CHERNYAYEV, I. I.

21449 CHERNYAYEV, I. I.; i MURAVEYSKAYA, G. S.

O reaktsiyakh soley tipa Blomstranda.
Izvestiya Sektora platiny i drugikh blagorod.
Metallov (In - t obshchey i neorgan. khimii im. Kurnakova),
Vyp. 23, 1949, s. 39. 71. Bibliogr: 9 NAZV.

SO: Letopis' Zhurnal'nykh Statey, No. 29, Moskva, 1949

CHERNYAEV, I. I.

Nek
3

Chernyaev, I.I., and Mashentsev, A.I.

Intracomplex compounds of acid hydrazides. I. Dithiocarbazic acid compounds of bivalent platinum.

Izvest. Sektora Platiny i Drugikh Blagorod. Metal., Inst. Obshchei i Neorg. Khim. Akad. Nauk USSR, Vol. 1949, No. 23, pp. 72-83

Chem. Abs., Vol. 45:2812b

The reactions of bivalent Pt compds. with $NH_4SCSNHNH_2$ (I) were studied. For the prepn. of I (m. 112-14°) 29 g. NH_3 was added to 41.4 g. $N_2H_4 \cdot H_2O$ dissolved in 100 ml. EtOH held in an ice-salt mixt.; 63 g. CS_2 was added with vigorous stirring, and stirring was continued 3-4 hrs. The product was filtered on a Büchner funnel, washed with abs. $EtOHEt_2O$, and dried over H_2SO_4, KOH, and paraffin.

CHERNYAYEV, I. I.

35197. O Geometricheskoy Izomeriitramina Sostava (En $NH_3PtClBrNO_2$)KH. Soobshch. 2. Izvestiya Sektora Platiny I Drugikh Blagorod. Metallov (In-T Obshchey I Neorgan. Khimii Im. Kurnakova), Vyp. 24, 1949 s. 79-99. --Bibliogr: 6 Nazv.

SO: Letopis' Zhurhal'Nykh Statey, Vol. 48, Moskva, 1949

CHERNYAYEV, I. I. and MURAVEYSKAYA, G. S.

"Geometric Isometry of Diamindinitro Compounds of Four-Valence Platinum," Iz. Sekt. Plat. i Blag. Met., 25, 1950

CHERNYAYEV, I. I.

Chemical Abst.
Vol. 48 No. 6
Mar. 25, 1954
Inorganic Chemistry

(3)

Internal complex compounds of hydrazides of acids. II. I. I. Chernyaev and A. I. Mashentsev. *Izvest. Sektora Platiny i Drug. Blagorod. Metal., Inst. Obshchei i Neorg. Khim., Akad. Nauk S.S.S.R.* 26, 62–8(1951); cf. *C.A.* 45, 2812*b*.—On the basis of a study of chem. and phys. properties, 4 configurations were established for the synthesized hydrazide dithiocarbonate of bivalent Pt. The nonelectrolytes $[(NH_3)_2(SCSN_2H_3)_2Pt]$ and $[(NH_3, SCSN_2H_3)(SCSNHNH_2)Pt]$ were obtained simultaneously from chlorotriammineplatinous chloride and from NH_4 trichloroammineplatinite.

J. R. Behrman

AF
11-5-54

CHERNYAYEV, I.I.

CA

6

Reactions of chloroammoniacal compounds of bivalent platinum with the hydrazide of dithiocarbonic acid. A. I. Mashentsev and I. I. Chernyaev (N. S. Kurnakov Inst. Gen. and Inorg. Chem., Acad. Sci. U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.S.R.* **70**, 803-6(1951).—Reaction between 1 mole $NH_4[(Cl_2)(NH_3, Cl)Pt]$ (**I**) and 4 moles $NH_2SSCNHNH_2$ (**II**) in cooled aq. soln. gives a flaky ppt. of a light-yellow $[(NH_3, N_2H_3CSS)(SSCNNH_3)Pt]$ (**III**), in which evidently the NH_3 of **I** has remained unsubstituted; consequently, only one of 2 radicals **II** forms an inner-complex cycle with Pt, while the other is bound to the Pt atom only by S. In NH_4OH or in alkali soln. **III** dissolves with difficulty, with a bluish green color. Mixing of 1 mole $[(Cl, NH_3)(NH_3)_2Pt]Cl$ (**IV**) with 3 or 4 moles **II** gives a yellowish white ppt. of $[(N_2H_3CSS)_2(NH_3)_2Pt]$ (**V**) identical with the product obtained from *trans*-$[Cl_2Pt(NH_3)_2]$ (*C.A.* **42**, 6004*g*). Reactions of **II** with Cl, NH_3 complexes of Pt (II) result always in nonelectrolyte complexes, on account of the tendency of hydrazides to form cycles, and the strong trans influence of its S bond. Substitution of the inner-sphere Cl (or other acid radical) by the sulfide group of **II** proceeds with the velocity of an ionic reaction; on the other hand, neither the S nor the NH_2 group of **II** will substitute the inner-sphere NH_3 of $[Pt(NH_3)_4]Cl_2$. Consequently, the obligatory primary step is the substitution of the single Cl by the S group of **II**, and NH_3 can be substituted only by virtue of the trans influence of that group. The course of the reactions is summarized in the following scheme (in which *th* stands for the cyclic and *th** for the noncyclic NH_2NHCSS group): I(*a*)$(NH_4)_2[(Cl_2)(Cl_2)Pt]$ + 2 **II** → *trans*-$[(th)_2Pt]$ + $4NH_4Cl$; (*b*) *trans*-$[(th)_2Pt]$ + 2NaOH → *trans*-$[(NHNHCSS)_2Pt]Na_2$ + $2H_2O$; (*c*) *trans*-$[(NHNHCSS)_2Pt]Na_2$ + 2HCl → *trans*-$[(th)_2Pt]$ + 2NaCl; (*d*) *trans*-$[(NHNHCSS)_2Pt](NH_4)_2$ + $[(NH_3)_2(NH_3)_2Pt]Cl_2$ → *trans*-$[(NHNHCSS)_2Pt][(NH_3)_4Pt]$ + $2NH_4Cl$; II (*a*) $NH_4[(Cl_2)(NH_3, Cl)Pt]$ + 2 **II** → *trans*-$[(th)(th^*, NH_3)Pt]$ + 3 NH_4Cl; (*b*) *trans*-$[(th)(th^*, NH_3)Pt]$ + NaOH → *trans*-$[(NHNHCSS)(th^*, NH_3)Pt]Na$ + H_2O. III(*a*)$[(NH_3, Cl)_2Pt]$ + 2 **II** → *cis*-$[(th)_2Pt]$ + $2NH_4Cl$ + $2NH_3$; (*b*) *cis*-$[(th)_2Pt]$ + 2NaOH → *cis*-$[(SSCNHNH)_2Pt]Na_2$ + $2H_2O$; (*c*) *cis*-$[(SSCNHNH)_2Pt]Na_2$ + 2HCl → *cis*-$[(th)_2Pt]$ + 2NaCl; IV.$[(Cl_2)(NH_3)_2Pt]$ + 2 **II** → $[(th^*)_2(NH_3)_2Pt]$ + $2NH_4Cl$; V.$[(Cl, NH_3)(NH_3)_2Pt]Cl$ + 2 **II** → $[(th^*)_2(NH_3)_2Pt]$ + $2NH_4Cl$ + NH_3; VI.$[(NH_3)_2(NH_3)_2Pt]Cl_2$ + 2 **II** → $[(NH_3)_4Pt]th_2$ + $2NH_4Cl$. N. Thon

1952

CHERNYAYEV, I.I.

3

Geometric and mirror-image isomerism of the triammines [enNH$_3$PtClBrNO$_2$]X. I. I. I. Chernyaev and O. N. Adrianova. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1953, 204–14; *Bull. Acad. Sci. U.S.S.R.*, Div. Chem. Sci. 1953, 183–91(Engl. translation); cf. *C.A.* 45, 1896*h*.—The isomers [enMeNH$_2$NO$_2$ClBrPt]Cl (I) and [enMeNH$_2$ClNO$_2$BrPt]Cl (II) were prepd. I is yellow, n_γ 1.75–1.76, n_α 1.714, extinction angle 45°. enNH$_3$ClNO$_2$BrPtCl (III) and enMeNH$_2$ClNO$_2$BrPtCl (IV) were resolved into optical isomers. The rotatory power was measured for *d*- and *l*-enNH$_3$ClNO$_2$BrPtCl (V), *d*- and *l*-enNH$_2$ClNO$_2$BrPt (VI), *d*-enMeNH$_2$ClNO$_2$BrPtNO$_3$ (VII), and *l*-enMeNHClNO$_2$BrPt (VIII). The amido-inversion coeff., ρ, is about 6 for the reaction $V \underset{OH^-}{\overset{H^+}{\rightleftarrows}} VI$ and about 5 for the reaction $VII \underset{OH^-}{\overset{H^+}{\rightleftarrows}} VIII$. In the presence of dichloronitrotriammines the corresponding values of ρ are 4–6 and 21–29, resp. $[\alpha]_D$, $[M]_D$, and α_F/α_C are tabulated for I–V and VII. The tabulated max. values of molar cond. for I and II are 141 and 107 mho-cm., resp.

J. W. Loweberg, Jr.

CHERNYAYEV, I.I.

(3) 4

Chemical Abst.
Vol. 48
Apr. 10, 1954
General and Physical Chemistry

Thermochemical investigation of isomeric compounds of platinum. I. I. Chernyaev, V. A. Palkin, and V. A. Sokolov. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1953, 215-9.—The heats of reaction (*q*) of *cis*-$Pt(NH_3)_2Cl_2$ (I), *trans*-$Pt(NH_3)_2Cl_2$ (II), $[Pt(NH_3)_3Cl][PtNH_3Cl_3]$ (III), $[Pt(NH_3)_3Cl]_2[PtCl_4]$ (IV), and $[Pt(NH_3)_4][PtNH_3Cl_3]_2$ (V) with aq. NH_3 were measured with an elaborate, illustrated, and fully described resistance thermometer sensitive to about 0.00005°. The values of *q* for I-V are 62.4, 52.2, 61.8, 54.9, and 59.5 cal./g., resp. Calcd. heat values for the isomeric transition I → II and the depolymerizations III → II, IV → II, and V → II are 3.0 ± 0.2, 5.8 ± 0.3, 2.5 ± 0.3, and 0.6 ± 1.2 kcal./mole, resp. J. W. Loweberg, Jr.

AF
6-27-54

CHERNYAYEV, I.I.

Complex compounds of platinum and acetamide. I. I. Chernyaev and L. A. Nazarova. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1953, 220-6; *Bull. Acad. Sci. U.S.S.R., Div. of Chem. Sci.* 1953, 199-203 (Engl. translations); *Izvest. Sektora Platiny* 28 (1952).—Compds. have been prepd. having the type formula $[Pt(NH_2COCH_3)(NHCOCH_3)(A)]X$, where A is NH_3 or $C_2H_4(NH_2)_2$, and X is nitrate, chloride, bromide, iodide, thiocyanate, or nitrite ion. Values of molar cond. at 25° for 0.25*M* solns. of imidoethylenediamineamminoplatinum(II) nitrate and the corresponding nitrite are 120 and 129.6 mho-cm.^{2}, resp. It is suggested that a H bond exists in ethylenediamine-acetamide compds. of Pt between the N atom of the free amide group and the O atom of the adjacent acetamide mol.

J. W. Loweberg, Jr.

VAYNSHTEYN, E.Ye.; KAVETSKIY, V.S.; CHERNYAYEV, I.I., akademik.

X-ray absorption spectra of Ni, Cu, and Zn ions in aqueous and non-aqueous solutions. Dokl.AN SSSR 91 no.4:775-778 Ag '53. (MLRA 6:8)

1. Akademiya nauk SSSR (for Chernyayev). 2. Institut geokhimii i analiticheskoy khimii im. V. I. Vernadskogo Akademii nauk SSSR (for Vaynshteyn and Kavetskiy). 3. Voronezhskiy gosudarstvennyy universitet (for Vaynshteyn and Kavetskiy).
(Absorption Spectra)

VAYNSHTEYN, E.Ye.; CHERNYAYEV, I.I., akademik.

Theory of the fine structure of X-ray absorption spectra of ions in solutions. Dokl.AN SSSR 91 no.5:1059-1062 Ag '53. (MLRA 6:8)

1. Akademiya nauk SSSR (for Chernyayev). 2. Institut geokhimii i analiticheskoy khimii im. V.I.Vernadskogo Akademii nauk SSSR.
(Absorption spectra)

MIKHEYEVA, V.I.; SURS, V.Yu.; CHERNYAYEV, I.I., akademik.

Reaction of magnesium boride with water. Dokl.AN SSSR 91 no.5:1133-1135 Ag '53. (MLRA 6:8)

1. Akademiya nauk SSSR (for Chernyayev). (Magnesium boride)

SEMENCHENKO, V.K.; CHERNYAYEV, I.I., akademik.

Pseudo-critical points and overcritical transitions. Dokl.AN SSSR 92 no.3: 625-627 S '53. (MLRA 6:9)

1. Akademiya nauk SSSR (for Chernyayev). (Phase rule and equilibrium)

MIKHEYEVA, V.I.; SURS, V.Yu.; CHERNYAYEV, I.I., akademik.

On the chemical characteristics of potassium hypoborate. Dokl. AN SSSR 93 no.1: 67-69 N '53. (MLRA 6:10)

1. Akademiya nauk SSSR (for Chernyayev). (Potassium hypoborate)

CHERNIAYEV, I.I., akademik.

Experimental basis for the transeffect regularities. Izv.Sekt.plat. i blag.met. no.28:14-44 '54. (MLRA 7:9)
(Compounds, Complex) (Platinum)

CHERNYAYEV, I.I.

GRINBERG, A.A. (Leningrad); BABAYEVA, A.V. (Moscow); YATSIMIRSKIY, K.B. (Ivanovo); GOREMYKIN, V.I. (Moscow); BOLIY, G.B. (Moscow); FIALKOV, Ya.A. (Kiyev); YAKSHIN, M.M. (Moscow); KEDROV, B.M. (Moscow); GEL'MAN, A.D. (Moscow); FEDOROV, I.A. (Moscow); MAKSIMYUK, Ye.A. (Leningrad); VOL'KENSHTEYN, M.V. (Leningrad); ZHDANOV, G.S. (Moscow); PTITSYN, B.V. (Leningrad); ABLOV, A.V. (Kishinev); VOLSHTEYN, L.M. (Dnepropetrovsk); TROITSKAYA, A.D. (Kazan'); KLOCHKO, M.A. (Moscow); BABAYEVA, A.V.; TRONEV, V.G. (Moscow); RUBINSHTEYN, A.M. (Moscow) CHERNYAYEV, I.I.; GRINBERG, A.A.; TANANAYEV, I.V.

Explanation of the transeffect. Izv.Sekt.plat.i blag.met. no.28: 56-126 '54. (MLRA 7:9)

(Compounds, Complex) (Platinum)

CHERNYAYEV, I.I.

AID P - 2256

Subject : USSR/Chemistry

Card 1/1 Pub. 152 - 1/19

Authors : Vol'fkovich, S. I., I. I. Chernyayev, and A. V. Nikolayev

Title : Orest Yevgen'yevich Zvyagintsev (On the occasion of his 60th birthday and the 35th anniversary of his scientific activities)

Periodical: Zhur. prikl. khim., 28, no.2, 121-122, 1955

Abstract : Biographic sketch with photograph.

Institution: None

Submitted : No date

CHERNYAYEV, I.I.; MURAVEYSKAYA, G.S.

[redacted]

Geometric isomerism of diamminedinitro componds of tetravalent platinum. Izv.Sekt.plat.i blag.met. no.31:5-25 '55. (MLRA 9:5)
(Platinum compounds) (Compounds, Complex) (Isomerism)

CHERNYAYEV, I. I.

C.

USSR/Inorganic Chemistry - Complex Compounds.

Abs Jour : Ref Zhur - Khimiya, No 9, 1957, 30315

Author : Chernyayev, I.I., Andrianova, O.N.
Inst : Institute of General and Inorganic Chemistry, Academy of Sciences. USSR.
Title : Geometric Isomerism of Triamine of Composition $[EnNH_3PtClBrNO_2]X$. Communication III.

Orig Pub : Izv. Sektora platiny IONKh AN SSSR, 1955, No 31, 34-38

Abst : To prove the correctness of the assumption of the instability of configuration with Br - Pt - Br coordinate in compounds of Pt(4+), it is shown that oxidation, with bromine, of $EnNH_3ClPtCl$ (I) results in the formation of cis-dibromotriamine $EnNH_3ClBr_2PtCl$ (II), and that the only reason of the formation of the cis-dibromocompound is isomerization of the transform which is always formed at first. I was obtained, with a 80% yield, by reduction of $EnNH_3Cl_3PtCl$ (III) with hydrazine hydrochloride

Card 1/2

Hydrated monocarbonate [illegible] was obtained from a solution of uranyl nitrate [illegible] pressure of CO_2, and the conditions for the production of uranyl-monocarbonate ($UO_2.CO_3$) from alcoholic solutions were determined.

PM

CHERNYAYEV, I.I

CHERNYAYEV, I.I., akademik; red.; STYRIKOVICH, M.A., red.; CHMUTOV, K.V., red.; SHKROB, M.S., doktor tekhn.nauk, red.; RAVICH, M.I., doktor khim. nauk, red.; PIROPOL'SKIY, Z.L., red. izd-va; SHAPRKIN, I.F., red. izd-va; KISELEVA, A.A., tekhn.red.

[Intra-boiler physical and chemical process, water preparation and water operations of boilers in electric power plants of high and ultrahigh parameters] Vnutrikotlovye fiziko-khimicheskie protsessy, vodopodgotovka i vodnye rezhimy kotlov na elektrostantsiiakh vysokikh i sverkhvysokikh parametrov. Moskva, 1957. 594 p. (MIRA 11:2)

1. Akademiya nauk SSSR. Komissiya po paru vsyokikh parametrov.
2. Chlen-korrespondent AN SSSR (for Styrikovich, Chmutov)
(Boilers) (Electric power plants)

CHERNYAYEV, Il'ya Il'ich, akademik; FAYNBOYM, I.B., redaktor; GUBIN, M.I., tekhnicheskiy redaktor.

[Pure substance] Chistoe veshchestvo. Moskva, Izd-vo "Znanie," 1957. 15 p. (Vsesoiuznoe obshchestvo po rasprostraneniiu politicheskikh i nauchnykh znanii. Ser.8, no.31) (MIRA 10:11)
(Chemistry)

CHERNYAYEV, I.I.

563

AUTHOR: Chernyaev, I.I. and Adrianova, O.N.

TITLE: Enantiomorphic Isomerism of Tetravalent-Platinum Compounds. I. Investigation of the Optical Activity of the Triamine $EnNH_3NO_2NO_2BrPtCl$. (Zerkal'naya Isomeriya Kompleksnykh Soedineniy Chetyrekhvalentnoy Platiny. I. Issledovanniye Opticheskoy Deyatel'nosti Triamina $EnNH_3NO_2NO_2BrPtCl$.)

PERIODICAL: "Zhurnal Neorganicheskoy Khimii" (Journal of Inorganic Chemistry, Vol. II, No. 2, pp. 298-306. (U.S.S.R.) 1957

ABSTRACT: This is a continuation of work to study the effect of the configuration and composition of enantiomorphic complex compounds of tetravalent platinum on the optical activity constants of the enantiomorphs, and deals particularly with the compound $EnNH_3NO_2NO_2BrPtCl$, recently prepared by the authors. The previous synthesis by Chernyaev and I.B. Litvak (2) of the corresponding chlorine compound $EnNH_3NO_2NO_2ClPtCl$ enables the effect of the replacement of chlorine by the more trans-active bromine to be found.

It was shown that in the fractional crystallization of d- and ℓ- camphorsulphonates of the triamine $[EnNH_3NO_2NO_2BrPt]^+$ its enantiomorphs are unstable and have the property of interconvertibility. 70-% yields of the d- and ℓ- isomers were obtained by fractional crystallization of the salts of d-camphorsulphonic acid and of ℓ-camphorsulphonic acid respectively.

Card 1/2

Enantiomorphic Isomerism of Tetravalent-Platinum Compounds.
I. Investigation of the Optical Activity of the Triamine
$EnNH_3NO_2NO_2BrPtCl$. (Cont.)

The rotating power and dispersion of the compounds
d(ℓ)-$EnNH_3NO_2NO_2BrPt$-d(ℓ-)$C_{10}H_{15}SO_4$, d(ℓ)-$EnNH_3NO_2NO_2BrPtCl$ and
ℓ(d)-$EnNH_2NO_2NO_2BrPt$.were determined; the rotating power of
the second compound was about one quarter of that of the
triamine with chlorine instead of bromine in the inner sphere.
For the amidoinversion coefficient for the reaction
d(ℓ)-$EnNH_3NO_2NO_2BrPtCl$ $\underset{HCl}{\overset{KOH}{\rightleftarrows}}$ ℓ(d)-$EnNH_2NO_2NO_2BrPt$ a mean
value of 3 was found, which is 2.5 times greater than that
for the chlorine analogue.

There are eight references, two of them Russian.

5 Tables.

Received 1 Nov.1956.

Card 2/2

CHERNYAYEV, I. I.

AUTHOR: Chernyayev, I. I. 78-3-1/35

TITLE: New Investigations of the Trans-Effect. (Novyye issledovaniya effekta transvliyaniya).

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1957, Vol.II, Nr.3, pp. 475-490. (USSR)

ABSTRACT: This is a survey of recent theoretical and experimental work on the trans-effect, but contains only two references to the many authors cited. Chernyayev claims to have observed the effect in tetravalent-platinum compounds as far back as 1926. The survey contains tabulations of reaction rates and other kinetic characteristics for chlorine substitution in tetravalent-platinum complex compounds in acetone solution, and various other relevant reactions both in tetra- and di-valent-platinum compounds. The effect in cobalt complex compounds is discussed and compared with that in the platinum compounds. This paper was presented at the Seventh All-Union Conference on the chemistry of complex compounds. There are 2 figures, 4 tables and 2 references, one of which is Slavic.

Card 1/2

CHERNYAYEV, I. I.

78-3-8/35

AUTHORS: Chernyayev, I. I. and Muraveyskaya, G.S.

TITLE: The Reactions of the Dinitrodimethylamine Compounds of Tetravalent Platinum $(CH_3NH_2NO_2)_2X_2Pt$.
(O reaktsiyakh dinitrodimetilaminovykh soyedineniy chetyrekhvalentnoy platiny $(CH_3NH_2NO_2)_2X_2Pt$.)

PERIODICAL: Zhurnal Neorganicheskoy Khimii, 1957, Vol.II, Nr.3, pp. 536-551. (USSR)

ABSTRACT: $(CH_3NH_2NO_2)_2(NO_2)_2Pt$ and $(CH_3NH_2NO_2)_2NO_2NO_3Pt$ have been obtained by the oxidation of $(CH_3NH_2NO_2)_2Pt$ with nitric acid of s.g. 1.35 and 1.50. Investigation of the properties of both these compounds confirmed the cis-diamine configuration attributed to them on the basis of synthesis. The chemical inertness of the platinum tetranitrodimethylamine $(CH_3NH_2NO_2)_2(NO_2)_2Pt$ molecule is proved by the absence of reaction with NH_3, dilute HCl, dilute KOH and H_2O. A change in the properties of the NO_2-group in compounds of tetravalent platinum

Card 1/3

The Reactions of the Dinitrodimethylamine Compounds of Tetravalent Platinum $(CH_3NH_2NO_2)_2X_2Pt$. 78-3-8/35

occurs independently of the method of formation of the NO_2-Pt-NO_2 coordinate. The nitrohydroxocompound $(CH_3NH_2NO_2)_2NO_2OHPt$ has been obtained by neutralisation of a solution of $(CH_3NH_2NO_2)_2NO_2NO_3Pt$ with alkali. The position of the NO_2-group in order of trans-activity of substitutes of tetravalent Pt compounds has been determined relative to hydroxyl by measurement of the pH of a 0.001 mol solution of $(CH_3NH_2NO_2)_2NO_2OHPt$. Indications are that the NO_2-group in tetravalent Pt compounds has a very small trans-influence. The methods of preparation and properties of methylamine-dihalogeno-compounds $(MeNO_2)_2X_2Pt$(X is equal to Cl, Br) are similar to thoseof previously studied ammonium compounds of the type $(NH_3NO_2)_2X_2Pt$. Proof of the existence of exchange between substitutes has been obtained.

Card 2/3

The Reactions of the Dinitrodimethylamine Compounds of Tetravalent Platinum $(CH_3NH_2NO_2)_2X_2Pt$. 78-3-8/35

On the basis of the study of the chemical reactions and pH of solutions of the compounds $(aNO_2)_2XOHPt$ ($X = Cl, Br, OH, NO_2$; $a = NH_3$, Me); $(NH_3NO_2)_2NO_2.XPt$ ($X = Cl, Br, OH\frac{1}{2}H_2O$) and $(aNO_2)_2X_2Pt$ ($X = Cl, Br, I$; $a = NH_3$, Me) the position of substitutes in order of trans-activity for tetravalent platinum compounds is determined by the following: $NH_3, OH, NO_2 < \ldots Cl < Br < I$. There are 3 tables, 1 figure and 12 references, 11 of which are Slavic.

SUBMITTED: November 20th, 1956.

AVAILABLE: Library of Congress.

Card 3/3

CHERNYAYEV, I.I.

CHERNYAYEV, I.I.

On B.F. Ormont's article "Preserve D.I. Mendeleev's traditions in contemporary inorganic chemistry." Zhur. neorg. khim. 2 no.5:1212 My '57. (MLRA 10:8)

(Chemistry, Inorganic)

CHERNYAYEV, I.I.; GOLOVNYA, V.A.; SHCHELOKOV, R.N.

Dioxalateuranylammonium hydrates. Zhur. neorg.khim. 2 no.8:1763-1767 Ag '57. (MIRA 11:3)

1. Institut obshchey i neorganicheskoy khimii im. N.S. Kurnakova AN SSSR.

(Ammonium compounds) (Hydrates)

CHERNYAYEV, I.I.; KRASOVSKAYA, N.N.

Part 1: Geometrical isomerism of tetravalent platinum diamminodinitrato dichlorides. Zhur. neorg. khim. 2 10:2349-2359 O '57.
(Platinum chlorides) (Isomers) (MIRA 11:3)

CHERNYAYEV, I.I.

54-4-19/20

AUTHOR: Chernyayev, I. I.

TITLE: Complexformation and Individual Properties of Chemical Elements of the Periodic System According to D. I. Mendeleyev - Mendeleyevian Eleventh Lecture on February 7, 1957 (Kompleksoobrazovaniye i individual'nyye svoystva khimicheskikh elementov periodicheskoy sistemy D. I. Mendeleyeva - Odinnadtsatoye mendeleyevskoye chteniye 7 fevralya 1957 g.).

PERIODICAL: Vestnik Leningradskogo Universiteta Seriya Fiziki i Khimii, 1957, Vol. 22, Nr 4, pp. 158-168 (USSR).

ABSTRACT: In his lecture Prof. Chernyayev aims at the verification of the thesis, that there is not less but rather more importance to the negative side of the natural laws than to the positive, affirmative side. The importance lies in the recognition of certain limits, which confine the possibility and impossibility of the phenomena on the field of the law in question. As with the first and second thermodynamic theorem also with the periodic law the starting-point can be a negative interpretation and not only the positive one. On the assumption, that it will be of special interest for the future historians in chemistry, the lecturer develops the thesis mentioned in the title based on the above cited viewpoint with the statement, that there is

Card 1/2

Complexformation and Individual Properties of Chemical Elements 54-4-19/20
of the Periodic System According to D. I. Mendeleyev .Mendeleyevian Eleventh
Lecture on February 7, 1957.

no chance of existence for elements, the properties of which would lie between the properties of the neighbor elements in the periodic system. Besides many other properties the difference, for instance, in the stability of the complex salts distinguishes one element from another. The periodic system denies the possibility of the existence of "intermediary elements", in the way as Werner's theory denies the possibility of existence of complex compounds with larger or smaller coordination numbers. The correlation between Mendeleyev's law and the theory of Werner is analysed and criticised. In 1924 the conception of the "transinfluence" at the formation of complex compounds was found by Prof. Chernyayev, the part, which the central atom plays in it, is explained, as well as some examples in connection with the distribution of the elements in the periodic system. The stability of the atom on the one hand, and of the molecule on the other is suggested to be the root of investigations of the lawfulness in the periodic system and of the regularities in the chemics of the complex compounds.

SUBMITTED: June 4, 1957.

AVAILABLE: Library of Congress.

Card 2/2

CHERNYAYEV, I.I.

A

USSR/General Problems. Methodology. History. Scientific
Institutions and Conferences. Teaching. Problems
of Bibliography and Scientific Documentation.

Abs Jour : Ref Zhur-Khimiya, No 6, 1958, 16683

Author : Chernyayev I. I.
Inst : Not given
Title : Forty Years of Development of Inorganic Chimistry
in the USSR

Orig Pub : Uspekhi khimii, 1957, 26, No 11, 1230-1240
Bibliography-31 titles.

Abstract : No abstract

Card 1/1

CHERNYAYEV, I., GOLOVNYA, V. and MOLODKIN, A.

"Thorium Complex Carbonate Compounds."

paper to be presented at 2nd UN Intl. Conf. on the peaceful uses of Atomic Energy, Geneva, 1 - 13 Sept 58.

CHERNYAYEV, I. I. (and V. A. Golovnya, G. V. Ellert, R. N. Shelokov, V. P. Markov)

"THE STRUCTURE OF COMPLEX URANYL COMPOUNDS".

By I. I. Chernyayev, V. A. Golovnya, G. V. Ellert, R. N. Shelokov and V. P. Markov.

Report presented at 2nd UN Atoms-for-Peace Conference, Geneva, 9-13 Sept. 1958.

AUTHORS: Chernyayev, I.I., Palkin, V.A., Baranova, R.A. SOV/78-3-7-8/44

TITLE: A Calorimeter for the Determination of the True Thermal Capacity of the Complex Compounds of Platinum Metals (Kalorimetr dlya opredeleniya istinnoy teployemkosti kompleksnykh soyedineniy platinovykh metallov)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol. 3, Nr 7, pp 1512-1520 (USSR)

ABSTRACT: The complex compounds of platinum metals decompose at temperatures of between 200 and 250°C. In order to determine thermal capacity it is necessary that investigations be carried out at temperatures below 200°C.
A calorimeter was constructed and the working scheme for its automatic adjustment to temperatures of from 200 to 250°C is described. The sensitivity of the calorimeter is 2.10^{-3} cal. The necessary quantity of complex platinum compound is 3.5 - 4 g. Calibration of the calorimeter was carried out with KCl at 25°C. The thermal capacity of cis- and trans-isomers of dichlorodiamine platinum complexes was determined, and it was found that both isomers have the

Card 1/2

A Calorimeter for the Determination of the True Thermal Capacity of the Complex Compounds of Platinum Metals

SOV/78-3-7-8/44

same thermal capacity within the temperature interval of 25-80°C. There are 8 figures, 5 tables, and 15 references, 13 of which are Soviet.

SUBMITTED: June 4, 1957

1. Complex compounds--Thermochemistry 2. Complex compounds --Decomposition 3. Platinum--Properties 4. Calorimeters --Calibration

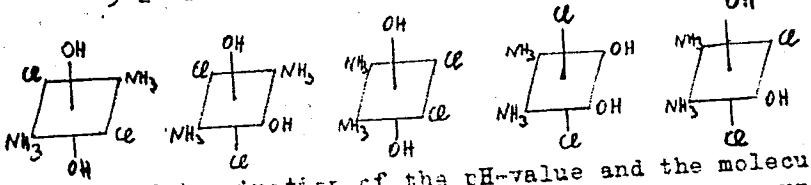
Card 2/2

AUTHORS: Chernyayev, I. I., Krasovskaya, N. N. SOV/78-3-9-6/38

TITLE: ~~On the Isomerism~~ of the Dihydroxo-Diamino-Dichloride of Tetravalent Platinum (O geometricheskoy izomerii digidroksodiammino-dikhloridov chetyrekhvalentnoy platiny)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol 3, Nr 9, pp 2024-2038 (USSR)

ABSTRACT: In the present paper the trans-effect of the hydroxyl in isomeric dihydroxo-diamino-dichloride of tetravalent platinum was investigated. The co-ordination theory assumes that the following geometrical isomers are existing for the compound $Pt(NH_3)_2Cl_2(OH)_2$:



By the determination of the pH-value and the molecular electric conductivity of the aqueous solution of the compounds 1 and 3

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SOV/78-3-9-6/38

On the Isomerism of the Dihydroxo-Diamino-Dichloride of Tetravalent Platinum

it is demonstrated that the hydroxo-group has a slight trans-effect. The investigation of the dependence of the pH-value and the molecular electric conductivity of the hydroxo-compounds on time indicates that no transition from the hydroxo-group to the aquo-group takes place in the hydration. In the interaction of dihydroxo-diamino-dichloride platinum-(IV) complexes with acids no isomerization occurs. In the interaction of $(NH_3)_2(ClNO_3)_3Pt$ with NaOH a modification in the structure of the molecules occurs. This effect was ascertained by determining the solubility of $(NH_3)_2(ClOH)_2Pt$. From the interaction of the compounds 2 and 3 with NH_3 it becomes evident that the compound $(NH_3)_2(ClOH)_2Pt$ was prepared from $(NH_3)_2(OHNO_3)_2Pt$. From the compound $(NH_3)_2(ClNO_3)_2Pt$ the compound $(NH_3)_2(ClOH_3)_2Pt$ is formed which belongs to the class of polynuclear compounds with oxygen bridges and water of crystallization. There are 1 figure, 17 tables, and 5 references, 5 of which are Soviet.

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SOV/78-3-9-6/38

On the Isomerism of the Dihydroxo-Diamino-Dichloride of Tetravalent Platinum

ASSOCIATION: I.O.N.Kh. Akademii nauk SSSR (I.O.N.Kh., AS USSR)

SUBMITTED: July 8, 1957

Card 3/3

AUTHORS: Chernyayev, I. I., Krasovskaya, N. N. SOV/78-3-10-10/35

TITLE: Some Questions on the Trans-Effect of the Hydroxy-Groups in the Complex Compounds of Quadrivalent Platinum (Nekotoryye voprosy transvliyaniya gidroksogruppy v kompleksnykh soyedineniyakh chetyrekhvalentnoy platiny)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol 3, Nr 10, pp 2281-2288 (USSR)

ABSTRACT: It is shown by the determination of the pH-value and the molecular electric conductivity of aqueous solutions of the compounds $(NH_3)_2(OH)_2Cl_2Pt$ and $(NH_3Cl)_2(OH)_2Pt$ that the hydroxy-groups have little trans-effect. It can be seen from table 1 that not one of the trans-dihydroxo compounds $(NH_3)_2(OH)_4Pt$, $(NH_3OH)_2(OH)_2Pt$ or $(NH_3Cl)_2(OH)_2Pt$ react upon ammonia or sodium nitrite and do not exchange the hydroxy-group against bromine when potassium bromide acts on it. The hydroxy-groups, combined with highly trans-effective addenda, are variable. The process of neutralization of hydroxo-compounds is also connected with the trans-effect. The change of the pH-value as a function of

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SOV/78-3-10-10/35

Some Questions on the Trans-Effect of the Hydroxy-Groups in the Complex Compounds of Quadrivalent Platinum

time was analyzed in the aqueous solutions of the compounds $(NH_3)_2Cl_2(OH)_2Pt$, $(NH_3)_2(ClOH)_2Pt$ and $(NH_3Cl)_2(OH)_2Pt$, and it was demonstrated that the pH-values of these compounds are similar to each other and do not depend on time. This effect shows that the hydration of these compounds is not connected with a transition of the hydroxy-group to the aquo-group. The determinations of electric conductivity also indicate that the hydroxy-group does not pass to the aquo-group in solving. There are 3 tables and 6 references, 5 of which are Soviet.

SUBMITTED: May 5, 1958

Card 2/2

SOV/78-3-12-14/36

AUTHORS: Chernyayev, I. I., Golovnya, A. V., Molodkin, A. K.

TITLE: Concerning the Hydrated Forms of Sodium Thorium Pentacarbonate (O gidratirovannykh formakh pentacarbotoreata natriya)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol 3, Nr 12, pp 2671-2686 (USSR)

ABSTRACT: The thorium carbonates of the alkali metals were systematically investigated and a new method for synthesizing $Na_6Th(CO_3)_5\cdot20H_2O$ and $Na_6Th(CO_3)_5\cdot12H_2O$ was developed. The syntheses of $Na_6Th(CO_3)_5\cdot(10-12)H_2O$ and $Na_6Th(CO_3)_5\cdot5H_2O$ were also worked out. The alkaline earth salts of sodium thorium pentacarbonate were isolated as the barium and calcium salts: $Ba_3Th(CO_3)_5\cdot7H_2O$ and $Ca_3Th(CO_3)_5\cdot7H_2O$.

The thermal stabilities of $Na_6Th(CO_3)_5\cdot20H_2O$ and $Na_6Th(CO_3)_5\cdot12H_2O$ were investigated and the corresponding thermograms were plotted. The course of the thermograms indicates that both crystal hydrates are converted to the non-aqueous $Na_6Th(CO_3)_5$

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SOV/78-3-12-14/36

Concerning the Hydrated Forms of Sodium Thorium Pentacarbonate

above 100°, and that above 300° they decompose to form ThO_2 and Na_2CO_3. Several crystallographic properties of the $Na_6Th(CO_3)_5 \cdot 20H_2O$ and $Na_6Th(CO_3)_5 \cdot 12H_2O$ were investigated. The properties of $Na_6Th(CO_3)_5 \cdot 20H_2O$ indicate that the crystals are monoclinic with the following parameters: a:b:c = 1.461:1:1.495 and $\beta = 106^\circ\ 12'$. The refractive indices are: $N_g = 1.476$, $N_m = 1.470$, $N_p = 1.462$. The crystallographic properties of $Na_6Th(CO_3)_5 \cdot 12H_2O$ differ sharply from those of the $Na_6Th(CO_3)_5 \cdot 20H_2O$. The refractive indices of $Na_6Th(CO_3)_5 \cdot 12H_2O$ are: $N_g = 1.504$, $N_p = 1.472$ and $N_m = 1.490$. The crystals of each hydrate differ greatly in terms of their stability in air. The $Na_6Th(CO_3)_5 \cdot 20H_2O$ crystals are unstable, losing their water very quickly and becoming opaque, while the $Na_6Th(CO_3)_5 \cdot 12H_2O$ crystals are completely stable. The behavior of both salts in water, alkali bases, acids, salts, and several organic solvents was investigated. Both crystals hydrolyze

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SOV/78-3-12-14/36

Concerning the Hydrated Forms of Sodium Thorium Pentacarbonate

easily in water to form white, amorphous precipitates. In alkali bases both hydrates are insoluble, while in acids they decompose spontaneously to give off CO_2 gas. In organic solvents (methyl and ethyl alcohols, ethyl ether, acetone, benzene, glycerin, and others) the crystals are insoluble. The crystals of $Na_6Th(CO_3)_5 \cdot 12H_2O$ are soluble in saturated solutions of the oxalates and carbonates of the alkali metals. The water molecules in sodium thorium pentacarbonate complexes are not identical. The last water molecule is the most stable in terms of its complex bond. The following new structural formula is suggested for sodium thorium pentacarbonate:

$[Na_6[Th(CO_3)_5 \cdot H_2O]] \cdot (n-1)H_2O$.

There are 7 figures, 13 tables, and 49 references, 3 of which are Soviet.

SUBMITTED: February 21, 1958

Card 3/3

YATSIMIRSKIY, Konstantin Borisovich; VASIL'YEV, Vladimir Pavlovich;
CHERNYAYEV, I.I., akademik, otv.red.; TRIFONOV, D.N., red.izd-va;
MARKOVICH, S.G., tekhn.red.

[Instability constants of complex compounds] Konstanty nestoikosti
kompleksnykh soedinenii. Moskva, Izd-vo Akad.nauk SSSR, 1959.
205 p. (MIRA 12:3)
(Complex compounds)

CHERNYAYEV, I.I.

PHASE I BOOK EXPLOITATION SOV/5084

International Conference on the Peaceful Uses of Atomic Energy. 2d, Geneva, 1958.

Doklady sovetskikh uchenykh. [t.4] Khimiya radioelementov i radiatsionnykh prevrashcheniy (Reports of Soviet Scientists. V. 4.: Chemistry of Radio- elements and Radiation Transformations) Moscow, Atomizdat, 1959. 323 p. 8,000 copies printed. (Series: Its: Trudy)

Ed. (Title page): A. P. Vinogradov, Academician; Ed.: V. I. Labaznov; Tech. Ed.: Ye. I. Mazel'.

PURPOSE: This collection of articles is intended for scientists and engineers interested in the applications of radioactive materials in science and industry.

COVERAGE: The book contains 26 separate studies concerning various aspects of the chemistry of certain radioactive elements and the processes of radiation effect on matter. These reports discuss present-day methods of reprocessing irradiated nuclear fuel, research in the chemistry of mercury, thorium, uranium, plutonium, and americium, problems related to the sorption and burying of radioactive wastes, the radiolysis of aqueous solutions and of organic compounds, the mechanism of polymer chain grafting, and the effect of radiation on natural and synthetic rubbers. V. N. Prusakov edited the present volume. Most of the reports are accompanied by references. Contributors to individual investigations are mentioned in annotations to the Table of Contents.

TABLE OF CONTENTS:

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5(2) SOV/78-4-4-7/44

AUTHORS: Chernyayev, I. I., Nazarova, L. A.,
Mironova, A. S.

TITLE: Nitrito Compounds of Tetravalent Platinum. Communication I. (Nitrosoyedineniya chetyrekhvalentnoy platiny) (Soobshcheniye I)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 4, pp 747-754 (USSR)

ABSTRACT: The mechanism of the reaction between sodium nitrite and sodium hexachloroplatinate was investigated. The synthesis of nitritoplatinum compounds and an investigation of the intermediate complex compounds formed were carried out. The reaction between sodium chloroplatinate and sodium nitrite apparently occurs first through a reduction of the tetravalent platinum compound to yield platinum (II) compounds in which the chloride ion is exchanged with the nitrito group and the Pt(II) is finally oxidized to Pt(IV). The preparation of the mononitrito- and dinitrito chloro compounds of platinum (IV) is very difficult. Tetra- and penta nitritoplatinates can be prepared more easily. Hexa nitritoplatinates cannot be prepared. The trinitrito-

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SOV/78-4-4-7/44

Nitrito Compounds of Tetravalent Platinum.
Communication I.

and tetranitrito chloro compounds of platinum (IV) were isolated in the purest form. The refractive indices of the crystals were determined, and specific reactions were carried out. The formation of the coordinates NO_2-NO_2 in chloronitrito compounds of Pt(IV) cannot be carried out by a substitution of the chlorine into the position trans to the nitrito group. The synthesis of potassium trinitrito trichloroplatinate is carried out by using a mixture of 3 g-moles $NaNO_2$ and 1 g-mole $Na_2PtCl_6.6H_2O$ with an excess of KNO_2. Yellow prismatic crystals are formed in this process. The compound formed has the composition $K_2[Pt(NO_2)_3Cl_3]$. By recrystallization from aqueous solution crystals of high purity were isolated. This compound crystallizes in two forms: facets and ribs. To ascertain each structure of the potassium trinitrito chloro platinate reactions with $AgNO_3$ and tetrammino platinum chloride were carried out. The synthesis of potassium tetranitrito dichloroplatinate

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SOV/78-4-4-7/44

Nitrito Compounds of Tetravalent Platinum.
Communication I.

was carried out using 4 g-moles of sodium nitrite and 1 g-mole of $Na_2PtCl_6.6H_2O$. The potassium salt produced has the homogeneous composition $K_2[PtCl_2(NO_2)_4]$. The synthesis of potassium pentanitrito chloroplatinate was carried out using 6 g-moles of $NaNO_2$ to 1 g-mole $Na_2PtCl_6.6H_2O$. The homogeneity of the compound was confirmed by crystal-optic investigations. The solubility of $K_2[Pt(NO_2)_5Cl]$ at 25° is 2.85 %. The crystal-optic investigations were carried out by E. Ye. Burova. There are 2 figures and 5 Soviet references.

SUBMITTED: January 30, 1958

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SOV/78-4-5-11/46

5(2)

AUTHORS: Chernyayev, I. I., Krasovskaya, N. N.

TITLE: On the Geometric Isomerism of the Halides of the Quadrivalent Platinum of the Diamine Series (O geometricheskoy izomerii galogenidov chetyrekhvalentnoy platiny diamminovogo ryada)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 5, pp 1002-1011 (USSR)

ABSTRACT: The three geometric isomers of $Pt(NH_3)_2Br_2Cl_2$ which had already been obtained by an earlier investigation carried out by the authors (Refs 1, 2) were synthetized, their structure was confirmed, and several properties described. The chemical properties of the isomers $Pt(NH_3)_2Br_2Cl_2$ are shown by table 1. For the purpose of determining the structure of the isomers, the reaction with ammonia was used. The interaction between $Pt(NH_3)_2Br_2Cl_2$ and NH_3 develops according to the following equations:

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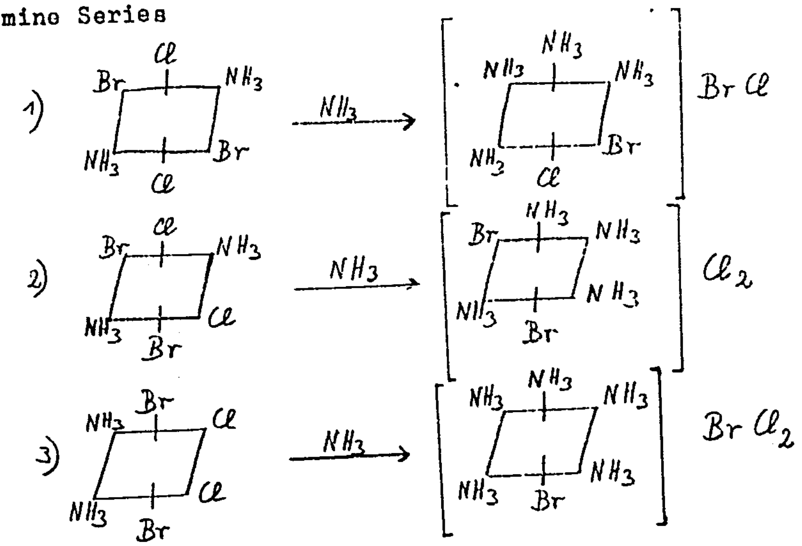
SOV/78-4-5-11/46

On the Geometric Isomerism of the Halides of the Quadrivalent Platinum of the Diamine Series



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SOV/78-4-5-11/46

On the Geometric Isomerism of the Halides of the Quadrivalent Platinum of the Diamine Series

In the interaction between $Pt(NH_3)_2Br_3Cl_2$ and $NaOH_2$ the following nitrito-compounds were obtained: $(NH_3)_2BrNO_2ClNO_2Pt$, $(NH_3)_2(BrNO_2)_2Pt$ and $(NH_3Cl)_2BrNO_2Pt$. The chemical analyses of the separated products (Tables 1, 2) showed that the interaction between $Pt(NH_3)_2Br_2Cl_2$ and $NaNO_2$ develops in complete accordance with the principle that by the action of halides mainly trans-configurations are formed according to the following equations:

$$(NH_3)_2Br_2Cl_2Pt + 2H_2O \rightleftarrows \left[(NH_3)_2BrH_2OCl_2Pt\right]^{+} + Br^{-} + H_2O \rightleftarrows$$

$$\rightleftarrows \left[(NH_3)_2BrH_2OClH_2OPt\right]^{2+} + Br^{-} + Cl^{-} ;$$

$$(NH_3)_2(BrCl)_2Pt + 2H_2O \rightleftarrows \left[(NH_3)_2BrH_2OCl_2Pt\right]^{+} + Cl^{-} + H_2O \rightleftarrows$$

$$\rightleftarrows \left[(NH_3)_2(BrH_2O)_2Pt\right]^{2+} + 2Cl^{-} .$$

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On the Geometric Isomerism of the Halides of the Quadrivalent Platinum of the Diamine Series

In the interaction of $(NH_3)_2Br_2Cl_2Pt$ and $(NH_3)_2(Br_2Cl)_2Pt$ with $AgNO_3$ nitrate compounds are formed. Cis-diamine $(NH_3Cl)_2Br_2Pt$ reacts with $AgNO_3$ with a formation of $(NH_3Cl)_2BrOHPt$. The solubility of the isomers $Pt(NH_3)_2Br_2Cl_2$ was determined, and it was found that the symmetric trans-diamine $(NH_3)_2Br_2Cl_2Pt$ is the least soluble and that the cis-isomer $(NH_3Cl)_2Br_2Pt$ is more easily soluble. The diammine-dichloro-dibromides of quadrivalent platinum belong to the class of non-electrolytes. The isomer $(NH_3)_2Br_2Cl_2Pt$ becomes hydrated more quickly than $(NH_3)_2(BrCl)_2Pt$. The hydration of $(NH_3Cl)_2Br_2Pt$ leads to the formation of binary electrolytes. Investigations of the conductivity and the variation of the conductivity of $Pt(NH_3)_2Br_2Cl_2$ and the solubility of this product are given by tables 2, 3, and 4. There are 5 tables and 5 references, 4 of which are Soviet.

SUBMITTED: February 8, 1958

Card 4/4

SOV/78-4-5-12/46

5(2)

AUTHORS: Chernyayev, I. I., Krasovskaya, N. N.

TITLE: On the Cis-triammines of Quadrivalent Platinum (O tsis-triammine chetyrekhvalentnoy platiny)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 5, pp 1012-1017 (USSR)

ABSTRACT: The hitherto unknown nitrate and chloride of the cis-isomer of triammino-trichloro-platinum $(NH_3Cl)_3PtCl$ and $(NH_3Cl)_3PtNO_3$ were prepared, their structure confirmed, and some of their properties investigated. The reaction of the interaction of $(NH_3Cl)_2Cl_2Pt$ with a mixture of CH_3COONH_4 and NH_4OH was investigated and the compound $(NH_3Cl)_2PtCl$ was isolated. In the interaction $(NH_3Cl)_2.(OH)_2Pt$ with a mixture of $(NH_4)_2CO_3$ and NH_4OH the compound $(NH_3Cl)2(NH_3OH)PtCl$ is formed. For the purpose of confirming the cis-structure of $(NH_3Cl)_3PtCl$ and $(NH_3Cl)_3PtNO_3$ the reduction of these compounds with oxalic acid and zinc was carried out in a hydrochloric acid medium. Oxalic acid exercises no reducing effect upon this compound. The analyses of the reduction products of $(NH_3Cl)_3PtNO_3$ and

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On the Cis-triammines of Quadrivalent Platinum SOV/78-4-5-12/46

(NH$_3$Cl)PtCl with oxalic acid and zinc are given by table 2. Under the action of AgNO$_3$, (NH$_3$Cl)$_3$PtNO$_3$ is converted into nitrate, and (NH$_3$Cl)$_3$PtNO$_3$ goes over into the corresponding chloride in the course of re-crystallization. The solution (NH$_3$Cl)$_3$PtNO$_3$ forms no precipitation with AgNO$_3$. Only after having stored for many hours does a weak opalescence occur in the solution. Experiments show that the configuration (NH$_3$Cl)$_3$Pt$^+$ is very stable. By determination of molecular electric conductivity it is shown that the cis-isomers of the triammines are binary electrolytes. The interaction of (NH$_3$Cl)$_3$PtCl with AgNO$_3$ is shown by figure 3. The solubility of (NH$_3$Cl)$_3$PtCl, (NH$_3$Cl)$_3$PtNO$_3$, (NH$_3$)$_2$·(NH$_3$Cl)$_2$PtCl$_2$ and (NH$_3$Cl)$_2$Cl$_2$Pt was determined, and results are shown by table 4. Table 1 shows the chemical reactions of the compounds formed with various agents. There are 4 tables and 6 references, 5 of which are Soviet.

SUBMITTED: February 8, 1958

Card 2/2

SOV/78-4-7-11/44

5(2)

AUTHORS: Muraveyskaya, G. S., Chernyayev, I. I.

TITLE: On Diammine-nitrochloropalladium $Pd(NH_3)_2NO_2Cl$ (O diammin-nitrokhlorpalladii $Pd(NH_3)_2NO_2Cl$)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 7, pp 1533-1541 (USSR)

ABSTRACT: The compound mentioned in the title is produced for the purpose of finding out whether in this case the same trans-effect rule holds as in the case of platinum. The plane configuration of the initial substances $Pd(NH_3)_2Cl_2$ and $Pd(NH_3)_2(NO_2)_2$ has been proved by means of X-ray examination of the structure and by the existence of geometric isomers. By the common crystallization of equivalent quantities of the initial substances the trans-nitrochlorocompound $Pd(NH_3)_2NO_2Cl$ was obtained. In the experimental part the production of the initial substances and of the trans-compound are described. The latter was obtained both by means of the aforementioned joint crystallization as also by the reaction of $Pd(NH_3)_2Cl_2$ with $NaNO_2$. Figure 1b shows microphotographs of the compound obtained in polarized light.

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SOV/78-4-7-11/44

On Diammine-nitrochloropalladium $Pd(NH_3)_2NO_2Cl$

In diluted solutions $Pd(NH_3)_2Cl$ undergoes hydrolysis , and excess of chloric ions substituting the nitro-group in the crystal lattice occurs, so that mixed crystals of low solubility and a composition of $Pd(NH_3)_2(NO_2)_{1-x}Cl_{1+x}$ are formed, the microphotograph of which is shown in figure 1a. Table 1 gives the properties of the initial substances and of the nitrochloric compound obtained in two ways. Table 2 shows the solubility of this compound at 25°, and table 3 shows their ratio during heating. Figures 2-6 show the heating curves of the compound mentioned. It was found that the formation of nitrochlorodiammines in palladium is analogous to that in the case of platinum. There are 6 figures, 4 tables, and 11 references, 4 of which are Soviet.

SUBMITTED: April 20, 1958

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5 (2) SOV/78-4-8-1/43

AUTHOR: Chernyayev, I. I.

TITLE: Mariya Semenovna Skanavi-Grigor'yeva (Deceased)
(Mariya Semenovna Skanavi-Grigor'yeva (Nekrolog))

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 8,
pp 1705 - 1707 (USSR)

ABSTRACT: Professor M. S. Skanavi-Grigor'yeva, Doctor of Chemical Sciences, died in July 1958. Her extensive scientific activity was devoted to the chemistry of the complex compounds (the special field of her first teachers A. Werner and L. A. Chugayev), the theory of the solutions, electrochemistry, investigations in the field of the isotopic composition of live substance (together with V. I. Vernadskiy), the determination of trace elements in biogenous material. She worked at 16 institutes, first at Zurich University, and at the end at the Moskovskiy gorodskoy pedagogicheskiy institut im. Potemkina (Moscow Municipal Pedagogical Institute imeni Potemkin). After having finished her secondary training she studied at the Department of History and Philosophy at the Vysshiye zhenskiye kursy (Women's School of Higher Education). She changed over to the Department of Natural Sciences and was then expelled from the studies be-

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Mariya Semenovna Skanavi-Grigor'yeva (Deceased) SOV/78-4-8-1/43

cause she participated in the revolutionary movement. She first went to Leipzig, then to Zurich where she worked under the supervision of A. Werner. In 1912 she returned to Petersburg and worked with Professor L. A. Chugayev. In 1919 she became Professor and holder of the Chair of Chemistry at Samara University. Later she taught at various universities of Leningrad and Moscow. There are 1 figure and 35 references, 28 of which are Soviet.

Card 2/2

5(0)

SOV/30-59-9-1/39

AUTHOR: Chernyayev, I. I., Academician

TITLE: The Tasks of the Chemistry of Complex Compounds

PERIODICAL: Vestnik Akademii nauk SSSR, 1959, Nr 9, pp 3-8 (USSR)

ABSTRACT: The chemistry of complex compounds is the chemistry of intermediates forming in a great number of technological processes. The number of complex compounds exceeds that of simple compounds by a multiple. Complex compounds of theoretical interest are characterized by three special features: the deviation from the usual valence correlations, the reduction of reaction rates, and the presence of a certain form of stability of the molecules. The author of the present paper describes phenomena occurring in the so-called interior sphere. The discovery of all characteristics of the chemistry of complex compounds according to the present concept of electrons is regarded as a task for the near future: their composition, form, reactivity, and the trans-effect (chelate effect). Finally, the author emphasizes that the entire progress of modern chemistry, including organic chemistry, depends on the understanding of the chemistry of complex compounds. For the

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The Tasks of the Chemistry of Complex Compounds SOV/30-59-9-1/39

technology of preparing pure substances it is necessary to select complex compounds suited for this purpose. Without the use of complex compounds, the possibilities of analytical chemistry would be within narrow limits. Complex compounds play an exceptionally important role in biochemistry. ✓

Card 2/2

GRUM-GRZHIMAYLO, Nikolay Vladimirovich; CHERNYAYEV, I.I., akademik, otv. red.; YASTREBOV, V.V., red.izd-va; YEGOROVA, N.F., tekhn.red.

[Chemical bonds in metallic alloys] Khimicheskie sviazi v metallicheskikh splavakh. Moskva, Izd-vo Akad.nauk SSSR, 1960. 106 p. (MIRA 13:6)

(Alloys) (Chemical bonds)

BAILAR, John Christian, editor; BUSH, D., assist.editor; ADRIANOVA, O.N. [translator]; CHERNYAYEV, I.I., red.

[Chemistry of the coordination compounds] Khimiia koordinatsionnykh soedinenii. Moskva, Izd-vo inostr.lit-ry, 1960. 695 p. Translated from the English. (MIRA 14:1)
(Coordination compounds)

5.2620
~~5 (2)~~

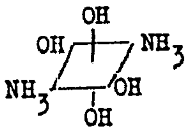
68106
SOV/78-5-1-8/45

AUTHORS: Chernyayev, I. I., Krasovskaya, N. N.

TITLE: On the Geometrical Isomerism of Diamminotetrahydroxoplatinum.IV

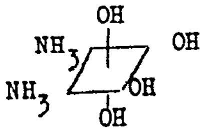
PERIODICAL: Zhurnal neorganicheskoy khimii, 1960, Vol 5, Nr 1, pp 39 - 47 (USSR)

ABSTRACT: In this paper the authors continue their investigation of the transeffect of the hydroxyl group in complex compounds of Pt(IV). They investigated the two theoretically possible isomers



Pt(NH$_3$OH)$_2$(OH)$_2$

and



Pt(NH$_3$)$_2$(OH)$_4$

, the analysis data of which are shown in tables 1,2. The reaction of the two isomers on heating with concentrated ammonia or NaNO$_2$ was investigated to prove the fact found earlier that the OH groups are passive on the axes OH-Pt-OH and NH$_3$-Pt-OH. No compounds with

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On the Geometrical Isomerism of Diamminotetrahydroxo-platinum.IV SOV/78-5-1-8/45

more than 2 ammino groups and no nitro compounds, respectively, were obtained even after a long treatment. In acid media, however, the OH groups easily pass over into aquo groups which are considerably mobile and are easily replaced by Cl, Br, or NO_3 (Tables 6-8), the sequence of substitution depending on the position of the group. The compounds $Pt(NH_3OH)_2(NH_3Cl)Cl_2$ and $Pt(NH_3OH)_2Cl_2$ were obtained by treatment with HCl (Table 9). 4 The structure of these compounds was determined by reaction with HBr (Table 10). Since no dibromides but only the tribromide $Pt(NH_3)_2B_3Cl$ and the tetrabromide $Pt(NH_3)_2Br_4$ were formed, the hydroxyl group is supposed to have a somewhat greater transeffect than the NH_3 group. Table 11 shows the solubility of the isomers $Pt(NH_3OH)_2(OH)_2$ and $Pt(NH_3)_2(OH)_4$. Tables 12, 13 show the dependence of the electrical conductivity of these two compounds

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On the Geometrical Isomerism of Diamminotetrahydroxo-platinum.IV SOV/78-5-1-8/45

on the age and the dilution of the solutions. These measurements were made by V. A. Tsingister. Both compounds are non-electrolytes. The authors mention L. A. Chugayev. There are 13 tables and 4 references, 3 of which are Soviet. 4

SUBMITTED: October 26, 1958

Card 3/3

68220

5.2.20

~~5(2)~~

S/078/60/005/02/006/045
B004/B016

AUTHORS: Chernyayev, I. I., Krasovskaya, N. N.

TITLE: Geometric Isomers of Diamminohydroxotrichloroplatinum (IV)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1960, Vol 5, Nr 2, pp 271-279 (USSR)

ABSTRACT: The paper reports on the preparation of three isomeric compounds $(NH_3)_2Cl_2ClOHPt$, $(NH_3Cl)_2ClOHPt$, and $(NH_3Cl)NH_3OHCl_2Pt$ which contain the coordinate Cl-Pt-OH, from the corresponding dihydroxo compounds by dropwise addition of the calculated quantity of HCl. The maximum yield was 30%. The data of the analyses are summarized in table 1. The structure of the isomers was determined by reduction with oxalic acid (Table 2) and by bromination with excess HBr (Table 3). The reaction with NH_3, $NaNO_2$, and $AgNO_3$ (Tables 4-8) indicated that the hydroxyl groups being in trans-position to a ligand with considerable trans-effect are readily substituted. In acid medium, the hydroxyl groups are easily transformed into aquo ions, with the aquo group being substituted by the acid anion. This reaction was investigated with HCl (Table 9) and HNO_3 (Table 10). The

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Geometric Isomers of Diamminohydroxotrichloro platinum (IV)

S/078/60/005/02/006/045
B004/B016

structure of the compounds with HNO_3 was confirmed by reaction with NH_3 (Table 11). Table 12 gives the electrical conductivity and pH of the solutions of the monohydroxo-, dihydroxo-, trihydroxo-, and tetrahydroxo compounds. All isomers of the compounds $Pt(NH_3)_2Cl_2OH$, $Pt(NH_3)_2Cl_2(OH)_2$, $Pt(NH_3)_2(OH)_3Cl$, and $Pt(NH_3)_2(OH)_4$ are non-electrolytes. The authors quote a paper by A. A. Grinberg and Yu. P. Mikhel's (Ref 2). There are 12 tables and 2 Soviet references.

4

SUBMITTED: October 29, 1958

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69015

S/078/60/005/04/010/040
B004/B007

AUTHORS: Chernyayev, I. I., Palkin, V. A., Baranova, R. A.

TITLE: The Heats of Formation and the Specific Heats of the Tetraammine and Triammine of Bivalent Platinum

PERIODICAL: Zhurnal neorganicheskoy khimii, 1960, Vol 5, Nr 4, pp 821 - 831 (USSR)

ABSTRACT: In the introduction, the authors refer to papers by A. F. Kapustinskiy, K. B. Yatsimirskiy, A. A. Grinberg, and B. V. Ptitsyn. For the purpose of determining the heats of formation of $[Pt(NH_3)_4]Cl_2$ and $[Pt(NH_3)_3Cl]Cl$, the heat effect produced by interaction between potassium- and ammonium-chloroplatinites with 9.4% aqueous ammonia solution was measured at 70°. For the purpose of conversion to 25°, the specific heats of all compounds taking part in the reaction as well as of their solutions were determined in a 9.4% ammonia solution within the interval of 25 to 70°, viz. for $K_2[PtCl_4]$, $(NH_4)_2[PtCl_4]$, $[Pt(NH_3)_4]Cl_2$, $[Pt(NH_3)_3Cl]Cl$, KCl, and NH_4Cl. The calorimeter and the method are described in references 1-4. Dehydration and treatment of hygroscopic tetraammine is dealt with in reference 2. Tables 1

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The Heats of Formation and the Specific Heats of the Tetraammine and Triammine of Bivalent Platinum

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B004/B007

and 2 give the measured heat effects of the reactions with an NH_3 solution as well as the solution heats. The results obtained by measuring specific heat are given in table 3, and are graphically represented in a figure. Within the investigated region, all specific heats depend linearly on temperature. The angle of inclination of the straight line in the diagram: specific heat - temperature increases with an increase in the number of ammonia molecules in the inner sphere of the ammine complexes of Pt(II). The authors mention their calculation of the heats of formation of $[Pt(NH_3)_4]Cl_2$ (177.1 kcal/mol) and $[Pt(NH_3)_3Cl]Cl$ (147.5 kcal/mol). As the heat of formation was calculated as the algebraic sum of a large number of summands, the authors estimate the error at ±1 kcal/mol or ±0.6%. The chemical analysis of the compounds investigated was carried out by M.N. Lyashenko. There are 1 figure, 3 tables, and 12 references, 9 of which are Soviet.

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SUBMITTED: January 23, 1959

Card 2/2

~~65998~~ 69538

S/078/60/005/05/13/037
B004/B016

5.2620

AUTHORS: Chernyayev, I. I., Mayorova, A. G.

TITLE: Complex Compounds of Rhodium With Thiosulfate and Ethylene Diamine

PERIODICAL: Zhurnal neorganicheskoy khimii, 1960, Vol. 5, No. 5, pp. 1074-1084

TEXT: The authors describe mixed thiosulfate-ammonia compounds of rhodium which are formed in the presence of ethylene diamine (En). These are polymeric complexes in which an S_2O_3 group forms the bridge. Here, En plays a stabilizing role, inhibits the reduction, and thus permits the isolation of these complex compounds from the solution. The reaction of $(NH_4)_3RhCl_6 \cdot H_2O$ with $Na_2S_2O_3 \cdot 5H_2O$ and En was investigated. The authors obtained the compound $\left[Rh_4 13S_2O_3 \cdot 2NaS_2O_3 \cdot 8En\right] Na_{10}(NH_4)_6 \cdot 11.5H_2O$. The water content of this compound was determined according to Yelitsur. The analysis made by E. Ye. Burova confirmed the homogeneity of this substance. When boiling a solution of this compound a cleavage occurred after 5-20 min to give $\left[Rh_2 6S_2O_3 \cdot NaS_2O_3 \cdot 4En\right] Na_4(NH_4)_3 \cdot 3H_2O$, and after 1 h the monomer $\left[Rh3S_2O_3 \cdot 2En\right] Na_2(NH_4)_3 \cdot 3.5H_2O$ resulted. The tetramer is cleft by ammonia to form the dimer. By reaction of $Rh3NH_3Cl_3$ with $Na_2S_2O_3 \cdot 5H_2O$ and En the dimer

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Complex Compounds of Rhodium With Thiosulfate and Ethylene Diamine

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$[Rh_27S_2O_3 \cdot 4En]Na_8$ was obtained which is split in aqueous and ammoniacal solution to give the monomer $[Rh3S_2O_3 \cdot 2En]Na_3$. The authors discuss the structures of these compounds which were identified by determining their electrical conductivity, molecular weight, pH, potentiometric titration, and magnetic susceptibility. Similar to the sulfite group also the thiosulfate group enters the inner sphere as NaS_2O_3. The authors refer to D. I. Ryabchikov and A. P. Isakova (Ref. 1). There are 8 references, 7 of which are Soviet.

ASSOCIATION: Institut obshchey i neorganicheskoy khimii im. N. S. Kurnakova Akademii nauk SSSR (Institute of General and Inorganic Chemistry imeni N. S. Kurnakov of the Academy of Sciences, USSR)

SUBMITTED: November 3, 1959

Card 2/2

CHERNYAYEV, I.I.; SHENDERETSKAYA, Ye.V.; Karyagina, A.A.

Monovalent rhodium formates. Zhur.neorg.khim. 5 no.5:1163
My '60. (MIRA 13:7)
(Rhodium compounds) (Formic acid)

S/078/60/005/06/04/030
B004/B014

5.2620

AUTHORS: Chernyayev, I. I., Mayorova, A. G.

TITLE: Thiosulfate Complex Compounds of Rhodium With Ammonia

PERIODICAL: Zhurnal neorganicheskoy khimii, 1960, Vol. 5, No. 6, pp. 1208 - 1220

TEXT: The authors of the present paper wanted to study ammonia compounds in order to clarify the composition of the previously prepared (Ref. 1) complex compounds of rhodium with thiosulfate and ethylene diamine. They obtained the following experimental results: Interaction between $(NH_4)RhCl_6 \cdot H_2O$ and $Na_2S_2O_3 \cdot 5H_2O$ + NH_4OH yields the tetrameric compound $[Rh_4 \cdot 13S_2O_3 \cdot 2NaS_2O_3 \cdot 12NH_3] \cdot Na_{14}(NH_4)_2$, which contains four additional ammonia molecules in its internal sphere, or the compound $[Rh_4 \cdot 13S_2O_3 \cdot 2NaS_2O_3 \cdot 10NH_3]Na_{12}(NH_4)_2 \cdot 2.5H_2O$ without excess ammonia. When these compounds are heated, they decompose into the monomer $[Rh3S_2O_32NH_3]Na_3$. In this process, the dimer $[Rh_26S_2O_3NaS_2O_36NH_3]Na_6(NH_4)$

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Thiosulfate Complex Compounds of Rhodium With Ammonia

S/078/60/005/06/04/030
B004/B014

which has two additional NH_3 molecules in its internal sphere, forms as intermediate of the first-mentioned tetramer with excess ammonia content. This dimer enters into reaction with ammonia and forms the compound $[Rh_25S_2O_36NH_3]Na_4 \cdot 3H_2O$. Interaction between $[Rh_23NH_3Cl_3]$ and $Na_2S_2O_3 \cdot 5H_2O$ + + NH_4OH yields the dimer $[Rh_27S_2O_36NH_3]Na_8$ which is split off by boiling into the monomer $[Rh3S_2O_32NH_3]Na_3$. In an ammoniacal medium this splitting takes place under simultaneous reaction with NH_4OH and formation of the compound $[Rh3S_2O_33NH_3]Na_3$. The compound $[Rh3S_2O_32NH_3]Na_3$ does not react with KI. Iodine does not enter the internal sphere, nor is the sodium of the external sphere replaced by potassium. The experiments performed are described, structural schemes are suggested, and analytical and physical data are given. The authors refer to a paper by V. V. Lebedinskiy and Ye. V. Shenderetskaya (Ref. 2). There are 2 Soviet references.

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Thiosulfate Complex Compounds of Rhodium With Ammonia

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B004/B014

ASSOCIATION: Institut obshchey i neorganicheskoy khimii im. N. S. Kurnakova Akademii nauk SSSR (Institute of General and Inorganic Chemistry imeni N. S. Kurnakov of the Academy of Sciences, USSR)

SUBMITTED: November 3, 1959

Card 3/3

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B004/B060

5 4700 1273 [illegible] 1018

AUTHORS: Chernyayev, I. I., Palkin, V. A., Baranova, R. A., Kuz'mina, N. N.

TITLE: Formation Heats and Specific Heats of Chloro Ammine Compounds of Bivalent Platinum

PERIODICAL: Zhurnal neorganicheskoy khimii, 1960, Vol. 5, No. 7, pp. 1428 - 1440

TEXT: The authors attempted to improve the accuracy of data so far available on the formation heat and specific heat of chloro ammine complexes of Pt^{II}, and to fill the gap for compounds hitherto left unconsidered. For their purposes, they made use of a specially designed calorimeter, a description of which is given in Ref.12. The heat effect of $NH_4[PtNH_3Cl_3]$ interaction with a 9.4% ammonia solution was measured at 70°C, as well as the specific heat of compounds $[Pt(NH_3)_3Cl]\cdot[PtNH_3Cl_3]$; $[Pt(NH_3)_3Cl]_2\cdot[PtCl_4]$; $NH_4[PtNH_3Cl_3]$, and $[Pt(NH_3)_4]\cdot[PtNH_3Cl_3]_2$ between

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86460

Formation Heats and Specific Heats of Chloro Ammine Compounds of Bivalent Platinum

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B004/B060

25° and 70°C. The synthesis of these compounds is briefly described, and analytical data are given. The crystallo-optical analysis (for $[Pt(NH_3)_3Cl]\cdot[PtNH_3Cl_3]$ made by M. M. Lyashenko) confirmed the absence of impurities. The specific heats found for compounds $[Pt(NH_3)_3Cl]\cdot[PtNH_3Cl_3]$ and $[Pt(NH_3)_3Cl]_2\cdot[PtCl_4]$ are given in Tables 1,2, Figs.1,2. Here, the spread of experimental data was ±1%. By allowing temperature in the calorimeter to rise more rapidly, the spread for the other compounds (Tables 3,4, Figs.3,4) was reduced to 0.5%. The formation heats of $NH_4[PtNH_3Cl_3]$ and of the isomers of the composition $(PtCl_2.2NH_3)_n$, (n = 1,2,3) were determined on the basis of the corresponding thermochemical cyclic processes according to Hess. Calculated heat effects of the interaction of the following compounds with gaseous NH_3 are indicated ($_{sd}$ = solid):

$$(NH_4)_2[PtCl_4]_{sd} + 4NH_{3\ gas} = [Pt(NH_3)_4]Cl_{2\ sd} + 2NH_4Cl_{sd} + 88.4\ \text{kcal/mole}$$

$$K_2[PtCl_4]_{sd} + 4NH_{3\ gas} = [Pt(NH_3)_4]Cl_{2\ sd} + 2KCl_{sd} + 86.9\ \text{kcal/mole}$$

$$NH_4[PtNH_3Cl_3]_{sd} + 3NH_{3\ gas} = [Pt(NH_3)_4]Cl_{2\ sd} + NH_4Cl_{sd} + 66.8\ \text{kcal/mole}$$

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86160

Formation Heats and Specific Heats of Chloro Ammine Compounds of Bivalent Platinum S/078/60/005/007/018/043/XX
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$$\text{cis-}[Pt(NH_3)_2Cl_2]_{sd} + 2NH_{3\ gas} = [Pt(NH_3)_4]Cl_{2\ sd} + 40.0\ \text{kcal/mole}$$
$$\text{trans-}[Pt(NH_3)_2Cl_2]_{sd} + 2NH_{3\ gas} = [Pt(NH_3)_4]Cl_{2\ sd} + 37.0\ \text{kcal/mole}$$
$$[Pt(NH_3)_3Cl]\cdot[PtNH_3Cl_3]_{sd} + 2\cdot 2NH_{3\ gas} = 2[Pt(NH_3)_4]Cl_{2\ sd} + 2\cdot 39.9\text{kcal/mole}$$
$$[Pt(NH_3)_3Cl]_2\cdot[PtCl_4]_{sd} + 3\cdot 2NH_{3\ gas} = 3[Pt(NH_3)_4]Cl_{2\ sd} + 3\cdot 37.9\ \text{kcal/mole}$$
$$[Pt(NH_3)_4]\cdot[PtNH_3Cl_3]_2 + 3\cdot 2NH_{3 gas} = 3[Pt(NH_3)_4]Cl_{2\ sd} + 3\cdot 39.2\ \text{kcal/mole}$$
$$[Pt(NH_3)_3Cl]Cl_{sd} + NH_{3\ gas} = [Pt(NH_3)_4]Cl_{2\ sd} + 18.5\ \text{kcal/mole.}$$

Fig.2 shows the molar specific heats of all compounds of the Werner-Miolatti series, and compares them with the values for $NaNO_3$ and KNO_3 supplied by V. A. Sokolov and N. Ye. Shmidt. The molar specific heats of trimer and dimer of the composition $n(PtCl_2.2NH_3)$ are shown in Fig.6: Molar specific heats.

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Formation Heats and Specific Heats of Chloro Ammine Compounds of Bivalent Platinum

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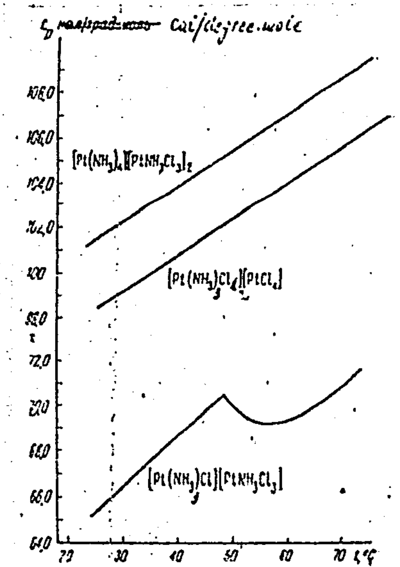

A striking aspect is the anomaly of $[Pt(NH_3)_3Cl]\cdot[PtNH_3Cl]$ at 48°C, as is characteristic of a phase transformation of the second order. Table 6 gives the following formation heats: $[Pt(NH_3)_4]Cl_2$, $-\Delta H = 177.1$ kcal/mole; $[Pt(NH_3)_3Cl]Cl$, $-\Delta H = 147.5$ kcal/mole; $NH_4[PtNH_3Cl_3]$, $-\Delta H = 152.6$ kcal/mole; cis-$[Pt(NH_3)_2Cl_2]$, $-\Delta H = 115.0$ kcal/mole; trans-$[Pt(NH_3)_2Cl_2]$, $-\Delta H = 118.0$ kcal/mole; $[Pt(NH_3)_3Cl]\cdot[PtNH_3Cl_3]$, $-\Delta H = 230$ kcal/mole; $[Pt(NH_3)_3Cl]_2\cdot[PtCl_4]$, $-\Delta H = 351$ kcal/mole; $[Pt(NH_3)_4]\cdot[PtNH_3Cl_3]_2$, $-\Delta H = 348$ kcal/mole. A paper by A. D. Gel'man is mentioned.

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S/078/60/005/007/022/043/XX
B004/B060

AUTHORS: Chernyayev, I. I., Golovnya, V. A., Shchelokov, R. N.

TITLE: Aquo-oxalato Sulfate Compounds of Uranyl

PERIODICAL: Zhurnal neorganicheskoy khimii, 1960, Vol. 5, No. 7, pp. 1454 - 1466

TEXT: The main results of this study were submitted to the Second International UNO Conference on the Peaceful Use of Atomic Energy. The authors first point out the difficulties involved in the synthesis of mixed acido complexes of uranyl which account for the scarceness of data available. In the work concerned here the authors started by investigating the possibility of substituting addenda by others (for the purpose of finding the rules governing relationships), and obtained the following series: $CO_3^{2-} > F^- > C_2O_4^{2-} > SO_4^{2-}$. On the basis of the result obtained, the mixed acido complexes were synthesized by addition reactions. The authors started from $UO_2C_2O_4 \cdot 3H_2O$ which was reacted with alkali sulfate, and obtained the oxalate-sulfate compounds of UO_2. For comparison, pure

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Aquo-oxalato Sulfate Compounds of Uranyl

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oxalate complexes were synthesized from uranyl oxalate and alkali oxalate, and pure sulfate complexes from uranyl sulfate and alkali sulfate. The following compounds were obtained: 1) $K_2[UO_2(C_2O_4)(SO_4)(H_2O)_2]\cdot H_2O$. The thermogram of this compound allows two effects to be identified: separation of the three H_2O molecules at 70 - 125°C, and destruction of the oxalate groups at 305 - 320°C. At 150°C, this substance loses all three H_2O molecules, which, however, are again added on standing in the air; this was confirmed both gravimetrically and analytically (Table 2). 2) $K_2[UO_2(C_2O_4)_2(H_2O)_2]H_2O$. This compound loses all three water molecules at 110°C. Two H_2O molecules are added stepwise on standing in the air, but not the third one. 3) $K_2[UO_2(SO_4)_2(H_2O)_2]$. In these three potassium compounds, a decrease in stability of the inner sphere of the complex ion was observed with an increase in molecular electrical conductivity μ:

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Aquo-oxalato Sulfate Compounds of Uranyl S/078/60/005/007/022/043/XX
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$K_2[UO_2(C_2O_4)_2(H_2O)_2] \rightarrow K_2[UO_2(C_2O_4)(SO_4)(H_2O)_2] \rightarrow K_2[UO_2(SO_4)_2(H_2O)_2]$

$\mu = 262\ ohm^{-1}.cm^2$ $\mu = 320\ ohm^{-1}.cm^2$ $\mu = 433\ ohm^{-1}.cm^2$

The same rule also holds for the following complex compounds: 4) $Rb_2[UO_2(C_2O_4)(SO_4)(H_2O)_2]$; 5) $Rb_2[UO_2(C_2O_4)_2(H_2O)_2]$; 6) $Rb_2[UO_2(SO_4)_2(H_2O)_2]$; 7) $Cs_2[UO_2(C_2O_4)(SO_4)(H_2O)_2]$; 8) $Cs_2[UO_2(C_2O_4)_2(H_2O)_2]$, and 9) $Cs_2[UO_2(SO_4)_2(H_2O)_2]$. Compound $Cs(NH_4)[UO_2(C_2O_4)(SO_4)(H_2O)_2]$ resulted from an attempt to obtain cesium oxalate sulfate as in the case of the rubidium compound by an exchange reaction between $UO_2C_2O_4.3H_2O$, $(NH_4)_2SO_4$, and Cs_2SO_4 as an aquo complex. Crystal microphotographs are given for some of the compounds, and for most of them the values of μ, pH, and thermograms of the water molecule loss on heating are given including gravimetric data for the re-addition of H_2O on standing. There are 13 figures, 18 tables, and 13 references: 3 Soviet, 1 Belgian, 2 French, and 5 German.

Aquo-oxalato Sulfate Compounds of Uranyl

S/078/60/005/007/022/043/XX
B004/B060

ASSOCIATION: Institut obshchey i neorganicheskoy khimii im. N.S.Kurnakova Akademii nauk SSSR (Institute of General and Inorganic Chemistry imeni N. S. Kurnakov of the Academy of Sciences USSR)

SUBMITTED: April 6, 1959

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S/078/60/005/007/025/043/XX
B004/B060

AUTHORS: Chernyayev, I. I., Golovnya, V. A., Ellert, G. V.

TITLE: The Complex Nature of Uranates

PERIODICAL: Zhurnal neorganicheskoy khimii, 1960, Vol. 5, No. 7, pp. 1481 - 1492

TEXT: This is a theoretical study of the complex formation of uranates on the basis of the coordination theory and in consideration of compounds synthesized by other researchers and by the authors themselves. After a general description of notions concerning the coordination theory by means of reactions of amphoteric hydroxides, the authors derive some genetic series of complex compounds of uranyl: Table 1. Genetic series of carbonates

Compound	mole U/mole CO_3	Compound	mole U/mole CO_3
$M_4^+[UO_2(CO_3)_3]$	1 : 3	$M_3^+[(UO_2)_2(OH)(CO_3)_3(H_2O)_5]$	1 : 1.5
$M_6^+[(UO_2)_2(CO_3)_5(H_2O)_2]$	1 : 2.5	$M^+[UO_2(OH)CO_3(H_2O)_3]$	1 : 1.0
$M_2^+[UO_2(CO_3)_2(H_2O)_2]$	1 : 2.0	$M^+[(UO_2)_2(OH)_3CO_3(H_2O)_7]$	1 : 0.5

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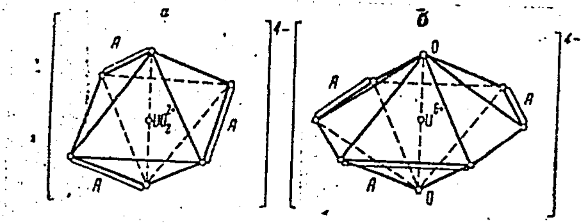
The Complex Nature of Uranates S/078/60/005/007/025/043/XX
B004/B060

The coordination number 6 results from this series for the uranyl ion. The various addenda are substituted according to the series: $CO_3^{2-} > F^- > OH^- > C_2O_4^{2-} > CH_3CO_2^- > SO_4^{2-}$. While the formation of binary compounds by means of bridges of CO_3^{2-}, $C_2O_4^{2-}$, SO_4^{2-}, and F^- is proved, that of polymer chains with more than two uranyl groups is called in question. The structure of binary complexes is discussed with Fig.1.



Legend to Fig.1: Structure of complex compounds of uranyl a - octahedral, b - dodecahedral, A = bivalent acid radical.

On the strength of crystal-optical and X-ray data, the dodecahedral structure is said to be the right one. Table 2 shows the genetic series

The Complex Nature of Uranates

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for the hydroxo compounds of uranyl.
Table 2. Genetic series of hydroxo compounds of uranyl.

No.	Type	U/OH	Example
1	$[(UO_2)_2(OH)]^{3+}$*	1:0,5	$M_3^+[(UO_2)_2(OH)(CO_3)_3(H_2O)_5]$
2	$[UO_2(OH)]^+$	1:1,0	$M^+[UO_2(OH)CO_3(H_2O)_3]$
3	$[(UO_2)_3(OH)_3]^+$	1:1,5	$M^+[(UO_2)_2(OH)_3CO_3(H_2O)\ x]$
4	$[UO_2(OH)_2]^0$	1:2,0	$[UO_2(OH)_2(NH_2OH)_2H_2O]$
5	$[(UO_2)_2(OH)_5]^-$	1:2,5	Нет 1)
6	$[UO_2(OH)_3]^-$	1:3,0	$M^+[UO_2(OH)_3(NH_2OH)_2]$
7	$[(UO_2)_2(OH)_7]^{3-}$	1:3,5	Нет 1)
8	$[UO_2(OH)_4]^{2-}$	1:4,0	$M_2^+[UO_2(OH)_4(NH_2OH)_2]$
9	$[(UO_2)_2(OH)_9]^{5-}$	1:4,5	Нет 1)
10	$[UO_2(OH)_5]^{3-}$	1:5,0	Нет 1)
11	$[(UO_2)_2(OH)_{11}]^{7-}$	1:5,5	Нет 1)
12	$[UO_2(OH)_6]^{4-}$	1:6,0	Нет 1)

Legend to Table 2:
1 = none

Compounds synthesized by other researchers, and the following compounds synthesized by the authors, are listed as examples of this series: $(NH_4)_3[(UO_2)_2(OH)(CO_3)_3(H_2O)_5]$ and the corresponding Ag, Ba, and Tl salt, as well as $(NH_4)[UO_2(OH)CO_3(H_2O)_2]$.

Analytical data are given. The X-ray structural analysis was performed by V. G. Kuznetsov at the authors' institute. The links of this series are

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discussed, and the difficulties met in synthesizing aquo-hydroxyl complexes are mentioned. Above all, the crystal-optical and X-ray identifications are rendered difficult by the microcrystalline structure of these compounds. As opposed thereto, the analogous genetic series of aquo-fluoro compounds is almost completely known (Table 3). The existence of the nonsynthesized compound $[(UO_2)_2F_{11}]^{7-}$ is dubious. The authors discuss the direct determination of hydroxyl groups in some of the compounds. Reference is made to papers by V. P. Markov and V. V. Tsapkin (Ref. 15), who performed the substitution of the OH group by means of fluorine following I. V. Tananayev's method, and titrated the resulting alkaline solution. The authors synthesized the compound $K_3[UO_2(OH)(CO_3)_2(H_2O)]$; whose analytical data are supplied. Fig.2 shows the dodecahedral structure for $[UO_2(OH)_2(H_2O)_4]$, and Fig.4 that for $M^+[UO_2(OH)_3(H_2O)_3]$. Fig.3 illustrates the structure of the binary complex $M^+[(UO_2)_2(OH)_5(H_2O)_6]$:

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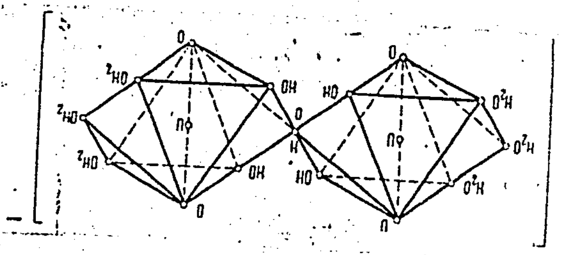
B004/B060



S. A. Brusilovskiy and O. Ye. Zvyagintsev are mentioned. There are 4 figures, 3 tables, and 30 references: 12 Soviet, 4 British, 2 Dutch, 3 French, 4 German, 1 Italian, and 1 Swiss.

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