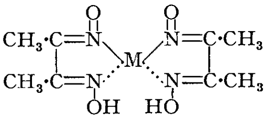
93. *A Contribution to the Chemistry of the Inner Complex Salts of Dimethylglyoxime.*

By Fritz Feigl and Hans A. Suter.

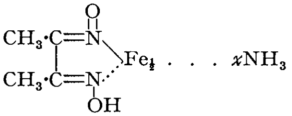
The constitution of various complexes of metals with dimethylglyoxime is discussed, and in particular a ferrous complex formerly supposed to be (II). Thilo and Friedrich had shown that both the oximino-groups of dimethylglyoxime are capable of entering into complex formation, and this is now further demonstrated by the preparation of several salts of dimethylglyoxime-palladium acid, $H_2[Pd(C_4H_6O_2N_2)_2]$.

Since Tschugaeff (*Ber.*, 1905, **38**, 2520) published the first of his papers on the insoluble red nickel salt of dimethylglyoxime, about 150 publications have appeared on the analytical applications of 1 : 2-dioximes (see Diehl, " The Applications of the Dioximes in Analytical Chemistry ", Columbus, Ohio, 1940) and on the constitution of their metal derivatives. The water-insoluble nickel and palladium compounds of dimethylglyoxime are of special interest. They are usually regarded as inner complex compounds and represented as shown in (I). This structure was fairly well validated by the experimental studies of Pfeiffer (*Ber.*, 1930, **63**, 1811). Tschugaeff and Orelkin (*Z. anorg. Chem.*, 1914, **89**, 401) described the preparation of a water-soluble ferrous compound of dimethylglyoxime; it results when dimethylglyoxime and ammonia are added to a tartrated ferrous solution. The compound, which is readily oxidized, has hitherto been written as in (II), *i.e.*, as an inner complex salt with co-ordinated ammonia molecules.

An examination of the structural formulæ (co-ordination formulæ) (I) and (II) reveals that only one of the two oximino-groups is capable of direct salt formation. The other is bound co-ordinatively to the metal atom, *i.e.*, by auxiliary valencies emanating from the nitrogen atom.



(I; M = Ni or Pd.)

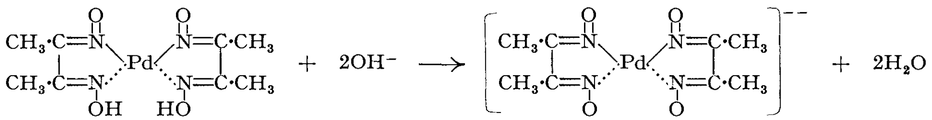


(II.)

Thilo and Friedrich (*Ber.*, 1929, **62**, 2998) were the first to obtain evidence that both these groups of dimethylglyoxime can function as salt-formers. They treated nickel dimethylglyoxime with sodium ethoxide in absolute alcohol and thus produced the compound $NaHNiD_2$.* This is a yellow-red crystalline substance that is easily decomposed by water and acids. Brown, unstable Li_2NiD_2 was obtained by an analogous procedure. It has now been found that all the oximino-groups of the inner complex palladium dimethylglyoxime also can take part in salt formation. Pure, intensely coloured, stable salts can be obtained, even when working in aqueous solution.

The starting point of the work reported here was the contradictory behaviour of dimethylglyoxime toward ammoniacal palladium solutions as opposed to the action of palladium dimethylglyoxime toward ammonia. Wunder and Thüringer (*Z. anal. Chem.*, 1913, **52**, 101) were the first to describe the quantitative precipitation of palladium dimethylglyoxime from mineral acid solution, and they also pointed out that no precipitate is obtained from ammoniacal solution. The reason for the non-precipitability is that the metal is present not as the reactive Pd^{++} ions but as the stable $[Pd(NH_3)_4]^{++}$ ions. Furthermore, palladium dimethylglyoxime is soluble in ammonia. Since the resulting solution is honey-yellow, it is evident that $[Pd(NH_3)_4]^{++}$ ions are not formed, for they are colourless.

The authors have found that addition of nickel salts to the yellow solution of $Pd(DH)_2$ in ammonia produces no red precipitate, and consequently there can be no unbound dimethylglyoxime present. It was further observed that the yellow solution remained unchanged after acidification with acetic acid followed by addition of potassium iodide. In contrast, this treatment produces insoluble, black palladium iodide, or brown-red solutions of $[PdI_4]^{--}$ ions, when applied to soluble palladium salts or aqueous suspensions of $Pd(DH)_2$. The complete masking of both the dimethylglyoxime and the palladium indicates that the action of ammonia on $Pd(DH)_2$ must produce a compound in which the ratio $Pd : DH_2 = 1 : 2$ has persisted. Consequently, a stable palladium dimethylglyoxime compound in ammoniacal solution can have only a composition which corresponds to that of the ferrous dimethylglyoxime (II) or to the formation of a water-soluble ammonium salt of palladium dimethylglyoxime of the same type as that of the unstable nickel dimethylglyoxime compounds isolated by Thilo and Friedrich. The assumption that an ammonium salt is formed is strengthened by Cooper's finding (*J. Chem. Met. Min. Soc. S. Africa*, 1925, **25**, 296) that $Pd(DH)_2$ dissolves in sodium hydroxide to produce a yellow solution. Confirmation of this supposition is supplied by the fact that compounds can be isolated which by virtue of their composition and chemical behaviour can be regarded as salts of a " dimethylglyoximepalladium acid ". The solubility of $Pd(DH)_2$ in alkalis to form salts, together with the concurrent masking of the palladium and dimethylglyoxime, can thus be plausibly explained by the following stoicheiometric formulations :



or

$$Pd(DH)_2 + 2KOH \longrightarrow K_2[PdD_2] + 2H_2O$$
$$Pd(DH)_2 + 2NH_4OH \longrightarrow (NH_4)_2[PdD_2] + 2H_2O$$

These equations and the isolation of *salts* of a dimethylglyoximepalladium acid represent the conversion of a water-insoluble inner complex salt into a water-soluble compound with an inner complex anion. These changes obviously occur because the two intact oximino-groups that remain in the inner complex palladium dimethylglyoxime form salts with strong alkalis. Accordingly, $Pd(DH)_2$ should be regarded as an amphoteric compound, which functions as an

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* The following abbreviations signify : DH_2 = dimethylglyoxime, $C_4H_8O_2N_2$; DH = monobasic residue of dimethylglyoxime, $C_4H_7O_2N_2$; D = dibasic residue of dimethylglyoxime, $C_4H_6O_2N_2$.

inner complex salt in neutral or acid media, and as an acid in alkaline surroundings. Hence, the compounds shortly to be described can be viewed as mixed salts of dimethylglyoxime, in which both oximino-groups exert an acidic function. In view of the fact that Feigl and Rubinstein (*Annalen*, 1923, **433**, 183) isolated cobalt compounds in which dimethylglyoxime is bound solely through the auxiliary valency of the nitrogen of the oximino-groups, it appears that dimethylglyoxime can react in three ways: (1) as neutral portion (DH_2 compounds); (2) as monobasic acid (DH compounds); (3) as dibasic acid (D compounds).

The experimental proof that palladium can form with dimethylglyoxime an inner complex salt as well as an inner complex anion, throws a new light on the ferrous compound of dimethylglyoxime, described by Tschugaeff and Orelkin (*loc. cit.*). There is but little support for the formulation (II) from analogous cases among complex compounds. Rather is it more in keeping with the facts to formulate the compound as an analogue of the water-soluble material produced from $Pd(DH)_2$ and ammonia, *i.e.*, as the ammonium salt of dimethylglyoximeferrous acid, furnishing the red $[FeD_2]^{--}$ ion.

Furthermore, the experimental proof that in the complex-bound dimethylglyoxime the acidic nature of the oximino-groups increases, is in accordance with the following previous findings of one of us (F. F.). The quadrivalent nickel compound $NiO(DH)_2$ (Feigl, *Ber.*, 1924, **57**, 758) and the compound CoS,DH_2,H_2O,NH_3 (Feigl and v. Tustanoswka, *ibid.*, p. 762) are soluble in alkalis and are precipitated from these solutions by addition of acids. Obviously the solubility of these two compounds in alkalis is due to the formation of water-soluble alkali salts.

EXPERIMENTAL.

(1) *Potassium Hydrogen Dimethylglyoximepalladium.*—Highly purified $Pd(DH)_2$ was added in small portions to aqueous potassium hydroxide solution, at 50°, until no more would dissolve. The suspension was filtered warm, and the filtrate, in a closed container, was kept overnight in the refrigerator. Yellow needles deposited and were collected in a glass filtering crucible. Since the salt is readily soluble in water, it was washed free from alkali with absolute alcohol, and the latter was then removed with ether. The material was analysed after 2—4 days' storage in an evacuated desiccator over calcium chloride.

A determination was made of the amount of $Pd(DH)_2$ that remains when the salt is decomposed by means of 0·5N-hydrochloric acid. The acid was allowed to react hot for 30 minutes and then at room temperature overnight. The residue of $Pd(DH)_2$ was collected in a dried, tared filter-paper and washed free from acid with 30% alcohol. After being dried at 105° and weighed, the solid was treated with sulphuric acid, evaporated to dryness, ignited to metallic palladium, and then weighed. The filtrate from the acid treatment was evaporated to dryness, and the residue gently ignited. If the potassium chloride was not perfectly white, the residue was dissolved in water and filtered through a weighed filtering crucible, which was then dried and weighed again. The difference between the weight of the ignited residue and the insoluble material collected on the filter was assumed to represent the weight of the potassium chloride. The analytical data correspond to a *potassium hydrogen* salt with 1·5 mols. of H_2O (after 2 days' drying) and an anhydrous acid salt (after 4 days' drying) (Found, after 2 days' and 4 days' drying, respectively: K, 9·66; 10·75; Pd, 26·80, 29·06; loss on acid treatment, 17·51, 10·91. $KH[PdD_2],1{\cdot}5H_2O$ requires K, 9·73; Pd, 26·54; H_2O, 6·72%. $KH[PdD_2]$ requires K, 10·43; Pd, 28·45%).

(2) *Barium Dimethylglyoximepalladium.*—The *barium* salt must be prepared with scrupulous exclusion of carbon dioxide because the latter readily decomposes the moist product. However, the dry salt is stable against this gas. An aqueous suspension of $Pd(DH)_2$ was boiled to drive off all the carbon dioxide and then allowed to cool. (The container was connected to a guard flask charged with concentrated potassium hydroxide solution.) The suspension was then treated with an excess of freshly prepared, filtered, carbonate-free alcoholic potash. The mixture was shaken until everything went into solution, and then an excess of freshly filtered barium hydroxide solution was added. A yellow, fine-grained precipitate appeared at once. The clear supernatant liquid was siphoned off (with exclusion of carbon dioxide) and the precipitate was washed several times with freshly boiled hot water. When free from alkali, the suspension was filtered through a fine filtering crucible (without exposure to carbon dioxide). The preparation was dried to constant weight in a vacuum over sulphuric acid.

For the analysis, a weighed quantity of the salt was transferred to a tared, fine glass filtering crucible and treated, without applying suction, with 0·5N-hydrochloric acid until the salt was completely decomposed. This point was easily ascertained, both by a change in colour and by an alteration in structure of the solid. The palladium dimethylglyoxime remaining in the crucible was washed thoroughly with water, dried at 105°, and weighed as such. The barium in the filtrate was determined as sulphate. {Found: Ba, 28·58, 28·99; $Pd(DH)_2$, 70·44, 70·55; loss on treatment with acid, 30·00, 29·88. $Ba[PdD_2], 0{\cdot}5H_2O$ requires Ba, 28·54; $Pd(DH)_2$, 70·01; H_2O, 1·90%}.

(3) *Palladium Dimethylglyoximepalladium.*—Barium dimethylglyoximepalladium, prepared by the procedure described in (2), was treated with an excess of a neutral solution of palladium chloride (prepared by dissolving ignited palladous chloride in aqueous sodium chloride solution). The mixture was kept on the water-bath, with occasional stirring, until no tiny yellow glistering particles could be seen (about one week). The evaporated water was replaced from time to time. The resulting brown salt was filtered on a glass crucible, the excess of palladous chloride removed by washing with water, and the salt brought to constant weight by drying at 105°. For analysis, the *salt* was decomposed with 0·5N-hydrochloric acid as outlined in (2). Both the residual $Pd(DH)_2$ and the palladium that passed into the filtrate were determined. The latter was precipitated as metallic palladium by making the filtrate basic

with ammonia and then adding formic acid. {Found: Pd, 23·19, 23·54; $Pd(DH)_2$, 72·60, 72·66; loss on treatment with acid, 27·83, 27·79. $Pd[PdD_2],H_2O$ requires Pd, 23·21; $Pd(DH)_2$, 73·30; H_2O, 3·93%.} These data indicate that the compound could be regarded as PdD, *i.e.*, as the palladium salt of dibasic dimethylglyoxime. The synthesis from barium dimethylglyoximepalladium demonstrates, however, that this product is a palladium salt of dimethylglyoximepalladium acid.

(4) *Manganese Dimethylglyoximepalladium.*—This *salt* was prepared as in (3) but by using manganous chloride. The product, dried at 105°, is dark olive green. After decomposition of the salt with 0·5N-hydrochloric acid, the manganese was precipitated as dioxide by treatment of the solution with ammonia and bromine. The dried precipitate was ignited and then converted into manganous sulphate by fuming with sulphurous acid and concentrated sulphuric acid. {Found: Mn, 14·32, 14·52; $Pd(DH)_2$, 85·93, 86·01; loss on treatment with acid, 11·58, 11·54. $Mn[PdD_2]$ requires Mn, 14·09; $Pd(DH)_2$, 86·42%.}

(5) *Lead Salts of Dimethylglyoximepalladium Acid.*—The procedures used in (3) and (4) did not produce pure lead salts of this acid, because $Pb[PdD_2]$ is very sensitive to acids. When barium dimethylglyoxime palladium is treated with an aqueous solution of a lead salt a red precipitate is formed at once. However, this lead salt is not pure; it contains either unreacted $Ba[PdD_2]$ or free $Pd(DH)_2$, depending on the conditions. If palladium dimethylglyoxime is treated with basic acetate ("liquor plumbi subacetici") a red salt is also formed, but this product likewise is not pure. It contains varying proportions of basic lead salts, probably resulting from the hydrolysis of the lead acetate. Nevertheless, by maintaining proper experimental conditions, a neutral and also a basic lead salt of dimethylglyoximepalladium acid were isolated. The products look alike; they are both scarlet when dry. It was found that solutions obtained by dissolving lead hydroxide in aqueous solutions of mannitol, glycerol, etc., react with $Pd(DH)_2$ to form the lead salts. When the mannitol or glycerol solutions are neutral, the normal salt is formed, whereas in the presence of free alkali, the product is a basic salt in which the ratio Pd : Pb = 1 : 2.

(a) *Neutral lead salt.* A solution containing 3·3 g. of lead nitrate in 50 ml. of water was mixed with 50 ml. of glycerol and then with dilute potassium hydroxide solution until the pH was 7·0—7·5. The liquid was then brought to the boil, allowed to cool in a closed container, and after 48 hours was filtered or centrifuged. Palladium dimethylglyoxime was stirred into this solution. The mixture, in a covered beaker, was digested on the water-bath for about 4 hours with occasional stirring. The solid was collected on a glass filtering crucible, washed free from lead with 50% glycerol, and the glycerol was then washed out with water. The solid was brought to constant weight at 105°. The *salt* was analyzed by dissolving the sample in 5—10 ml. of concentrated nitric acid in a beaker. The solution was then cautiously treated with 5 ml. of concentrated sulphuric acid. After the violent reaction had subsided, the mixture was warmed gently, and as soon as no more nitrous gases were evolved the temperature was raised and the solution brought to definite fuming. After cooling, the residue was diluted with 1N-sulphuric acid, to which a little hydrochloric acid had been added in order to dissolve the anhydrous palladium sulphate. The suspension was then heated to boiling, cooled, the lead sulphate collected on a glass filtering crucible, washed, and dried at 120°. The palladium in the filtrate was precipitated by formic acid after the solution had been made alkaline with ammonia (Found: Pb, 38·93, 38·85; Pd, 18·91, 19·21. $Pb[PdD_2]$ requires Pb, 38·22; Pd, 19·68%).

(b) *Basic lead salt.* The *compound* was prepared by the procedure given in (a) except that the addition of potassium hydroxide was continued until the glycerol–lead solution became quite basic to phenolphthalein. {Found: Pb, 51·83, 52·46; Pd, 11·23, 10·50. $Pb[PdD_2],Pb(OH)_2$ requires Pb, 52·90; Pd, 13·62%}.

Attempts to prepare the methyl ester of dimethylglyoximepalladium acid, by refluxing a chloroform solution of methyl iodide along with $Pb[PdD_2]$, were unsuccessful: no yellow lead iodide was formed, nor did evaporation of the chloroform solution yield a noticeable residue.

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