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THEORY OF ORGANIC ANALYTICAL REAGENTS

I. M. Korenman,  
Gor'kiy State U

[A Digest]

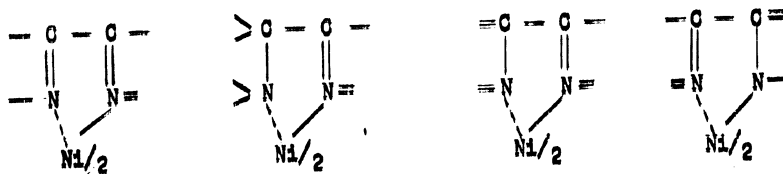
Not only dimethylglyoxime, but also other alpha-dioximes react with nickel [1, 2, 3]. Alpha-dioximes react with other ions besides nickel. Thus, dimethylglyoxime is capable of reacting with salts of ferrous iron, cobalt, palladium, platinum, and copper [2]. Colored compounds are also yielded by salts of rhodium [4], iridium [5], rhenium [6], gold [7] and bismuth [8]. Other alpha-dioximes exhibit activity within approximately the same range. For instance, alpha-benzaldioxime forms colored, difficultly soluble compounds with salts of nickel, ferrous iron, palladium [9], platinum, silver [10], copper [11], and bismuth [12]. Methylglyoxime reacts with salts of nickel, palladium, silver, copper, and ferrous iron [13], while alpha-furildioxime yields precipitates with salts of nickel, palladium, rhodium, platinum, and ruthenium [14]. Generally speaking, Fe<sup>++</sup>, Co, Ni, Pd, and Cu ions react with all alpha-dioximes. Ru, Rh, Pd, Ir, Re, Bi, Au, and Ag ions react with only some of them. Fe<sup>++</sup> gives with the reagents in question a reaction which is highly specified and more sensitive than that yielded by the nickel cation; substances reacting in this manner may be described as specific reagents for Fe<sup>++</sup> or some other ion with greater justification than naming them reagents for nickel.

A number of organic substances which does not contain the alpha-dioxime grouping still reacts with nickel ions and cations of other elements lying within the range indicated above [15, 16, 17, 18, 19, 20, 21, 22]. The five-ring inner complex shown below is common to the products formed by the compounds involved, which possess the groupings indicated in the formulae.

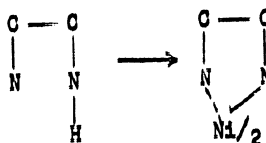
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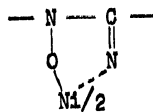
Irrespectively of the position of the double bonds, the following formation of a cyclic complex salt takes place in all of the four cases thus formulated:



Depending on the position of double bonds and the nature and position of the radicals combined with the basic functional group which is common to all of the reagents discussed hitherto, we have subgroups of reagents and individual reagents exhibiting specific properties as far as their application in analysis is concerned.

It has already been noted that nickel in the five membered ring may be replaced by other ions. The atoms of carbon and nitrogen may also be replaced by other atoms without affecting the general range of reactive ability of the compound [24, 25, 26, 27]. In regard to analogous compounds of this class, investigations carried out in our laboratory by S. A. Orlova have shown that crystals of nickel and palladium nitrosoguanidine are very similar in shape to the corresponding compounds of the cations in question with dimethylglyoxime.

A number of monooximes of dioxocompounds exhibits a reactivity similar to that of the substances mentioned above and forms five-ring complex salts in which the complex-forming atom of nitrogen is replaced by oxygen [24, 25, 26]. N'-hydroxy-N-(3-nitrophenyl)-N'-benzamidine [27] gives an orange-yellow precipitate with nickel salts, forming the complex



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Thus, 2-pyridylhydrazine exhibits reactions of limited sensitivity towards Fe<sup>++</sup> and Co<sup>++</sup> [32, 33].

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