durchgeführt, die es gestatten, die Geschwindigkeitskonstante der Rückreaktion abzuschätzen. Daraus lässt sich ein ungefährer Wert für folgende Grössen berechnen:

a/ die Gleichgewichtskonstante des vorgelagerten Gleichgewichts

b/ die in der Lösung vorhandene Konzentration an Hydroxylradikalen

c/ das Normalpotential des Systems Hydroxylradikale-Hydroxylionen

Auch die Aktivierungsenergie des ersten Reaktionsschrittes wurde bestimmt, während diejenige der Rückreaktion und des zweiten Reaktionsschrittes ebenfalls abgeschätzt wurde. Die daraus berechnete Aktivierungsentropie war insbesondere für den zweiten Reaktionsschritt stark negativ, was den vorgeschlagenen Reaktionsmechanismus stützt bzw. Hinweise auf eine der zur Verfügung stehenden Möglichkeiten für den Mechanismus des zweiten Reaktionsschrittes gibt.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

$MnO_4^{=}$

$MnO_4^{=}$

MnO_2

$\frac{a-x}{x^{1/2}}$

$a-x$

$a-x^2$

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

INVESTIGATIONS OF LIGANDS EXCHANGE IN COMPLEX COMPOUNDS OF Cr^{III} BY MEANS OF VOLTAGE SWEEP CHRONOAMPEROMETRY

W. Kemula and E. Rakowska

A new method of investigation of the influence of Cr^{II} ions on ligands exchange in complex compounds of Cr^{III} using the hanging mercury drop electrode [1] was preposed. This enables the electrolytic generation of Cr^{II} "in situ" in solutions of complex compounds and the simultaneous investigation of products formed using voltage sweep chronoamperometry [2,3]. Thus it was possible to study the reduction of Cr^{III} and the oxidation of Cr^{II}. The following compounds were investigated: $[Cr/H_2O/_6]Cl_3$, $[Cr/H_2O/_4Cl_2]Cl$, $[Cr/NH_3/_5H_2O]/NO_3/_3$ and $[Cr/NH_3/_5Cl]Cl_2$ in various supporting electrolytes. It was stated, that in solutions containing halogen ions owing to electroreduction of $[Cr/H_2O/_6]^{3+}$, $[Cr/NH_3/_5H_2O]^{3+}$ or $[Cr/NH_3/_5Cl/]^{2+}$ -ions and subsequent oxidation another species of Cr^{III} complex ion is formed, which is reduced at the less negative potential, than Cr^{III} complex ions present in the bulk of solution. The intermediate species causes a new reduction maximum during the second cycle of electrode polarisation. This new secondarily formed Cr^{III}/Cr^{II} system is considerably more reversible /particularly in solutions of bromides/, than the system of primarily present complex ions. It was observed, moreover, that in solutions of sulphates and perchlorates as supporting electrolytes the irreversibility of the process increases. The influence of different factors on the formation of new species was investigated;

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

in particular the relationship between the variation of pH, presence of surface active substances, temperature, change of voltage rate and the appearance of the maximum was studied. The chronovoltamperometric curves recorded oscillographically show the increase of the secondary maximum in consecutive cycles of electrode polarisation, this being related with the steady increase of concentration of new complex species at the electrode surface in the course of electrolysis.

The results are discussed on the basis of Taube's hypothesis of bridged activated complexes.

REFERENCES

1. Kemula W., Kublik Z., Anal. Chim. Acta, 18, 104 /1958/.
2. Kemula W., Rakowska E., Bull. Acad. Polon. Sci., 9, 657 /1961/
3. Kemula W., Rakowska E.; Roczniki Chem. 36, 203 /1962/

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Page Denied

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Abstract

THE INFLUENCE OF MEDIUM AND LIGAND EXCHANGE ON THE ABSORPTION SPECTRA OF THE URANYL ION IN SOLUTIONS

Z. Libuś, St. Minc, Poland

Absorption spectra of the complex $[UO_2/NO_3/_2/TBP/_2]$ in various organic solvents /benzene, cyclohexane, isooctane, n-decane, undecane, n-butyl ether, tri-n-butyl phosphate, carbon tetrachloride, chloroform/ between 370 and 480 mμ were determined. The position of the absorption band and the distribution of intensities among the component vibrational bands in the spectrum of $[UO_2/NO_3/_2/TBP/_2]$ complex when dissolved in different solvents remained practically unaffected, whereas the differences in intensity amounted to several score per cent.

Absorption spectra of $[UO_2/CH_3COO/_3]^-$ complex in water solutions of Li, Na, K, Ca and Ba acetate buffers were determined. No effect of ionic medium on the absorption spectrum of this complex were found.

The stepwise formation of uranyl acetate and uranyl sulphate complexes in water solutions was followed spectrophotometrically. It was found that the first additions of the acetate buffer to a solution of $UO_2/ClO_4/_2$ result in a small and gradual shift of the absorption band of the hydrated uranyl ion toward longer wavelengths, accompanied by an increase of its intensity and blurring of the vibrational structure. Very similar spectral effects were observed on increasing concentration of the sulphate ions in solutions containing UO_2^{++}. Much more pronounced changes of the spectrum were observed at higher concentrations of acetate ions concomitant with the formation of the limiting triacetate complex. These spectral effects could be explained by assuming that within the region of lower concentrations of the anions only the outer-sphere association of acetate or sulphate anions

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

with $[UO_2/H_2O/_6]^{++}$ aquo complex takes place. The exchange of water molecules coordinated by the uranyl ion for anions should be assumed to take place only when the limiting triacetate complex begins to form.

From the observed changes of the spectrum of the UO_2^{++} ion taking place on exchanging its ligands the conclusion was drawn, that the absorption band between 370 and 480 mμ corresponds to electron process localised on the UO_2 group.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

ÜBER DIE RAUMSTRUKTUR DER KOVALENTEN URANYL-KOMPLEXE.

J. Szöke - Hungary

Nach den Arbeiten von Horton /JACS 1956./ Sacconi und Ciampoli /J.Chem.Soc. 1954./ ferner Bullwintel und Noble /JACS 1958./ ist es wahrscheinlich, dass das Uranyl-Ion sechskoordinativ. Im Jahre 1959 /Acta Phys et Chem Szeged/ wurde ein Stereomodell von uns entwickelt um die Raumstruktur der Uranylkomplexe zu erklären. Diesem Modell nach nehmen die Bindungen um dem Uranyl-Ion bei der Spitze eines unregelmässigen Oktaeders Platz. Wir haben mit Hilfe dieses Modells die bisher bekannten Komplex Uranyl-Verbindungen aufbauen können.

In dieser Arbeit wollen wir die Richtigkeit dieses Modells mit spektroskopischen, thermoanalytischen, praeparativen und anderen analytischen Methoden kontrollieren. Unsere Forschungsergebnisse sind zusammenfassend Folgende:

Die Ausbildung der Komplexverbindungen lässt die Thermostabilität der Liganden ändern. Komplexe, die aus flüssigen, oder leicht sublimierbaren Liganden aufgebaut sind, können ein oder zwei Liganden ohne Änderung des verbleibenden Liganden /oder Liganden/ abgeben. In einigen Komplexen zersetzt sich die Struktur der Liganden infolge des Thermoeffektes.

Die symmetrischen Komplexmoleküle absorbieren nur auf dem Gebiet der Uranylabsorption. Bei den asymmetrischen Molekülen meldet sich eine über 500 nm bedeutsame Absorption.

Die aus bidentaten Ligandenaufgebauten, gemischten Komplexe vom Typ /$ML'L''_2$/ oder /$M\,L'L''L'''$/ sind auf dem Wege direkter Synthese nicht herstellbar. Reaktionsfähiger Zwischen-produkte kann man gewinnen durch partielle, thermische Zersetzung, wodurch die indirekte Synthese der obgenannte Komplextypen ermöglicht wird.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Auf Grund der Erfahrungen, die wir bei den Synthesen der gemischten Komplexe gewonnen haben, können wir annehmen, dass die räumliche Kupplungsstätte der Liganden um das Uranyl-Ion bei den Komplex-typen /KM_2l_2/ und /ML_3/ /L = bidentat, l = monodentates Ligand/ verschieden ist.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

ON THE THEORY OF SPECTROSCOPY OF URANYL COMPOUNDS IN SOLUTIONS

A. Bartecki, B. J.Trzebiatowska - Poland

In the course of our extensive researches during the last four years on the basis of literature concerning the problem of molecular spectroscopy of uranyl compounds, we have elaborated a general theory which allows us to understand the principle lines connecting the absorption spectra and chemistry of these compounds in solutions.

This theory may be applied to elucidate the influence of the following parameters:

I/ Kind of anion and its concentrations
II/ Coordination phenomena
III/ Concentration of hydrogen ions
IV/ Solvent effect
V/ Bond type

It was possible to state that:

a/ the absorption spectra of uranyl compounds exhibit a distinct vibrational structure caused by the superposition of uranyl vibrations on the electronic tran sitions,

b/ the principal electronic transition about 20500 cm^{-1} arises from a transition from a level located on oxygen to the empty uranium shell inside uranyl group,

c/ at least one further electronic transition appears in the ultraviolet range and may be assumed as caused by a transition from ligand molecules to uranyl group,

d/ the vibrational structure is best understandable in terms of a unique progression $0'' - v'$ of the totally symmetric vibrations ν_1,

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

e/ this structure is apparently influenced by solvent effects, hydrogen ions and bond type. It was also found that the anion type and the water content in the solvation sphere, exhibit a considerably lesser effect,

f/ the increase of the electrostatic forces between uranyl ion and ligand molecules makes the spectrum less diffuse the reverse being true for cases where there is a great participation of covalency.

g/ bands intensities may be connected in some degree with the stability constants of compounds formed in solutions.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Abstract

STUDIES ON THE ABSORPTION SPECTRA OF THE U^{+3} ION.

J.Drożdżyński and B.Jeżowska-Trzebiatowska - Poland

The absorption spectrum of the U^{+3} ion was examined in anhydrous methyl alcohol and glacial acetic acid, saturated with hydrogen chloride /0.2 to 0.3 M HCl/. The data were recorded in the range 250 mμ - 1000 mμ

The UCl_4 solution was first freed from dissolved oxygen by repeated freezing and evacuation in a special apparatus. This solution was then transferred to a spectrophotometric cell provided with a vacuum stopper and reduced with zinc amalgam /2.4% by weight/ in situ. The measurements were taken after the evolution of hydrogen had stopped, which took place in 1-2 hours. The solution then had a violet-red colour and did not show any change during the experiment. The volumetric estimation of U^{+3} ion, showed that the reduction was complete. The frequencies and extinction coefficient of the absorption bands are tabulated below:

in methyl alcohol

/cm^{-1}/	10204	11236	13513	16525	18348	20000	22222	24900
ε	75,3	166.6	25.6	332	1121	580	480	580
/cm^{-1}/	26250	28090	29850	31800	33150			
ε	705	862	849	640	265			

in glacial acetic acid

/cm^{-1}/	10101	11485	13333	16200	18518	23900	24390	25750
ε	108.7	322.5	43.5	405	1238	1980	2044	2180
/cm^{-1}/	26178	26850	27173	27932	28409	28901	30810	
ε	2220	2190	2249	2290	2285	2325	1038	

Thus the spectrum of violet-red U^{+3} chloro-complexes was obtained for the first time in the range 250 mμ - 1000 mμ

The observed absorption bands correspond to the f^3 transition in the visible and f^2d transition in the ultraviolet region.

IPUW Wrocław z.77/62 A-4 300

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Abstract

LICHTABSORPTIONSEIGENSCHAFTEN UND MAGNETISCHE MOMENTE VON KOMPLEXVERBINDUNGEN DES DREIWERTIGEN TITANS

H.L. Schläfer - Deutsche Demokratische Republik

Die effektiven magnetischen Momente von $[TiA_6]^{3+}$ -Komplexen /A=H_2O, NH_3, $CO/NH_2/_2$, CN^-/ wurden bei den Temperaturen 99,295 und 293°K bestimmt. Die Temperaturabhängigkeit der Suszeptibilität lässt sich nach dem CURIE-WEISSchen Gesetz darstellen, die θ-Werte liegen zwischen 20 und 45°. Die μ_{eff}-Werte bei 293° liegen im Bereich zwischen 1.74 und 1.82 B.M., zeigen also einen geringen Bahnmomentbeitrag.

Mit Hilfe der KOTANI'schen Theorie[1] /Kristallfeld kubischer Symmetrie und Spin-Bahn-Kopplung/ gelingt es nicht die μ_{eff}- Werte und insbesondere deren Temperaturabhängigkeit zu verstehen. Dazu muss dem kubischen Kristallfeld noch eine niedrigsymmetrische /tetragonale bzw. rhombische/ Feldkomponente überlagert werden.

Aus den Absorptionsspektren der Verbindungen, die an Lösungen bzw. an Kristallpulvern /refelxionsspektren/ aufgenommen wurden, folgt ebenfalls, dass der Symmetrie des Ligandenfeldes nicht rein oktaedrisch/O_h/ sein kann. Der /t_{2g} /^2E_g-Zustand ist in zwei Zustände aufgespalten, wobei die Aufspaltung je nach der Art der Liganden A zwischen 2000 und 4600 cm^{-1} liegt.

Die experimentellen Befunde sind mit den Forderungen des JAHN-TELLER-Theores[2] in Übereinstimmung, wonach bei mehratomigen nicht linearen Molekülen Strukturen mit bahnentarteten Elektronenzuständen nicht stabil sind. Durch Symmetrieerniedrigung wird die Bahnentatung aufgehoben. Es wird die Frage diskutiert, ob es sich bei den $[TiA_6]^{3+}$ -Verbindungen um statische Verzerrungen der Oktaederstruktur handelt, oder ob dies für

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

den Titanalaun zutrifft - um einen dynamischen Effekt/3/.

/1/ M.Kotani, J.Phys.Soc. /Japan/ 4, 293 /1949/

/2/ H.A.Jahn u.E.Teller, Proc.Roy.Soc. A161, 220 /1937/
H.A.Jahn, Proc.Roy.Soc. A164, 117 /1938/

/3/ vergl.z.B.T.M.Dunn in Modern Coordination Chemistry Interscience Publ.Inc.New York, London 1960 S. 253

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

SPECTRES DE VIBRATION ET STRUCTURE DE NITRITES COMPLEXES

J.P. Mathieu, France

On a étudié les spectres d'absorption infrarouges et quelques spectres de diffusion des nitrides doubles de métaux alcalins et de M=Ca, Ba, Pb, Cu, Ni, Co, Rh, Ir, Pd, Pt. On examinera les questions suivantes:

1/ Dans les complexes parfaits, les fréquences internes du groupe NO_2 ont des valeurs voisines de celles qu'elles possèdent dans les dérivés nitrés organiques. La fréquence ν_a est très différente de celle de l'ion NO_2^-

2/ On peut distinguer par les spectres de leurs solutions dans H_2O ou D_2O les sels doubles /Ca, Ba, Pb, Cu, Ni/ et les complexes parfaits /Co, Rh, Ir, Pd, Pt/

3/ Classement des vibrations fondamentales des complexes $[M/NO_2/_4]$ et $[M/NO_2/_6]$

4/ Influence de la structure cristalline sur la constitution des spectres.

5/ Considérations sur les nitroammines.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Abstract

DIE BINDUNGSVERHÄLTNISSE DER SEITENERD-METALLIONEN AN EINEM IONENAUSTAUSCHER MIT VERANKERTER IMINODIESSIGSÄURE

R. Hering - Deutsche Demokratische Republik

Während zweiwertige komplexbildende Metallionen mit Iminodiessigsäure-Ionenaustauscherharz /IDE-Harz/ im schwach sauren Gebiet ausschliesslich 1:1-Komplexe bilden und durch Elution mit verdünnter Mineralsäure getrennt werden können, ist dies bei den Seltenerd-Metallionen nicht möglich, da diese verschiedene pH-abhängige Komplexe bilden. Bei einer pH-Änderung von 3 bis 7 konnten für Lanthan- und Ytterbiumionen bisher folgende Komplexbindungsformen ermittelt werden.

$*-[LaY]\,[HY]-*$ bzw. $*-[LaY]^{+} + *-[HY]^{-}$

$\{[*-LaY]_2\,YH-*\}^{+} + NO_3^{-}$ bzw. $*-[LaY]\,[HY]-*$ neben $*-[LaY]\,NO_3$

$*-[LaY\,OH]^{-}$ neben $*-[HY]^{-}$ bzw. $*-[LaY_2]^{-}-*$ neben La^{+++}

$*$ - deutet die Ankerstellen im Harzgerüst an.

Y steht für Iminodiessigsäure.

Zur Untermauerung wurde das Monomere des IDE-Harzes, die Benzyliminodiessigsäure /BILDE/ in Gegenwart von Seltenerd-Ionen untersucht. Die potentiometrisch verfolgten Neutralisationskurven deuten ebenfalls auf die oben angeführten Bindungsverhältnisse.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Page Denied

Next 3 Page(s) In Document Denied

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Abstract

IONOPHORETIC STUDIES OF COMPLEX FORMATION BETWEEN FERRIC AND THIOCYANATE IONS IN AQUEOUS SOLUTIONS

R.Józefowicz, J.Masłowska - Poland

Complex formation in aqueous solutions of ferric and thiocyanate ions was studied by ionophoresis on paper strips. The migration velocity of the complex ions $Fe(SCN)_n^{3-n}$ was determined at various SCN^- concentrations. The concentrations SCN^- limits were found corresponding to the predomination of the separate complex in solution. The partition of total Fe /III/ in the ionopherograms among the various ionic species was determined photometrically and hence approximate values of instability constants of the individual complexes were calculated.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

THE DETERMINATION OF THE POLISUBSTITUTED COMPLEXES BY MEANS OF THE POTENTIOMETRIC SUFRACE METHOD

J.Wojtczak, A.Swinarski - Poland

Lefebvres potentiometric sufface method of the determination of complexes was developed and adapted to the investigation of bisubstituted complexes.

As a base of calculation the change of the potentiometric sufrace was taken. The change was obtained during the decomposition of simple complex with the acid. The anion of that acid should be the component of polisubstituted complex. This anion forms simple complexes more stable than the addend of the initial simple complex.

The changes of the potentiometric sufrace obtained in this manner were compared with the changes that appear during the titration of initial simple complex with an acid that did not contain the complexometric components.

In the parallel sets the bisubstituted complex already formed was titrated with an acid which was not able to form complexes. Adapting the base equations of Lefebvre's method to the changed experimental conditions it is possible to calculate the stability constans of polisubstituted complexes.

The values obtained are between the values of the stability constans of simple complexes. This is in agreement with theoretical predictions.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

THE INFLUENCE OF THE COMPONENT ELECTRONEGATIVITIES ON THE VALUE OF INSTABILITY CONSTANT OF COMPLEX COMPOUNDS

A. Łodzińska - Poland

This paper presents the relation between the pK value of halogens complexes with different cations and the electronegativity of halogens. It has been established that pK value is a linear function of the halogens. If the instability constants of two halogen complexes are known, the pK value for other halogen complexes with the same coordination number may be determined.

Besides, it has been stated that the stability of halogen complexes with predominated covalent bound increases linearly with the decreasing of the electronegativity of coordinated halogen. For the compounds with predominated electrostatic bound the stability increases linearly with the increasing of the electronegativity of halogens.

Complexes with the difference of electronegativity between cation and fluoride is greater than 2,5 show an increase of stability together with the increase of halogen electronegativity. If that difference is lower than 2,5 the stability of the complex varies in the opposite direction.

On the diagrams No 1-4 we have shown that the pK values as a function of electronegativity of the halogen are linear. The slope of the line /pK/ $El_{halog.}$/ is characteristic for the properties of the cation. On the base of changes of the slope the parameters which influence the stability of the complexes with a predominated electrostatic or covalent bound have been determinated.

Transiting from complexes of a lower to a higher coordination number parameters have been determined which change the tangent value.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Abstract

REFRACTOMETRIC METHOD OF DETERMINATION THE INSTABILITY CONSTANT OF COMPLEX COMPOUNDS

W.Brandel, A.Swinarski - Poland

The instability constant of some complex compounds was calculated on the base of Spacu, Popper and Yermolenko's refractometric method in connection with Job's method for determination the coördination number. It has been assumed, that the maximal deviation from the additivity of the refraction index, depends on the stability of the complex compound. On that assumption an empirical equation is proposed :

$$K = \frac{\Delta n_2 (\Delta n_2 - \Delta n_1)^2}{\Delta n_1^2 C_o} (p + q)$$

Δn_2 - is the theoretical, maximal deviation from the additivity, the value of which is propotional to the general concentration of the complex compound,

Δn_1 - is the experimental deviation from the additivity, proportional to the concentration of the undissociated compound,

p and q - are the volumes of the mixed solutions, equal with the mole quantities /p+q = const./,

C_0 - is the general concentration of the metal ion or the ligand.

This equation can be only used for instable compounds.

Another equation is proposed for the calculation of the pK on the base of the proportionality of the surface to the stability of the complex compound.

$$pK = \frac{S \cdot 10^2}{\left(\frac{p-q}{10}\right)^2 \cdot C_o^2}$$

S - is the surface between the curve of the deviation from the additivity of the refraction index and the axe of concentrations.

The last equations is more universal. Both equations were verified:

a/ on the zinc, cadmium and lead complexes with acetic acid and

b/ on iron /III/, and aluminium complexes with fluorides.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

CONDITIONS OF FORMATION AND STABILITY OF POLYSUBSTITUTE COMPLEXES

A. Swinarski - Poland

The formation constants of complexes forming successively in water characterize the disubstitute complex compounds, one of whose ligands is water. It has been found that for a large number of electrostatic bond complexes there is a linear correlation between their successive formation constant values and their coordination number. If only two of the successive formation constant values are known, the formation constant value for the initial aquo-complex of a given central ion may be found by extrapolation. Only a few values determined by experimental methods coincide well with the results obtained by this graphic method.

Polycomponent complex compounds form by displacement of the ligand forming less stable complexes by another one forming more stable complexes. In a system containing two components forming complexes of various stability with the central ion a stable disubstitute complex can not be obtained unless such a concentration of the components in the reaction medium is maintained that the ratio of their concentrations should be inversely proportional to the ratio of their constants of simple complexes formation.

Studies on chloride complexes of Fe^{3+} in water indicate that the failure to obtain a coordination number higher than n= 4 in compounds of the $/Fe(H_2O)_{6-n}Cl_n/^{3-n}$ type in a number of works known from literature is due to inadequate ratio of H_2O to Cl^- in the medium.

This also probably accounts for the fact known from earlier observations that a complex compound passing from the solution into a solid phase shows a higher coordination number as a solid than in the solution.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Abstract

STUDIES ON THE POLYNUCLEAR COMPLEXES. THE HYDROLYSIS OF V^{3+} ION IN NaCl MEDIUM

L. Pajdowski - Poland

The hydrolysis of V^{3+} ion has been hitherto studied by Meites[1/] /1953/ and Pajdowski[2/] /1959/ and the existence of two complexes: VOH^{2+} and $V/OH/_2^+$ in very diluted solutions was established. It is possible however, that in the more concentrated solutions of metal salt new complexes appear, whose concentrations at low B are so small, that they would not be identified. The present investigation was undertaken in an effort to obtain more information on this point.

The experiments were carried out as potentiometric titrations at 20°C in 3 M and 1 M NaCl as high salt-back ground with a calibrated glass electrode. Assuming the activity factors to be constant[3/] the emf of the cell can be written:

$$E = E_g^0 + 58.2 \log h + E_j$$

In all experiments B /metal salt concentration/ and Cl^- were kept constant and H varied by the addition of equal volumes of $NaHCO_3$ and B M vanadium /III/ solutions in the right medium. With E_g^0 and E_j known from the acid titrations, log h, the analytical hydrogen ion concentration H and the average number of OH^- groups bound per vanadium /III/ cation Z can be calculated.

Since the curves $Z/\log h/_B$ for different values of B in the investigated metal concentration range /0.001 M-0.102 M/ do not coinside, at least one polynuclear hydroxyl vanadium /III/ complex must be formed. The curves for highest titrations: 0.102 M, 0.050 and 0.0306 M are practically parallel and show agreement with the theoretical Z/log h/ curve for $V_2/OH/_2^{4+}$:

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

$$X_{22} = \log/1-Z/-1/2 \log Z = \log h - 1/2 \log/2 \beta_{22} B/$$

The data have been recalculated and plotted in the form of normalised variables y/x/ with x = log B-2 log h and y=Z/2. From "direct analysis"[4/] a straight line of slope: dlog g/dlog u = 1.0 was obtained, where

$$\log u = x - y \log e - \int^{x} y dx \quad \text{and}$$
$$\log/1+g/ = -\int^{x} y dx + \log/1-y/ + y \log e$$

This show that only one polynuclear complex: $V_2/OH/_2^{4+}$ in studied range is formed.

For lower values of B deviations appear from core-links mechanism[4/] which should be due to mononuclear VOH^{2+} and $V/OH/_2^{+}$ species. From the position of "best fit" between the normalised curves Z/x/ and the experimental curvesZ/log h/$_B$ the numerical values of the preliminary equilibrium constants β_{11} and β_{22} were obtained. Assuming that no serious error is introduced by neglecting $V/OH/_2^{+}$ species the better values of equilibrium constants:

$\log \beta_{11} = -3.15 \pm 0.05$ $\log \beta_{22} = -4.1 \pm 0.1$ /in 3 M NaCl/

$\log \beta_{11} = -2.87 \pm 0.05$ $\log \beta_{22} = -3.9 \pm 0.1$ /in 8 M NaCl/

were obtained by using the equation:

$$Zh^2 - \beta_{11} /1-Z/h - 2B \beta_{22} /1-Z/^2 = 0$$

From the given data it seems that β_{11} and β_{22} are affected by changes in Cl^- /and perhaps by ionic strength/ and this would imply that in the more concentrated NaCl solutions at least one chloro complex of vanadium /III/ is formed.

The dimerisation constant of the VOH^{2+} ion is considerably lower than the dimerisation constant of similar iron /III/ species:

$\log K_d$ VOH^{2+} = $\log / \beta_{22}/\beta_{11}^2 /$ = 1.8

$\log K_d$ $FeOH^{2+}$ = - " - = 3.2

The calculations of equilibrium constant β_{21} for the reaction:

$$V^{3+} + 2H_2O \rightleftharpoons V/OH/_2^{+} + 2 H^{+}$$

and the refinement of β_{11} and β_{22} values are continuing.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

1/ L. Meites, J.Am.Chem. Soc., 75 /1953/ 6059
2/ L. Pajdowski, Komunikaty, VI Jubil.Zjazd P.T.Chem. Warszawa, 56
3/ G. Biedermann, L.G. Sillen, Arkiv Kemi, 2 /1953/ 425
4/ L.G. Sillen, Acta Chem.Scand., 8 /1954/ 318

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

COMPLEXES OF CHROMIUM /III/ IONS WITH DL-alpha-ALANINE

J. Starosta, L.Pajdowski and B.Jeżowska-Trzebiatowska-Poland

The system chromium /III/ - alanine was spectrophotometrically investigated in the acid medium. Reaction between chromium /III/ and alamine was obtained by heating the mixtures up to 100°C. The existence of complexes $[Cr/AnH/_n/H_2O/_{6-n}]^{+3}$ /where n = 2 - 6/ was proved by examining a series of isomolar solutions /Job's series/ with total concentrations equal to 0,062, 0,124 and 0,248 M. The existence of complex $[Cr/AnH//H_2O/_5]^{+3}$ has been demonstrated on the basis of Bjerrum's formation curve. It was shown that in the system Cr^{+3} - AnH - H_2O several complexes are formed, which exist in a state of equilibrium. To determine the stability constans of these complexes a few series of solutions of identical chromium /III/ concentration and incressing amount of alanine, were propared.

Chromium /III/ concentration in these series was maintained in the range of $5,15.10^{-3}$ - $1,2.10^{-2}$ M.

The absorption measurements were carried out at the wavelengths 520, 545 and 560 m. From the series of "corresponding solutions" the Bjerrum's formation curve was ostimated and the stability constants $\beta_1 = 5,62,10^3$, $\beta_2 = 2,51.10^6$, $\beta_3 = 3,43.10^8$, $\beta_4 = 1,94.10^{10}$, $\beta_5 = 5,23.10^{11}$ and $\beta_6 = 7,54.10^{12}$ of the six complexes were calculated. The measurements were made at 19 ± 0,5°C and ionic strength $\mu = 1,0$ controlled by the admixture of $NaClO_4$ solutions.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

ÜBER EINIGE KOMPLEXEVERBINDUNGEN IN LÖSUNGEN

A. Okáč - ČSSR

Manche in der analytischen Chemie schon lange verwendete Komplexreaktionen sind noch nicht eindeutig erklärt. In den roten oxydierten Lösungen von Ni/II/-dimethylglyoxim haben wir schon früher durch physikalisch chemische Messungen die Hauptreaktion

$$\left[Ni^{II}D_3\right]^{4-} \rightleftharpoons \left[Ni^{IV}D_3\right]^{2-} + 2\,e$$

erfasst. Nun hat es uns gelungen die Produkte $Na\left[NiD_3\right]$ und $K_2\left[NiD_3\right]$ im kristallinen Zustand zu isolieren und ihre Identität mit denen in roten oxydierten Lösungen durch Analyse, Eigenschaften und potentiometrische und magnetische Messungen zu bestätigen.

Durch Reduktion der roten Lösungen in stark alkalischem Milieu in inerter Atmosphäre wurden rückgängig die gelben Komplexe $\left[NiD_2\right]^{2-}$, $\left[NiD/OH/\right]^{-}$ und $\left[NiD_3\right]^{4-}$ potentiometrisch, photometrisch und magnetochemisch vervolgt, die die Zwischenreaktionen bei Oxydation des Čugajewschen Salzes erklären. Dadurch konnte das Reaktionmechanismus dieser Oxydation ergänzt werden. Die bisherige Verschiedenheit der Ansichten auf die Zusammensetzung des oxydierten Čugajewschen Ni-Salzes wurde dadurch beseitigt. Die Ursache verschiedener Meinungen liegt nicht nur in komlizierenden Nebenreaktionen, sondern auch darin, dass die Autoren in ziemlich stark alkalischem Milieu die Ionen DH^{-} und nicht die richtigen Ionen D^{2-} voraussetzen.

In nicht wässerigen Lösungen entstehen durch Einwirken von Halogenen andere Komplexe, von denen $Ni/DH/_2Br_2$, $Ni/BH/_2$ Br und $Ni/BH/_2$ J isoliert wurden. Diese zweite Reihe von Ni-Komplexen besitzt ganz andere Eigenschaften. Sie sind im Wasser unbeständig, ihre chemische und magnetische

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Eigenschaften sind verschieden von Verbindungen die durch verschiedene Oxydationsmittel in wässeriger Lösung entstehen.

Bei der alten Reaktion des Formaldoxims mit Metallionen haben wir die Reaktionen der Ni/II/⁻, Mn/II/⁻ und Co/II/⁻ Salzen polarographisch, potentiometrisch, konduktometrisch und magnetochemisch verfolgt und die Ladung der Komplexionen elektrophoretisch und mit Hilfe von Ionexen untersucht. Die komplexierende, aktive Form des Formaldoxims, bildet die farbigen Komplexe $[Ni^{IV}R_6]^{2-}$, $[Mn^{IV}R_6]^{2-}$ und $[Co^{III}R_6]^{3-}$, die auch in kristallinem Zustand isoliert und identifiziert wurden. Bei dieser Reihe von Komplexsalzen, die gleichzeitig in Warschau von Minczewski und Marczenko mit übereinstimmenden Resultaten studiert wurden, ist die Struktur der aktiven Form des Formaldoxims noch nicht erklärt worden. Wir sind der Ansicht, dass es sich um ein trimeres Formaldoxim handeln könnte, das den oben angeführten Ni^{IV}-Dioximaten ähnliche Komplexe von der Zusammensetzung $[Me^{I}(oxim)_3]^{2-}$ bildet.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Abstract

THE OXYGEN CARRYING BY MANGANESE /II/ PHTALOCYANINE

[illegible] and B.Jeżowska-Trzebiatowska - Poland

Manganese /II/ Phtalocyanine in pyridine solution can combine reversibly with molecular oxygen, forming a blue intermediate compound. It loses this ability after prolonged heating in an oxygen atmosphere.

Earlier investigations showed that the uptake of oxygen is one molecule per two molecules of manganese phtalocyanine. From the analysis of solid, infrared absorption spectra and from polarography of the blue complex in pyridine the following formula has been suggested: PcMnO.py. These investigations do not fully explain the reversible oxygen bonding by manganese /II/ phtalocyanine.

In the present investigations we have obtained manganese phtalocyanine in the reaction of phtalonitryl with manganese /II/ acetate in undecyl alcohol. The blue oxidation product forming purple crystals in the solid has been isolated from the pyridine solution of manganese phtalocyanine, oxidised by the molecular oxygen, and diluting it with water. According to analysis and magnetic measurements the obtained purple product is a binuclear complex. Magnetic moment μ_{eff}=1,79 BM/1Mn corresponds to the electronic structure $d^2 s^2 d^{1} p^2 sr^3$. The complex empirical formula is:

$$\left[C_{32}H_{16}N_8MnO_2\ MnN_8H_{16}C_{32}\ .2py\right]\ .\ 4H_2O$$

The purple compound heated in air at 200°C changes into manganese /II/ phtalocyanine.

Polarographic investigations of the blue complex in pyridine containing 0,05 lithium chloride show only one reduction step, with the half-wave potential at -0,9v corresponding to the second reduction wave of oxygen.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

The absorption spectra analysis shows that one characteristic band dominates in the three related complexes: in the manganese phtalocyanine at $\lambda = 725$ mμ, in the blue complex at $\lambda = 620$ mμ and in the final green oxidation product at $\lambda = 670$ mμ. The above band probably corresponds to the electronic transitions from phtalocyanine to manganese. The changes in the band position are caused either by oxygen coordination, or by the alteration of manganese oxidation state in the case of the final irreversibly oxidized product. Inactive green complex has two additional bands: at $\lambda = 825$ mμ and $\lambda = 925$ mμ, caused by the electronic structure change from $d^2e^2d^1p^2sp^3$ to $d^1d^1e^1p^2sp^3$.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

THE URANIUM /VI/ COMPLEXES FORMED DURING THE SYNERGIC EXTRACTION OF URANYL SULPHATE BY SOLUTIONS OF AMINES AND ALKYLPHOSPHORIC ACIDS

C.Deptuła, S.Minc - Poland

The extraction of uranium /VI/ from sulphuric acid solutions by mixtures of tri-n-octylamine /TnOA/ and alkylphosphoric compounds /neutral and acid alkylphorphoric esters/ or tri-n-octylamine with tri-n-octylphosphine oxide in benzene and carbontetrachloride, has been investigated.

It was found that during this extraction by a mixture of TnOA and the alkylphosphoric acids [mono- /H_2MBP/ di-n-butylphorphoric /HDBP/ - mono-2,6,8, tri-methyl-nonyl-4-phosphoric -/H_2DDPA/, di- 2-ethyl-hexylphosphoric /HD_2EHPA/] synergic or antagonistic phenomena appear to take place, depending on the concentration of sulphuric acid. The addition of the neutral phosphoric compounds [tri-n-butylphosphate (TBP) or tri-n-octyl-phosphine oxide /TOPO/] does not influence greatly the extent of the uranium extraction.

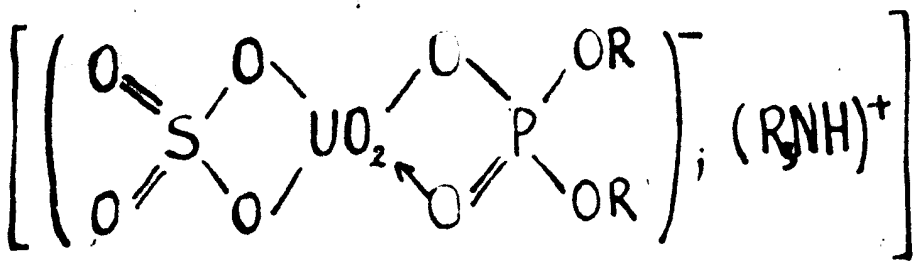
From the relation between the extraction coefficient /E^o_v/ and the concentration of one of the extractants, while the concentration of the other is maintained constant, it was found the in the complex extracted one mole of the uranium associates with one mole of alkylphosphoric acid and with one mole of TnOA.

Using the Fischer's method it was found that the organic phase contains no water.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

On the basis of the data obtained so far the authors assume that the complex extracted has the following structure:



To get more information on this complex an infrared study is now in progress.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

WYZNACZANIE WZGLEDNEJ TRWAŁOŚCI KOMPLEKSÓW CYNKU, KADMU, I NIKLU Z KWASEM WINOWYM METODA ELEKTROCHROMATOGRAFICZNA

B. Hurnik - Poland

W referowanej pracy wykorzystano metodę elektrochromatograficzną do wyznaczania względnej trwałości związków kompleksowych. Przedmiotem badania były kompleksy winianowe cynku, kadmu i niklu w środowisku słabo kwaśnym /pH 3 - 6/. Zarówno skład jak i stałe nietrwałości wymienionych kompleksów mają różne wartości liczbowe u różnych autorów. Ponieważ elektrochromatograficznie można ustalić warunki, w których w roztworze istnieje jon dodatni, w których jon ujemny a kiedy cząstka obojętna, można więc w zależności od warunków doświadczenia ustalić, kiedy kwas winowy z badanymi kationami tworzy kompleks o składzie $[Me/Win/]$ a kiedy o składzie $[Me/Win/_2]^{--}$.

Doświadczenia wykonano przy napięciu 200 V i średnim czasie t = 2 godz. Zostały one wykonane w seriach. W ramach jednej serii doświadczeń pozostawał stały stosunek kwasu winowego do jonu metalu a zmieniało się jedynie pH roztworu. Początkowo przy niskim pH /3,0 - 3,5/ jon badanego metalu wędrował jako kation. Następnie przy wyższym pH, pozostawał w punkcie startowym, aż przy jeszcze wyższym pH, wędrował w postaci wyraźnej plamy w kierunku elektrody dodatniej, był więc anionem. Na tej podstawie wyciągnięto wniosek, że w środowisku słabo kwaśnym Zn^{++}, Cd^{++} i Ni^{++} tworzą z kwasem winowym zarówno kompleks obojętny jak i ujemny w zależności od pH roztworu i od stężenia kwasu winowego. Graficznie wyznaczono dokładną wartość pH, przy której w roztworze istnieje w 100% kompleks obojętny typu $[Me/Win/]$. Ponieważ przy wzroście pH w roztworze tworzy się kompleks typu $[Me/Win/_2]^{=}$ więc

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

wg. założeń teoretycznych Bjerruma dla $\bar{n} = 1$, to jest, gdy kompleks utworzony jest w 50% zachodzą równości:

$$k = \frac{1}{A} \qquad K = /A/^2$$

gdzie k - średnia stała tworzenia
K - stała nietrwałości
A - stężenie wolnego ligandu
$\bar{n}$ - średnia liczba koordynacyjna

Znając wartość pH, przy którym $\bar{n} = 1$ t.zn. gdy w roztworze badanym istnieje cząstka obojętna, oraz znając stężenie kwasu winowego wziętego do doświadczenia i jego stałe dysocjacji elektrolitycznej, można wyliczyć stężenie wolnego jonu Win^{--}.
Dla kompleksów cynku, kadmu i niklu z kwasem winowym otrzymano następujące wartości liczbowe:

Win^{--}	$= 1,41.10^{-2}$	g-jonu	dla	Zn
Win^{--}	$= 1,89.10^{-2}$	"	"	Ni
Win^{--}	$= 3,89.10^{-2}$	"	"	Cd

Można na tej podstawie uważać że w podobny sposób zmieniają się stałe nietrwałości wymienionych kompleksów:

$$K_{Zn} < K_{Ni} < K_{Cd}$$

Stąd wniosek, że trwałość wymienionych kompleksów maleje w kierunku od cynku do kadmu /zgodnie z literaturą/.
Na podstawie uzyskanych wyników wnioskuje się o przydatności elektrochromatografii do wyznaczania względnej trwałości niektórych typów kompleksów.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

THE STRUCTURE AND PROPERTIES OF Re - O - Re NUCLEUS IN BINUCLEAR COMPLEXES

B.Jeżowska-Trzebiatowska, W.Wojciechowski
Poland

Binuclear Re IV complexes are diamagnetic. This was first discovered by B.Jeżowska-Trzebiatowska and S. Wajda in the instance of μ-oxochlororhenate $K_4Re_2OCl_{10}$. Diamagnetism of that kind of complex is undoubtedly connected with the properties of Me - O - Me nucleus.

In the present work the length of Re - O - Re bond has been calculated on the basis of the theory of covalent bonds. This length equals to 3,5 A, while the sum of ionic radii amounts to 4,12 A.

So great a contraction of Re - O - Re bond may be caused by the interaction of 2 rhenium atoms through oxygen atom. Therefore the theory of molecular orbitals has been applied to this nucleus arriving at the following orbital scheme:

$$E_g^b \quad E_u \quad A_{1g} \quad A_{2u} \quad E_g^a$$

It explains the magnetic properties of binuclear complexes of rhenium IV, ruthenium IV, chromium III et c.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

DIPOLE MOMENTS OF NITRATES OF CERTAIN HEAVY ELEMENTS COMPLEXES WITH TRIBUTYLPHOSPHATE

J.Kurwic, J.Michalczyk - Poland

Tributylphosphate /TBP/ extraction of uranyl nitrate is of great teoretical and practical importance. The dipole moment value of complexes formed by uranyl nitrate with TBP has a decisive influence on the process. In this communication some investigations will be presented, whose purpose is to evaluate the dipole moments of these complexes. The main difficulties in the achievment of this task consisted in : 1° - the difficulty to obtain anhydrous solutions of $UO_2/NO_3/_2$ in TBP; 2° - the impossibility of separation of different hypotetical complexes that seem to be formed in solutions.

Diluted solutions of TBP in CCl_4 have been prepared and their dielectric constant / ε /, density /d/ and refraction index /n/ at 20°C have been measured. On the basis of experimental results the dipole moment of the molecule TBP was evaluated by extrapolation /3,24 D/.

A method has been elaborated to dehydrate the $UO_2/NO_3/_2$ solutions in TBP with uranyl oxide without to introduce any foreign materials. The concentration of uranium in the saturated solution of $UO_2/NO_3/_2$ in TBP, which was dehydrated in this way, was measured spectrophotometricaly at 20°C. The mol fraction of $UO_2/NO_3/_2$ was found to be 0,4260. The water content in the solution determinated by K.Fischer's method was 0,19 % by weight.

To a sample of the solution the TBP was added and by dissolving of this system in different quantities of benzene we prepared a series of solutions in benzene with constant ratio of $UO_2/NO_3/_2$ to TBP content.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

ε ,d and n have been determined for every solution investigated. On the basis of these results, the specific polarisation of orientation of the system in the infinite dilution in benzene has been calculated by extrapolation.

Assuming that the whole $UO_2/NO_3/_2$ present in solution forms the complex $UO_2/NO_3/_2.2TBP$, we have calculated the contents of free TBP. Assuming the additivity of the polarisation of orientation of the mixture related to following constituents : TBP, water and the complex investigated we evaluated 3,22 D as a value of the dipole moment of this complex.

The $UO_2/NO_3/_2$ mol fraction in satured solution in TBP is higher than 0,33 - which is the value corresponding to pure $UO_2/NO_3/_2.2TBP$ complex. As the existence of free $UO_2/NO_3/_2$ in this solution is rather not probable,so we tried to assume an existence of still another complex, namely $UO_2/NO_3/_2.TBP$. If this is the case, the system consists of the mixture of both complexes and of free TBP /and some water/. Different quantities of TBP were added to the samples of this solution and the systems obtained in this way were dissolved in different quantities of benzene. Then ε , d and n have been measured. Dipole moments of both complexes : $UO_2/NO_3/_2.TBP$ /2,98D/ and $UO_2/NO_3/_2.2TBP$/3,42D/, have been calculated by double extrapolation method.

The possibility of formation of greater complexes:$2UO_2/NO_3/_2.3TBP$ and $3UO_2/NO_3/_2.4TBP$ seems to be more probable. Such a hypotesis was confirmed by the results of our investigations which consisted on the criometric depression of the freezing point of benzene when a saturated $UO_2/NO_3/_2$ solution in TBP was dissolved in it. Taking into account the water contents,we received a value of 948,9 as the mean molecular weight of saturated anhydrous $UO_2/NO_3/_2$ solutions in TBP, while the molecular weight of $UO_2/NO_3/_2.2TBP$ complex is 926,7.

Similar investigations of solutions of the system $Th/NO_3/_4$-TBP in CCl_4 led us to evaluate 4.3 D as the dipole moment of $Th/NO_3/_4.2TBP$.

From our experiments in the system: $La/NO_3/_3$ - TBP - CCl_4 the value of the dipole moment 6,7 was determined for : $La/NO_3/_3.3TBP$.

Now we are investigating zirconium nitrate complexes with TBP.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

SPECTROPHOTOMETRIC STUDY OF THE REACTION BETWEEN CUPRIC ION AND NICOTINIC ACID HYDRAZIDE /NAH/ AND ISOPROPYLIDENEHYDRAZIDE NICOTINIC ACID /INA/

S. Zommer, T. Lipiec - Poland

Structure of molecules of NAH and INA indicated the presence of free unshared electron pairs by oxygen and nitrogen atoms suggest that it is possible to form a coloured complex. Two tautomeric forms of NAH and INA are possible and under this condition of investigation the enol structure is active.

Aqueous solution of NAH with Cu^{2+} ions is green or blue depending upon the concentration of $Cu/NO_3/_2$ and NAH. The blue color, turned after some time, in green. Absorption of aqueous solution did not change during about 6 h, subsequently become turbid and produced brown precipitate.

INA with cupric ion give immediately in every condition green complex stable for over 12 h. Presence of $-CH_3$ group and second double bond stabilizes probable the complex with cupric ions.

Analysis of absorption curves $A = f/\lambda/$, take into account differential curve, indicated the formation of one complex with absorption maxima at $\lambda = 680-720$ mμ. The composition of complex was investigated by the method of continuous variation /Job/ and spectrophotometric titration. The component ratio is equal to 1:2

$$2\ RH + Cu^{2+} \longrightarrow R_2Cu + 2\ H^+$$

Influence of pH on the absorbance of the complex is large; it increases with the growth of pH until it forms a precipitate of $Cu/OH/_2$. The stability of this complex has been calculated and the value of $K_c \approx 1{,}64.10^{-5}$. The sensitivity of the reaction is 13 μg Cu^{2+}/ml.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Ions Fe^{3+} and VO_3^- interfere.
The complex was found to obey Beer's law.
The spetrophotometric measurements have been done using Coleman-Junior spectrophotometer type 14.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

ON THE FORMATION OF TETRAHEDRAL COBALT /II/ COMPLEXES IN SOLUTIONS

W. Libuś - Poland

Among other divalent transition metal ions cobalt /II/ shows the highest tendency to the formation of tetrahedral complexes. Exceptionly characteristic spectral effects in the visible absorption spectra accompanying the formation of succesive tetrahedral complexes of cobalt /II/ make it especially suitable for a study of factors controlling the symmetry of complexes in solution.

Basing on spectral changes observed in sets of absorption curves corresponding to varying ratio of the ligand in question to cobalt /II/ concentration, in some cases supported by other measurements, the formulas of successive tetrahedral complexes were deduced. In addition isosbestic points observed in these sets of absprption curves enabled us to compute the concentrations and thus to construct the diagrams of formation of individual complexes.

The main results obtained in these investigations as regards the composition of complexes formed in various systems and various solvents are summarised in the tables below.

	Solvent	Solutions of CoX_2	Solutions of CoX_2+MeX
		Co/II/ + Cl^-	
1	water	octahedral complexes	o.c. , $[CoCl_4]^{2-}$
2	ethyl alcohol	$[CoCl_2L_2]$ + o.c.	$[CoCl_3L]^-$, $[CoCl]^{2-}$
3	isopropyl alc.	$[CoCl_2L_2]$	$[CoCl_3L]^-$, $[CoCl_4]^{2-}$
4	acetonitrile	$[CoCl_2L_2]$ + $[CoL_6][CoCl_3L]_2$	$[CoCl_3L]^-$, $[CoCl_4]^{2-}$

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

5	water	octahedral complexes	O.C. , $[CoBr_4]^{2-}$
6	ethyl alcohol	$[CoBr_2L_2]$ O.C.	$[CoBr_3L]^-$, $[CoBr_4]^{2-}$
7	isopropyl alc.	$[CoBr_2L_2]$	$[CoBr_3L]^-$, $[CoBr_4]^{2-}$

Co /II/ + I^-

8	water	octahedral complexes	O.C. , $[CoI_4]^{2-}$
9	ethyl alcohol	$[CoI_2L_2]$	$[CoI_3L]^-$, $[CoI_4]^{2-}$

Co /II/ + NCS^-

10	pyridine	Co $/NCS/_2L_4$	octahedral complexes
11	water	octahedral complexes	o.c. , $[Co/NCS/_4]^{2-}$
12	methyl alc.	octahedral complexes	o.c. , $[Co/NCS/_4]^{2-}$
13	acetonitrile	$[Co/NCS/L_5]^+$ $[Co/NCS/_3L]^-$	$[Co/NCS/_3L]^-$, $[Co/NCS/_4]^{2-}$

X = Cl^-, Br^- , I^- , NCS^- respectively
L = solvent molecule
Me= Li^+ or R_4N^+

In some instances in the solutions of cobalt /II/ salts in organic solvents /cases 4 and 13/ the coordination disproportionation was shown to take place.

Basing on the experimental material obtained the properties of the complex forming agent and that of the solvent responsible for the symmetry of cobalt /II/ complexes in solution are discussed.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Page Denied

Next 1 Page(s) In Document Denied

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

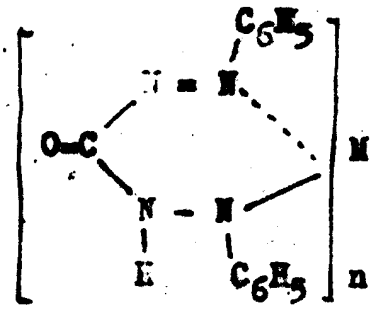
Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

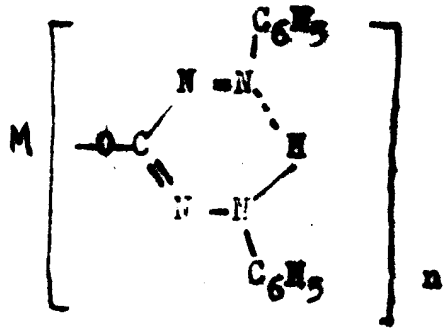
STRUCTURE INVESTIGATION OF METAL-DIPHENYLCARBAZONE COMPLEXES BY INFRARED SPECTROSCOPY

W. Kemula and K. Jankowski

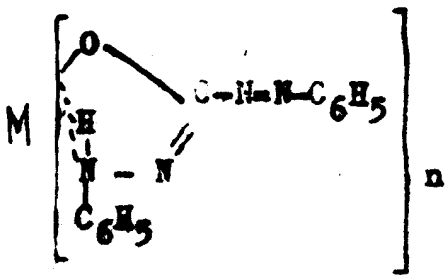
The aim of the present paper was to investigate the structure of diphenylcarbazone /DCO/ complexes with mercury, copper, nickel, zinc and cobalt by infrared spectroscopy. The structure of these, analytically important, complexes of diphenylcarbazone as well as of dithizone /diphenylthiocarbazone/ was until now not definitely elucidated. For diphenylthiocarbazone complexes four different formulae were until now proposed:



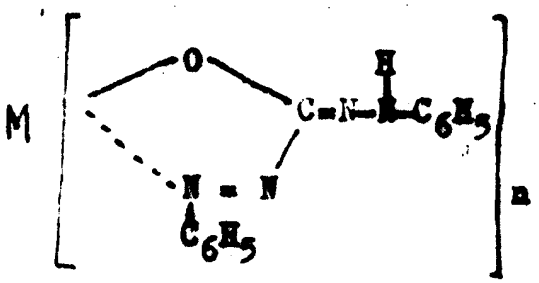
I - Fischer's



II - Irving's



III - Geiger's



IV - Harding's

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

We can assume that for DCO complexes similar structures are possible. It was found that for Cu, Zn, Ni and Co complexes of DCO the structure II can be attributed, taking into account the following facts:

1/ in the IR spectrum of these complexes disappears the stretching frequency of C=O observed in the DCO spectrum, and a new intense and broad band in the region of about 1200 cm^{-1} is recorded, corresponding to v/C-O/;

2/ in the spectra of complexes an intense band in the region of about 1550 cm^{-1} is observed, which corresponds to the C=N bond in the chelate ring;

3/ the stretching frequency of the group N-H in complexes is decreased from 52 to 90 cm^{-1}, in comparison with the shortest band v/N-H/ in the DCO spectrum, while the intensity of this band is very small. This indicates the presence of the intramolecular hydrogen bond N-H....N. The stretching frequency of N-H in the spectra of complexes increases with the falling stability of the complexes in the series Cu > Ni > Zn > Co;

4/ the spectra of above mentioned metal complexes are similar to the spectrum of the sodium salt of DCO.

The mercury complex has a different spectrum. Thus, the formula IV can be attributed to this compound, because:

1/ in the spectrum of the complex the stretching frequency of C=O disappears, and a broad band v/C-O/ is observed, indicating linking of the metal through oxygen;

2/ in the spectrum, the band 1644 cm^{-1} indicates that the C=N bond does not participate in formation of chelate ring;

3/ the stretching frequency of N-H equals in the complex spectrum the stretching frequency of N-H in DCO spectrum in dilute chloroform solution. Neither hydrogen bond nor coordination bond between metal and nitrogen of the imino group is therefore present in the molecule of the mercury complex, indicating the invalidity of formulae II and III.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

THE SZILARD-CHALMERS EFFECT IN SOME COMPLEXES

J. MIKUlski, T. Senkowski and I. Streński - Poland

Irradiation of stable nuclides by thermal neutrons leads, in the reaction /n, γ /, to the formation of radioisotopes which in some cases may be separated from the target by the Szilard-Chalmers method[1/].

A radium-berylium source in a paraffin wax block with an activity of 0,5 curie was used for the irradiation by thermal neutrons of potassium hexacyanomanganate and potassium pentacyanonitrosylmanganate with the purpose of determining the enrichment coefficient /C_e/ and the retention coefficient /C_r/.

The target substances in crystalline form or in solution, prepared by the method of Hieber et al.[2/], were irradiated during five periods of half-life of the radionuclide ^{56}Mn /$T_{1/2}$ = 2,6 h./ i. e. 13 hours[3/]. The activity /A_1/ was measured using a VAZ-410 type G-M counter.

To the irradiated solution of $K_3/Mn/CN/_5NO/$ a diluted solution of $MnSO_4$ as a carrier was added and the atoms of radiomanganese recoiled from the complex of pentacyanonitrosylmanganate were precipitated by methylated hexamethylenediamine. The precipitate was filtered off and the activities of the filtrate /A_2/ and of the enriched preparation /A_3/ were determined.

From the equation:

$$C_r = \frac{A_2 \cdot 100}{A_1}$$

the retention coefficient was calculated. It amounted to 25 $\pm$ 1 per cent.

The enrichment coefficient C_e characterised by the ratio of the relative concentrations of radionuclide ^{56}Mn in the

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

enriched preparation and in the target was calculated from the equation:

$$C_e = \frac{100 - C_r}{100} \cdot \frac{m_1}{m_2},$$

where m_1 denotes the mass of manganese in the target and m_2 the mass of enriched preparation.

A single irradiation of 10 g of $K_3/Mn/CN/_5NO/$, containing 1,65 g of manganese, to which 1,2 mg of manganese as a carrier was introduced, led to an enrichment of the range of 10^3. A similar enrichment was achieved on irradiation of tungsten hexacarbonyle[4/].

Comparing the usefulness of potassium hexacyanomanganate and of potassium pentacyanonitrosylmanganate as targes for the Szilard-Chalmers reaction, the latter proved to be more convenient because, unlike potassium hexacyanomanganate it does not hydrolize in water.

In future we intend to study the Szilard-Chalmers reaction using potassium octocyanotungstate and potassium octocyanomolibdate.

The authors would like to express their thanks to Prof. Henryk Niewodniczański and Prof. Wiktor Jakób for theirs interest in these investigations.

References

1. L. Szilard, T.A.Chalmers, Nature, 134, 462 /1934/
2. W. Hieber, R. Nast, E. Proeschl, Z.anorg.Chem., 256, 159 /1948/
3. I. Strońska, Wiad. Chem., 12, 65 /1958/
4. V.D. Niefiedov, M.A. Toropova, Z.Nieorg.Chim., 2, 175 /1958/

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

A SERIES OF DERIVATIVES IN THE GROUP OF OXIME-CYANIDES OF MOLIBDENUM

W. Jakób, E. Hejmo and A. Kanas - Poland

The paper to be presented is concerned with investigations on the products of oxidation and hydrolysis of the violet $[Mo/CN/_5NO]^{4-}$ ion, contained in $K_4/Mo/CN/_5NO/$. A detailed discussion of the composition and of some properties of this compound has been published previously /communication to the VI-th Congress of Polish Chemical Society; a more complete article has been sent to "Roczniki Chemii" for a possible publication/.

In the paper we succeeded to show that the radical NO contained in the complex anion is a triply charged negative group with 14 electrons, of the hydroxylaminic origin. We suggest to call it the "deproto-oximic" group.

Titration of the solution of $K_4/Mo/CN/_5NO/$ with $K_3/Fe/CN/_6/$ gives only a single, sharp change of the potential which appears after one equivalent of the oxidant has been used. The solution obtained is green. Titration with the solution of KOBr leads to a potential change and a simultaneous yellowing of the solution, after two equivalents of the oxidant have been added. Undoubtedly it is the central atom, Mo which is oxidized in the processes considered, for the presence of unaffected NO group in the products can be shown with chemical methods and from the analysis of the absorption spectrum. The above oxidation processes are reversible; the oxidized solutions can be reduced in alkaline medium with the help of $Na_2S_2O_4$ or hydroxylamine, whereby the violet colour of the original complex is regained.

The investigations on the composition of isolated products of oxidation and of their magnetic properties, and also the investigations of the magnetic properties of the oxidized

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

solutions, allow us to draw a conclusion on existence of the following series of complexes:

$[Mo/CN/_5NO]^{4-}$, violet, diamagnetic,

$[Mo/CN/_5NO]^{3-}$, green, paramagnetic

$[MoO/CN/_4NO]^{3-}$, yellow, diamagnetic.

/The composition of the last complex is not yet certain./ Undoubtedly all these complexes belong to inorganic oximes.

The "deproto-oximic" group contained in the complexes exhibits a small only deprotonising agency: the pH-metric titration leads to a diffuse change of potential at about pH = 6. Concentrated solutions with this value of pH are intensively blue. The blue solutions however, evolve rapidly HCN, changing the colour to green. It is likely that the blue solution contains $[/Mo/CN/_5NOH]^{3-}$. A stronger acidification results in a decomposition with a simultaneous evolution of HCN. The products of decomposition are coloured gels of a variable composition; the relation of Mo to NO is approximately 1:1

We think that such a subborn bonding of the deproto-oximic group with molybdenum both in the products of oxidation and of hydrolysis result of a probable transfer of two electronic pairs from NO to molecular π-orbitals with the participation of the central atom.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

THE COMPLEX SALTS OF TETRAZOLIUM ION WITH IONS OF TETRACHLOROGALLIC, INDIC, THALLIC AND CHLOROACIDS OF OTHER METALS

T. Pukas - Poland

Complex compounds of ions of the chlorogallic, indic, thallic, sincic, auric and platinic acids with 2,3,5-triphenyltetrazolium ion have been obtained. The composition of these compounds have been determined analytically and according to the Job's method : /TPT//$GaCl_4$/, /TPT//$ZnCl_4$/, /TPT//$TlCl_4$/, /TPT//$AuCl_4$/ and /TPT/$_2$/$PtCl_6$/.

The ultraviolet light absorption of the aqueous solutions of these compounds and the benzene solution of the gallic compound, since only this compound is soluble in benzene, has been investigated.

It has been stated that the maximum of the light absorption for the aqueous solutions is at the wave length ca.252 mμ and for the m benzene solution at the wave length ca.278 mμ.

The molar absorptivity for the aqueus solution of /TPT/Cl and /TPT//$GaCl_4$/ has been found. It is about 30 000.

The 2,3,5-triphenyltetrazolium tetrachlorogallates with some substituents in benzene ring /$-CH_3$, $-OCH_3$, $-NO_2$, -Cl/ have been obtained.

The curves of light absorption for the aqueous solutions of these salts in the region 200 mμ - 320 mμ have been determined. The molar absorptivities have been calculated. It has been stated that the $-OCH_3$ groups shifts the absorption maximum of the aqueous solutions to the wave length ca.270 mμ and increases the molar absorptivity by about 20 per cent, and the Cl substituent in benzene ring decreases the molar absorptivity by ca.20 per cent.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

The infrared spectra for these compounds in the region 3 500-675 cm^{-1} have been investigated.

The measurements have been carried out by means of the Unicam SP-500 spectrophotometer and the double beam spectrophgtometer with automatic recording Hilger Model H-800/sodium chloride prism/.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

THE ELECTRON SPIN RESONANCE AS PROOF OF ELECTRONIC STRUCTURE OF BINUCLEAR CHROMIUM III COMPLEXES.

W. Wojciechowski, B. Jeżowska-Trzebiatowska, I. Bójko
Poland

Binuclear complexes of transition metals with nucleus Me-O-Me possess some interesting magnetic properties. Some of them are diamagnetic, for example $K_4Ru_2OCl_{10}$, $K_4Mo_2OCl_{10}$, and ReIV with oxy- and phenolo-acids. Binuclear complexes Cr III with Me-O-Me and Me-OH-Me bonds are however paramagnetic.

In the course of the present investigations we carried and the measurments of magnetic susceptibility, the absorption spectra and paramagnetic resonance for the following complexes of Cr III: I. Rhodochloride, II. Basic rhodochloride, III. Erythrochloride, IV. Basic erythrochloride.
The results of these measurments are given in table I.

Table I.

	μ_{eff} in BM	χ_g		H in Gauss		The position of absorption bands
		293°K	84°K	293°K	84°K	
Rhodochloride	1,85	1,986		336		18120 cm^{-1} 24600 cm^{-1}
Erythrochloride	2,26	2,009	2,04	316	431	18500 cm^{-1} 24300 cm^{-1}
Basic erythrochloride	2,3	1,993	2,01	315	360	

The basic rhodochloride reveals some interesting and curious magnetic properties. At a temperature of 300°K its gram susceptibility $\chi_{g\,300°K} = 1,958\ 10^{-6}$. Then as temperature decreases the susceptibility also decreases according to equation:

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

$$\chi_g = 0,88 \sqrt{\frac{T^2}{\theta} - 1}$$

At T = θ = 125°K the compounds become diamagnetic.

The above measurements are in agreement with the results obtained by EPR method. Basic rhodochloride is not liable to paramagnetic absorption either at the liquid air or room temperature.

The non-existence of the paramagnetic absorption in case of basic rhodochloride /at room temperature/ may be explained as follows: the electron of nucleus Cr-O-Cr or two molecular orbitals are too close to each other.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Application of the Hanging Mercury Drop Electrode to an Investigation of Halogen Complexes of Chromium (III)

by

W. KEMULA and E. RAKOWSKA

Presented by W. KEMULA on July 31, 1961

In the past years a number of papers appeared concerning investigations of the exchange rate of ligands in various complex compounds and the electron transfer rate in red-ox reactions of the type: Co (III) $\rightleftarrows$ Co (II), Fe (III) $\rightleftarrows$ Fe (II), $\rightleftarrows$ Cr (III) $\rightleftarrows$ Cr (II) [1]—[5].

It was established, that in several processes the presence of Cr (II) ions has a catalytic influence on the exchange of ligands and electrons. For example aquo-chloro-complexes of Cr(III) exchange very slowly chloride ions with water molecules $[Cr(H_2O)_4Cl_2]^+ + 2\,H_2O \rightarrow [Cr(H_2O)_6]^{3+} + 2\,Cl^-$, while in the presence of Cr(II) the loss of one Cl^- ion is almost instantaneous [2].

A significant influence of Cr(II) was observed also in the case of various Co(III) and Fe(III) complexes [2]. In the spontaneous reaction of the $[(NH_3)_5CrX]^{2+}$ ion (X — halogen) $[(NH_3)_5Cr(H_2O)]^{3+} + X^-$ is produced, but in the presence of Cr^{2+}, we obtain $[(H_2O)_5CrX]^{2+}$ and 5 NH_4^+ ions [3].

However, these investigations with the use Cr(II) are inconvenient, because Cr(II) obtained from reduction of Cr(III) with metallic Zn or Al is very unstable and it readily oxidizes reacting even with water. Therefore it is necessary to use special experimental conditions.

It seemed, that the application of electrolytic generation of Cr(II) with the use of a "hanging" mercury drop electrode (HMDE) [6] should facilitate these investigations. If we, moreover, take into consideration, that the Cr(III) complexes with various ligands are reduced at various potentials, then by using HMDE it will be possible to generate simultaneously Cr(II) and study the products of ligand exchange. In our previous papers [7]—[9] it has been demonstrated, that cyclic voltammetry has been successfully used for studying intermediate stages or unstable products of electrode reactions, because the ion or molecule formed on the electrode surface may immediately undergo the reverse reaction (oxidation or reduction).

From polarographic investigations of the Cr(III)—Cr(II) system it is known that Cr(III) is reduced irreversibly in two waves to Cr(II) and Cr, in most electrolytes with the exception of saturated $CaCl_2$ aq. and 1 M KCNS.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

It was found, moreover, that various aquo-complexes of Cr(III) are reduced at different potentials, for example: green $[Cr(H_2O)_4Cl_2]$ Cl is reduced more easily, i.e., at more positive potential, than the violet $[Cr(H_2O)_6]^{3+}$. The papers concerning polarographic oxidation of Cr(II) are less numerous; these investigations are, as already mentioned, most difficult owing to the low stability of aqueous solutions of Cr(II).

Experimental

Equipment and reagents

The previously [illegible] was used. The cyclic voltammetric curves were recorded by the [illegible] A thermostatic cell (27°C) with an external saturated calomel electrode [illegible] was the same, as in previous studies [7], [9].

[illegible] water were used. Fresh and "aged" solutions of [illegible] 15 H_2O were used. In order to obtain a green [illegible] a suitable [illegible] H_2O was thrown into the solution directly before recording. The [illegible] green solution after a 10-days aging process. The so obtained [illegible] was hydrolysed. pH of this solution was 2.9 and a [illegible] was observed. The test-solutions were taken from the above [illegible] of Cr^{3+} was determined colorimetrically.

Results

Curve 1 (Fig. 1) shows the successive cyclic voltammetric curves of 0.1 N KC[illegible] to which the violet solution of $[Cr(H_2O)_6]$ Cl_3 was added. When the electrode was polarized the first time from 0 to negative potentials, we recorded maximum I at —0.85 V caused by the one-electron reduction of the $[Cr(H_2O)_6]^{3+}$ species. When at the potential —1.2 V the direction of the polarization is reversed and the oxidation currents recorded — we observe a maximum of anodic current II at —0.45 V. This current [illegible] the oxidation of the Cr(II)-species formed during the preceding cathodic [illegible] the second cycle a new maximum III appears [illegible] positive potential than I (i.e. at —0.65 V). By further [illegible] curves, [illegible] the height of the [illegible] does not [illegible] the reduction of a Cr(III) [illegible] species [illegible] the reduction [illegible] during the oxidation process. [illegible]

[illegible] and the [illegible] on curve 1 [illegible] it is known, that the [illegible] is more stable in acid solutions [illegible] be expected that after dissolution of the crystal of $[Cr(H_2O)_4Cl_2]$ Cl·2 H_2O before

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

the recording in more acid solutions, the maximum III should be considerably higher than maximum III on curve 2. The curve 3 has been recorded in these conditions. It is evident, that in 0.1 N HCl we observe on the cathodic branch one high maximum at a potential nearly equal to that of maximum III on curves 1 and 2. At —0.85 V we observe also a slightly visible deviation of the curve, which corresponds to the presence of the minute amount of the $[Cr(H_2O)_6]^{3+}$ species in the solution.

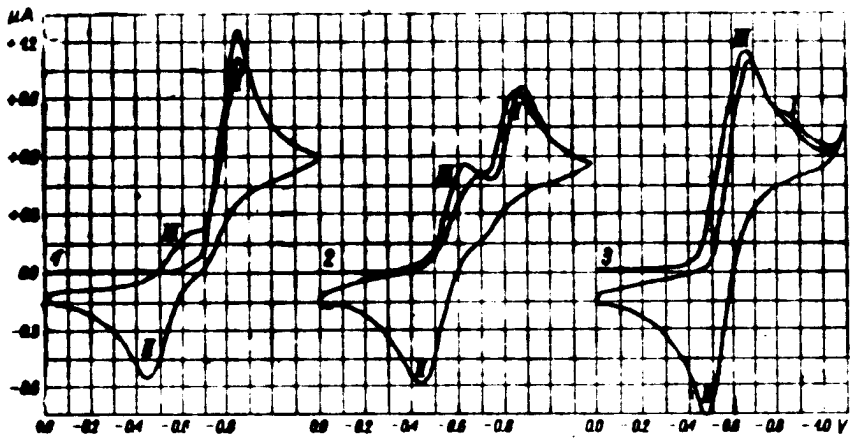


Fig. 1. Cyclic voltammetric curves of: 1. 1.10^{-3} M $[Cr(H_2O)_6]Cl_3$ in 0.1 N KCl; 2. freshly dissolved 1.10^{-3} M $[Cr(H_2O)Cl_2]Cl$ in 0.1 N KCl; 3. freshly dissolved 1.10^{-3} M $[Cr(H_2O)Cl_2]Cl$ in 0.1 N HCl.

These results enable us to state, that in the solution surrounding the electrode such Cr(II)-species are formed, which are oxidized afterwards not only to a primary solved complex, i.e. $[Cr(H_2O)_6]^{3+}$, but also to another one with a lower number of H_2O molecules. It is not clear as yet, whether the formed complexes are $[Cr(H_2O)_4Cl_2]^+$ or $[Cr(H_2O)_5Cl]^{2+}$. To simplify we shall use in the following part

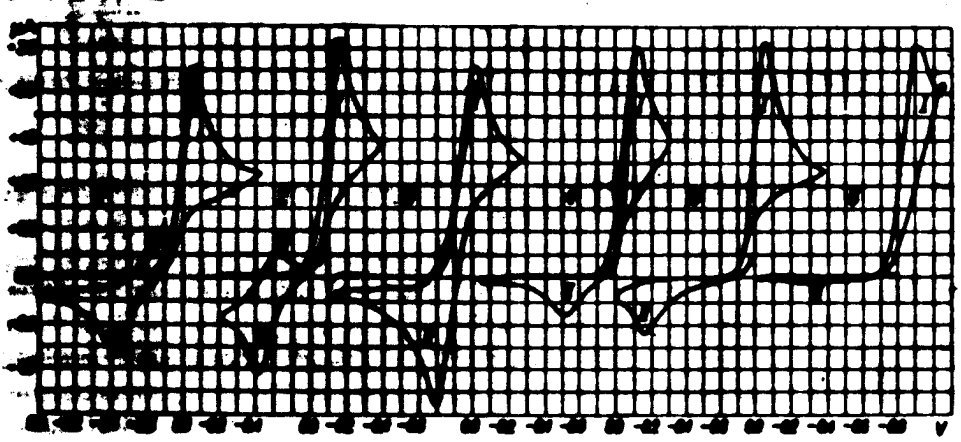


Fig. 2. Cyclic voltammetric curves of violet 1.10^{-3} M $Cr_2(SO_4)_3$ in 0.1 N solutions of: 1. KCl, 2. KBr, 3. KCNS, 4. K_2SO_4, 5. $NaClO_4$, 6. KNO_3.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

of the paper the formula $[Cr(H_2O)_5Cl]^{2+}$, because, as results from the literature data, the existence of this species is more probable in the presence of Cr(II). The kind of supporting electrolyte has a significant influence on the formation of maximum III during the second and following cycles of polarization of the electrode. In Fig. 2 the voltammetric curves corresponding to the electrode reactions of Cr(III)—Cr(II) system in 0.1 N solutions of KCl, KBr, KCNS, K_2SO_4, $NaClO_4$, KNO_3 are compared. To each solution a violet solution of $Cr_2(SO_4)_3$ was added. In 0.1 N KCl (curve 1) as well as in 0.1 N KBr (curve 2) maximum III appears at a potential more positive than the primary maximum I. In 0.1 N KCNS-solution (curve 3) we observe only a slight deviation on the reduction curve. This gives evidence, that formation of a new species reduced at a somewhat less negative potential also occurs, contrary as in the case of 0.1 N K_2SO_4 (curve 4) and 0.1 N $NaClO_4$ (curve 5) solutions where the cyclic curves are overlapping and no new maxima and minima appear. In 0.1 N KNO_3 (curve 6) also the secondary maxima on the following cyclic curves are not observed, and the very slight oxidation current of Cr(II) → Cr(III) (maximum II) is hardly visible.

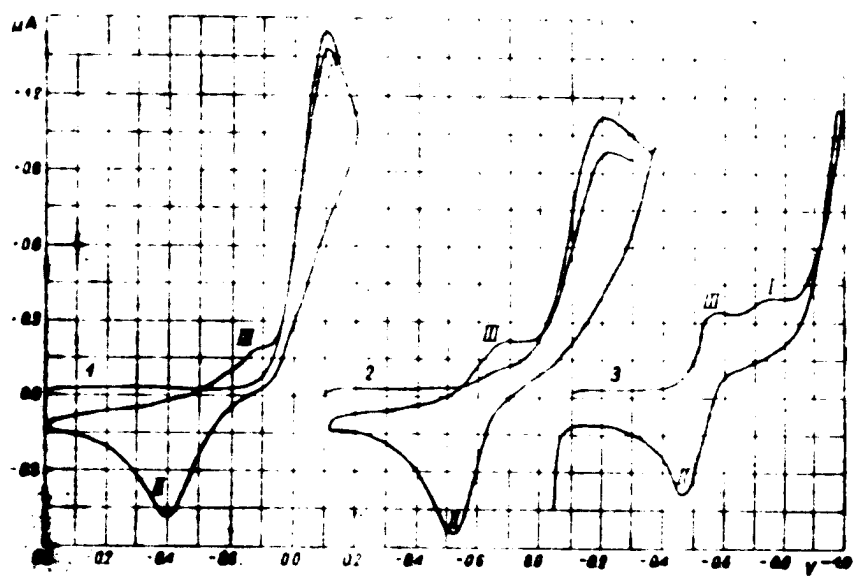


Fig. 3. Cyclic voltammetric curves of 1·10⁻³ M $[Cr(H_2O)_6]Cl_3$ solution in $CaCl_2$: 1. 0.1 N, 2. 3 N, 3. 10 N

From the above mentioned results an influence of halogen on the formation maximum III may be reduced. However, the rise of concentration of KCl from 0.1 N to 3 N does not induce an essential change of the shape of the voltammetric curves. We obtain another shape of the curves by using $CaCl_2$ as supporting electrolyte (Fig. 3): the reduction of Cr(III) in more diluted solution i.e. in 0.1 N $CaCl_2$ (curve 1) has the same character, as in KCl of the same concentration. The increase of $CaCl_2$ concentration to 3 N causes the appearance of maximum III already in

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

the first polarization cycle of the electrode (curve 2); thus the electrode process, which was secondary in 3 N KCl, is in 3 N $CaCl_2$ a primary one. A further increase of $CaCl_2$ concentration to 10 N produced a corresponding increase of the primary maximum III (curve 3). Probably the dehydrating action of concentrated $CaCl_2$ solutions takes place here.

Discussion

It follows from the described experiments that the formation of a new, secondary maximum in the second cycle on the voltammetric curve is caused by the reduction of the green complex $[Cr(H_2O)_5X]^{2+}$ ($X = Cl^-$ or Br^-). This form appears as the result of the electrode process, i.e., after the oxidation of the cathodically reduced violet ion $[Cr(H_2O)_6]^{3+}$ present in the bulk of the solution.

It is evident, that the secondary maximum III is considerably lower than the oxidation maximum II. Secondary systems of a similar type, namely the phenylhydroxylamine—nitrosobenzene or *p*-phenylenediamine—*p*-quinonediimine obtained by Kemula and Kublik as the result of irreversible reduction of nitrobenzene [7] and *p*-nitroaniline [8] showed the ratio $\frac{i_{anodic}}{i_{cathodic}} \cong 1$. On the contrary, in our case this ratio is equal to about 2 although the reaction in 0.1 N KBr is reversible like the above-mentioned reactions.

It may be concluded from this, that only a part of the ions Cr(II) present near the electrode is oxidized to $[Cr(H_2O)_5Cl]^{2+}$.

The formation of the $[Cr(H_2O)_5Cl]^{2+}$ complex from the $[Cr(H_2O)_6]^{3+}$ complex as the result of electrode reaction was not confirmed in the literature. In many papers concerning the exchange of ligands in complexes in the presence of Cr^{2+} the transition $[Cr(H_2O)_6]^{3+} \rightarrow [Cr(H_2O)_5Cl]^{2+}$ or $[Cr(H_2O)_4Cl_2]^+$ was not observed. The influence of Cr^{2+} aq connected with its great lability (half time of ligand exchange $t_{1/2} = 10^{-5}$ sec. [1]) was observed mainly in the reactions of hydrolysis of complexes richer in halogens or other groups, for instance:

$$[Cr(H_2O)_4Cl_2]^+ + H_2O + Cr^{*2+} \rightarrow [Cr^*(H_2O)_5Cl]^{2+} + Cr^{2+} + Cl^- \qquad [2].$$

$$[(NH_3)_5CrCl]^{2+} + 5H_2O + 5H^+ + Cr^{*2+} \rightarrow [Cr^*(H_2O)_5Cl]^{2+} + Cr^{2+} + 5NH_4 \qquad [3].$$

and, as it results from the above equations the hydrolysis was not complete, but produced the $[Cr(H_2O)_5Cl]^{2+}$ complex. If the presence of Cr(II) could also produce $[Cr(H_2O)_5Cl]^{2+}$ in the reverse reaction during the exchange of one water molecule in the $[Cr(H_2O)_6]^{3+}$ complex for a halogen, the formation of a secondary maximum in the second cycle of polarization would be understandable. However, the results of Taube and Myers [2] did not confirm this possibility. They investigated the reaction:

$$[Cr(H_2O)_4Cl_2]^+ + Cr^{2+}\,aq \rightarrow [Cr(H_2O)_5Cl]^{2+} + Cr^{2+}\,aq + Cl^-$$

and in a Cl^- labeled solution established that the exchange of the non-radioactive halogens bound in the complex with the radioactive halogens in the solution was very slow. This fact also suggests a very slow rate of exchange between Cl^- ions

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

from the solution and the water molecules bound in the complex in the case of the $[Cr(H_2O)_6]^{3+} + Cr^{2+}$ reaction.

Indeed, Plane and Taube [4] observed a considerable acceleration of the exchange reaction of electrons between $[Cr(H_2O)_6]^{3+}$ and Cr^2 in the presence of Cl^- ions, but in these investigations very high concentrations of Cl— (3—4 M) were used and, moreover, the other anions (NO^-) had a similar influence. From this some other cause of the growth of exchange rate may be concluded. Moreover, Anderson and Bonner [5] observed only a 12 per cent increase of the exchange rate when Cl^- ions were present, contrary to Plane's and Taube's results.

It is possible that the divergences between our results and those of the above mentioned authors are caused by different experimental conditions: for example the difference in Cr (III) concentrations (in our case 10^{-3} M, in some of the above cited papers — 1 M). In view of this, our method is more convenient, because it enables investigations in more diluted solutions.

The formation of $[Cr(H_2O)_5Cl]^{2+}$ from $[Cr(H_2O)_6]^{3+}$ is possible in very concentrated chloride solutions (4 M) [10], whereas the discussed effect of formation of the green isomer appears also in diluted solutions of Cl^- and Br^- (0.1 N). It is, however, necessary to take into consideration the possibility of existence in Helmholtz's layer of a different concentration of these anions than in the bulk of the solution. The complex $[Cr(H_2O)_5Cl]^{2+}$ might also be formed not as the result of exchange reaction between Cr(III) and Cr(II) in the electrode layer, but in consequence of the interaction between Cr(III) or Cr(II) and the electrode

Investigations concerning this problem are in progress.

DEPARTMENT OF INORGANIC CHEMISTRY, UNIVERSITY, WARSAW
(KATEDRA CHEMII NIEORGANICZNEJ, UNIWERSYTET, WARSZAWA)
INSTITUTE OF PHYSICAL CHEMISTRY, POLISH ACADEMY OF SCIENCES
(INSTYTUT CHEMII FIZYCZNEJ, PAN)

REFERENCES

[1] H. Taube, Can J. Chem., 37 (1959), 129.
[2] H. Taube, H. Myers, J. Am. Chem. Soc., 76 (1954), 2103.
[3] A. E. Ogard, H. Taube, J. Am. Chem. Soc., 80 (1958), 1084.
[4] R. A. Plane, H. Taube, J. Phys. Chem., 56 (1952), 33.
[5] A. Anderson, N. Bonner, J. Am. Chem. Soc., 76 (1954), 3826.
[6] W. Kemula, Z. Kublik, Anal. Chim. Acta., 18 (1958), 104.
[7] — , Roczniki Chem., 32 (1958), 941.
[8] — , Bull. Acad. Polon. Sci., Cl. III, 6 (1958), 653. Nature, 182 (1958), 793.
[9] W. Kemula, E. Rakowska, Z. Kublik, Coll. Czechosl. Chem. Commun., 25 (1960), 3105.
[10] H. Gates, E. L. King, J. Am. Chem. Soc., 80 (1958), 5011.

LIV → disproportionation

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

THE PROPERTIES OF SOLID PHASES OF $M_2^{II}\,M^{IV}/CN/_8R_2 \cdot x\,H_2O$ /M^{II} = Cd, Mn; M^{IV} = Mo, W; R = NH_3, N_2H_4 or H_2O/

W. Żakób, A. Samotus and Z. Stasicka - Poland

We have the photochemical reactions of aqueous solutions of $K_4[Mo/CN/_8] \cdot 2\,H_2O$ and $K_4[W/CN/_8] \cdot 2\,H_2O$, particularly in presence of NH_3 or N_2H_4. We succeeded to isolate the following crystalline red photoproducts:

$Cd_2[Mo/CN/_8/NH_3/_2] \cdot 4\,H_2O$ $\quad$ $Cd_2[W/CN/_8/NH_3/_2] \cdot xH_2O$

$Cd_2[Mo/CN/_8/N_2H_4/_2] \cdot 4\,H_2O$ $\quad$ $Cd_2[W/CN/_8/N_2H_4/_2] \cdot xH_2O$

$Mn_2[Mo/CN/_8/NH_3/_2] \cdot x\,H_2O$ $\quad$ $Mn_2[W/CN/_8/NH_3/_2] \cdot xH_2O$

These solid phase precipitate from red solutions obtained as a result of what has been called the first photochemical reaction. We have proved without any doubt the ligands NH_3 and N_2H_4 are contained in the anion, while H_2O is a zeolytic water of the crystal lattice.

Crystals of all the mentioned photoproducts have the same shape, are optically single axial, and probably belong to the tetragonal system. The Debye x-ray diagrams are all identic undepending of the particular metal atoms M^{II} and M^{IV} and undepending of the ligand, NH_3 or N_2H_4. However, they differ distinctly from the Debye diagrams of normal, yellow salts: $Cd_2[Mo/CN/_8] \cdot 8H_2O$. $Mn_2[Mo/CN/_8] \cdot 8H_2O$ and appriopriate tungsten compounds.

Reciprocally, the infrared spectra of the normal, yellow cadmium salts have much in common with the appriopriate photoproducts. As regards the differences: the red photoproducts both of molybdenum and tungsten show additionally a complex band in the range 1200-1500 cm^{-1} owing to the deformation vibration modes of ammonia or hydrazine;

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

the band above 3200 cm^{-1} is now much broadened from the longer wave side owing to the stretching vibrations of N-H; the band at about 2100 cm^{-1} which corresponds to the stretching vibration of CN^- is distinctly narrowed.

The electronic absorption spectra of the cadmium salt in diluted KCN or NH_3 solutions are exactly the same for R = NH_3 and R = N_2H_4. They show three bands with distinct maxima at 242 mμ /Mo/ or 251 mμ /W/, 374 mμ /Mo and W/, ca 500 mμ /Mo and W/. The last band is very diffuse and vanishes at about 600 mμ . These results are to be compared with the spectrum of the solution of normal, yellow salts, prepared in the same way: their spectra show the same first two maxima practically unchanged, but the third band, a diffuse one, has a maximum shifted to 420-445 mμ , vanishing at about 570 mμ .

The acolytic properties of the red solid phases, particularly strong in case of crystallization water, to some extent refer also to the ligands allowing for a partial exchange of NH_3 or N_2H_4 by H_2O. Also an isomorphic exchange of $[Mo/CN/_8R_2]^{2-}$ ions by other ones like $[Mo/CN/_4/OH/_2]^{2-}$ seems to be possible, particularly as the result of what has been called the second photochemical reaction. Both these kinds of defects show no influence on the Debye diagram and essentially also on the electronic absorption spectrum; only the long wave absorption band is slightly affected.

According to our hypothesis $[Mo^{IV}/CN/_8R_2]^{2-}$ ions have a shape of an Archimedean atriprism with two tetrahedrons put upon the square planes of the antiprism; the R-ligands would then occupy the free peaks of the two tetrahedrons.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

STABILITY, SPECTRA AND STRUCTURE OF IRON - α-DIIMINE COMPLEXES

P. Krumholz - Brasil

The iron/II/ complexes of 2,2'-bipyridine /bipy/ and o-phenanthroline /phen/ differ in a characteristic manner from those of aliphatic 1,2-diamines and from the bipy and phen complexes of other bivalent transition metal ions of the first series, in that: a/ $K_3 \gg K_2 < K_1$ b/ the tris-complexes are of the low-spin type, and c/ that these complexes display new and strong absorption bands in the visible. It has been demonstrated by the preparation and the properties of iron/II/ complexes of aliphatic α-diimines that the characteristic ligand-behaviour of bipy and phen is due to the presence of the α-diimine grouping -N=C-C=N-.

The iron/II/ complexes of aliphatic α-diimines, /glyoxal-bis-methylimine, biacetyl-bis-methylimine/ are more stable than the complexes of their heteroaromatic analogues, bipy and phen. The iron/II/ complexes of pyridine-2-aldimines provide the link between the two aforementioned classes of complexes.

Since now a great variety of iron/II/ α-diimine complexes can be prepared, the influence of structural changes on the stability and the spectra of these complexes can be systematically investigated which, in turn, may provide information on the nature of the metal-ligand bond. Some recent results of such investigations are reported.

As pointed out early in 1950, the properties of iron/II/ α-diimine complexes suggest a/ a radical structural change as passing from the mono- and bis-, to the tris-complexes, and b/ a partial double bond character of the metal-ligand bonds as possible reason for those structural changes. The partial

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

double bond character can be pictured either in resonance formulations involving structural rearrangements of the ligands, or else by formation of dative π-bonds through combination of the /filled/ t_{2g} orbitals of the metal with /empty/ antibonding π^*-orbitals of the ligands.

Stability relations among different iron/II/ α-diimine complexes as well as their spectra are discussed in terms of those bonding pictures.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

THE RELATION BETWEEN THE COORDINATION NUMBER AND THE DISTRIBUTION OF PROTONS

J.Chojnacki - Poland

While "core and link" hypothesis seems to be unsuitable in the case when the linking does not progress gradually, but leads immediately to comparatively high polimerised, e.g. pentamolybdate ion; moreover when the "core" and ligands have charges of like sign, the electrostatic expulsion ought to prohibit any linking.

A complementary theory proposed below bases on the assumption that the ions $[MeO_4]^{2-}$ or $H[MeO_4]^{-}$ do not appear successively in the solution acidified increasingly, but there exist simultaneously many protonated complexes, as $[MeO_3/OH/]^{-}$, $[MeO_2/OH/_2]^{0}$ $[MeO/OH/_3]^{+1}$, $[Me/OH/_4]^{+2}$ or $[Me/OH/_6]^{0}$, $[Me/OH/_5H_2O]^{+1}$ and so on.

If h means the concentration of free hydrogen ions, $c_0, c_1 \ldots c_i \ldots c_n$ - are the concentrations of i-protonised monomers and $C = \sum c_i$ is the total concentration of Me, then :

$$c_i = C \frac{k_i h^i}{F/h/}$$

where $F/h/ = \sum_{i=0}^{i=n} k_i h^i$ is the partition function of protons, $k_0 = 1$ and k_i - are the equilibrium constants.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Simple electrostatic theory leads to the conclusion, that $[MeO_4]^{-2}$ and $[MeO_3/OH/]^{-}$ exist only in the tetrahedral form T, unable to any linkage with like complexes. On the contrary, the $[MeO_2/OH/_2]^{o}$ and $[MeO/OH/_3]^{+}$ should appear in the hydrated octahedral forms Oh : $[Me/OH/_6]^{o}$ and $[Me/OH/_5H_2O]^{+}$ resp. having bond strength 1 /mesodesmid/ and therefore suitable to link illimitably each other. In mixed complexes /pOh+qT/ the amount of linked T-s is limited by the number of free mesodesmic bonds of the octahedral groups.

The stoichiometry of polyion depends of the ratio of octahedral forms to tetrahedral ones, and therefore is determined by the distribution function only, eg. in the series OhT, OhT_2, OhT_3, ...OhT_6 the ratio amounts; 1; 0,5; 0,33; 0,25; 0,20; 0,167; resp. and therefore the last compound OhT_6 having the least ratio 0,167 appears as the first in the acidified solution.

The theory verified by the measurements on molybdates executed by Chojnacka gives the correct value for pH required to obtain the paramolybdate ion.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

[redacted] U/IV/ AND VARIOUS HALOGENATES

G. Gordon - USA

[redacted] of U/IV/ with BrO_3^-, ClO_2^-, ClO_2 and [redacted] are certainly complex and the ensuing disproportionation of the halogenate which accompanies the oxidation of U/IV/ makes the system difficult but extremely interesting to study. The purpose of this report is to indicate the progress which has been made in the study of both the stoichiometry of the reaction and the transfer of oxygen from the oxidising agent to the product uranyl ion. With ClO_2^- and ClO_2 extensive oxygen transfer to uranium takes place for each of the oxidising agents and under some conditions the transfer exceeds one atom of oxygen per UO_2^{++}. The study of the mechanisms of these reactions is complicated by the formation of intermediate halogen species of high oxidising power and these species interact with each other as well as with uranium /IV/ and uranium /VI/. The apparent order of rates of oxidation of U/IV/ by halogenate would appear to be $ClO_2^- > ClO_2 > OCl^- > Cl_2 > ClO_3^-$. The association between ClO_2^- and UO_2^{++}

$$UO_2^{++}/H_2O/_n + ClO_2^- = \left[UO_2^{++}/H_2O/_{n-1}\ ClO_2^-\right] + H_2O$$

to form a charge transfer complex will also be discussed.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

APPLICATION OF THE MÖSSBAUER EFFECT FOR THE INVESTIGATION OF COMPLEX IRON COMPOUNDS IN CRYSTALLINE FORM

A.Z.Hrynkiewicz, H.Lizurej, J.Sawicki, T.Senkowski - Poland

The apparatus for the in investigation of the Mössbauer spectra of iron compounds was built /1/. It can be used for the observation of the fine structure of the 14.4 keV γ line in the transition of Fe^{57} nucleus from the ground state /I= 1/2/ to the first excited state /I= 3/2/.

The uniform motion of the absorber is provided by a properly shaped cam driven by a DC motor. The range of the fine structure investigation covers velocities from -10mm/sec to + 10mm/sec corresponding to the energy interval of ca. 1 μeV.

The investigation of a group of crystalline complex ferro- and ferri- cyanides was carried out. It was found that the coupling between the nuclear quadrupole moment and the electric extranuclear field gradient depends on the type of the ligand. The energy of the quadrupole interaction was calculated for different compounds. The isomeric shift observed in some cases enables to drow conclusions concerning the s electron density in the nuclear volume.

/1/ J. Bara, A.Z.Hrynkiewicz. H.Lizurej, D.Kulgawczuk. in the press in Nucleonics.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

SOME NEW ASPECTS OF THE REDUCTION MECHANISM OF MANGANESE OXYANIONS

M. Wrońska, M. Baranowska, E. Jeżowska-Trzebiatowska-Poland

The mechanism of the reduction of MnO_4^- ions by OH^- ions was solved in our Institute for the concentrations of hydroxides smaller than 1 M/l and greater than 6 M/l. The present results comprise an investigation of the reduction process in the concentrations of hydroxides smaller not yet investigated /1 M/l - 6 M/l/.

It was demonstrated that in these conditions the velocity of the reduction $MnO_4^- \rightarrow MnO_4^{2-}$, increases with increasing of hydroxide activity, which confirms that the reaction occours between the ions of the same sing. The progress of the reaction was determined magnometrically, which permitted to study the pure reduction process and to eliminate the disproportionation reaction of manganese /VI/.

The observed systematical change of the reaction order / -1 in 1 M/l hydroxide, 0 in 3 M/l Hydroxide and 1/2 in 5 M/l hydroxide/ and the kinetic laws used:

$V = k\frac{a-x}{x^2}$, $V = k\frac{a-x}{x}$, $V = k\frac{a-x}{\sqrt{x}}$, could not be explained by the change of the structure of activated complex, it is rather to be ascribed to the influence of the concurrent disproportionation reaction on the velocity of the reduction process.

The obtained results allowed the determination of the catalytic influence of cations of alkaline metals group and others ions such as Ca^{++}, Ba^{++}, and SiO_3^{2-} on the rate of the reaction.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

$MnO_4^- + OH \rightleftharpoons MnO_4^= + OH$

$OH + OH^- \rightleftharpoons H_2O + O^-$

$MnO_4^- + O^- + \cancel{OH^-} = MnO_4^= + O$

$O - OH^- = HO_2^- \quad H_2O_2$

$\downarrow OH$

$$U = \frac{dMnO_4^-}{dt} = k\left(\frac{[MnO_4^-]_0 - x}{x}\right)$$

$$\left(\frac{a_2}{a_1}\right)^{n-1} = \frac{T'}{T^2}$$

$FeO_4^=$ FeO_4

Na

$Fe(OH)_3$ K

$k = 4 \pm 1.07 \times 10^{-8}$

1.02×10^{-8}

$1.07 \times 10^{-8}\ m^2 l^{-2} min^{-1}$

10^{-4}

KOH om

KOH G.R.

Rt

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Page Denied

Next 1 Page(s) In Document Denied

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

PHOTOCHEMICAL PROPERTIES OF $[Mn/CN/_5NO]^{2-}$

W. Kakób, A. Gołębiowski, T. Senkowski - Poland

Investigating the redox properties of $[Mn/CN/_5NO]^{3-}$ /I, say/ and $[Mn/CN/_5NO]^{2-}$ /II, say/ we have noticed that in aqueous solutions a photochemical reaction of II takes place which depends on p_H. If $p_H < 4$, the originally yellow solution of II becomes discoloured /decomposition of the complex/; if $p_H > 4$, II is reduced to I, the reduction being accompanied by a colour change to violet. We assume the following reaction scheme of the photoreduction:

$$2\,[Mn/CN/_5NO]^{2-} + 2H_2O + n_1h\nu = 2\,[Mn/CN/_5NO]^{3-} + H_2O_2 + 2H^+$$

$$[Mn/CN/_5NO]^{2-} + 3H^+ + H_2O + n_2h\nu = Mn^{2+} + 5HCN + NO_2^-\,,$$

$$H_2O_2 + NO_2^- = NO_3^- + H_2O$$

Summarising,

$$3\,[Mn/CN/_5NO]^{2-} + 2H_2O + H^+ + /n_1 + n_2/h\nu = 2\,[Mn/CN/_5NO]^{3-} + Mn^{2+} + 5HCN + NO_3^-$$

The product of photoreduction was identified by a comparison of the absorption spectrum in the region 200-750 m with that of I and II /s. table/. We infer that the photoproduct is identic with I.

$K_3[Mn/CN/_5NO]$	photoproduct	$K_2[Mn/CN/_5NO]$
226 mμ	213 mμ	206 mμ
353-356 mμ	350 mμ	314 mμ
566-574 mμ	568-572 mμ	395-396 mμ
-	-	980-990 mμ

The electronic configuration of the central atom in I and

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

It is not yet certain. One of two different extremal configurations is often assumed:

d^4/Mn^{III}, NO^-/ or d^6 /Mn^I, NO^+/ for I, and d^3 /Mn^{IV}, NO^-/ or d^5/Mn^{II}, NO^+/ for II. We tried to answer on the basis of the spectral data which of the possibilities seem unlikely. With this purpose we made a qualitative, group-theoretical discussion of the ligand field transitions in terms of the pure electrostatic theory in the strong field limit, allowing for two extremal situations only: NO^- or NO^+.

Excluding the spin-forbidden transitions we find two types of ligand field transitions in II and I: a/ forbidden transitions which can get allowed only by a coupling with vibration modes, b/ weakly forbidden transitions which owing to a strong polarisation of d orbitals by NO^+ become allowed even in the equilibrium configuration of nuclei.

The qualitative predictions are as follows:

I /Mn^{III}/ should show three weakly forbidden bands, one of them in the near infrared,

I /Mn^I/ should show two pairs of ligand field transitions; in each pair however, one of the transitions would be forbidden and so likely hidden by the other one which is forbidden weakly.

II /Mn^{IV}/ should show altogether 12 weakly forbidden transitions, four of them in the near infrared.

II /Mn^{II}/ should show, qualitatively, a similar spectrum to that of I /Mn^I/ except that a new band, weakly forbidden, in the far infrared should appear.

Comparing these predictions with the table we see that the configuration II /Mn^{IV}/ is rather improbable. By analogy, the same should be true for I. Therefore, within the validity of our assumptions, configurations I/Mn^I, NO^+/ and II/Mn^{II}, NO^+/ are more probable than I/Mn^{III}, NO^- /. This conclusion is in accordance with the IR studies carried out by J. Lewis, R.J. Irving and G. Wilkinson.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

INVESTIGATIONS OF CYANONITROSYL COMPLEXES OF FIRST SERIES TRANSITION METALS BY RADIOISOTOPIC EXCHANGE METHOD

B.Jeżowska-Trzebiatowska, J.Ziółkowski
Po-land

The exchange reactions of cyanides groups in the following three complex ions of manganese, iron and cobalt were investigated:

$Mn/CN/_5NO^{-3}$, $Fe/CN/_5NO^{-2}$, $Co/CN/_5NO^{-3}$

$KCN^{14}N$ has been used. The influence of light, temperature, reagents concentration and pH solutions on the rate of exchange reaction has been examined. We confirmed the photochemical character of the exchange reactions in all these complexes. The photosensitivity of the complexes rises in the series :

$Mn/CN/_5NO^{-3} \gg Co/CN/_5NO^{-3} \sim Fe/CN/_5NO^{-2}$

The relation of the rate constant reaction of the exchange tested in the darkness to the rate constants at the standart illumination in individual complexes is as follows :

$Mn/CN/_5NO^{-3}$	17.8	
$Co/CN/_5NO^{-3}$	1.08 /trans/	5.15 /cis/
$Fe/CN/_5NO^{-2}$	1.32 /trans/	1.12 /cis/

The activation energy of the exchange reaction in the complexes investigated amounts to :

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

$Mn/CN/_5NO^{-3}$	22.8 kcal/mole	
$Co/CN/_5NO^{-3}$	trans- 8.1 kcal/mole	cis-21.2 kcal/mole
$Fe/CN/_5NO^{-2}$	trans-14.7 kcal/mole	cis-24.6 kcal/mole

The rate of the exchange increases with the rise of complex concentration and that of cyanides which indicates the complexity of the reaction mechanism. The rate increase of the reaction exchange following the concentration of hydrogen ions has been confirmed in iron and manganese complexes. A marked unequivalency of the cyanide groups in the "trans" position has been noted in the complexes of iron and cobalt. It is evident in the difference of the rate constants of the exchange reaction of the cyanogen exchanging quicker in the "trans" position to the NO-group and the slower exchanging groups in the "cis" position. The attempt has been made to explain the electronic structure of the examined complexes and the structure of the coordinated NO group.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

THE CHEMICAL BOND AND ELECTRONIC STRUCTURE OF OXALATORHENATE/IV/ BY RADIOISOTOPIC EXCHANGE METHOD

S. Wajda - Poland

To obtain the additional informations regarding the structure and character of bonds in the binuclear rhenium /IV/ complexes, obtained by us, the isotopic exchange method was applied. The results will be presented of the investigations of ^{14}C exchange in the systems $\left[Re_2O/OH/_6/C_2O_4/_2\right]^{4-}/\ ^{14}C_2O_4^{=}$ and $\left[Re_2O/OH/_2/C_2O_4\right]^{4-}/\ ^{14}C_2O_4^{=}$.

On the previous investigations it was necessary to accept that oxalatorhenates /IV/ possess the co-valent bonds D^2SP^3 and that these complexes are diamagnetic both in solid phase and in solution.

In the dioxalatorhenate /IV/ complex-oxalic acid system the isotopic exchange proceeds at the measurable rate and corresponds to the monomolecular reaction. This indicates that the oxalato groups in the complex are equivalent. The exchange rate decreases with the increase of the complex concentration, is not however actually dependent on the ligand concentration.

This result according to both A.A. Grinberg and A.W. Adamson does not determine the mechanism of the process. Nevertheless a fairly high activation energy /E = 25,0 kcal/mol/ as well as the absence of the exchange in tetraoxalatorhenate /IV/ point unequivocally to the dissociation mechanism S_{N1} being a determinant here, and the exchange proceeding through the intermediate aquo-complexes.

The results obtained for a few experimental series are represented in the table:

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Temper measur. °C	Concentrat. of compl. M/1	Concentrat. $C_2O_4^=$ M/1	Half-time exchange hour	Exch.constant R M/1. hour
37,0	0,00978	0,08333	105	$9,4.10^{-5}$
37,0	0,00496	0,08333	29	$21,2.10^{-5}$
37,0	0,00978	0,03333	122	$7,0.10^{-5}$
37,0	0,00489	0,04545	23,3	$23,9.10^{-5}$
47,6	0,00489	0,04545	6,1	$92.\ 10^{-5}$
47,6	0,00978	0,09040	31	$36.\ 10^{-5}$
18	0,00465	0,500	59	$10,7.10^{-5}$

The exchange constant R according to the above results is therefore a complicated function of the constituents concentration. It should be stressed, that the process rate does not change in a wide range of hydrogen ions concentration because the oxalate ion has been introduced into the system in the form of oxalic acid.

In case of tetraoxalatorhenate /IV/ the exchange was investigated in a similar way as in dioxlatorhenate /IV/ and during about 200 hr. the increase of activity of the precipitate of quinoline salt was not observed. The values obtained did not exceed the limit of experimental faults.

According to facts represented the replacement of chelate groups by hydroxide groups decreases the covalency of bonds in a complex. It is possibly connected with the spatial structure of the two complexes discussed. That is today: one of the oxygen atoms of the oxalato-group is bound with the central ion along the axis of binuclear complex, which causes the bond fission and formation of an aquocomplex. The chelate groups in tetraoxalatorhenate /IV/ on the other hand are bound on a plane perpendicular to the bridge bond direction, which makes dissociation impossible or at any rate very difficult.

This interpretation is rather corroborated by the fact that these complexes form simultaneously during the dissolution of ReO_2 in oxalic acid and do not transform themselves into each other.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

MECHANISMS OF ONE-ELECTRON REDOX REACTIONS INVOLVING DESTRUCTION OF THE MO_2^+ STRUCTURE*

J.C. Sullivan and E.H. Appelman - USA

Based on discussion of mechanisms for analogous reactions and theoretical considerations it is predicted that important terms in the rate laws for the reactions; Np/V/ + Ti/III/ = = Np/IV/ + Ti/IV/ and Np/V/ + Eu/II/ = Np/IV/ + Eu/III/ should be $-dNp/V//dt \gg 0.3 [Np/V/][Ti/III/]$ and $-dNp/V//dt = \gg 0.08 [Np/V/][Eu/II/][H^+]$, at 25°C in molar perchloric acid.

A detailed mechanism is presented for the reduction of Np/V/ by V/III/. Comparison of specific rate constants measured and calculated in terms of the proposed mechanism is presented. The necessity of focussing attention on specific rate constants, rather than free energies of activation, when judging the degree of reliability to be assigned any purported mechanism for a redox process is demonstrated.

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

POTENTIOMETRIC INVESTIGATION OF METAL-TRIS /HYDROXYMETHYL/ AMINOMETHANE COMPLEXES

W. Komala, W. Brzobaczek, A. Malanicki - Poland

Tris/hydroxymethyl/ -aminomethane, $/HOCH_2/_3CNH_2$, finds an increasing practical application in various fields, among them also in analytical chemistry as primary acidimetric standard, for pH-standardization, for preparation of buffer solution for electrophoresis, spectrophotometry, biochemical research and others. Very scarce data have been available until now, concerning the complexing properties of this compound. The presence of a primary amine group suggests the possibility of formation of complexes of the ammonia type, but presumably some influence can be exerted by three hydroxyl groups. The reactivity of these groups nevertheless should be diminished by formation of intra-molecular hydrogen bonds.

In this paper formation of silver and copper /II/ complexes has been investigated potentiometrically with the glass membrane electrode, basing on the pH effects accompanying the formation of these compounds. On this basis, from the course of the calculated formation function, follows that complexes with maximal number of liganding molecules have the formulae: $Ag/Tris/_2^+$ and $Cu/Tris/_4^{++}$, respectively.

Evaluation of the formation function of these complexes, carried on at varying pH values and at varying concentrations of metal ion led to conclusion that in the investigated range neither polynuclear complexes may be formed, nor hydrolysis disturbs the metal complexation. The last factor, can to some extent introduce some complications, nevertheless experiments for calculations of stability constants were performed in conditions

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

where this effect can obviously be neglected. Evaluation of the stability constants was carried on by means of the Bjerrum approximation method, basing on the value of the average stability constant and the midpoint slope of the formation curve. For silver complexes at 20°C and the ionic strength μ =1.0/KNO_3/ the successive pK_n values equal 3.0[illegible] and 3.67, respectively. Measurements for copper /II/ complexes performed in the same conditions give the following pK_n values: 4.30, 3.62, 2.98 and 2.30, respectively for all four intermediate complexes.

For the check of the stability constant values of silver complexes the measurements were performed with the silver electrode, using and excess of Tris. This procedure, performed at various ionic strengths μ = 0.05, 0.10, 0.25, 0.50, 1.00 at the temperature 20°C made possible at least calculation of the overall stability constants, which was found /in $p\beta_2$ values/ 6.5[illegible]; 6.70; 6.75; 6.76; 6.78. These results are in fair agreement with the value 6.70 obtained with the glass membrane electrode for μ = 1.0 using the Bjerrum method.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

POLAROGRAPHIC PROPERTIES OF AQUEOUS SOLUTIONS OF MOLYBDOSILICIC ACIDS

W. Kemula and S. Rosołowski

As we have indicated previously the silicic acid reacts in definite conditions with molybdate ions forming there heteropolyacids, namely the α, β and γ acid. For α - and β -molybdosilicic acids the formula $H_4[Si/Mo_2O_7/_4] \cdot nH_2O$ can be ascribed, but the γ -acid should be formulated as $H_4[Si/Mo_3O_{10}/_4] \cdot nH_2O$. Formation of α - and β -acids proceeds at room temperature, and their existence depends on the proper concentration of hydrogen ions . The γ -molybdosillicic acid is formed when β acid is heated shortly at temperature 100°, or kept at room temperature during 90 mins.

Polarographic study of molybdosilicic acids on the droping mercury electrode has indicated that α and β acids are polarographically inert, but the γ acid is reduced in the presence of a buffer solution containing hydrochloric acid, sodium formate and n-butanol, giving a characteristic reduction wave. The presence of n-butanol is in this case necessary, because without it no polarographic wave of the acid could be recorded.

Polarographic measurements were performed after 90 mins from mixing solution to provide that the polarographically inert acid is completely converted into the γ acid. So prepared solution is stable and no changes of wave shape or height during one month were observed. Obtained results have confirmed conclusions given previously concerning the stability of various forms of molybdosilicic acid in solution.

The polarographic wave is a kinetic one. This can be concluded taking into account the effect of the height of the mercury

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

reservoir above the capillary and the magnitude of temperature coefficient. The half-wave potential depends on pH.

On the acidity of solution depends also the shape and height of the polarographic wave of γ acid. Best results we have obtained using as a supporting electrolyte 0.5 M buffer containing hydrochloric acid and sodium formate in the pH range from 1.9 to 2.6.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

POLAROGRAPHISCHES VERHALTEN DER CIS UND TRANS DICHLORO-BIS-ÄTHYLENDIAMIN - Co/III/ LÖSUNGEN

L. Kiss - Hungary

Im Falle von zwei en Gruppen enthaltenden Co/III/ Komplexen spielt sich die Co/III/-Co/II/ Reduktion an der Quecksilbertropfelektrode in zwei Stufen ab, welche in den I-V Kurven zwischen 0 und -1 V erscheinen. Der Zweck gegenwärtiger Arbeit ist die Untersuchung dieses Teiles der Strom-Spannung Kurven im Falle von cis und trans $/Coen_2Cl_2/^+$ Ionen enthaltenden Lösungen. Zur Feststellung des Charakters der einzelnen Stufen wurden die Zusammenhänge i - Konz., i- $\sqrt{h}$ und i- T, sowie die pH Abhängigkeit der polarographischen Ströme bestimmt.

Bekanntlich werden die obigen Ionen in wässerigen Medien hydrolisiert. Dementsprechend ändert sich der erste Abschnitt der I-V Kurven mit der Zeit, während die Höhe und das Halbstufenpotential der zweiten Stufe konstant bleiben. Die Hydrolise wird durch Gegenwart von metallischem Quecksilber katalysiert und das Gleichgewicht der in der Lösung vorhandenen Ionen vollständig in der Richtung des $[Coen_2/OH/_2]^+$ Ions verschoben. Diese Annahme scheint dadurch unterstüzt, dass die Gestalt der Kurven und die Halbstufenpotentiale in 1 n NaOH -wo nur mit dem Vorhandensein des obigen Ions zu rechnen ist - sowie in Lösungen, die 48 Stunden über einer Quecksilberoberfläche gestanden haben, übereinstimmen.

Auf Grund der in den I-V Kurven auftretenden zeitlichen Änderungen wurde versucht, über den Mechanismus der Elektrodenvorhänge und die Geschwindigkeit der Hydrolise Folgerungen zu ziehen.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

THE EVALUATION OF THE STABILITY CONSTANTS OF COMPLEXES FROM POLAROGRAPHIC DATA IN THE CASES OF IRREVERSIBLE ELECTRODE REACTIONS

J. Biernat - Poland

The polarographic method can be advantageously applied to the study of complex metal ions, when the reductions of both metal ion and metal ion complex take place reversibly at the dropping electrode. Therefore the interesting group of transition elements and other complexes could not be examined polarographicaly.

The adding of a ligand to a solution diminishes the activity of the free metal ion causing the shift of electrode potential to the more negative value. When the shift is large the rate of back electrode reaction can be ommited and then the polarographic wave becomes irreversible. Similar effect is observable when the amalgam is deactivated /Fe, Mn/.

The problem of irreversibility of polarographic currents has been solved about tenyears ago. The relation between the complex formation function and the change of half-wave potential has been found by present author by employing the above results. From that relation the stability constants can be evaluated. The overall formula is

$$\sum_{0}^{N} \beta_i /L/^i = \exp\left[\frac{F}{RT} \int_{E^k}^{E^w} f/E/\, dE\right]$$

1. When both waves are reversible the old formula is obtained

$$\sum = \exp\left[\frac{nF}{RT} /E^w - E^k/\right]$$

2. When the waves are irreversible the function f/E/ is also constant and equal to n

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

$$\sum = \exp\left[\frac{\alpha n F}{RT}/E^{w} - E^{k}/\right]$$

3. In the case of reversible wave of free metal ion and irreversible wave of metal ion complex the value of f/E/ changes from n to αn. To evaluate the stability constants an auxiliary potential E^{p} /potential of change/ and two formulae are used: one for revesible and another for irreversible wave.

$$\sum = \exp\left\{\frac{F}{RT}\left[n\ /E^{w} - E^{p}/ + \alpha n/E^{p} - E^{k}/\right]\right\}$$

The E^{p} value is found experimentaly. With a particular concentration of ligand the half-wave potential of complex ion is equal E^{p}. When the complexes are insoluble in the region of E^{p}, the E^{p} value can be evaluated but only if the complex formation formula is simple /e.g. $K/L/^{q}/$.

The above integral can be determined graphicaly from the plot αn versus $E_{1/2}$. The αn may be calculated from the slope of each wave.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

THE SPECTROPHOTOMETRIC INVESTIGATION OF THE COMPLEX FORMATION IN THE SYSTEM Pb^{4+} - Cl^-

J.Szychliński - Poland

The problem of the formation of complexes in the aqueous solutions containing Pb^{4+} and Cl^- was studied by Wescott /1/, Heal, May /2/ and Szychliński, Latowski, Korewa /3/. The non-aqueous solutions were investigated by Matthews /4/ and Szychliński, Latowski /5/. These investigations did not finally solve this problem.

The absorption spectra of the Pb^{4+} solutions in the 2M - 10 M HCl_{aq} and $PbCl_4$ in the benzene or the petroleum ether/λ = 2000 - - 5000 Å; VSU-1 Zeiss spectrophotometer/ are measured in this work.

The characteristic peak of the Pb^{4+} absorption in the HCl_{aq} solutions is found at 3080 Å. It does not shift with the change of HCL concentration. The molar extinction coefficient decreases with the increase of the concentration. The absorption maximum of $PbCl_4$ in the benzene or the petroleum ether solution is found in the 2800 - 2900 Å region. In the benzene solution the second maximum in the 3750 - 3900 Å region is also observed. The addition of the aromatic hydrocarbon to the solution of $PbCl_4$ in CCl_4 or the petroleum ether causes the colour of this solution.

The obtained experimental datas suggest, that the Heal and May's hypothesis concerning the equilibrium /in aqueous solutions/

$$PbCl_4 + Cl^- \rightleftharpoons PbCl_5^-$$

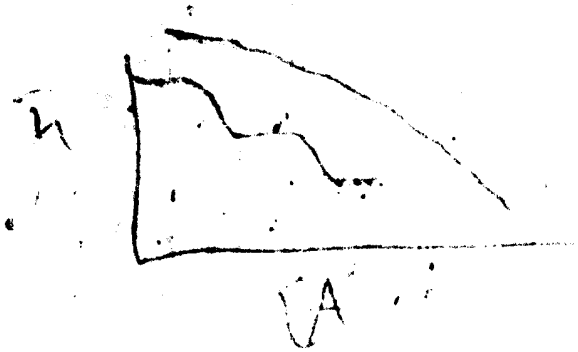
is not probable. It is possible that in the non-aqueous solutions the complexes of $PbCl_4$ with the aromatic hydrocarbons are formed.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Literature cited

1. Wescott E.W., J.Am.Chem.Soc., 1920, 42, 1335.
2. Heal H.G., May J., ibid., 1958, 80, 2374.
3. Szychliński J., Latowski T., Korewa R., Roczniki Chem., 1958, 32, 1013
4. Matthews J., J.Am.Chem.Soc., 1898, 20, 832.
5. Szychliński J., Latowski T., Roczniki Chem., 1958, 32, 997.



$\bar{n} = \frac{C_A \; A}{C_n}$ $\quad B_1 [A] + (\bar{n}-1) B_2 A + \ldots$

$\bar{n}$ as $f(A)$

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

THE STRUCTURE OF URANYL COMPLEXES WITH SOME β-DIKETONES

B. Jeżowska-Trzebiatowska, W. Kąkołowicz-Poland

Uranyl forms with acetyloacetone two complexes yellow and red of identical composition $UO_2/Acac/_2.H_2O$, but only the red complex occurs in aqueous solutions and the organic solvents. Benzoyloacetone forms an orange complex, probably a mixture of yellow and red complexes $UO_2/Bacac/_2.3H_2O$. Dibenzoylomethane forms in solid phase a dark red complex $UO_2/Dbm/_2.2H_2O$.

The magnetic susceptibility of each of these complexes was defined by Gouy method, which gave

$$\chi_{UO_2/Acac/_2} = +0,018.10^{-6}$$

$\chi_{UO_2/Bacac/_2} = -0,044.10^{-6}$, $\chi_{UO_2/Dbm/_2} = -0,054.10^{-6}$ respectively.

The calculated susceptibilities UO_2^{+2} amount to 151, 133, 111.

The paramagnetism of the uranyl group being independent of temperature points to 5f orbital participation in π donor bond.

The paramagnetism changes in conformity with ligands and the bond character in chelation.

Uranyl complexes with diketones are very stable. The instability constants, calculated by the modiffied method, amount to

$K_{UO_2/Acac/_2} = 7,1.10^{-15}$, $K_{UO_2/Dbm/_2} = 8,3.10^{-15}$,

$K_{UO_2/Bacac/_2} = 9.8.10^{-15}$

The stability is caused by the covalency of bonds and the effect of π bonds originated by ligands. The action of electrons of these bonds on the uranium energy levels probably strenthens the π bonds between uranium and oxygen in the nucleus UO_2 and enhances the paramagnetic contribution to sus-

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

THE CRYSTAL STRUCTURE OF COPPER TETRATHIOCYANATOMERCURATE
$Cu/Hg/SCN/_4/$

A. Kdrczyński – Poland

The space group Pcan – D_{2h}^{14} has been established for orthorombic $Cu/Hg/SCN/_4/$ by the X-ray oscillating method. The unit cell contains four molecules. The coordinate of Cu, Hg and S has been studied previously[1/]. Four S atoms form a distorted tetrahedron around the Hg atom. The mean bond lenghts and bond angles in the $Hg/SCN/_4$ unit are: Hg–S = 2,56 ± 0,014 Å, S–C = 1,72 ± 0,05 Å, C–N = 1,21 ± 0,06 Å, S–Hg–S = 108°06' Hg–S–C = 101°15' and 83°[illegible], S–C–N = 180°.

Four N atoms and two S atoms from SCN groups are co-ordinated to each Cu atom, thus giving it a total of six fold co-ordination. The mean dimensions of the CuN_4S_2 unit are : Cu – N = 1,90 ± 0,04 Å, Cu – S = 3,00 ± 0,017 Å, with N – Cu – N angles about 74 and 106°, and Cu – N – C angle = 160°.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

THE LATTICE CONSTANTS AND SPACE GROUP OF $Na_2BiJ_5.4H_2O$ CRISTALS

T. Bałczak - Poland

Sodium pentaiodobismuthate /III/ has been prepared by dissolving equivalent amounts of Bi_2O_3 and Na_2CO_3 in 38 % aqueous solution of HJ and slow crystallisation at room temperature. The hydriodic acid contained some free iodine. The compound $Na_2BiJ_5 \cdot 4H_2O$ crystallizes in red, monoclinic prisms or needles.

Rotation and Weissenberg photographs were taken by equi-inclination method using small crystals shaped as cylinders by treatment with acetone. The lattice constants are :
a = 9,47 ± 0,02 Å , b = 16,38 ± 0,02 Å, c = 13,06 ± 0,02 Å,
$= 106^{\circ} \pm 0,5$
With four molecules per unit cell the density was calculated to 3,28 g/cm^3, the experimental value is 3,27 g/cm^3.
Weissenberg photographs were taken with rotations about the /010/-axis and about the /001/-axis by means of CuK radiation. For /010/-axis three layer lines /0-2/ were recorded. Systematic extinctions were found for h01 reflections with l odd and 0k0 reflexions with k odd.
The space group is thus № 14 $C_{2h}^5 = P2_1/c$.
The work is being continued.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

RÖNTGENSPEKTROSKOPISCHE UNTERSUCHUNGEN AN KOMPLEXVERBINDUNGEN DER ÜBERGANGSELEMENTE

A. Meisel - Deutsche Demokratische Republik

Es wird ein fokussierender Hochvakuum-Röntgenspektrograph beschreiben, der nach der Johann-Methode eine grosse Lichtstärke mit einem hohen Auflösungsvermögen vereinigt. Die stärksten Linien des Röntgen-K-Emissionsspektrums von Komplexen der Elemente der ersten Übergangsreihe wurde sekundär angeregt und photographisch-photometrisch auf Lage, Form und Breite untersucht. Die Linienverschiebung $\delta\lambda$ wurde mit einer Genauigkeit von 0,04 X gemessen. Zum Vergleich von Linienbreiten und -formen wurden das Verhältnis der Halbwertsbreiten der Verbindung und des Elementes $/\Delta\lambda/_V/ /\Delta\lambda/_E$ und die relative Änderung des Asymmetrieindex der Verbindung $/\alpha_V - \alpha_E/ /\alpha_E$ betrachtet. Der Einfluss der chemischen Bindung auf Form und Breite der $K_{\alpha_{1,2}}$- Linien konnte auch dort noch festgestellt werden, wo sich keine Änderung in der Linienlage ergab. Bei Berücksichtigung der Wechselwirkung der 2p-Eletronen mit den 3d- bzw. 4s-Elektronen und der damit verbundenen Aufspaltung des 2p--Niveaus soll bei den Übergangselementen die Änderung des Asymmetrieindex gleichsinnig mit der Anzahl der ungepaarten d-Elektronen, d.h. in gleicher Weise wie das magnetische Moment oder auch die magnetische Suszeptibilität verlaufen. Dieses Gesetz lässt sich auch auf chemische Verbindungen anwenden. Für die Linienbreiten ergab sich ebenfalls ein Anstieg mit wachsender Anzahl ungepaarter d-Elektronen. Ferner wurden Zusammenhänge ermittelt zwischen Linienbreite und Asymmetrieindes einerseits und Komplexstabilität andererseits sowie zwischen Dublettabstand der $K_{\alpha_{1,2}}$-Linien und Art der chemischen Bindung.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

ON THE INSTABILITY CONSTANTS OF PLATINUM COMPLEXES

A.A. Grinberg, G.A. Shagisultanova and M.I. Gel'fman

USSR

Stepwise constants.- /1/ The published data on the instability constants of platinum complexes are surveyed briefly. /2/ A very simple method is described for the determination of those instability constants /concentration/ which correspond to the dissociation of one Cl^- or Br^- from the complexes $PtCl_4^{2-}$, $PtNH_3Cl_3^-$, cis- and trans-$Pt/NH_3/_2Cl_2$, $PtBr_4^{2-}$, $PtNH_3Br_3^-$, cis- and trans-$Pt/NH_3/_2Br_2$ $PtNO_2Cl_3^{2-}$, $PtPyCl_3^-$ and $PtBr_3^-$. The instability constants decrease regularly in the series from $PtCl_4^{2-}$ to trans-$Pt/NH_3/_2Cl_2$. There is also a general decrease from $PtBr_4$ to $Pt/NH_3/_2Br_2$, but the instability constant of $PtNH_3Br_3^-$ is somewhat larger than that of $PtBr_4^{2-}$. /3/ All the bromides studied were more stable than the corresponding chlorides. /4/ The trans-diammines studied were more stable than the cis-compounds. /5/ The kinetic and thermodynamic properties of cis- and trans- $Pt/NH_3/_2X_2$ are compared.

Total /cumulative/ constants.- /6/ Instability constants /concentration/ have been determined by a potentiometric method for the ions $PtCl_4^{2-}$, $PtBr_4^{2-}$, PtI_4^{2-}, $Pt/CN/_4^{2-}$, $Pt/NH_3/_4^{2-}$, $Pt/C_2H_5NH_2/_4^{2+}$, $Pt/CH_3NH_2/_4^{2+}$, $Pten_2^{2+}$, and also for $PtNH_3Cl_3^-$, $Pt/NH_3/_2Cl_2$, $Pt/NH_3/_3Cl^+$, $Pt/NH_3/_2I_2$ and $Pt/CH_3NH_2/_2I_2$. /7/ It is shown, that a platinized platinum electrode in platinum /II/ salt solution reacts $Pt^{2+} + 2e^- \rightleftharpoons Pt/s/$. /8/ It is also shown, that there is an exchange between platinum metal and $PtCl_4^{2-}$ and $Pt/NH_3/_4^{2+}$. /9/ The total instability constant decreases regularly from

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

$PtCl_4^{2-}$ to $Pt/NH_3/_4^{2+}$. /10/ The total instability constants determined by us are compared with literature data and correlated with the general chemical behavior of the complexes. /11/ The mechanism of Gros's reaction, i.e. the transformation of Magnus's salt into Gros's salt and platinum metal, is explained. /12/ Cis-$Pt/NH_3/_2Cl_2$ is observed to be isomerised in the presence of platinum metal.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Резюме

О КОНСТАНТАХ НЕСТОЙКОСТИ КОМПЛЕКСНЫХ СОЕДИНЕНИЙ ПЛАТИНЫ

А.А.Гринберг, Г.А.Магисултанова, М.И.Гельфман - СССР

А. Ступенчатые константы

I. Краткий обзор имеющихся в литературе данных по константам нестойкости платиновых комплексов.

2. На основе весьма простого метода определены значения концентрационных констант нестойкости, отвечающих отщеплению одного иона хлора или брома от ионов $PtCl_4^{2-}$, $PtNH_3Cl_3^-$, цис- и транс- $Pt(NH_3)_2Cl_2$, $PtBr_4^{2-}$, $PtNH_3Br_3^-$, цис- и транс- $Pt(NH_3)_2Br_2$, а так же $PtNO_2Cl_3^{2-}$, $PtPyCl_3^-$, $PtPyBr_3^-$.

В ряду $PtCl_4^{2-}$-$Pt(NH_3)_2Cl_2$ имеет место закономерное падение констант от $PtCl_4^{2-}$ /максимальное значение/ до транс- $Pt(NH_3)_2Cl_2$ /минимальное значение/. В ряду $PtBr_4^{2-}$-$Pt(NH_3)_2Br_2$ положение в общем такое же, но константа нестойкости $PtNH_3Br_3^-$ несколько больше, чем у $PtBr_4^{2-}$.

3. Бромиды во всех изученных случаях более устойчивы, чем соответствующие хлориды.

4. Транс-диаммины в изученных случаях более устойчивы, чем цис-диаммины.

5. Дается сопоставление кинетических и термодинамических характеристик цис- и транс- соединений $Pt(NH_3)_2X_2$.

Б. Общие /тотальные/ константы

6. Потенциометрическим методом определены значения общих концентрационных констант нестойкости для ионов $PtCl_4^{2-}$, $PtBr_4^{2-}$, PtI_4^{2-}, $Pt(CN)_4^{2-}$, $Pt(NH_3)_4^{2+}$, $Pt(C_2H_5NH_2)_4^{2+}$, $Pt(CH_3NH_2)_4^{2+}$, $PtEn_2^{2+}$, $PtNH_3Cl_3^-$, $Pt(NH_3)_2Cl_2$, $Pt(NH_3)_3Cl^+$, $Pt(NH_3)_2J_2$ и $Pt(En,NH_2)_2J_2$.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

7. Показано, что в растворах солей Pt/II/ платинированный платиновый электрод ведет себя как электромоторно-активный электрод.

8. Показано, что имеет место обмен между металлической платиной и платиной в составе комплексных ионов $PtCl_4^{2-}$ и $Pt(NH_3)_4^{2+}$.

9. Значения общих констант нестойкости в переходном ряду $PtCl_4^{2-}$-$Pt(NH_3)_4^{2+}$ закономерно уменьшаются от $PtCl_4^{2-}$ /максимальное значение/ до $Pt(NH_3)_4^{2+}$ /минимальное значение/.

10. Вновь полученные значения общих констант сопоставлены с литературными данными и общей характеристикой химического поведения соответствующих комплексов.

11. Разъяснен механизм реакции Гро превращения соли Магнуса в соль Гро и металлическую платину.

12. Обнаружен процесс изомеризации цис- $Pt(NH_3)_2Cl_2$ в присутствии металлической платины.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Резюме

ОБ АЦЕТАТАХ И ФОРМИАТАХ РОДИЯ НИЗШЕЙ ВАЛЕНТНЛСТИ

И.И.Черняев, Е.В.Шендерецкая, Л.А.Назарова, А.С.Анцышкина - СССР

При взаимодействии хлорородиата аммония с муравиной кислотой получено соединение $Rh(HCO_2)_2 \cdot \frac{1}{2} H_2O$. Уксусная кислота с этиловым спиртом дает ацетат состава $Rh(CH_3CO_2)_2 \cdot H_2O$, строение которого определено рентгенографически. Оно оказалось тождественным со строением ацетата меди или хрома /II/.

Реакции и ацетата и формиата родия ограничиваются только обратимым замещением воды на другой адденд из-за трансвлияния краевого атома родия, дополняющего до шести координационное число другого атома родия. Совершенно аналогично химическое поведение ацетатамидных соединений двухвалентной платины, указывающее на возможность такого же димерного строения с координационным числом шесть, сильным трансвлиянием по координатам вода-платина-платина-вода, отсутствием реакции окисления и наличием пяти связей между атомами платины.

Стереохимическое положение атомов родия /и платины/ в димерах совершенно подобно координационному положению атомов углерода в органических соединениях, где каждый атом одновременно имеет положение и центрального и краевого. Центр молекулы димера занимает электронное облоко в отличие от обычных координационных соединений, имеющих в центре положительно /или иногда отрицательно/ заряженный атом. Механизм возникновения димеров родия /и платины/ неясен. Соединения диамагнитны.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

L I S T o f P U B L I C A T I O N S

from the

Dpt's of Inorganic Chemistry- INSTITUTE of TECHNOLOGY

and UNIVERSITY

of

W R O C Ł A W

with the associated

Dpt of Structural Research - INSTITUTE of PHYSICAL CHEMISTRY

POLISH ACADEMY of SCIENCES

1 9 4 7 - 1 9 6

Directory: Prof.W.Trzebiatowski and Prof.B.Jeżowska-Trzebiatowska

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

1. Trzebiatowski W.
"The Existence and Properties of New Discovered Chemical Elements". (pol.Rev.)
Przegląd Chemiczny 5, 84-89 (1947).

2. Trzebiatowski W., Płoszek H., Łobzowski J.
"X-ray Examination of the System Cr-Mo and Cr-W". (pol. engl.sum).
Roczniki Chemii 21, 22-28 (1947).

3. Trzebiatowski W.
"Chemical Compounds of Variable Composition". (pol. -Rev.)
Roczniki Chemii 22, 206-219 (1948).

4. Trzebiatowski W., Wojciechowska J., Damm J.
"The Synthesis of Barium Titanate". (engl.).
EXPERIENTIA VI/4 137, (1950).

5. Jeżowska-Trzebiatowska B., Nawojska J., Wrońska M.
"On Quinquevalent Manganese". (pol.engl.sum.).
Roczniki Chemii 25, 405-416 (1951).

6. Jeżowska-Trzebiatowska B.
"The Chemistry of Rhenium". (pol.-Rev).
Wrocławskie Towarzystwo Naukowe. Seria B. Nr 36 (1951).

7. Jeżowska -Trzebiatowska B.
"Complex Compounds of Rhenium (IV) and (V)". (pol.)
Wrocławskie Towarzystwo Naukowe, Seria B. Nr 39 (1953).

8. Jeżowska-Trzebiatowska B., Nawojska J., Wrońska M.
"The Mechnism of Reduction of $KMnO_4$ by concentrated KOH Solution" (engl.).
Bulletin de L'Academie Pol. des Sci.Cl.III-Vol.I No 7 (1953).

9. Trzebiatowski W., Wojciechowska J., Damm J.
"The Mechanism of the Synthesis of Barium Titanate" (pol.engl.sum.).
Roczniki Chemii 26, 12 (1952).

10. Trzebiatowski W., Śliwa A., Staliński B.
"Magnetic properties od metallic Uranium and Uranium Hydride". (pol.engl.sum).
Roczniki Chemii 26, 110 (1952).

11. Trzebiatowski W., Pigoń K.
"Electric Conductivity of Barium Titanate". (pol.engl.sum)
Roczniki Chemii 26, 494 (1952).

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

12. Staliński B., Damm J.
"The Usefulness of Titanium and his Compound" (pol.Rev.).
Wiadomości Chemiczne 7, 62 (1952)

13. Trzebiatowski W., Staliński B.
"Magnetic Properties of Titanium Hydrides". (russ.).
Bull.Pol.Akad.Nauk kl.III - T.1 No 3-4 (1953).

14. Trzebiatowski W., Staliński B.
"Magnetic Properties of Titanium Hydrides". (engl.).
Bull. de L'Acad.Pol. des Sc.Cl.III - Vol.1 Nos 3-4 (1953).

15. Trzebiatowski W., Staliński B.
"Magnetic Susceptibilities of Niobium Hydrides". (engl).
Bull. de L'Acad.Pol.des Sci. Cl.III. Vol.1 No 7, (1953).

16. Trzebiatowski W., Staliński B.
"Magnetic Susceptibilities of Niobium Hydrides". (russ).
Bull.Pol.Akad.Nauk. kl.III - T.1 No 7, (1953).

17. Wojciechowska J.
"Synthesis of Strontium Titanate". (pol.egl.sum.).
Roczniki Chemii 27, 218 (1953).

18. Trzebiatowski W., Berak J., Romotowski T.
"The Copper-Titanium System". (pol.engl.sum.).
Roczniki Chemii 27, 426 (1953).

19. Trzebiatowski W., Dryś M., Baran W.
"The System Beryllium Oxide-Titanium Dioxide". (pol.engl. sum.).
Roczniki Chemii 27, 438 (1953).

20. Trzebiatowski W.
"The Methods and Problems of Magnetochemistry". (pol.Rev.).
Wiadomości Chemiczne 7, 150 (1953).

21. Śliwa A.
"The Chemistry of Transuranium Elements". (pol.Rev).
Wiadomości Chemiczne 7, 338 (1953).

22. Trzebiatowski W., Berak J.
"The Platinum-Rhenium System". (russ.).
Bull.Pol.Akad.Nauk kl.III - T.II, No 1, (1954).

23. Trzebiatowski W., Śliwa A., Staliński B.
"Magnetic properties of Uranium Hydride and Deuteride".
(pol.engl.sum.).
Roczniki Chemii 28, 12 (1954).

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

24. Trzebiatowski W., Dryś M., Berak J.
"The System Barium Oxide-Titanium Dioxide". (pol.engl.sum.).
Roczniki Chemii 28, 21 (1954).

25. Trzebiatowski W., Łukaszewicz K.
"The Structure of Titanium Arsenide". (pol.engl.sum.)
Roczniki Chemii 28, 150 (1954).

26. Trzebiatowski W.
"The Occurrence, Properties and Application of Some Rare Chemical Elements". (Article in pol.).
Problemy Nr 3, 158 (1954).

27. Staliński B.
"X-Ray Analysis and Magnetic Susceptibilities of Tantalum Hydrides". (engl.).
Bull.de L'Acad. Pol.des Sciences Cl.III - Vol.II. No 5 (1954).

28. Jeżowska-Trzebiatowska B., Wajda St.
"The Behaviour and Constitution of Active Re (IV)-Complexes". (eng.).
Bull. de L'Acad.Pol.des Sc.Cl.III - Vol.II, No 5 (1954).

29. Łukaszewicz K., Trzebiatowski W.
"Crystal Structure of Titanium Arsenide, TiAs" (engl).
Bull. de L'Acad.Pol.des Sciences Cl.III - Vol.II, No 6, (1954).

30. Jeżowska-Trzebiatowska B., Wajda St.
"The Behaviour and Constitution of Active Re (IV)-Complexes" (russ.).
Bull.Pol.Akadem.Nauk kl.III - T.II,No 5, (1954).

31. Trzebiatowski W., Berak J., Niemiec J.
" High Temperature Laboratory Furnaces" (pol).
Przemysł Chemiczny 10, 458 (1954).

32. Jeżowska-Trzebiatowska B., Nawojska J., Wrońska M.
"Kinetics of $KMnO_4$ Reduction with OH - Ions". (russ.).
Bull.Pol.Akad.Nauk. kl.III - T.II No 9, (1954).

33. Biernat J., Jeżowska-Trzebiatowska B.
"Polarographic Reduction of Hypomanganate". (pol.engl.sum.).
Roczniki Chemii 29, 182 (1955).

34. Jeżowska-Trzebiatowska B., Nawojska J., Wrońska M.
"Kinetics and Reaction Mechanism of consecutive Reductions of $Mn^{VII} \rightarrow Mn^{IV}$ by OH^- Ions". (pol.engl.sum.).
Roczniki Chemii 29, 259 (1955).

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

35. Trzebiatowski W., Niemiec J.
"The Structure of $Re_{24}Ti_5$". (pol.engl.sum.).
Roczniki Chemii 29, 277 (1955).

36. Trzebiatowski W., Dryś M.
"The System Strontium Oxide-Titanium Dioxide". (pol.engl. sum.).
Roczniki Chemii 29, 964 (1955).

37. Jeżowska-Trzebiatowska B., Wajda St.
"Binucleary Complex Compounds of Re(IV)" (germ).
Presented at the Annual Meeting of The Chemical Society in the German Democratic Republic 1954.

38. Jeżowska-Trzebiatowska B., Pajdowski L.
"Trinuclear vanadium (III) Complexes". (germ.).
Presented at the Annual Meeting of The Chemical Society in the German Democratic Republic 1954.

39. Łukaszewicz K., Trzebiatowski W.
"Unit Cells of Barium Titanates $BaO.2TiO_2$ and $BaO.4TiO_2$". (pol.engl.sum.).
Roczniki Chemii 29, 943 (1955).

40. Trzebiatowski W., Rozdział P.
"Studies on the Content of Tracer Elements in Polish Phosphat Rocks". (pol.engl.and russ.sum).
Przemysł Chemiczny 11, 614 (1955).

41. Trzebiatowski W., Terpiłowski J.
"Thermodynamic Properties of the Silver-Zinc System and the Related beta-AgMg Phase". (engl.).
Bull. de L'Acad.Pol.des Sciences Cl.III - Vol.III No 7, 391 (1955).

42. Jeżowska-Trzebiatowska B., Przywarska H.
"Peroxycomlexes as Intermediate States in the Electron Transfer Reaction". (engl.).
Bull. de L'Acad.Pol.des Sciences Cl.III - Vol.III, No 8, 429 (1955).

43. Trzebiatowski W.
"Inorganic Chemistry in Wrocław". (pol.).
KOSMOS (seria B: Przyroda nieożywiona) Rok.I, 1,348,(1955)

44. Staliński B.
"X-Ray Analysis of Lanthanum Hydrides". (engl.).
Bull. de L'Acad.Pol.des Sciences Cl.III - Vol.III, No 11 613 (1955).

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

45. Biernat J., Jeżowska-Trzebiatowska B.
"Polarographic Reduction of Hypomanganate". (pol.engl.sum.).
Roczniki Chemii 29, 182, (1955).

46. Trzebiatowski W.
"The Development of Inorganic Chemistry". (pol.-Rev.).
KOSMOS B. Rok.II,1, 31-41 (1956).

47. Trzebiatowski W., Węglowski St., Łukaszewicz K.
"The Crystal Structure of Zirconium Arsenides". (pol.engl. sum.).
Roczniki Chemii 30, 353 (1956).

48. Rozdział P., Trzebiatowski W.
"Notes on some Tracer Elements Contents in Calcium Cyanamide Fertilizer". (pol.engl.sum.).
Roczniki Chemii 30, 321 (1956).

49. Trzebiatowski W., Damm J., Romotowski T.
"Studies on the Reaction of Anhydrite with Quartz.I Thermodynamical Calculations". (pol.engl.sum.).
Roczniki Chemii 30, 431 (1956).

50. Trzebiatowski W., Damm.J., Romotowski T.
"Studies on the Reaction of Anhydrite with Quartz.II. Progress of the Reaction in the System $CaSO_4 + SiO_2$". (pol.engl.sum).
Roczniki Chemii 30, 443 (1956).

51. Niemiec J.
"The System Gold-Rhenium". (pol.).
Roczniki Chemii 30, 619 (1956).

52. Bezak J.
"The Production of defluorised Thermophosphates on the basis of new Studies on the Ternary System $CaO-P_2O_5-SiO_2$". (pol.).
Przemysł Chemiczny 12, 478-484 (1956).

53. Romanowski W.
"The Electronic Factor in heterogenous Catalysis". (pol.-Rev).
Wiadomości Chemiczne 10, 439 (1956).

54. Trzebiatowski W., Staliński B.
"X-Ray Investigations of the Zirconium-Hydrogen System". (pol.engl.sum.).
Roczniki Chemii 30, 691 (1956).

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

55. Niemiec J. and Trzebiatowski W.
"The Existence of σ - and χ -Phases in Rhenium Alloys" (engl.).
Bull de L'Acad.Pol.des Sciences Cl.III - Vol.IV, 9, 601 (1956).

56. Trzebiatowski W.
"The Structure of Chemical Elements and Compounds".
II Conference on Theoretical Chemistry - Spała 1954 (pol.).
Państwowe Wydawnictwa Naukowe 1956 - Warszawa.

57. Trzebiatowski W., Staliński B.
"Outlines of Methodes and Applications of Magnetochemistry". (pol.). II Conference on Theoretical Chemistry-Spała 1954.
Państwowe Wydawnictwa Naukowe - Warszawa 1956.

58. Jeżowska-Trzebiatowska B.
"The Chemical Bond and Stability of Complex Coumpounds".
II Conference on Theoretical Chemistry - Spała 1954. (pol.)
Państwowe Wydawnictwa Naukowe - Warszawa 1956.

59. Wojciechowska J. Berak J., Trzebiatowski W.
"Investigations of the System $CaO-P_2O_5-SiO_2$. I.Partial System: $3CaO.P_2O_5-CaO.SiO_2-SiO_2$". (pol.engl.sum.).
Roczniki Chemii 30, 743 (1956).

60. Berak J., Wojciechowska J.
"Investigations of the System $CaO-P_2O_5-SiO_2$.II. Partial System: $3CaO.P_2O_5-2CaO.SiO_2-CaO.SiO_2$". (pol.engl.sum.).
Roczniki Chemii 30, 757 (1956).

61. Wojciechowska J.
"Iso- and Polymorphism of A_2XO_4 Compounds" (pol.Rev).
Wiadomości Chemiczne 10, 649 (1956).

62. Trzebiatowski W., Terpiłowski J.
"The Thermodynamic Characteristic of some Intermetallic Phases of extensive Composition Ranges". (pol.engl.sum.).
Roczniki Chemii 31, 333 (1957).

63. Trzebiatowski W.
"Remarks on the Content of some Tracer Elements in technical Calcium Cyanamide (discussion)". (pol.germ.sum.).
Roczniki Chemii 31, 359 (1957).

64. Trzebiatowski W., Kubicka H.
"The Magnetic Properties of Platinum Catalysis with $\gamma-Al_2O_3$ as Carrier". (engl.).
Bull. de L'Acad.Pol.des Sciences Cl.III - Vol.V,No 4, 429 (1957).

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

65. Jeżowska-Trzebiatowska B.
"New Researches of Rhenium Complex Compounds".(germ.).
Chem.Techn. 9 Jg.,8, 470 (1957).

66. Jeżowska-Trzebiatowska B., Wróńska M.
"Decomposition of Potassium Ferrate(VI) in Concentrated KOH Solutions". (engl.).
Bull. de L Acad.Pol.des Sciences Cl.III - Vol. V, 6, 659 (1957).

67. Dryś M., Trzebiatowski W.
"The System Strontium Oxide-Titanium Dioxide". (pol.engl. sum).
Roczniki Chemii 31, 489 (1957).

68. Trzebiatowski W., Kubicka H., Śliwa A
"The Structure and Magnetic Properties of Palladium Catalysts with γ - Al_2O_3 as Carrier" (pol.engl.sum.).
Roczniki Chemii 31, 497 (1957).

69. Trzebiatowski W.
"Some Remarks on Polish Researches in Kinetics". (pol.).
KOSMOS B - Rok III, 2, 181 (1957).

70. Trzebiatowski W., Rozdział P.
"Researches on the Content of Tracer Elements in Polish Mineral Raw Materials". (pol.russ. and engl.sum.).
Przemysł Chemiczny 13, 452 (1957).

71. Staliński B.
"The Structure and Magnetic Properties of Transition Metal Hydrides". (pol. russ.and engl.sum.).
Zeszyty Naukowe Politechniki Wrocławskiej, Chemia IV, 25 - 78 (1957).

72. Tarnizowski J.
"Thermodynamical and Structural Characteristic of Ag-Zn System". (pol.russ. and engl.sum.).
Zeszyty Naukowe Politechniki Wrocławskiej - Chemia III 3-40 (1956).

73. Tarnizowski J.
"Thermodynamical Properties and the Order State of β - Phase in the Au-Zn System". (pol.russ. and engl.sum.).
Zeszyty Naukowe Politechniki Wrocławskiej - Chemia IV 13-23 (1957).

74. Jeżowska-Trzebiatowska B., Pajdowski L.
"Polynuclear Vanadium (III) Complexes. I. Complexes of Vanadium (III) with Chloroacetic Acid". (pol.engl.sum.).
Roczniki Chemii 31, 769 (1957).

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

75. Jeżowska-Trzebiatowska B., Nawojska J., Wajda St.
"A Study of Radiochlorine Exchange by Hexachlororhenate (IV)". (engl.).
Bull. de L'Acad.Pol.des Sciences Cl.III - Vol.V, No 11, 1081 (1957).

76. Żdanowicz W.
"The Purification of Substances by the Zone Melting Method". (pol.Rev.).
Postępy fizyki - T.VIII, 2, 147-164 (1957).

77. Terpiłowski J.
"Thermodynamical Properties of Liquid Metallic Solutions. I. The Ag-Pb System". (pol.russ.and engl.sum.).
Archiwum Hutnictwa T.II, 4, 289-304 (1957).

78. Trzebiatowski W.
"Radioactive Chemical Elements". (pol. - Lecture).

79. Trzebiatowski W., Romanowski W.
"Studies on the Structure of Ni/Al_2O_3 Catalysts with low Nickel Content". (pol.engl.sum.).
Roczniki Chemii 31, 1123 (1957).

80. Łukaszewicz K.
"The Crystal Structure of Barium Tetratitanate, $BaO.4TiO_2$". (pol.engl.sum.).
Roczniki Chemii 31, 1111 (1957).

81. Staliński B.
"Electric Conductivity of Lanthanum Hydride LaH_2-LaH_3". (engl.).
Bull. de L'Acad.Pol.des Sciences Cl.III - Vol.V, 10, 1001 (1957).

82. Staliński B.
"Magnetic Susceptibilities of Lanthanum and the Lanthanum-Hydrogen System". (engl.).
Bull.de L'Acad.Pol.des Sciencies Cl.III - Vol.V, 10, 997 (1957).

83. Trzebiatowski W., Kubicka H.
"The Structure and Magnetic Properties of Platinum Catalysts with γ-Al_2O_3 as Carrier". (pol.engl.sum.).
Roczniki Chemii 32, 3 (1958).

84. Trzebiatowski W.
"Problems arising with the Production and Exploatation of Nuclear Energy-Inaugural Lecture delivered at the Institute of Technology, Wrocław". (pol.).
Wiadomości Chemiczne 12, 31-38 (1958).

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

85. Barak J.
"The System Magnesium Oxide - Phosphorus Pentoxide". (pol.engl.sum.).
Rocznik Chemii 32, 17 (1958).

86. Trzebiatowski W., Różyczka J.
"Electric Properties of Silver Subfluoride Ag_2F". (pol. engl.sum.).
Roczniki Chemii 32, 183 (1958).

87. Trzebiatowski W., Węglowski St., Łukaszewicz K.
"The Crystal Structure of Zirconium Arsenides ZrAs and $ZrAs_2$". (pol.engl.sum.).
Rocznik Chemii 32, 189 (1958).

88. Jeżowska-Trzebiatowska B., Wajda S.
"The Diamagnetic Oxooxalatorhenate (IV)". (engl.).
Bull.de L'Acad.Pol. des Sciences Cl.III - Vol.VI, 4, 217 (1958).

89. Niemiec J., Trzebiatowski W.
"Solid Solutions of σ - Phases with Rhenium Contents". (engl.).
Bull. de L'Acad.Pol.des Sciences Série des sci.chim géol. et geogr. Vol.VI, 4, 223 (1958).

90. Jeżowska-Trzebiatowska B. Wrońska M.
Mechanism and kinetisc of the Cerrate (VI) Reduction". (french.). XVI Congres International de Chimie Pure et Appliqué, Paris 1957.

91. Jeżowska-Trzebiatowska B., Wajda St.
"Diamagnetic Rhenium (IV) Complexes". (germ.).
XVI Congres Inter. de Chimie Pure et Appl. Paris 1957.

92. Jeżowska-Trzebiatowska B., Przywarska M.
"Peroxy-Compounds of Rhenium". (french).
XVI Congres Int. de Chimie Pure et Appl. Paris 1957.

93. Terpiłowski J., Trzebiatowski W.
"Thermodynamical Characteristic of Intermetallic Phases of the Daltonide and Bertohollide Type". (pol.russ. and engl.sum.).
Archiwum Hutniotwa T.III. 2, 97-112 (1958).

94. Jeżowska-Trzebiatowska B., Bartecki A., Chmielewska M., Przywarska H., Mikulski T., Bukietyńska K., Kokołowicz W.
"Studies on the Chemistry of Sesquivalent and Quadrivalent Uranium in Organic Solvents". (engl.).
Nukleonika T.III, 39-58 (1958).

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

95. Damm J., Trzebiatowski W.
"Studies on the Reaction of Anhydrite with Quartz. III Kinetics of the Reaction up to 1230°". (pol.engl.sum.).
Roczniki Chemii 32, 441 (1958).

96. Damm J., Trzebiatowski W.
"Studies on the Reaction of Anhydrite with Quartz. IV Kinetics of the Reaction between 1250° -1310°". (pol.engl. sum.).
Roczniki Chemii 32, 455 (1958).

97. Jeżowska-Trzebiatowska B., and Przywarska H.
"The Kinetics of Reaction between Oxochlororhenate (IV) and Hydrogen Peroxide".
Bull. de L'Acad.Pol. des Sciences Série des sci.chim., Vo.VI,No 6,345 (1958).

98. Jeżowska-Trzebiatowska B., Przywarska H.
"Oxygen Carrying Capacity of Binuclear Rhenium (IV) Complex".
Bull. de L'Acad.Pol. des Sciences Serie des sci.chim., Vo.VI, No 6, 349 (1958).

*) 99. Biernat J.
"Polarographic Investigations of manganates" (pol.engl.sum.).
Prace Konferencji Polarograficznej, Warszawa 282, (1956).

*) 100. Jeżowska-Trzebiatowska B., Biernat J.
"Polarographic Reduction of Ferrates" (pol.engl.sum.).
Prace Konferencji Polarograficznej Warszawa, 278 (1956).

*) 101. Jeżowska-Trzebiatowska B., Nawojska J.
"Polarographic Reduction of Cyanorhenates (V)" (pol.engl. sum.)
Prace Konferencji Polarograficznej, Warszawa 274 (1956).

*) 102. Terpiłowski J.
"Electrochemical Investigations of the β- phase of Ag-Mg alloys" (pol.engl.sum.).
Zesz. Naukowe Politechniki Wrocław.Chemia IV, 3-11 (1957).

103. Kubicka H.
"Crystallochemistry and Ferrimagnetic Properties of Ferrites". (pol. engl.sum.).
Wiadomości Chemiczne 3, 141 (1958).

104. Żdanowicz W.
"Purifying of met . Bismuth by Zone Melting" (pol.engl.sum.).
Zesz.Nauk. Politechniki Wrocław. - Chemia V, 25-35, (1958).

*) Publications omited from the years 1956 - 1957.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

105. Terpiłowski J.
"Thermodynamic Properties of Liquid Metal Solutions Part II. The Bi-In System". (pol.engl.sum).
Archiwum Hutnictwa T.III. 3 227-237 (1958).

106. Damm J.
"Studies on the Reaction of Anhydrite with Quartz - Part V. The influence of the heating rate on the Kinetic of the reaction" (pol.engl.sum.).
Roczniki Chemii 32, 1033-1044, (1958).

107. Jeżowska-Trzebiatowska B., Przywarska H.
"Kinetics of the Reaction between Oxochlororhenate (IV) and Molecular Oxygen Catalyzed by Nitrates".
Bull.de L'Acad.Pol.des Sciences Lettres, Ser.Sc.Chim.VI. 611-615 (1958).

108. Jeżowska-Trzebiatowska B., Bartecki A.
"The Absorption Spectra of Uranyl Nitrate in Some Organic Solvents".
Bull. de l'Acad.Pol.des Sciences Lettres Ser.Chim. VI. 567-574 (1958).

109. Jeżowska-Trzebiatowska B., Pajdowski L.
"Polynuclear Vanadium III Complexes. II. Structure of vanadium III Complexes with Monochloroacetic Acid".
Roczniki Chemii 32, 1061-1072 (1958).

110. K.Łukaszewicz
"The Crystal Structure of Strontium Titanates - $2SrO.TiO_2$ and $3SrO.2TiO_2$". (pol.engl.sum.).
Roczniki Chemii 33, 239 - 242 (1959).

111. Wojciechowska i J.Berak
"The System $MgO - P_2O_5 - SiO_2$" (pol.engl.sum.).
Roczniki Chemii 33, 21 - 31 (1959).

112. W.Trzebiatowski and A.Sepichowska.
"Magnetic Properties of Uranium Tellurides".
Bull. De L'Acad.Pol.Des Scien. Série des sci.chim., géol. et géogr. - Vol.VII, No.3 181 - 182 (1959).

113. W.Trzebiatowski
"Über magnetische Eigenschaften einiger Metallkatalysatoren".
Mitteilungsblatt der Chemischen Geselschaft in der Deutschen Demokratischen Republik Sonder Heft Katalyse 307 - 310 (1959).

114. B.Staliński
"Magnetic Properties of Cerium and of the Cerium-Hydrogen System.Electric Conductivity of Cerium Hydride".
Bull.De L'Acad. Pol.Des Scien. Serie des sci chim., géol. et géogr. Vol.VII, No.5 (1959) 269 - 274.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

115. W.Trzebiatowski, A.Szaynok i P.Rozdział
"Semiquantitative Spectrographic Determination of Some Lanthanides in Thoria" (pol.engl.sum.).
Chemia Analityczna 4, 563-569 (1959).

116. B.Jeżowska-Trzebiatowska und J.Danowska.
"Reduktionsmechanismus und Elektronenstruktur des Oxycyanorhenats (V)".
"Zeitschr.für Physikalische Chemie" 212, 29-39 (1959).

117. B.Jeżowska-Trzebiatowska, A.Bartecki and M.Chmielowska.
"The Potassium Permanganate-Stannous Chloride System in Acetone".
Bull.De L'Acad.Pol.Des Scien.Série des sci.chim., géol.et geogr. - Vol.VII,No.7 485-490 (1959).

118. B.Jeżowska-Trzebiatowska and J.Kaleciński
"The MnO_4^- - MnO_4^{2-} Equilibrium in Alkaline Solutions".
Bull.De L'Acad.Pol. Des Scien.Série des sci.chim., géol et geogr. - Vol.VII, No 6, 417-420 (1959).

119. B.Jeżowska-Trzebiatowska and J.Kaleciński.
"Kinetics and Mechanism of the Disproportionation of Manganate (VI)".
Bull. De L'Acad.Pol. Des Scien.Série des sci.chim.,.géol. et geogr. - Vol.VII, No.6, 411-416 (1959).

120. B.Jeżowska-Trzebiatowska and J.Kaleciński
"Kinetisc and Mechanism of Reduction of Permanganate to Manganate by OH^- Ions.
Bull, De L'Acad.Pol.Des Scien. Série des sci.chim., géol et geogr. - Vol.VII, No.6, 405-410 (1959).

121. J.Terpiłowski
"Thermodynamical Properties of Liquid Metallic Solutions V. The In-Sb System" (pol.engl.sum.).
Archiwum Hutnictwa Tom IV Zeszyt 4, 355-370 (1959).

122. W.Trzebiatowski and A.Kisza
"Electrode Potentials of Uranium in Molten Salts"
Bull.De L'Acad.Pol. Des Scien.Série des sci. chim.,géol. et geogr. - Vol.VII, No.11, 781-787 (1959).

123. M.Dryś and W.Trzebiatowski
"Phase Equilibria in the System Ba_2TiO_4 - Sr_2TiO_4".
Bull. De L'Acad.Pol.Des Scien.Série des sci.chim.,.géol. et geogr. - Vol.VII, No.9, 605 - 606 (1959).

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

124. W.Trzebiatowski, A.Bogacz, I.Baryoka
Investigations on the Reduction of Uranium /IV/ Fluoride by Liquid Aluminium in Molten Salt Mixtures.
Nukleonika Vol.IV (1959) 591-598.

125. B.Jeżowska-Trzebiatowska and J.Kaleciński
X-Ray Inducad Reduction of Potassium Permanganate and Manganate in Akaline Solution.
Bull. De L'Acad.Pol.Des Scien.Série des scien.chim.
Vol.VIII No. 2 (1960) 27-31.

126. W.Romanowski
Magnetic Method of Determination of Dispersion Grade of Metal in Nickel and Cobalt Catalysts.
Roczniki chemii 34 (1960) 239 -249.

127. W.Trzebiatowski
The Present State and Development Prospects of Inorganic and Physical Chemistry in Poland.
The Review of the Polish. Ac. of Sciences (1960) 32-52.

128. A.Bartecki,M.Chmielowska, B.Jeżowska-Trzebiatowska
Inorganic compounds in acetone Part I. (pol.engl.sum.).
Przemysł Chemiczny 39 (1960) 210-214.

129. A.Bartecki, M.Chmielowska, B.Jeżowska-Trzebiatowska
Inorganic compounds in acetone Part II. (pol.engl.sum.).
Przemysł Chemiczny 39 (1960) 215-218.

130. W.Trzebiatowski
The structure and magnetic properties of some metallic catalysts.
Problemy kinetyka i kataliza (russ) X (1960) 155/163.

131. W.Trzebiatowski and W.Romanowski
Structure and Activity of Nickel Catalysts Supported on Zinc oxide.
Bull.De L'Acad.Pol.Des Scien.Série des scien.chim.
Vol.VIII.No.3. (1960) 113-116.

132. J.Terpiłowski and W.Trzebiatowski
Thermodynamic Properties of Indium Antimonide
Bull.De L'Acad.Pol. Des Scien.Série des scien.chim.
Vol.VIII. No. 3 (1960) 95-98.

132. W.Trzebiatowski , K.Pigoń and J.Różycka
Electronic Properties of Zinc Arsenide Zn_3As_2
Bull. De L'Acad.Pol.Des Scien. Série des scien.chim.
Vol.VIII.No. 4 (1960) 197-200.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

134. M.Dryś and W.Trzebiatowski
Some Phase Equilibria in the Ternary System BaO - SrO-TiO_2
Bull. De L'Acad.Pol. Des Scien. Série des scien.chim.
Vol.VIII. No.4 (1960) 173-176.

135. W.Trzebiatowski
The Development of Basic Research on the Chemistry of Reactor Fuels and Materials in Poland. (pol.engl.sum.)
Wiadomości Chemiczne 7 (1960) 453-460.

136. B.Staliński and Z.Biegański
Heat Capacity and Thermodynamical Functions of Titanium Hydride TiH_2 within the Range of 24° to 363° K.
Bull. De I'Acad.Pol. Des Scien.Série des scien.chim.Vol.VIII. Nr.5, (1960) 243-248.

137. B.Jeżowska-Trzebiatowska, J.Ziółkowski
Investigations on the Structure of Complex Compounds by Radioisotopic Exchange.Structure of Cyanonitrosyl Complexes
Conference on the Use of Radioisotopes in the Physical Sciences and Industry - RXCC/116 Copenhagen (1960) 1-17.

138. L.Pajdowski
Polynuclear Vanadium (III) Complexes. III. Potentimetric Investigations of Equilibrium and Stoichiometric Coefficients of Hydroxocomplexes in Solution.
Roczniki Chemii 34 (1960) 763-744 (pol.engl.sum.).

139. L.Pajdowski and B.Jeżowska-Trzebiatowska
Polynuclear Vanadium (III) Complexes.IV. Determination of the Stability of Polynuclear Complexes.
Roczniki Chemii 34 (1960) 775-785 (pol.engl.sum.).

140. B.Jeżowska-Trzebiatowska and L.Pajdowski
Polynuclear Vanadium (III) Complexes.V.Determination of the Instability and Equilibrium Constants in the Nonbuffered System VCl_3 - $ClCH_2COOH$.
Roczniki Chemii 34 (1960) 787-797 (pol.engl.sum.).

141. B.Jeżowska-Trzebiatowska
The Mechanism and Kinetics of some Oxidation-Reduction Reactions in Solutions-Catalysis and Chemical Kinetics Lecture given an the Polish -Russian Conference Wrocław 1959 (Warsaw-PWN 1960 p. 196 (211 - polish.engl.sum.).

142. W.Trzebiatowski
Magnetic Properties and Structure of some Metallic Catalysts an Chemical Kinetics Lecture given at the Polish-Russian Conference Wrocław 1958 (Warsaw -PWN 1960) p.175/82 polish,engl.sum.).

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

143. W.Trzebiatowski and A.Jabłoński
Some Phase Relations of the $BaO-UO_2-O_2$ System
Nukleonika 5(1960) 587/96 (engl.).

144. W.Trzebiatowski and W.Żdanowicz
Some Electrical Properties of Cadmium Arsenide - Cd_3As_2
Bull. de L'Acad. Pol.des Sciences, Série d, sc chimiques -Vol.VIII, 511-16 (1960) - engl.

145. W.Trzebiatowski and A.Sepichowska
Magnetic Properties of Uranium-Tellurium Alloys.II.
Bull.de L'Acad.Pol.des Sciences, Ser. d. sc.Chimiques Vol.VIII 457-60, (1960).

146. A.Idzikowski and W.Trzebiatowski
Occurence certain Trace Elements in the Ashes of Upper Silesian Bituminous - Coal-Part.I.
Bull.de L'Acad.Pol.de Sciences, Ser.sc. géologiques 8 (1960) No.4. (engl) 225-234.

147. A.Idzikowski
Occurence of certain Trace Elements in the Ashes of Upper Selesian Bituminous Coal - Part II.
Bull. de L'Acad.Pol.Sciences, Ser.sc. geologiques 8-(1960) No 4 (engl.) 235-243.

148. K.Łukaszewicz
The Crystal Structure of beta-$Mg_2P_2O_7$
Roczniki Chemii 35 (1961) 31-5 (pol.engl.sum).

149. B.Staliński, Z.Biegański
Adiabatic Semimicrocalorimeter for the Temperature Range 23-370°K. Heat Capacities Measurements on Titanium in the Range 27-360°K.
Roczniki Chemii 35 (1961 273-83 (pol.engl.sum),

150. H.Kubicka
Magnetic Properties of the Cerous Ion in the System CeF_3 - LaF_3
Roczniki Chemii 35 (1961) 385-8 (pol.engl.sum.).

151. J.Berak
Phase Equilibria in the System $CaO-P_2O_5-CaF_2$
Part I The System $Ca_3/PO_4/_2-CaF_2$
Roczniki Chemii 35 (1961) 23-30 (pol.engl.sum).

152. J.Berak
Part II The System $CaO-Ca_3/PO_4/_2-CaF_2$
Roczniki Chemii 35 (1961) 69-78 (pol.engl.sum).

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

153. B.Jeżowska-Trzebiatowska, St.Wajda
Para- and Diamagnetic Rhenium (IV) Complexes. Part III. Complex Compounds of Rhenium (IV) with Organic Hydroxydacids
Bull.Ac.Sc.Pol. Ser.Sc.Chim. IX (1961) 57-64.

154. B.Jeżowska-Trzebiatowska, St.Wajda, W.Wojciechowski
Para- and Diamagnetic Rhenium (IV) Complexes Part IV. Re (IV) Complexes with Phenol Carboxylic Acids
Bull.Ac.Sc.Pol. Ser.Sc.Chim. IX (1961) 65-70.

155. B.Jeżowska-Trzebiatowska, A.Bartecki
The Solvent Effect in Absorption Spectra of Uranyl Nitrate
Bull.Ac.Sc.Pol. Ser.Sc.Chim. IX (1961) 87-90.

156. A.Bartecki, B.Jeżowska-Trzebiatowska
The Vibrational Structure of Electronic Spectra of Uranyl Nitrate. Part I. Force Constants and U-O Distances in Organic Solvents.
Nukleonika VI (1961) 267-276 (pol.engl.sum.).

157. A.Bartecki, B.Jeżowska-Trzebiatowska
Part II. The Dissociation Energy of Uranyl Ion
Nukleonika VI (1961) 277-286 (pol.engl.sum.).

158. A.Bartecki, B.Jeżowska-Trzebiatowska
Part.III. Transition Intensities in the Spectra of Uranyl Nitrate Nukleonika VI (1961) 287-294 (pol.engl.sum.).

159. J.Damm
The Kinetics of Optical Bleaching of F-Centres in gamma-Coloured KCl Crystals.
Bull.Ac.Sc.Pol. Ser.Sc.Chim. IX (1961) 91-6.

160. J.Terpiłowski, I.Barycka
Thermodynamical Properties of Liquid Cadmium Magnesium Solutions.
Bull.Ac.Sc.Pol. Ser.Sc.Chim. IX (1961) 175-178.

161. W.Trzebiatowski, W.Suski
Magnetic Properties of Uranium-Selenium Alloys
Bull.Ac.Sc.Pol. Ser.Sc.Chim. IX (1961) 277-280.

162. Z.Biegański, B.Staliński
Heat Capacities and Thermodynamic Functions of Vanadium and Vanadium Hydride within the Range 24-340°K. The Hydrogen Contribution to the Heat Capacity of Transition Metals Hydrides.
Bull.Ac.Sc.Pol. Ser.Sc.Chim. IX (1961) 367-372.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

163. B.Stalliński
Nuclear Magnetic Resonance and its Application in Chemistry Part I.
Wiadomości Chemiczne XV (1961) 295-312 (pol.engl.sum.).

164. B.Stalliński
Nuclear Magnetic Resonance and its Application in Chemistry Part II.
Wiadomości Chemiczne XV (1961) 403-418 (pol.engl.sum.).

165. W.Trzebiatowski, J.Niemiec, A.Sepichowska
Magnetic Properties of Uranium Tellurides. III. The Preparation, Crystal Structure and Magnetic Behaviour of Uraniumoxytelluride.
Bull. Ac.Sc.Pol. Ser.Sc.Chim. IX (1961) 373-377.

166. K.Łukaszewicz, E.Nagler
Lattice Constants and Space Group of Copper Pyrophosphate.
Roczniki Chemii 35 (1961) 1162-3.

167. K.Łukasiewicz and R.Smajkiewicz
The Crystal Structure of Manganese Pyrophosphate $Mn_2P_2O_7$.
Roczniki Chemii 35 (1961) 741-744 (pol.engl.sum.).

168. W.Żdanowicz
Thermoelectric Properties of Cadmium Arsenide - Cd_3As_2.
Acta Physica Polonica Vol.XX (1961) 647-655 (engl).

169. W.Romanowski
Investigations on the Structure and Composition of Cobalt Contacts Supported on Carriers.
Chemia Stosowana 2 (1961) 225-236 (pol.engl.sum.).

170. B.Jeżowska-Trzebiatowska and K.Bukietyńska
The Electronic Structure of Uranium (IV) in Complex Compounds - I Comparison of the Absorption Spectra of Uranium (IV) and Praseodymium (III) Coumpounds.
J.Inorg.Nucl. Chem.Vol. 19 (1961) 38-42.

171. W.Trzebiatowski i H. Kubicka
K Voprosu o suscestvovanii sverchparamagnetizma v rasbavlennych slojach metallov.
Žurnal Fizičeskoj Chimii Ak.N.SSSR XXXV, vyp.3/1961/682-683 (russ.).

172. L.Paidowski
Stability of Metal-ion Complexes in Solution I.Potentiometric Methods for Computating Succesive Stability Constants of Mononuclear Complexes.
Wiadomości Chemiczne XV (1961) 369-402 (pol.engl.sum).

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

173. L.Pajdowski
Stability of Metal-ion Complexes in Solutions II. Potentiometric Methods for Computating Stability Constants of Polynuclear Two-Component Complexes (A_pB_q).
Wiadomości Chemiczne 15 (1961) 463-481 (pol.engl.sum.).

174. L.Pajdowski
Stability of Metal-ion Complexes in Solution III. Potentiometric Methods For Computating Stability Constants of Polynuclear Three-Component Complexes ($M_q/OH/_pA_s$).
Wiadomości Chemiczne 15 (1961) 529-542 (pol.engl.sum.).

175. J.Niemiec
X-Ray Analysis of the Rhenium-Thorium System
Bull. Ac.Sc.Pol. Ser.Sc.Chim.
Vol.IX, No 8 (1961) 501-506.

176. W.Romanowski, H. Dreyer und D. Mehring
Magnetische Eigenschaften von aus Mischsalzen dargestellten Nickel-Trägerkontakten. I.
Zeitschrift für anorganische und allgemeine Chemie
Bd.310 Heft 4-6 (1961) 286-297.

177. B.Jeżowska-Trzebiatowska and M.Chmielewska
The Behaviour and Structure of Uranyl Nitrate in Organic Solvents - I.
The Studies of Uranyl Nitrate Hexahydrate Organic Solutions by Conductivity Method.
J.Inorg.Nucl.Chem. Vol. 20 (1961) 106-116.

178. W.Trzebiatowski and A.Kisza
Thermodynamic Properties of Cobalt (II) Chloride in Fused Alkali Chlorides.
Bull. Ac.Sc.Pol. Ser.Sc.Chim.
Vol.IX, No 10 (1961) 605-612.

179. J.Wesołowski, J.Jarmuła and B.Rosenfeld
Diffusion and Mobility of Tritium in Tantalum.
Bull. Ac.Sc.Pol. Ser.Sc.Chim.
Vol.IX, No 10 (1961) 651-655.

180. J.Z.Dams
Diffusion Induced Bleaching of Colour Centres in γ - Irradiated KCl Crystals.
Bull. Ac.Sc.Pol. Ser.Sc.Chim.
Vol.IX, No 10 (1961) 647-650.

181. K.Łukaszewicz and T. Głowiak
The Crystal Structure of Potassium Oxycyanorhenate.
Bull. Ac.Sc.Pol. Ser.Sc.Chim.
Vol.IX, No 10 (1961) 613-617.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

182. J.Z. Damm
Some Relation between Optical and Thermal Bleaching of Colour Centres in γ - Irradiated KCl Crystals.
Bull. Ac.Sc.Pol. Ser.Sc.Chim.
Vol.IX, No 10 (1961) 639-645.

183. J.Barak
On Possibilities of Fluorine Substitution by Oxygen in Apatite.
Chemia Stosowana 5 (1961) 565-573 (pol.engl.sum.).

184. B.Jeżowska-Trzebiatowska, J.Kaleciński
The Radiation Chemistry of Oxyanions of Transition Elements Part. I.The Reduction of Potassium Permangenates in Aqueous Solutions by Co^{60} Rays.
Bull. Ac.Sc.Pol. Ser.Sc.Chim.
Vol.IX, No 12 (1961).

185. B.Jeżowska-Trzebiatowska, H.Przywarska
The Acid Base and Structural Equilibria of Binucleus Re (IV) Complexes.
Bull.Ac.Sc.Pol. Ser.Sc.Chim.
Vol.IX, No 11 (1961) 679-684.

186. B.Jeżowska-Trzebiatowska, W.Wojciechowski
Para- and Diamagnetic Re(IV) Complexes
Part V - The Complex of Re(IV) with the Ethylene Diamine Tetracetic acid.
Bull.Ac.Sc.Pol. Ser.Sc.Chim.
Vol.IX, No 11 (1961) 685-691.

187. B.Jeżowska-Trzebiatowska, W.Wojciechowski
Para- and Diamagnetic Re(IV) Complexes
Part VI - The Racah Coefficients and Energy Levels of some Complexes $5d^3$ Elements.
Bull.Ac.Sc.Pol. Ser.Sc.Chim. Vol.IX,No 11 (1961) 693-698.

188. K.Pigoń
Semiconducting Properties of Zinc Arsenide
Bull.Ac.Sc.Pol. Ser.Sc.Chim.
Vol.IX,No 11 (1961) 751-760.

189. K.Pigoń
Some Remarks on Semiconductivity of The $Me_3^{II}X_2^{V}$ Compounds
Bull.Ac.Sc.Pol. Ser.Sc.Chim.
Vol.IX, No 11 (1961) 761-765.

190. B.Jeżowska-Trzebiatowska, W.Wojciechowski
Part VII - The Energy and Lenght of the Oxygen Bond Bridge in Binuclear Re(IV) Complexes.
Bull.Ac.Sc.Pol. Ser.Sc.Chim.
Vol.IX,No 12 (1961) 699-704.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

191. B.Jeżowska-Trzebiatowska, S.Waida and W.Wojciechowski
Para- and Diamagnetic Rhenium (IV) Complexes.
Part VIII. The Absorption Spectra of Oxalatorhenates (IV).
Bull. Ac.Sc.Pol. Ser.Sc.Chim.
Vol.IX, no 12 (1961) 767-772.

192. B.Jeżowska-Trzebiatowska, L.Pajdowski and J.Starosta
Complexes of Chromium (III) Ions and Amino-Acids
I.Optical Investigations of Chromium (III) Complexes With Glycine Roczniki Chemii 35 (1961) 433-444 (pol.engl. sum.)

193. B.Jeżowska-Trzebiatowska, L.Pajdowski and J.Starosta
Complexes of Chromium (III) Ions and Amino-Acids.
II. Stability of Chromium (III) Complexes With Glycine
Roczniki Chemii 35 (1961) 445-456 (pol.engl.sum.)

[redacted]

[redacted]

[redacted]

[redacted]

[redacted]

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

163. B.Staliński
Nuclear Magnetic Resonance and its Application in Chemistry Part I.
Wiadomości Chemiczne XV (1961) 295-312 (pol.engl.sum.).

164. B.Staliński
Nuclear Magnetic Resonance and its Application in Chemistry Part II.
Wiadomości Chemiczne XV (1961) 403-418 (pol.engl.sum.).

165. W.Trzebiatowski, J.Niemiec, A.Szpichowska
Magnetic Properties of Uranium Tellurides. III. The Preparation, Crystal Structure and Magnetic Behaviour of Uraniumtelluride.
Bull. Ac.Sc.Pol. Ser.Sc.Chim. IX (1961) 373-377.

166. K.Łukaszewicz, E.Nagler
Lattice Constants and Space Group of Copper Pyrophosphate.
Roczniki Chemii 35 (1961) 1162-3.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

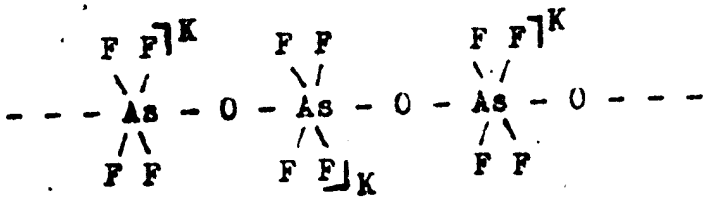
Abstract

ZUR STRUKTUR DER POLYMEREN FLUOROARSENATE

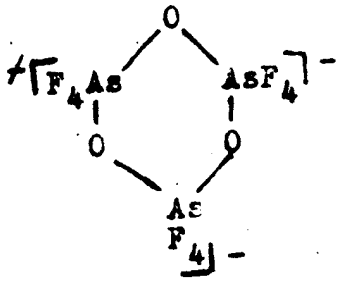
L. Kolditz

Jena, Deutsche Demokratische Republik

Polymere Fluorarsenate entstehen durch thermische Kondensation von Fluorohydroxoarsenaten $[AsF_5OH]^-$, $[AsF_4(OH)_2]^-$, die unter HF - Abspaltung verläuft. Pentafluoromonohydroxoarsenate kondensieren zunächst zu einer kettenförmigen Verbindung. Dabei kommen die zu den OH - Gruppen transständigen Fluoratome zur Reaktion.



Bei höherer Temperatur erfolgt eine Umlagerung der Sauerstoffatome von der trans- in die cis-Stellung, wodurch Ringe vorgebildet werden. In Lösung wurde das Ion



nachgewiesen. Auch die entsprechende Säure ist mit Hilfe von Ionenaustauschern in verdünnter Lösung zu erhalten. Die potentiometrische Titration beweist, dass sie zu den starken Säuren gehört. Tetrafluorodihydroxoarsenate kondesieren unter HF - Abspaltung zu flächenartig vernetzten Polymeren, die nach vorsichtiger Hydrolyse zu räumlich vernetzten Verbindungen weiter kondensiert werden können.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Die Kondensationsreaktionen werden durch Nebenreaktionen des abgespaltenen Fluorwasserstoffes kompliziert, der z.B. $[AsF_4/OH/_2]^-$ in $[AsF_5OH]^-$ umwandelt.

Die Substanzen wurden unter anderem thermographisch, salzkryoskopisch, papierchromatographisch, IR-spektroskopisch und röntgenographisch untersucht.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

BESTIMMUNG VON KOMPLEXZUSAMMENSETZUNGEN IN WÄSSRIGER LÖSUNG DURCH AMINEXTRAKTION

D. Richter und H. Grosse-Ruyken, - Deutsche Demokratische Republik

Die Aminextraktion erlaubt durch Untersuchung der Abhängigkeit der Verteilungskoeffizienten von der Ligandenkonzentration ebenso wie der Anionenaustausch mit festen Austauscherharzen Aussagen über die Komplexbildung und -zusammensetzungen des sich verteilenden Metallions in der wässrigen Phase, wobei insbesondere auch das Gebiet der anionischen Komplexe erfasst wird. Die Genauigkeit der Aussage ist dabei jedoch wegen der Unsicherheit in der Kenntnis der Aktivitätskoeffizienten der an den Reaktionen beteiligten Komponenten in der Austauscher- und wässrigen Phase begrenzt. Da die "flüssigen Anionenaustauscher" im Gegensatz zu den festen Anionenaustauscherharzen keiner Salzinvasion unterliegen, ist es u.a. möglich, bei variabler Ligandenkonzentration in der wässrigen Phase die Bedingungen in der organischen Phase /Aktivitätskoeffizienten, Säurebeladung usw./ exakt konstant zu halten, wenn die Aktivität der Säure im Säure-Salz-Paar HX-MeX in der wässrigen Phase konstant bleibt. Die Änderung des Verteilungskoeffizienten mit der Ligandenkonzentration ist dann ein eindeutiger Ausdruck der Komplexbildung in der wässrigen Phase. Diese Bedingung kann ohne vorherige Kenntnis der Aktivitätskoeffizienten der Säure im Säure-Salz-Paar HX-MeX auf experimentellem Wege dadurch erreicht werden, dass man die organische Phase bis zur Gleichgewichtseinstellung im Kreislauf o.ä. durch Lösungen von HX-MeX verschiedener Konzentrationen leitet.

Es wird über die bisherigen Ergebnisse zur Komplexbildung des Th/IV/ und Hf /IV/ mit Nitrationen berichtet, die durch das Studium der Systeme Tri-n-octylamin/Benzol - Th^{234}, H_2SO_4, Na_2SO_4/H_2O, Tri-n-octylamin/Benzol-Hf^{181}, H_2SO_4, Me_2SO_4/H_2O und Tri-n-octylamin/Benzol - Th^{234}, HNO_3, $MeNO_3/H_2O$ erhalten wurden.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

UNTERSUCHUNG ÜBER DEN EXTRAKTIONSMECHANISMUS BEI DER DIBUTYLPHOSPHORSÄUREEXTRAKTION VON Zr UND Nb

H. Grosse-Ruyken, A. Hermann und H. Krug - Deutsche Demokratische Republik

Die Aufklärung von Extraktionsmechanismen geschieht häufig durch Bestimmung der Abhängigkeit des Verteilungsverhältnisses von der Konzentration der beteiligten Reaktionspartner. Dieses Verfahren, dessen experimenteller Aufwand gering ist, erlaubt z.B. bei der Extraktion von Chelatkomplexen gleichzeitig Aussagen bezw. Berechnungen über die in der wässrigen Lösung vorliegenden Komplexe.

Entsprechende Untersuchungen mit Dialkylphosphorsäuren sind bisher kaum durchgeführt worden, obwohl diese Substanzen bereits seit Jahren als wirksame Extraktionsmittel zur Trennung der verschiedensten Metallionen benutzt werden. Es wurde darum versucht den, Reaktionsablauf bei der HDBP-Extraktion von Mikromengen Zr und Nb aus $HClO_4$-saurer Lösung aufzuklären.

Obwohl bisher die in der organischen Phase vorliegenden Zr- und Nb-Verbindungen nicht isoliert wurden, und auch die Nb- Species in $HClO_4$-saurer Lösung nicht genau bekannt sind, lassen sich als Ergebnis der Extraktionsversuche die Zahl der zu erwägenden Reaktionsabläufe weitgehend einschränken.

Als wahrscheinlichste Reaktion werden z.Zt. angenommen

$$Zr/DBP/_2^{2+} + 3/HDBP/_2 \text{ ====== } Zr/H/DBP/_2/_4 + 2\ H^+$$

$$NbOOH^{2+} + 2/HDBP/_2 \text{ ------ } NbOOH/H/DBP/_2/_2 + 2\ H^+$$

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

ZUR KENNTNIS DER CLATHRATE DER Me/4-ÄTHYLPYRIDIN/$_4$/SCN/$_2$ - KOMPLEXE MIT C_8-AROMATEN

G. Gemlek - Deutsche Demokratische Republik

Koordinierte Metallverbindungen vom Typ der Me/Alkylpyridin/$_4$ /SCN/$_2$ bilden mit Aromaten und deren Derivate Clathrate. Auf Grund der selektiven Clathratbildung lassen sich stellungsisomere Aromaten, z.B. p- und m-Xylol, voneinander trennen.

Wir untersuchten vor allem die Komplexe des Mn, Fe, Co, Ni mit 4-Äthylpyridin als Liganden und Thiocyanat als Anion. Zur Clathratbildung wurden die C_8-Aromaten /p-, m-, o-Xylol und Äthylbenzol/ eingesetzt.

Durch Bestimmung der Bildungsenthalpien, Dampfdrucke, magnetischer Momente und der Molvolumenkontraktionen der Komplexe und Clathrate wurde versucht, den Reaktionsmechanismus und die Art der Bindung aufzuklären und die Gründe für die selektive Clathratierung kennenzulernen. An Hand der Ergebnisse lässt sich erkennen, dass die Zentralionen einen bedeutenden Einfluss auf die Stabilität und die Bildungsenthalpien der Clathrate ausüben. Ausserdem ändert sich die Stabilität der Clathrate mit den addierten C_8-Aromaten. Die Unterschiede der Bildungsenthalpien, Dampfdrucke und Molvolumenkontraktionen sind einmal auf Änderungen der permanenten Dipolmomente der Zentralionen und zum anderen auf die Polarisierbarkeit der C_8-Aromaten durch das Zentralion zurückzuführen. Die Clathratbildung ist ohne Einfluss auf die magnetischen Momente der Komplexe. Mehr oder weniger starke Wechselwirkungsenergie zwischen Zentralion und C_8-Aromat führt zu unterschiedlichen Molvolumenkontraktionen.

Auf Grund mikroskopischer Beobachtungen wird die Ansicht vertreten, dass die Clathrate aus Lösungen kristallisieren

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

und nicht, wie bisher angenommen, dass sich die C_8-Aromaten in das bestehende Kristallgitter des Komplexes unter Änderung der Kristallstruktur einlagern.

Röntgenographische Strukturuntersuchungen der Clathrate führten bisher zu keinem endgültigen Ergebnis. Aus den J.R. Spektren der Komplexe und der Clathrate liessen sich keine Aussagen über die Bindungsverhältnisse machen.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

COORDINATION PROPERTIES OF MOLYBDENUM AND TUNGSTEN

W. Jakób - Poland

This will be a review based on a part of investigations carried out in the Department of Inorganic Chemistry of the Jagiellonian University of Kraków. It is mainly concerned with photo-cyanides of Mo(IV) and W (IV), which coordinate ten ligands each, and with some inorganic oximes of Mo(IV), Mo(V).

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Page Denied

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

ZUR KOMPLEXCHEMIE DER o-HYDROXYCYCLOHEXYLIMINODIESSIGSAURE /I/ UND DER o-HYDROXYANILINDIESSIGSAURE /II/

L.Wolf, W.Metzel, H.Schreiber - Deutsche Demokratische Republik

Durch die potentiometrische Titration der genannten Sauren in Gegenwart von Erdalkali-, Ubergangsmetall- und Seltenerd-Ionen wurden die Komplexeigenschaften ermittelt. Die Ubergangsmetalle und die Erdalkalimetalle bilden mit /I/ und /II/ bevorzugt 1:1-Komplexe, wahrend die Seltenerd-Ionen sowohl stabile 1:1- also auch stabile 1:2-Komplexe bilden. Die pK-Werte von /I/ und /II/ und die Komplexstabilitatskonstanten von /I/ wurden berechnet.

Naherer Einblick in die Struktur der Metallkomplexe wurde durch die Darstellung kristallisierter Verbindungen ermoglicht. Die Analyse der Komplexe ergab Ubereinstimmung mit den auf potentiometrischem Wege gewonnenen Ergebnissen. Mit 2-wertigen Metallionen bildet /I/ neutrale Komplexe des Typs $[Me^{++}X]$, wahrend /II/ anionische Komplexe des Types $[Me^{++}X]^{-}$ ergibt.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

INVESTIGATIONS OF THE COMPLEX COMPOUNDS OF SO_2 AND SeO_2 WITH HCl , HBr, HJ, HF and STUDIES ON COMPOUNDS OF MOLYBDIC ACID AND COMPLEX CYANIDES IN AQUEOUS SOLUTIONS

S. Witekowa - Poland

On the base of the analysis of dependence - curves of pryper conductivity, pH and absorption of light radiation of systems $HCl-SO_2-H_2O$, $HBr-SO_2-H_2O$, and $HJ-SO_2-H_2O$ from the molar relation of components in the permanent temperature 25°C was stated the creation of not durable compounds in composition $SO_2.HCl$, $SO_2.HBr$ and $SO_2.HJ$. The analysis of dependence-curves of proper conductivity of system $H_2F_2-SO_2-H_2O$ from the molar relation of components proved, that H_2F_2 and SO_2 did not create complex compounds.

The comparison of absorption-curves of light radiation of systems $HCl-SO_2-H_2O$, $HBr-SO_2-H_2O$ and $HJ-SO_2-H_2O$ containing halogen - hydrogen and SO_2 in molar proportion 1:1 pointed to the "deepening of colour" of the tested complexes, parallel to the increase of the atomic number of halogen, as well as the difference between the dipolmoment SO_2 and dipolmoment of the conform halogen-hydrogen, that is to increase of the polarity of created complexes.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Analogous investigation of systems $HCl-SeO_2-H_2O$, $HBr-SeO_2-H_2O$ and $H_2F_2-SeO_2-H_2O$ proved of existence of complexes in compositions $SeO_2.4HCl$, $SeO_2.4HBr$ and $SeO_2.4,5\ H_2F_2$. From the absorption-curves of light radiation follows that the "deepening of colour" from $SeO_2.4HCl$ to $SeO_2.4HBr$ increases.

The measuring of the proper conductivity and pH of the mentioned compositions permit to state, that the increase of dilution has an the gradual decomposition of complexes. Investigations carried out in the temperature 0°C and 25°C show on the diminution of durability of this complexes in higher temperature.

Qualitative studies on the reaction between ammonium molybdate and complex cyanides in an acid medium proved that under these conditions, beside $K_4[Fe(CN)_6]$ all these complex cyanides react which have their equivalent in the higher oxidation state. The complexes formed are redox systems.

With the aid of spectrometric measurements coloured solutions of complex compounds of molybdic acid with the following complex cyanides were examined $K_4[Fe(CN)_6]$, $K_4[Fe(CN)_5NO]$, $K_3[Fe(CN)_5NH_3]$, $K_3[Fe(CN)_5H_2O]$, $K_3[Mn(CN)_6]$ and $K_4[W(CN)_8]$. The studies led to the observation that these complexes are very similar to one another.

Ammonium molybdate, in an acid medium, combines with the mentioned complex cyanides in the ratio I:I. During the reactions only this kind of complexes is formed, regardless of the pH of the acid reaction medium. It was found that in the formation with the mentioned complex cyanides the $Mo_6O_{21}^{6-}$ ions take part.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

The curves of light absorption of the studied complexes show a similar shape, and they have analogical higher and lower maxima.

The place of maximum depended on the kind of principal ion of complex cyanides and on the character of group which is going on the place of CN. Mol coefficients of absorption of the studied complexes have been determined. Their values increase with the increase of length of the wave for which light absorption reaches maximum.

The author suggests that the change of dipole moment of the examined complexes brings about the change in value of the mol coefficient of absorption and deepening of colour.

As a result of qualitative examinations it was found that tungstic acid does not react with complex cyanides, whereas chromic acid reacts with some complex cyanides which are in lower state of oxidation.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract.

THERMODYNAMISCHE EIGENSCHAFTEN VON CHARGE-TRANSFER-MOLEKÜL-KOMPLEXEN

G. Junghähnel

Deutsche Demokratische Republik

Die Donator-Acceptor-Molekülkomplexe, die sich durch eine charakteristische, nur dem Molekülkomplex als Ganzes zuzuordnende Absorption im nahen Ultraviolett auszeichnen, lassen sich mit der Theorie von R.S. Mulliken gut beschreiben. Nach dieser Auffassung besteht ein enger Zusammenhang zwischen den optischen und den thermodynamischen Eigenschaften in der Form, dass im allgemeinen einem stabilerem Komplex eine stärker rotverschobene charge-transfer-Bande entspricht.

Ausgehend von einer sehr allgemeinen Gleichung wird gezeigt, dass die Gleichung von Rose und Drago und die viel benutzten Gleichungen von Ketelaar und von Hildebrand und Benesi Sonderfälle dieser Gleichung darstellen.

An den Molekülkomplexen des Jods mit den Halogenbenzolen ist zu erkennen, dass die Stabilität dieser Komplexe in der Reihenfolge F . Bz ⟶ Cl . Bz ⟶ Br . Bz ⟶ J . Bz wächst. Diese Reihenfolge konnte auch durch Verwendung der Löslichkeitsmethode zu Gleichgewichtsbestimmung des Komplexgleichgewichtes bestätigt werden.

An einigen Beispielen kann gezeigt werden, dass die Komplexbildung das Ultrarot-Spektrum der Komponenten beeinflusst und dass dieser Einfluss zur Bestimmung von Gleichgewichtskonstanten verwendet werden kann.

Aus den Änderungen des Ultrarot-Spektrums der Komponenten lassen sich auch Aussagen zur Struktur der charge-transfer-Komplexe machen.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

SPECTROPHOTOMETRIC STUDY OF THE REACTION BETWEEN FERRIC ION AND ACETYLOACETOANILIDES /AAA/

A.Kerkuć, T.Lipiec - Poland

β - diketones reacts in aqueous solution with ferric ions, forming a deep red coloured complex, slightly soluble in water.

Acetyloacetoanilides /$CH_3.CO.CH_2.CO.NH.C_6H_5$/ containing in molecule also nitrogen atom, forms with ferric ions violet coloured complex, soluble in water. The color develops rapidly and is stable for over 24 h.

Analysis of absorption curves $A = f(\lambda)$ indicated formation of one complex with absorption maxima very sharp at $\lambda = 390$ mμ and mild at $\lambda = 530-600$ mμ

Influence of pH on the absorbance of the complex is very large; it increases with the growth of pH until it forms a precipitate of $Fe/OH/_3$.

The absorbance of the mixture was measured at 560 mμ and pH ≈ 2,7, without buffer mixture.

The composition of complex was investigated by the method of continuous variation /Job/, spectrophotometric titration and straight line /Asmus/.

The curves established by means of continuous variation method have not a sharp maximum but indicated the component ratio equal to 1:1 .

With the increase of the concentration the maximum absorption remains unchanged.

The curves of spectrophotometric titration did not show a well defined break and similar results were obtained from reverse measurements; it was indicated by the weak complex /dissociated/.

The Asmus method, which is very useful for such a complexes indicated also the component ratio equal to 1:1.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Results are confirmed by the method of continuous variation in 50% ethanol in which the dissociation of the complex is considerably withdrawn and the curves have a sharp maximum by the ratio 1:1 .

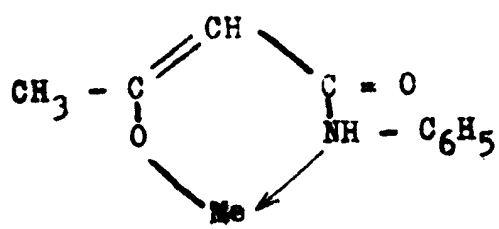
The stability of this complex has been calculated and the value of $K_c \approx 4,087,10^{-3}$, and the molar absorption coefficient for $\lambda = 560$ mμ equals to 1234.

The sensitivity of the reactions is 2,3 μg Fe^{3+}/ml and concentration limit is 1 in 400.000.

Other common metallic ions do not interfere in aqueous solution. Such anions as J^-, $S_2O_3^{2-}$, SCN^-, F^- and organic acids interfere, giving decolourisation or weakness of color.

The complex was found to obey Beer's law between the concentration limits of 1-100 μg Fe^{3+}/ml and AAA may be employed as reagent for a colorimetric determination of Fe^{3+}.

The 1:1 mole ratio of reagent to iron /III/ was found experimentally and the color of complex indicates that the formed complex is other than common typical β-diketones complex with metallic ions and probably the nitrogen atom closed the ring as follows :



Farther investigations are being carried out.

The spectrophotometric measurements have been done using Coleman - Junior spectrofotometer.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

RESEARCH ON THE MIXED MERCURIC THIOCYANATE-SULPHITE COMPLEXES

M. Czakis-Sulikowska - Poland

Mercuric thiocyanate when dissolved in Na_2SO_3 solutions with pH <7,30, forms a complex $\left[Hg\left[SCN\right)_2SO_3\right]^{2-}$. The formation of the complex is proved by a lowering of pH of the initial solution.

By the potentiality method the concentration equilibrium constant (K_r) of the reaction :

$$Hg(SCN)_{2\,solid} + SO_3^{-} \rightleftharpoons \left[Hg(SCN)_2SO_3\right]^{-} \qquad 1.$$

as well as the secondary dissociation constant (K_{wt}) were determined. At 21°C and a ionic strength 0,5 maintained by $NaClO_4$: $K_r = 8{,}91.10^3$, $K_{wt} = 1{,}20.10^{-12}$.

The Na_2SO_3 solution, saturated with $Hg(SCN)_2$, decomposes at pH = 10,63 and precipitates HgO. The reaction of acidolysis with formation of $Hg(SCN)_2$, follows the equation :

$$\left[Hg(SCN)_2SO_3\right]^{-} + H_3O^{+} \rightleftharpoons Hg(SCN)_2\downarrow + HSO_3^{-} + H_2O \qquad 2.$$

In order to characterize the stability of the mixed complex $\left[Hg(SCN)_2SO_3\right]^{-}$ in solution, the equilibrium constant (K_d) of disproportionation was calculated :

$$\left[Hg(SCN)_2SO_3\right]^{-} \rightleftharpoons 2/3\left[Hg(SCN)_3\right]^{-} + 1/3\left[Hg(SO_3)_3\right]^{-4} \qquad 3.$$

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

The exponent the constant $pK_d = -0,49$. The negative value of pK_d indicates that the complex $[Hg(SCN)_2SO_3]^{--}$ is unstable in solution, regardless of the constant K_{wt}. This unstability can be attributed to the large difference between the oxidation-reduction potentials of the coordinated groups SCN^- and SO_3^{--}.

The unstability of the complex under investigation was also confirmed by paper ionophoresis. The investigation was carried out in 30 mins. On strips of Whatman paper No 1, 1 x 40 cm., in a chamber of the moist type, at field intensity 8,82 V/cm., with 0,1 m $NaClO_4$ as ground electrolyte. The electro-osmosis value was 5 mm. Three mercury bands were obtained shifted to the anode by 35 mm, 24 mm and 12 mm from the start point. The two first are connuted with the sulphite band shifted to the anode by 47 mm and the third one - with the thiocyanate bands, shifted to the anode by 12 mm. The ionopheregram obtained shows the simultaneous presence of homogeneous mercury sulphite and thiocyanate complexes in the solutions.

The presence of $[Hg(SCN)_4]^{--}$ ions in solution was also proved by analysis. The molar ratio of mercury precipitated in the form of $Zn[Hg(SCN)_4]$ to that remaining in the solution was found as 2:3.

The above system is an example of the complicated character of equilibrium in solutions containing mixed complexes.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

SOME INFLUENCES DETERMINING COORDINATION NUMBER OF CATIONS*

L. I. Katzin - USA

Since the early interpretations of directional bonding by Pauling and others, it has been understood that the number and geometry of bonds in central atom-ligand configurations depend on the electronic configurations of the central atom /generally a metallic cation/. Only in the context of the changes which appear in the coordination configuration of a given central cation with different ligands has it become apparent that ligands may have characteristic effects on the coordination configuration assumed by the central atom. This does not refer to the purely geometric limitations imposed by the internal structure of a polydentate ligand, but to electronic effects of even monatomic ligands.

The most obvious examples are furnished by the halide ligands. It is now well understood for example that the blue colors of cobaltous halides in organic solvents, or in crystals such as the double CsCl-$CoCl_2$ salts, are due to cobalt having tetrahedral coordination configuration. The common configuration /the red-colored forms/ is 6-coordinate octahedral . The effect of halide on the coordination geometry of not only the first-row transition metals but on others is to facilitate the formation of a lower coordination-number structure than the normal. Conversely, the "normal" is found in aqueous solution, with nitrate, perchlorate or sulfate salts, and these ligands-water, nitrate ion, perchlorate ion, sulfate ion and many others--favor the higher coordination states of acceptor ions.

---

*Based on work performed under the auspices of the U.S. Atomic Energy Commission.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Specific influences have also been identified for ligands with phosphoryl groups /e.g., phosphine oxides, alkyl dialkylphosphonates, tri-organic esters of phosphoric acid etc./. These reduce the coordination of cations with potential f-electron contribution to the hybridization from higher numbers /e.g., 8/ to six. There is a suggestion from recent literature that there may be some specific effects of certain arsines, but these may be linked with conventional steric effects.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

THE MAGNETIC PROPERTIES OF SOME URANIUM IV COMPOUNDS

B.Jeżowska-Trzebiatowska and K.Bukietyńska-Poland

The magnetic susceptibility of some U/IV/ compounds was investigated. It was found that compounds of cubic symmetry are distinguished by the value of magnetic moment μ_{eff} = 2,8 BM Such compounds are: $U/C_2O_4/.2H_2O$ μ_{eff}=2,8 BM and $U/EDTA/.2H_2O$ μ_{eff} = 2,8 BM.
Compounds of orthorombic symmetry /antiprism structure/ have a considerably higher magnetic moment i.e. μ_{eff}=3,3-3,6BM. In this group are: $U/Acac/_4$ μ_{eff} = 3,3 BM, $U/TTA/_4$ μ_{eff} = 3,6 BM and $U/SO_4/_2 \cdot 4H_2O$ μ_{eff} = 3,6 BM.

On the grounds of present author's investigations, the literature data and assuming the $5f^2$ structure for U/IV/ /the ground state $^3H_4$/, the U /IV/ compounds may be systematized as follows:

1. Compounds with cubic symmetry, marked either by a strong dependence of magnetic susceptibility on the temperature and the magnetic moment value μ_{eff} = 2,84 BM, or only by weak paramagnetism which is unaffected by the temperature.
2. The U/IV/ compounds, with the orthorombic symmetry of the antiprism type, having the magnetic moment value μ_{eff} = 3,3-3, 7BM. In this case, the degeneracy of $^3H_4$ state is quenched by the action of crystal field on the $5f^2$ electrons.

According to calculations of L. Natkaniec and W.Wojciechowski the $^3H_4$ level splits into 5 levels. The difference between the two lowest levels is ΔE=192,5 cm^{-1} /comparable with kT/. Based on these results, the explanation of the higher values of magnetic moment for some U/IV/ compounds is in good agreement with the experimental data.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1 STAT

Abstract

ADVANCES IN ORGANO - METALLIC COMPOUNDS CATALYSIS

A. Goudot - France

The theoretical study of complex compounds can be deepened by means of molecular-orbital method.
In the formation of organo-metallic compounds the metallic cation strongly "electrophile" proceeds to a delocalisation of π-electrons on the ligands atoms. The distribution of charges can be calculated for a case of breaking off of a bond between two atoms which become heavily positive.
Energy-levels calculations allow to determine when two unlike ligands are coordinated, one of them are a "donor", and the other an "acceptor". That can allow us to forsee the transfer of an atom or molecule from "donor" to the "acceptor".
It is with this method that the study of complex compounds in catalysis has been involved.
In the first place a study has been made with two organo--cupric complex catalysing the reaction: $2H_2O_2 = 2H_2O + O_2$, of which L. Nicolaev has made the experimental studies /organo- compounds are trimethyl-diamine and biuret/. The ligand field due to the ligands determines the electronic structure of the complex catalyst. From electromagnetic property of the ligands-metal-complex depends the catalytic power in the charge complex addend-metalsubstrat.
Delocalisation energy calculations in charge transfer complexes allow us to obtain the "activation potential".

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

THE MAGNETIC PROPERTIES OF "ADDITIONAL" COMPOUNDS OF CHROMYL CHLORIDE WITH HYDROCARBONS

A. Bartecki, S. Wajda - Poland

The compounds formed between chromyl chloride and hydrocarbons were well known for a long time. As it was frequently assumed chromium remains sixvalent in these compounds. This suggestion is in evident contradiction with some experimental facts, for instance that after the hydrolysis, chromium /IV/ compounds on the one side and oxidation products of hydrocarbons /aldehydes, ketones/ on the other are obtained. But unfortunately in spite of many ideas concerning the forming mechanism and structure of these compounds, the electronic structure of chromium was not directly determined. There is especially a complete lack of magnetochemical measurements.

Starting from this point we have carried out measurements of magnetic susceptibility, using Guy's method, of two compounds:

$$2 \cdot CrO_2Cl_2 \cdot C_8H_{18} \text{ and } 2\ CrO_2Cl_2 \cdot C_6H_{12}$$

in both the solid and liquid states. The measurements in the solid state were performed in the temperature range from 80 to 300°K at fourmfield strenghts. It was stated that both compounds are paramagnetic, and the calculated magnetic moments is equal μ = 4,40 B.M. for isooctane- and μ = 4,41 B.M. for cyclohexane-complexes. These compounds follow the Curie-Weiss law, the Weiss-constant beeing θ = -2,5° and θ = +7,0°K.

The measurements in dioxane solutions, carried out in room temperature show that the magnetic moments are here very close to the theoritical value for Cr/IV/ e.g. d^2 system. The corresponding values are μ = 5,1 BM and μ = 5,0 BM.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

The investigations lead to following principal conclusions:

1/ chromium does not remain in its initial oxidation state /VI/; assuming the T_d arrangment and d^3 s hybridisation it seems that chromium appears here to be four-valent;

2/ the compounds of chromyl chloride with hydrocarbons could not be treated as additional compounds. They should be accepted as true coordination compounds arising during the dismutation process between chromium atom and hydrocarbon molecule. This is followed by protonation of one oxygen atom in the chromyl group and forming a binuclear complex with double oxygen bridges between chromium and carbon atoms.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

THE DIAMAGNETIC OXOHALOGENORHENATES /V/.

S. Wajda and B.Jeżowska-Trzebiatowski - Poland

The only known up to-date oxohalogenorhenate /V/ compound is $K_2/ReOCl_5/$, which appears as an intermediate step in the reduction of $KReO_4$ by hydrogen iodide.

Owing to the application of SO_2 as a reducing agent we have obtained $/ChinH/_2/ReOBr_5/$ and $/ChinH/_2/ReOJ_5/$. These compounds are the final product of the reduction of Re/VII/ in the medium of a suitable acid.

Measurements of magnetic susceptibility in the temperature range 80° to 300°K demonstrated that these compounds are diamagnetic like $K_2/ReOCl_5/$. The magnetic susceptibility of the quinoline salt of oxobromorhenate /V/ and oxoiodorhenate /V/ changes slightly according to temperature, namely to $\chi_M^{292} = -288.10^{-6}$ and $\chi_M^{80} = -245.10^{-6}$ for oxobromorhenate/V/ or $\chi_M^{295} = -405.10^{-6}$ and $\chi_M^{81} = -346.10^{-6}$ for oxoiodorhenate /V/.

The determination of oxobromorhenate /V/ molecular weight in acetone solution with Berger Rast's isothermic distillation method showed that it is a molecular compound. The results obtained preclude the suggestion that spin-spin coupling of two rhenium atoms through the oxygen bridge has been the cause of diamagnetism.

Diamagnetism in the above compounds may only be caused by the Re/V/ d^2 electron pairing on the b_{2g} level as a result of the t_{2g} orbitals splitting in octahedral field rhombically distorted.

These conclusions are confirmed by analysis of the absorption spectra. There occur - as was to be expected - the tho-

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

three absorption bands, typical for the transitions between the split levels, i.e. oxobromorhenate /V/ at λ = 450 mμ, ε = 52,3/, λ = 535 mμ / ε = 65,1/ and at λ = 820 mμ / ε = 25,9/. In the case of oxoiodorhenate /V/ these maxima are shifted in the hypsochromic direction i.e. λ = 415 mμ /ε=1840/ and λ = 525 mμ / ε = 350/.

In oxoiodorhenate /V/ the position of these band is the same as in the case of oxocyanorhenate /V/. The shifting of the absorption bands in the hypsochromic direction in oxoiodorhenate /V/ and oxocyanorhenate /V/ proves their greater thermodynamic stability. The stability of these complexes therefore changes in the following order.

$$Cl < Br < J = CN$$

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1

STAT

Abstract

ON ACETATES AND FORMIATES OF LOW-VALENCY RHODIUM

I.I. Chernyaev, E.V.Shenderetskaya, L.A. Nasarova and A.S. Antsyshkina - USSR

Ammonium chlororhodiate reacts with formic acid to give the compound $Rh/HCO_2/_2/H_2O/_{1/2}$. With acetic acid in ethanol it yields the acetate of composition $Rh/CH_3CO_2/_2H_2O$. By X-ray methods, the latter compound has been shown to have the same structure as the dimeric copper/II/ and chromium /II/ acetates.

The only reactions of rhodium/II/ acetate and formiate seem to be the reversible substitution of water by another addend; this fact is ascribed to the trans-effect which each rhodium atom exerts upon the other rhodium atom which occupies one corner of its coordination octrahedron. A fully analogeus chemical behavior is shown by the acetamide compounds of platinum /II/. This indicates the possibility that these are also dimers with the coordination number 6, with a strong trans-effect along the line H_2O-Pt-Pt-H_2O, no tendency to oxidation, and five bonds between the platinum atoms.

The sterochemical position of the Rh/and Pt/ atoms in the dimers is very similar to the coordination position of carbon atoms in organic compounds, in which each atom acts both as a coordination center and as a ligand. Unlike usual coordination compounds, in which the center is a positively /or sometimes negatively/ charged atom, the center of these dimeric molecules is occupied by an electronic cloud. The mechanism of formation of the Rh /and/Pt/ dimers is not clear. The compounds are diamagnetic.

Declassified in Part - Sanitized Copy Approved for Release 2011/11/07 : CIA-RDP80T00246A017300080001-1