48. *The Basis of the Selectivity of Dimethylglyoxime as a Reagent in Gravimetric Analysis.*

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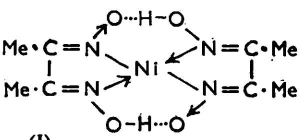
The factors which determine the relative solubilities in water of dimethylglyoxime complexes of stable dipositive cations are considered. Further support is provided for Rundle's suggestion that the insolubility of bisdimethylglyoxime nickel is attributable mainly to metal–metal bonding between planar molecules of the complex in the solid state; a similar conclusion is reached for the palladium(II) and platinum(II) derivatives. Bisdimethylglyoxime copper(II) has previously been shown to crystallise with a structure different from that of the nickel complex; cobalt(II), which might be expected to resemble nickel(II), forms a derivative which contains two firmly bonded molecules of water and appears to contain an octahedrally co-ordinated cobalt ion, thus precluding metal–metal bonding. Since the copper and cobalt complexes are soluble, and since no other metal in a stable oxidation state is likely to form a planar four-co-ordinated complex, the value of dimethylglyoxime in analysis becomes comprehensible.

Some new physical data for metal derivatives of dimethylglyoxime and ethylmethylglyoxime are reported.

ALTHOUGH dimethylglyoxime has been used in the gravimetric determination of nickel and palladium for many years, it is only recently that understanding of its selectivity has been possible. The structure (I) for bisdimethyglyoxime nickel was proposed by Brady and Muers [1] on the basis of the absence of reaction between the compound and phenyl *iso*cyanate,[2] acetic anhydride,[3] or methylmagnesium iodide; [1] the hydroxyl groups were shown as participating in what would now be called very strong intramolecular hydrogen bonding. The planar configuration round the nickel ion in complexes with other vicinal dioximes was demonstrated later by the isolation of *cis*- and *trans*-forms of complexes with benzylmethylglyoxime, methyl-*n*-propylglyoxime, and *n*-butylmethylglyoxime.[4, 5]



(I)

The *X*-ray determination of the structure of bisdimethylglyoxime nickel [6] has revealed

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[1] Brady and Muers, *J.*, 1930, 1599.

[2] Tschugaev, *J.*, 1914, 2187.

[3] Barker, *Chem. News*, 1925, **130**, 99.

[4] Sugden, *J.*, 1932, 246.

[5] Cavell and Sugden, *J.*, 1935, 621.

[6] Godycki and Rundle, *Acta Cryst.*, 1953, **6**, 487.

two features of outstanding interest. Planar molecules of the compound are so arranged, with planes parallel and nickel atoms of adjacent molecules only 3·24 Å apart (alternate molecules being rotated through 90° to allow room for the methyl groups), as to indicate weak metal–metal bonding This conclusion appears to be supported by the peculiar dichroism exhibited by the complex.[6,7] Furthermore, the oxygen–oxygen distance (2·44 Å) is the shortest known separation of hydrogen-bonded oxygen atoms. Comparison of the infrared absorption spectra of the complex (I) and the corresponding compound containing OD in place of OH groups led Rundle and Parasol [8] to identify a band at 1775 cm.$^{-1}$ as the O–H vibration frequency (the lowest value yet reported); and from the presence of only a single N–O vibration frequency (at 1560 cm.$^{-1}$) they further deduced that the hydrogen bonds were symmetrical.

Bisdimethylglyoxime palladium(II) is isomorphous with the nickel complex and also contains very strong and symmetrical hydrogen bonds.[8] Bisdimethylglyoxime copper(II), which is soluble, has a planar structure [9] and molecular dimensions almost identical with those of the nickel derivative; [6] the arrangement of the molecules in the lattice, however, precludes any metal–metal interaction. On this evidence, Godycki and Rundle [6] suggest an explanation of the difference in solubility between the copper and the nickel complex: the extra lattice energy resulting from metal–metal interaction in the latter stabilises the solid phase relatively to a solution of isolated molecules. Since the solubility, S, of a non-electrolyte and the difference in free energy between the solid and the solution are related by the equation $\Delta G^{\circ} = \mathbf{R}T \ln S$, a small increase in lattice energy would account for a large decrease in solubility.* They also suggest that the intramolecular hydrogen bonding may exert some desolubilising effect, but since they report that the copper compound contains very strong and symmetrical hydrogen bonds (a conclusion with which we do not agree), they have no evidence to support this hypothesis.

Two other metals are well known to exhibit planar four-co-ordination in stable di-positive oxidation states: platinum and cobalt. In an attempt to extend Godycki and Rundle's suggestions so as to provide a general explanation of solubility relations among metal derivatives of dimethylglyoxime, we have therefore studied the platinous and cobaltous complexes; and we have examined the importance of metal–metal bonding by introducing a larger alkyl group into the dioxime, thus forcing metal atoms in derivatives which contain metal–metal bonds further apart, and thereby weakening their interaction.

Bisdimethylglyoxime platinum(II) is very sparingly soluble and may, indeed, be used as a weighing form for platinum [13] (in the dimethylglyoxime separation of palladium and platinum, it is essential that the latter metal should be in the tetra-positive oxidation state). A partial determination of its structure by X-ray powder photography shows it to be isomorphous and very nearly isodimensional with the palladium complex, and the infrared spectra of the two substances are almost identical. The similarity in the complexes of nickel, palladium, and platinum is therefore complete.

Bisdimethylglyoxime cobalt(II) appears to have been prepared by Mellor and Craig,[14] who quoted a satisfactory analysis for cobalt in the compound, but gave no indication of

* The insolubility of the nickel complex is the more remarkable in that the stabilities of the bisdimethylglyoxime complexes in aqueous dioxan follow the normal Irving–Williams order $Co < Ni < Cu > Zn$, though the difference between log K (average) for the nickel and the copper compound (10·8 and 11·7 respectively at 25°) is small.[10] The relation between these stability constants and solubilities has been admirably discussed by Irving and Rossotti,[11] and Godycki and Rundle's discovery of the principal reason for the specificity of the reagent for nickel was, indeed, foreshadowed in a penetrating discussion by Irving and Williams.[12]

[7] Yamada and Tsuchida, *J. Amer. Chem. Soc.*, 1953, **75**, 6351.

[8] Rundle and Parasol, *J. Chem. Phys.*, 1952, **20**, 1487.

[9] Bezzi, Bua, and Schiavinato, *Gazzetta*, 1951, **81**, 856.

[10] Charles and Freiser, *Anal. Chim. Acta*, 1954, **11**, 101.

[11] Irving and H. S. Rossotti, *Analyst*, 1955, **80**, 258.

[12] Irving and Williams, *ibid.*, 1952, **77**, 822.

[13] Cooper, *J. Chem. Met. Mining Soc. S. Africa*, 1925, **25**, 296.

[14] Mellor and Craig, *J. Proc. Roy. Soc. New South Wales*, 1941, **74**, 495.

how it was obtained. Their value for the magnetic moment (2·6 B.M.) is shown by Figgis and Nyholm [15] (in a review of the magnetic properties and stereochemistry of cobaltous compounds) to be an almost conclusive indication of a square-planar configuration round the cobalt ion. Our attempts to prepare this substance, however, have been uniformly unsuccessful: from aqueous or aqueous dioxan solutions we have invariably obtained solvated complexes, $(C_4H_7O_2N_2)_2Co,2H_2O$ and $(C_4H_7O_2N_2)_2Co,2C_4H_8O_2$ respectively, which decomposed when attempts were made to remove the solvent by warming *in vacuo*. The magnetic moments of these complexes (1·92 and 1·90 B.M. respectively) indicate the presence of octahedrally co-ordinated bivalent cobalt. It thus seems clear that the dihydrate is the phase in equilibrium with a saturated solution of bisdimethylglyoxime cobalt: the well-established tendency of cobalt to assume the co-ordination number six, and the strength of the two extra bonds, must compensate for the loss of the metal–metal interaction energy which might have been expected to stabilise the lattice of the anhydrous planar compound. (In this connection it is significant that the nickel complex is appreciably soluble in solvents, such as pyridine, 2 : 6-lutidine, and dimethylaniline, which are better donors than water). Since the phases in equilibrium with saturated solutions of the nickel and the cobalt complex are not analogous, the great difference in solubilities is not surprising. The presence of a peak at 1751 cm.$^{-1}$ in the infrared spectrum of the dihydrate indicates the presence of very strong hydrogen bonding, and suggests that the dimethylglyoxime molecules are coplanar and that the water molecules therefore occupy *trans*-positions.

Bisethylmethylglyoxime nickel * is considerably more soluble than the dimethylglyoxime complex.[16] The very close similarity in the infrared spectra of these substances shows that the strengths of the hydrogen bonds in them are identical. The compounds are isomorphous, and the increase in the *c* side of the orthorhombic unit cell on going from the dimethylglyoxime to the ethylmethylglyoxime derivative strongly suggests that the distance between the metal atoms (*c*/2 in the dimethylglyoxime complex [6]) is increasing. This lends powerful support to Godycki and Rundle's theory of metal–metal interaction as an important factor in determining the solubility of bisdimethylglyoxime nickel, since the normal effect of increase in the size of the alkyl group would be expected to be a decrease in solubility. Conversely, the slightly shorter nickel–nickel distance in bis*cyclo*hexanedionedioxime nickel (3·20 Å, as against 3·24 Å in the dimethylglyoxime compound [6]) may be correlated with a decrease in the solubility of the nickel derivative,[17] despite the solubility of the dioxime in water.

Palladous and platinous derivatives of ethylmethylglyoxime are also more soluble than those of dimethylglyoxime; in each instance the increase in solubility is accompanied by a significant increase in metal–metal distance (as deduced from lattice constants), but the infrared spectrum indicates no change in the hydrogen bonding.

Our investigation of the infrared spectrum of bisdimethylglyoxime copper reveals the presence of two N–O vibration frequencies (at 1590 and 1541 cm.$^{-1}$) and a broad peak around 2500 cm.$^{-1}$. When these results are considered in conjunction with those for the nickel complex, they suggest the presence of quite strong, but not symmetrical, hydrogen bonds. Information of a totally different kind supports this suggestion: Charles and Freiser [10] noticed that for the interaction of cobaltous, nickel, or cupric ion and dimethylglyoxime the successive constants for complex formation are not very different; and they inferred that for complexes of all three metals the dichelate compound is stabilised (relative to the monochelate) by intramolecular hydrogen bonding. It seems likely, therefore, that although the hydrogen bonding is stronger in the nickel than in the cupric complex, it must

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* This discussion refers to the isomer which is precipitated from aqueous media—presumably the *trans*-form, but this is not established.

[15] Figgis and Nyholm, *J.*, 1954, 12.

[16] Cox, Sharratt, Wardlaw, and Webster, *J.*, 1936, 129.

[17] Wallach, *Annalen*, 1924, **437**, 148, 175.

still be important in the latter substance, and that it plays only a subsidiary part in determining relative solubilities. The decisive factors are the metal–metal bonding in the nickel, palladium, and platinum complexes, and the fact that the phase in equilibrium with a saturated solution of the cobalt complex is a stable dihydrate.

EXPERIMENTAL

Bisdimethylglyoxime Platinum(II).—Potassium chloroplatinite, dimethylglyoxime, and ammonium acetate were allowed to react in aqueous alcoholic solution[18] (the formation of this complex was found to be very much slower than that of the analogous palladium compound) (Found: C, 22·2; H, 3·5; N, 12·8; Pt, 46·6. Calc. for $C_8H_{14}O_4N_4Pt$: C, 22·5; H, 3·3; N, 13·2; Pt, 45·9%). Peaks at 1720 and 1550 cm.$^{-1}$ in the infrared spectrum corresponded to those (discussed above) at 1733 and 1550 cm.$^{-1}$ in the palladium, and 1775 and 1560 cm.$^{-1}$ in the nickel, compound. An X-ray powder photograph (taken using Cu-K_α radiation) was indexed (by comparison of the pattern with that of the palladium compound, which was almost identical) on the basis of an orthorhombic unit cell with $a = 16{\cdot}9$, $b = 10{\cdot}5$, $c = 6{\cdot}5$ Å; the values reported[6] for the palladium compound are $a = 16{\cdot}9$, $b = 10{\cdot}6$, $c = 6{\cdot}5$ Å.

Bisdimethylglyoxime Cobalt(II).—Hydrated cobalt chloride, dissolved in the minimum amount of water, was added to an equivalent amount of dimethylglyoxime in hot acetone. The resulting brown liquid was evaporated in a stream of oxygen-free nitrogen (to avoid oxidation to the cobaltic compound), and the brown *dihydrate* filtered off by suction, washed with acetone, and dried *in vacuo* (Found: C, 30·0; H, 5·2; N, 16·8. $C_8H_{18}O_6N_4Co$ requires C, 29·6; H, 5·5; N, 17·2%). The *addition compound* with two molecules of dioxan was obtained from saturated solutions of cobalt acetate in water and dimethylglyoxime in dioxan by the same procedure (Found: C, 41·7; H, 6·1; N, 12·4. $C_{16}H_{30}O_8N_4Co$ requires C, 41·3; H, 6·4; N, 12·0%). Magnetic susceptibilities were determined by the Gouy method at 22°, correction being made for the diamagnetism of the ligands.

Bisdimethylglyoxime Copper(II).—This was prepared by Tschugaev's method[18] (Found: Cu, 21·3; C, 33·6; H, 5·2; N, 19·2. Calc. for $C_8H_{14}O_4N_4Cu$: Cu, 21·6; C, 32·7; H, 4·8; N, 19·1%). The infrared spectrum has already been described.

Bisethylmethylglyoxime Nickel.—The dioxime of pentane-2 : 3-dione (obtained by oxidation of diethyl ketone with selenium dioxide) reacted with nickel chloride in aqueous alcohol to yield the compound as orange crystals (Found: Ni, 17·7; C, 37·5; H, 6·0; N, 17·7. Calc. for $C_{10}H_{18}O_4N_4Ni$: Ni, 18·5; C, 37·8; H, 5·7; N, 17·7%). Its X-ray powder diagram was indexed on an orthorhombic unit cell with $a = 19{\cdot}6$, $b = 10{\cdot}7$, $c = 6{\cdot}8$ Å (probably accurate within $\pm 0{\cdot}1$ Å). If the reasonable assumption is made of similar packing in the unit cell to that obtaining in the dimethylglyoxime derivative, the nickel–nickel distance ($c/2$) is 3·4 Å. The infrared spectrum closely resembles that of the dimethylglyoxime complex, the O–H and (single) N–O stretching frequencies being 1783 and 1564 cm.$^{-1}$ respectively. The compound is diamagnetic.

Cox *et al.*[16] reported interplanar spacings which cannot be reconciled with the lattice constants given above; we are unable to account for this, since their spacings for the copper derivative (see below) agree with ours. They did not, however, evaluate lattice constants; without the information given in Godycki and Rundle's work on bisdimethylglyoxime nickel,[6] we too would have been unable to proceed beyond measurement of the powder photograph.

Bisethylmethylglyoxime Palladium(II).—This was obtained as a dark ochre precipitate from an alcoholic solution of ethylmethylglyoxime and potassium chloropalladite (Found: C, 32·7; H, 5·0; N, 15·4. Calc. for $C_{10}H_{18}O_4N_4Pd$: C, 32·9; H, 4·9; N, 15·3%). Its X-ray powder diagram indicated an orthorhombic unit cell with $a = 19{\cdot}5$, $b = 10{\cdot}9$, $c = 6{\cdot}8$ Å. The infrared spectrum contains peaks at 1735 and 1550 cm.$^{-1}$ analogous to those in the dimethylglyoxime complex.

Bisethylmethylglyoxime Platinum(II).—The compound separated very slowly as a dark brown precipitate when solutions of ethylmethylglyoxime and potassium chloroplatinite were mixed (Found: C, 25·2; H, 3·8. Calc. for $C_{10}H_{18}O_4N_4Pt$: C, 26·5; H, 4·0%). The unit cell is orthorhombic and isodimensional with that of the palladium compound. The infrared spectrum shows peaks at 1730 and 1540 cm.$^{-1}$ and is almost identical with that of the palladium complex.

Bisethylmethylglyoxime Copper(II).—An X-ray powder photograph of this substance, made

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[18] Tschugaev, *Z. anorg. Chem.*, 1905, **46**, 144.

by a method similar to that used for the dimethylglyoxime complex, showed that it is not isomorphous with the nickel compound (Found: C, 37·9; H, 5·6; N, 17·3. Calc. for $C_{10}H_{18}O_4N_4Cu$: C, 37·4; H, 5·6; N, 17·4%). The compound showed diffuse absorption in the 2500 cm.$^{-1}$ region, but it cannot be said with certainty that there is more than one N–O vibration frequency.

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