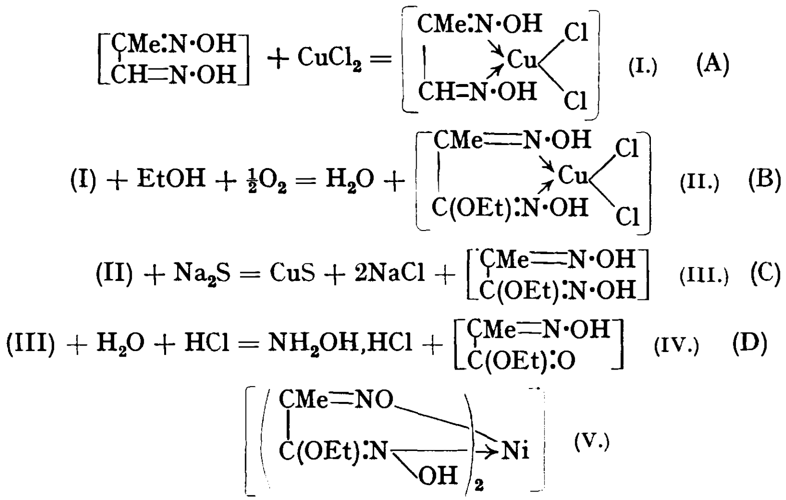
122. *Methylalkoxyglyoximes as Chelate Groups.*

By E. Sharratt and W. Wardlaw.

In a recent investigation (this vol., p. 129) we isolated as green crystalline substances four complexes of the type (I). These were obtained from the reaction [*e.g.*, (A)] between anhydrous cupric chloride and a glyoxime in ethyl-alcoholic solution. When dimethyl-, methylethyl-, or benzylmethyl-glyoxime was used, only one product resulted in each case, but with monomethylglyoxime the reaction was more complex. From the mixture of the cold concentrated alcoholic solutions of (anhydrous) cupric chloride and methylglyoxime, (I) crystallised within an hour as already described. It has since been found that the mother-liquor afforded emerald-green crystals (II) during the course of the next few days; these differed from (I), not only in colour, but also in that they were soluble in benzene and in chloroform, and a preliminary analysis suggested that (II) was (I) with alcohol of crystallisation. However, it was not possible to remove alcohol from (II), either by maintaining it at 100° for some hours or by placing it in a vacuum desiccator over calcium chloride for a week. Moreover, a complete analysis of (II) revealed that the molecule had only 10 hydrogen atoms instead of the 12 demanded by the structure suggested above. Further investigation indicated that the *product* (II) had an entirely different constitution from that of (I). A new chelate group (III) had been formed in the reaction, and had produced the co-ordination compound (II). The experimental data upon which these formulæ are based are as follows.

When an alcoholic solution of (II) was treated with aqueous sodium sulphide [reaction (C)], and the copper sulphide removed, the new *oxime* (III) was isolated from the filtrate as a white substance which crystallised from chloroform in silky needles. It was soluble in benzene, acetone, and alcohols, but only slightly soluble in water. With nickel salts it gave an orange-yellow *compound* (V), which melted without decomposition at 197°—a reaction typifying its glyoxime structure. If (I) was similarly treated with sodium sulphide, the original methylglyoxime was liberated, and isolated as its characteristic nickel derivative (see table; also Tschugaeff, *Chem. Zentr.*, 1911, **82**, i, 871).



$$\begin{bmatrix}\text{CMe:N·OH}\\ \text{CH=N·OH}\end{bmatrix} + \mathrm{CuCl_2} = \left[\begin{array}{l}\text{CMe:N·OH}\searrow\ \ \text{Cl}\\ \quad|\qquad\qquad \text{Cu}\\ \text{CH=N·OH}\nearrow\ \ \text{Cl}\end{array}\right] \quad \text{(I.)} \quad \text{(A)}$$

$$\text{(I)} + \text{EtOH} + \tfrac{1}{2}\mathrm{O_2} = \mathrm{H_2O} + \left[\begin{array}{l}\text{CMe=N·OH}\searrow\ \ \text{Cl}\\ \quad|\qquad\qquad\quad \text{Cu}\\ \text{C(OEt):N·OH}\nearrow\ \ \text{Cl}\end{array}\right] \quad \text{(II.)} \quad \text{(B)}$$

$$\text{(II)} + \mathrm{Na_2S} = \text{CuS} + 2\text{NaCl} + \begin{bmatrix}\text{CMe=N·OH}\\ \text{C(OEt):N·OH}\end{bmatrix} \quad \text{(III.)} \quad \text{(C)}$$

$$\text{(III)} + \mathrm{H_2O} + \text{HCl} = \mathrm{NH_2OH,HCl} + \begin{bmatrix}\text{CMe=N·OH}\\ \text{C(OEt):O}\end{bmatrix} \quad \text{(IV.)} \quad \text{(D)}$$

$$\left[\left(\begin{array}{l}\text{CMe=NO}\\ \quad|\\ \text{C(OEt):N}\diagdown\text{OH}\end{array}\right)_2 \rightarrow\text{Ni}\right] \quad \text{(V.)}$$

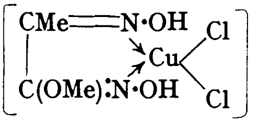
When (II) was decomposed with hydrogen sulphide, the filtrate obtained on removal of copper sulphide and excess of gaseous reagent produced no precipitate with nickel acetate, but gave, on concentration, hydroxylamine hydrochloride and ethyl α-oximinopropionate (IV), identified by comparison with the ester synthesised from pyruvic acid (Meyer and Janny, *Ber.*, 1882, **15**, 1527). Product (I), when decomposed with aqueous hydrogen sulphide, again yielded the original methylglyoxime. These experimental results indicate the above scheme of reactions.

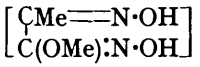
If decomposition (C) is effected with hydrogen sulphide, instead of the sodium salt, free hydrochloric acid is liberated, which hydrolyses (III), as shown in (D). According to this scheme, (II) should be formed only in the presence of an oxidising agent such as air. We find that, by exclusion of air, product (I) alone results from the reaction between cupric chloride and methylglyoxime in ethyl alcohol. Moreover, (I) should be convertible into (II) on treatment with alcohol, and this proves to be the case if free access of air is permitted [reaction (B)].

When other compounds of type (I), *i.e.*, from dimethyl-, methylethyl-, or benzylmethylglyoxime, were used, there was no evidence of any reaction, even after refluxing with ethyl or methyl alcohol for seven hours. The absence of such reaction is readily understood from the mechanism suggested for the production of (II). This substance is obtained from (I) by a process involving the elimination of the elements of water, one hydrogen atom being obtained from the glyoxime molecule itself. As no other compound of type (I) contains a hydrogen atom in the requisite position, such a reaction could not occur with these compounds—in fact, the non-formation of such substances affords an interesting proof that the explanation offered is correct.

In order to determine whether the reactions for the formation of (II) were general, methyl alcohol was substituted for ethyl alcohol. On mixing cupric chloride and methylglyoxime in this solvent, no material separated until, after three days, the *product* (VI) commenced to crystallise. Analysis of this substance indicated that it was the analogue of (II). The non-precipitation of (I) is due to its greater solubility in methyl than in ethyl alcohol.

(VI.)





$$\left[\begin{array}{l}\text{CMe}{=}\text{N·OH}\\ \text{C(OMe)}{:}\text{N·OH}\end{array}\right]$$

(VII.)

Decomposition of (VI) with sodium sulphide produced *methylmethoxyglyoxime* (VII), whereas hydrogen sulphide gave hydroxylamine hydrochloride and methyl α-oximinopropionate.

Compounds (III) and (VII) may readily be distinguished from the dialkylglyoximes, especially by means of their *nickel* derivatives :

Glyoxime	Monomethyl.	Dimethyl.*	Methylethyl.	Methylmethoxy.	Methylethoxy.
M. p.	154°	236° (decom.)	170°	148°	142°
		Nickel derivatives.			
	Deep crimson, readily reverting to orange (decomp. 243°).	Crimson; sublimes at 250°.	Tangerine (decomp. 260°).	Orange; reverts to yellow at 223° (decomp. 285°).	Orange-yellow (m.p. 197°).

* Tschugaeff, *Z. anorg. Chem.*, 1905, **46**, 145.

The two new organic compounds (III) and (VII) are oxime derivatives of esters (*viz.*, ethyl and methyl α-oximinopropionates). Alternatively, they may be regarded as esters of substituted hydroxamic acids, and it is most interesting that their preparation involves an oxidation, as does that of the hydroxamic acids themselves from nitroxyl and aldehydes (Angeli and Angelico, *Gazzetta*, 1904, **34**, i, 50) :

$$\text{R·CHO} + \text{HN(OH)}_2 = \text{R·C(OH)}{:}\text{N·OH} + \text{H}_2\text{O}.$$

EXPERIMENTAL.

Copper Methylethoxyglyoxime Dichloride (II).—Copper methylglyoxime dichloride (I) was prepared as already described (this vol., p. 131), and the filtrate was set aside in a vessel so as to permit access of air. Emerald-green needles began to separate after 24—30 hours; 6 hours later they were removed, further yields being removed daily. The needles were washed with a little alcohol, and dried; m. p. 165° (decomp.) [Found: Cu, 22·68; Cl, 25·22; N, 9·8; C, 21·22; H, 3·6. $C_5H_{10}O_3N_2,CuCl_2$ requires Cu, 22·67; Cl, 25·28; N, 9·98; C, 21·39; H, 3·59%. $C_5H_{12}O_3N_2,CuCl_2$, *i.e.*, (I) with EtOH of crystallisation, would require Cu, 22·51; Cl, 25·10; N, 9·91; C, 21·24; H, 4·28%]. On recrystallisation from acetone, chloroform, or benzene, (II) separated unchanged in emerald-green needles (Found: from acetone, Cu, 22·5; from benzene, Cl, 24·9%). A sample of (II) was placed on a small dry watch-glass, and the total weight recorded (4·7632 g.); after 6 hours' heating at 100°, no change in weight could be detected (4·7631 g.). Analysis of a fraction of the *dichloride* (II) which had been kept over calcium chloride in a vacuum desiccator for a week again proved that it was unaltered (Found: Cl, 25·12%).

Like other similar complexes of type (I), substance (II) was decomposed by water, and the results of molecular-weight determinations in phenol and electrical-conductivity measurements in acetone prove it to be a true 4-covalent compound.

Cryoscopic determination in phenol (constant = 7·27° per 1000 g.) : 6·29 g. per 1000 g. gave Δt = 0·190°, whence M = 241 (Calc. : 281).

Conductivity. A solution in acetone (3·620 g./l.) had $\kappa = 3{\cdot}471 \times 10^{-5}$ mho at 25°, whence μ = 2·69.

Attempted Preparation of (II) *in Absence of Air.*—A solution of copper chloride and methylglyoxime in ethyl alcohol, in the same proportions as in the foregoing experiment, was placed in a flask with exclusion of air. Product (I) separated rapidly as before, but was allowed to remain, since its removal would necessitate exposure of the mother-liquor to air. A week later, there was no sign of any further reaction, and the product then removed consisted solely of (I) (Found: Cu, 27·0; Cl, 29·9%). The filtrate was then divided into two fractions, and to one free access of air was permitted; from this, emerald-green needles characteristic of (II) appeared after 30—36 hours, but from the fraction from which air was excluded no crystals separated.

Copper Methylmethoxyglyoxime Dichloride (VI).—A cold solution of anhydrous copper chloride (1 g.) in methyl alcohol (40 c.c.) was mixed with a solution of methylglyoxime (1 g.) in the same solvent. After 3 days, bright emerald-green crystals appeared. These were removed four days later, and dried; m. p. 176° (decomp.) (Found: Cu, 23·6; Cl, 26·67; C, 18·0; H, 3·2. $C_4H_8O_3N_2,CuCl_2$ requires Cu, 23·8; Cl, 26·61; C, 18·0; H, 3·0%). The *substance* was only slightly soluble in chloroform and in benzene, and not readily soluble in acetone [contrast (II)].

Methylethoxyglyoxime (III).—A solution of the crystals (II) in ethyl alcohol (0·2 g. in 20 c.c.) was treated with aqueous sodium sulphide (0·2 g.; 5 c.c.). After removal of the precipitated copper sulphide, the filtrate was evaporated to dryness, and the residual *glyoxime* twice recrystallised from chloroform or benzene; m. p. 142° (Found: C, 40·8; H, 7·0; N, 19·4. $C_5H_{10}O_3N_2$ requires C, 41·1; H, 6·9; N, 19·2%). Reaction of the oxime with nickel acetate in aqueous-alcoholic solution gave an orange-yellow precipitate of the *nickel* derivative [Found: Ni, 16·8. $(C_5H_9O_3N_2)_2Ni$ requires Ni, 16·8%]. After recrystallisation from alcohol, this melted to a red liquid at 197° without decomposition.

Methylmethoxyglyoxime (VII).—Decomposition of (VI) with sodium sulphide in a similar manner to that just described yielded *methylmethoxyglyoxime* as a white solid, crystallising from chloroform in silky needles, m. p. 148° (Found: C, 36·23; H, 5·8; N, 20·9. $C_4H_8O_3N_2$ requires C, 36·36; H, 6·11; N, 21·2%). On addition of an alcoholic solution of this oxime to aqueous nickel acetate, an orange precipitate of the *nickel* complex was obtained; it was recrystallised from alcohol [Found: Ni, 18·5. $(C_4H_7O_3N_2)_2Ni$ requires Ni, 18·3%].

Decomposition of (I), (II), *and* (VI) *with Hydrogen Sulphide.*—The sap-green crystals (I) (0·2 g.) were dissolved in cold alcohol (20 c.c.), and the solution diluted with an equal volume of water. Hydrogen sulphide was then passed through the solution till precipitation of the metal was complete. The mixture was boiled and filtered, excess hydrogen sulphide and copper sulphide thus being removed. Addition of aqueous nickel and ammonium acetates to the cold filtrate produced a scarlet precipitate which became orange after an hour, or on heating. This reaction proves the presence of the original methylglyoxime in the filtrate, and so establishes formula (I).

Similar treatment of substances (II) and (VI) with hydrogen sulphide produced filtrates which did not react with nickel acetate. These solutions were therefore evaporated to dryness, and the resulting residues extracted with a little alcohol. The undissolved material in both cases proved to be hydroxylamine hydrochloride. The alcoholic extracts were evaporated, and the white solid so obtained twice recrystallised from light petroleum (b. p. 60—80°). The colourless needles so produced proved to be respectively ethyl (m. p. 95°) and methyl (m. p. 71°) α-oximinopropionates (Found, for ethyl ester: C, 45·97; H, 7·08; N, 11·3. Calc. for $C_5H_9NO_3$: C, 45·80; H, 6·92; N, 10·7%. Found, for methyl ester: N, 12·4. Calc. for $C_4H_7NO_3$: N, 12·0%); for the latter, Lepercq (*Bull. Soc. chim.*, 1894, **11**, 299) gives m. p. 69°.

Ethyl α-Oximinopropionate (IV).—This ester was synthesised by a modification of Meyer and Janny's method (*loc. cit.*). Aqueous solutions of hydroxylamine hydrochloride (10 g.; 30 c.c.) and lead nitrate (24 g.; 50 c.c.) were mixed, and the resulting lead chloride removed. Sodium hydroxide solution (30 c.c.; 5*N*) was added to the filtrate, and lead hydroxide was filtered off. The filtrate was mixed with pyruvic acid (10 g.) dissolved in sodium hydroxide (80 c.c.; 5*N*), and the cooled solution set aside over-night and then twice extracted with ether (50 c.c.) to remove impurities. The aqueous solution was acidified with acetic acid (20 c.c.; 5*N*), and silver nitrate solution (25 g.; 60 c.c.) added. The voluminous white precipitate of silver α-oximinopropionate which resulted was removed by filtration, care being taken to minimise access of light to the substance. After being washed with water, the silver salt was transferred to a desiccator (containing calcium chloride), which was then evacuated and placed in a dark cupboard for a week. The dried silver salt (10 g.) was then mixed with ethyl iodide (20 g.) and alcohol (30 c.c.), the whole being heated under reflux for 3 hours. After silver iodide had been separated, the solvent was removed by distillation, and the residue recrystallised twice from light petroleum (Found: C, 46·1; H, 6·8%).

A sample of the ester thus synthesised was melted with a similar amount of the ester (IV) obtained by decomposition of (II), and the mixed melt cooled. Samples of this mixture and of the two separate substances were heated together in an oil-bath : all three melted simultaneously at 95° (Meyer and Züblin, *Ber.*, 1878, **11**, 693, give 94°; Meyer and Janny give 95°).

Treatment of Compounds of Type (I) *with Alcohols.*—Copper methylglyoxime dichloride (I) (1 g.) was heated under reflux with ethyl alcohol (50 c.c.) for an hour. The hot solution was then filtered, and emerald-green needles separated later; these were identical with (II) (Found : Cl, 25·1%).

The other three compounds of type (I) were similarly treated with ethyl alcohol, but even after 7 hours no reaction could be observed. Methyl alcohol was also used as solvent, but in no case was there any indication of reaction : copper dimethylglyoxime dichloride was recovered unchanged (Found : Cu, 25·6. Calc. : Cu, 25·4%) and so also was the methylethyl analogue (Found : Cu, 23·7. Calc. : Cu, 24·0%).

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