27. *The Planar Configuration of Quadricovalent Compounds of Bivalent Copper and Nickel.*

By E. G. Cox, E. Sharratt, W. Wardlaw, and K. C. Webster.

In a recent communication by two of us (J., 1935, 731) it was shown that, in a number of 4-covalent compounds of bivalent copper, the metal valencies are coplanar, as in bivalent nickel, palladium, and platinum. Further support for this view has been obtained by an investigation of the simple derivative, dipyridinocupric chloride, Cu py_2Cl_2. This substance, which crystallises well from methyl alcohol, has been prepared under various experimental conditions with the object of discovering the theoretically possible *cis*- and *trans*-isomerides. Under all conditions, we find that it crystallises in the same form, which possesses a *trans*-planar configuration. This result follows from a consideration of the cell dimensions of the substance as determined by *X*-ray methods. The short length of the *c*-axis (3·84 Å.) shows that the two pyridine rings must be coplanar (or very nearly so), since its value is of the same order as the distance of approach of $=$CH$-$ groups in different molecules. Reference to a model shows that this can only be so in a molecule of *trans*-planar configuration, for with a *cis*-planar configuration the parallel arrangement of the pyridine rings shown in Fig. 1 is impossible on account of the proximity of the two rings (minimum distance 1·9 Å. instead of 3·7 Å.). In order to obtain the requisite clearance between the rings, they must be rotated about the N–Cu bonds through approximately 40°, thus increasing the thickness of the molecule and necessitating a *c*-axis of at least 4·5 Å. On the same grounds, a molecule in which the distribution of copper valencies is

Fig. 1.

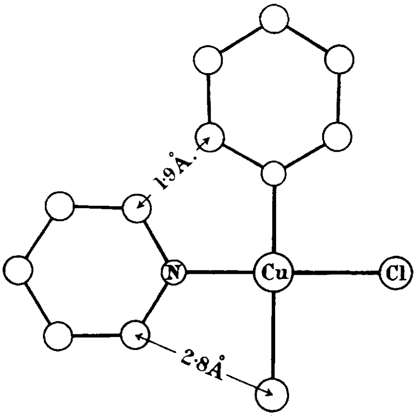
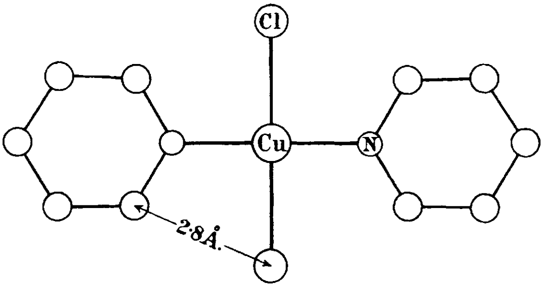


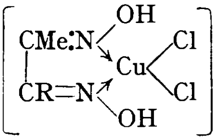
Fig. 2.

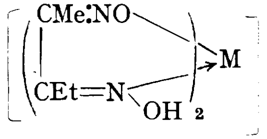


tetrahedral is excluded : in this case the projection of the chlorine atoms in a plane at right angles to that of the nitrogens would also exclude so short a *c*-axis as 3·8 Å. The molecule therefore has a planar *trans*-configuration in which the pyridine rings are coplanar : as Fig. 2 shows, however, the rings are probably rotated slightly out of the plane of the copper valencies (while remaining parallel to each other) in order that the minimum Cl–CH distance may be about 3·0 Å.

The inability to obtain the *cis*-derivative recalls the similar difficulty experienced with palladium, which from aqueous solutions yields only a *trans*-derivative, Pd.py_2Cl_2, by the use of pyridine : although, in the latter case, a *cis*-compound can be obtained by using potassium chloropalladite and pyridinium acetate (Grünberg, *Compt. rend. Acad. Sci. U.R.S.S.*, **1933**, 218; *A.*, **1934**, 379), yet it readily reverts to the α(*trans*)-form. That the *cis*-form of the copper salt is also very unstable has been clearly demonstrated by a reaction between pyridine and a copper compound in which the chlorine atoms must be in *cis*-positions. We have isolated as green crystalline substances four complex *salts* of the type (I), where

(I.)





(II.)

R = H, CH_3, C_2H_5, or $C_6H_5{\cdot}CH_2$; these 4-covalent compounds were readily soluble in alcohols, in acetone, and (except the first) in chloroform and benzene. Furthermore, *copper methylglyoxime dichloride* (I; R = H) was found to be unimolecular in acetone and phenol, and to have a negligible electrical conductivity in the former solvent. A crystallographic study of the dimethylglyoxime compound (I; R = CH_3) strongly suggests a planar form for this substance.

Addition of pyridine to a solution of any of these substances in alcohol or acetone displaces the oxime, and must form *cis*-Cu py_2Cl_2 initially. However, the product isolated is always the *trans*-planar form. Quadricovalent copper compounds of *cis*-configuration, like those of palladium, are therefore undoubtedly unstable when chelate groups are absent.

Since the distribution of valencies is planar in both cases, and the metal atoms are not greatly different in radius, it is to be expected that corresponding copper and nickel compounds will sometimes be isomorphous. This has proved to be the case with the methylethylglyoxime *derivatives* (II; M = Cu or Ni). These substances are microcrystalline, but microscopic examination and *X*-ray powder photographs show that they are undoubtedly isomorphous. The table (p. 133) shows the close correspondence between the lattice spacings of the two derivatives. Theoretically, these compounds should exist in *cis*- and *trans*-modifications, but an examination of the products resulting from interaction of the oxime with the acetates of nickel and copper has shown that only one substance is obtained. Again, as both substances were decomposed by heat, without melting, it is not possible to obtain isomerides of them as Sugden (J., **1932**, 246; **1935**, 621) was able to do in the case of the nickel derivatives of some other unsymmetrical oximes.

EXPERIMENTAL.

Methylglyoxime.—This was prepared by Tschugaeff's method (*Chem. Zentr.*, 1911, **82**, i, 871). Acetoacetic ester (90 g.), sodium nitrite (50 g.), and potassium hydroxide (42 g.) were dissolved in water (1800 c.c.), and the pale yellow mixture kept over-night; it was then cooled to 0°, air was bubbled through it, and 5*N*-sulphuric acid (*ca.* 150 c.c.) added slowly until it was acid to methyl-orange. After standing for an hour (still at 0°), the mixture was extracted with ether (5 × 100 c.c.), the ether removed, and the resulting *iso*nitrosoacetone dried in a vacuum desiccator; yield, 46 g. The whole of this product was dissolved in sodium hydroxide solution (46 g.; 200 c.c.), and hydroxylamine hydrochloride (100 g.) added. The mixture was warmed on the water-bath for 2 hours; on cooling, white crystals of methylglyoxime separated; yield, 44 g.; m. p. 154° (Found : N, 27·8. Calc. for $C_3H_6O_2N_2$: N, 27·5%).

Methylethylglyoxime.—Ethyl ethylacetoacetate ("Organic Syntheses," Vol. VII, p. 36) was converted into methyl *iso*nitrosopropyl ketone by the method described above. Introduction of the second oxime group was also effected similarly. The oxime, which was much more readily soluble than dimethylglyoxime in alcohol, melted at 170—171° (Schramm, *Ber.*, 1883, **16**, 181, gives 170°).

Benzylmethylglyoxime.—Ethyl benzylacetoacetate was synthesised by a method similar to that for the ethyl derivative. The glyoxime was then prepared by Sugden's method (J., 1932, 249). Our oxime melted at 183°; Sugden gives 194°, but Schramm (*loc. cit.*) gives 180—181°.

Copper Methylglyoxime Dichloride (I; R = H).—A cold alcoholic solution of anhydrous copper chloride (7 g.; 150 c.c.) was mixed with methylglyoxime (5 g.) dissolved in alcohol (50 c.c.). Sap-green crystals of the *dichloride* began to appear almost immediately, and were removed after an hour. They were washed with a little alcohol and dried; m. p. 156° (decomp.) (Found: Cu, 26·8; Cl, 29·7; C, 15·45; H, 2·6; N, 11·8. $C_3H_6O_2N_2,CuCl_2$ requires Cu, 26·9; Cl, 30·0; C, 15·2; H, 2·5; N, 11·8%). The substance was soluble in alcohols and acetone, but was decomposed by the addition of cold water, with the liberation of some of the oxime. The results of the molecular-weight determinations and of electrical conductivity measurements in acetone leave no doubt that this substance is a true 4-covalent compound :

Cryoscopic determination in phenol (*constant* = 7·27° *per* 1000 *g.*). 10·54 G. per 1000 g. gave $\Delta t = 0{\cdot}318°$, whence $M = 241$ (Calc. : 236).

Ebullioscopic determination in acetone (*constant* = 2·22° *per litre*). 16·90 G. per 1000 c.c. gave $\Delta t = 0{\cdot}158°$, whence $M = 237$.

Conductivity.—A solution of the dichloride in acetone (7·384 g./l.) had $\kappa = 8{\cdot}74 \times 10^{-5}$ mho at 25°, whence $\mu = 2{\cdot}80$.

Copper Dimethylglyoxime Dichloride (I; R = CH_3).—Cold alcoholic solutions of anhydrous copper chloride (2 g.; 80 c.c.) and dimethylglyoxime (2 g.; 120 c.c.) were mixed. Deep green crystals of the required compound separated rapidly; they were washed with alcohol and dried (Found: Cu, 25·44; Cl, 28·39; N, 10·8. Calc. for $C_4H_8O_2N_2,CuCl_2$: Cu, 25·39; Cl, 28·34; N, 11·18%). This substance was also prepared by warming to 60°, for 5—7 minutes, aqueous cupric chloride (10 g.; 100 c.c.) and solid dimethylglyoxime (3 g.). When the deep green solution was filtered and allowed to cool, it deposited crystals of the dichloride (Found : Cu, 25·40%). It is important not to wash this product with pure water since this causes decomposition, the oxime separating from the mixture. This compound had been prepared by Paneth and Thilo (*Z. anorg. Chem.*, 1925, **147**, 196) by passing dry hydrogen chloride over dry copper dimethylglyoxime; these authors considered the chlorine atoms to be ionised, since the halogen could be precipitated with cold alcoholic silver nitrate; but since this reagent contains water, which decomposes the product, this reaction provides no evidence as to the structure of the compound, which is clearly similar to that of the methylglyoxime derivative just described. Again, this substance is soluble in chloroform and benzene.

If copper dimethylglyoxime dichloride is boiled with water for 10 minutes, or aqueous cupric chloride (10 g.; 150 c.c.) is boiled with dimethylglyoxime (5 g.) for 15 minutes, cuprous chloride separates, and if this is removed, and the filtrate cooled, fine yellow needles are deposited. These are very readily oxidised by air, and for analysis they were removed in an atmosphere of nitrogen (Found: Cu, 27·7; Cl, 17·6. $C_4H_8O_2N_2,CuCl$ requires Cu, 29·6; Cl, 16·5%); they appear, therefore, to be the *cuprous* derivative.

Copper Methylethylglyoxime Dichloride (I; R = C_2H_5).—When cold alcoholic solutions of methylethylglyoxime (3 g.; 40 c.c.) and anhydrous cupric chloride (3 g.; 50 c.c.) were mixed, emerald-green crystals of the required *compound* separated rapidly; they were removed and dried (Found: Cu, 24·0; Cl, 26·65. $C_5H_{10}O_2N_2,CuCl_2$ requires Cu, 24·0; Cl, 26·8%). This compound resembles the dimethyl derivative in its solubility in organic solvents. Water decomposes it, with liberation of the original oxime.

Copper Benzylmethylglyoxime Dichloride (I; R = CH_2Ph).—Cold alcoholic solutions of the glyoxime (3 g.; 60 c.c.) and anhydrous cupric chloride (3 g.; 60 c.c.) were mixed. The complex, which separated almost immediately, crystallised in pale green leaflets possessing a silvery reflex. Its properties were similar to the two compounds just described (Found: Cu, 19·3; Cl, 21·45. $C_{10}H_{12}O_2N_2,CuCl_2$ requires Cu, 19·5; Cl, 21·7%).

Reaction of Pyridine with the Glyoxime Compounds of Cupric Chloride.—Solutions of these glyoxime derivatives of cupric chloride (I) in acetone or alcohol, at 15°, were treated with pyridine. From the methylglyoxime compound, dipyridinocupric chloride separated almost immediately in pale blue, microscopic needles. These were removed and examined by *X*-ray powder photographs without recrystallisation, so as to preclude any possibility of the product reverting to a more stable isomeride, for it is well known that recrystallisation of *cis*-dipyridinopalladium chloride effects such a transformation. This reaction was also carried out at − 10°, but a similar product was obtained [Found, for compound formed at 15° : Cu, 21·5; Cl, 23·8; for compound formed at − 10° : Cu, 21·5. Calc. for $Cu(C_5H_5N)_2Cl_2$: Cu, 21·7; Cl, 24·2%]. Addition of pyridine to the other glyoxime derivatives also produced the same compound, but the reaction was much slower in these cases, especially when the dimethylglyoxime compound was used (Found, from dimethyl compound : Cu, 21·4; from methylethyl compound : Cu, 20·9; from benzylmethyl compound : Cu, 20·8%). The last two derivatives were contaminated with a little of the hexapyridinocupric chloride.

Dipyridinocupric Chloride.—This substance was then prepared by Lang's method (*Ber.*, 1888, **21**, 1580), *i.e.*, by the direct action of pyridine on cupric chloride in alcoholic solution; it crystallised from methyl or ethyl alcohol in fine blue needles (Found : Cu, 21·7%). Addition of acetic acid to the alcoholic copper chloride did not affect the product obtained on the addition of pyridine, even when the reaction was effected at − 10°.

Copper Bismethylethylglyoxime (as II).—An aqueous solution of copper acetate (1 g.; 100 c.c.) was acidified with a few drops of acetic acid, and an alcoholic solution of methylethylglyoxime (1·3 g.; 50 c.c.) added. After being heated for 30 minutes, the solution was filtered and cooled; dark brown microscopic needles then separated; m. p. 179° (decomp.) [Found : Cu, 19·8. $(C_5H_9O_2N_2)_2Cu$ requires Cu, 19·8%]. A saturated solution of *copper bismethylethylglyoxime* in chloroform or benzene was fractionally precipitated with light petroleum. All fractions melted at the same temperature as the original, *viz.*, 179° (decomp.). When plunged in an oil-bath at 175°, none of the fractions melted, showing that the true m. p.'s had been recorded (cf. Sugden's experiments with the nickel compounds, *loc. cit.*).

This compound was also prepared by the addition of cold aqueous copper acetate (1 g.; 25 c.c.) to an alcoholic solution of the oxime (1·3 g.; 50 c.c.). Cold water (50 c.c.) was then added, and after being stirred for a few minutes, the mixture was filtered. On standing, the filtrate deposited dark brown needles, which were much larger than those prepared by the previous method; they were, however, otherwise identical; m. p. 179° (decomp.). This substance was soluble in organic solvents, but did not give good crystals on recrystallisation.

Nickel Bismethylethylglyoxime.—Methylethylglyoxime (1 g.) was dissolved in warm alcohol (140 c.c.) and added to a hot aqueous solution of nickel sulphate (2 g.; 200 c.c.) containing a few drops of dilute sulphuric acid. Ammonia was then added slowly, till precipitation was complete. After the hot solution had stood for an hour, the tangerine-coloured *complex* was removed, and dried in an oven [Found : Ni, 18·35. $(C_5H_9O_2N_2)_2Ni$ requires Ni, 18·5%]. A remarkable feature of this substance was its ready solubility in alcohols and benzene, in which it was about 50 times as soluble as nickel dimethylglyoxime. Attempts to isolate two isomerides of this substance failed; all fractions obtained from acetone–water decomposed at the same temperature as the original, *viz.*, 260°.

Reaction between Copper Acetate and Methyl- or Benzylmethyl-glyoximes.—When either of these glyoximes was used in place of methylethylglyoxime in the preparation of a copper derivative as above, the product was of a different type : only one oxime group was associated with the metal atom, which had replaced the hydrogen atoms from both oxime groups of the glyoxime. The *substances* were black and hygroscopic, analysis indicating that they were hydrated (Found for methylglyoxime compound : Cu, 35·8. $C_3H_4O_2N_2Cu,H_2O$ requires Cu, 35·0%; for benzylmethylglyoxime compound : Cu, 21·2. $C_{10}H_{10}O_2N_2Cu,2H_2O$ requires Cu, 21·9%). These compounds are evidently similar to the α-benzoinoxime derivative of copper which we recently studied (J., 1935, 818). They were not further examined, as they were of no use for stereochemical purposes.

Crystallographic and X-*Ray Results.*

X-Ray investigations were carried out by means of single-crystal rotation and oscillation photographs using copper K_α radiation.

Copper Dimethylglyoxime Dichloride.—This compound forms triclinic combinations of $a\{100\}$, $b\{010\}$, $c\{001\}$, and $p\{0\bar{1}1\}$; tabular on $b\{010\}$, and sometimes elongated along $[c]$. Angles observed : $a(100) : b(010) = 64° 17'$; $b(010) : c(001) = 69° 37'$; $c(001) : p(0\bar{1}1) = 51° 35'$. From *X*-ray measurements, $a = 7·96$, $b = 8·10$, $c = 7·54$ Å., $\alpha = 100° 23'$, $\beta = 109° 52'$, and $\gamma = 109° 18'$.

The crystals are non-pyroelectric, and there are two molecules in the unit cell (*d*, calc. = 2·00 g./c.c.; obs. = 1·98). The space-group is therefore $P\bar{1}$ (C_i^1) and the molecules asymmetric.

Optical properties : the minimum refractive index in the (010) plane is 1·57 ($\lambda = 5461$) and is inclined at 29° to the *a*-axis in the obtuse angle β. The birefringence is very high, the maximum index not being accurately measurable owing to strong absorption.

These results, combined with the observation that the a-axis rotation photograph shows weak odd-layer lines, strongly suggest that the molecules are flat and equally spaced along the a-axis, so that their thickness is approximately $\frac{1}{2}a$.cos 29°, *i.e.*, 3·5 Å.

Dipyridinocupric Chloride.—This substance crystallises in poorly developed monoclinic combinations of $a\{100\}$, $m\{110\}$, and $p\{011\}$, greatly elongated parallel to $[c]$. Refractive indices : α (parallel to $[c]$) $= 1{\cdot}60$, $\gamma = 1{\cdot}75$ ($\lambda = 5461$). Strongly dichroic.

X-Ray measurements give $a = 34{\cdot}0 \pm 0{\cdot}5$, $b = 8{\cdot}4 \pm 0{\cdot}1$, and $c = 3{\cdot}84 \pm 0{\cdot}05$ Å. The angle β is apparently close to 90°. With four molecules in the unit cell, $d = 1{\cdot}76$ g./c.c. (obs. 1·76). The space-group was not determined, but the lattice is probably uncentred, and the absence of pyroelectric effects shows the class to be C_{2h} or C_s.

Copper Bismethylethylglyoxime.—This compound forms very small dark brown elongated plates, having a rhomboidal outline with an angle of 58°. The slow vibration is inclined at about 48° to the direction of elongation in the acute angle of the rhomboid. An X-ray powder photograph was taken with copper K_α radiation in a camera of 3 cm. radius; the measured spacings (in Å.) are recorded in the table.

Nickel Bismethylethylglyoxime.—This substance forms small red crystals of the same appearance as those of the copper derivative (angle of rhomboid 58°, slow vibration inclined at approx. 43° to the direction of elongation). The lattice spacings measured in the same way as for the copper derivative are shown in the table (I = intensity).

Copper compound.				Nickel compound.			
d.	*I.*	*d.*	*I.*	*d.*	*I.*	*d.*	*I.*
8·50	v.s.	3·10	v.w.	8·50	v.s.	—	—
7·18	v.w.	2·91	m.s.	7·13	v.w.	2·92	s.
6·00	m.s.	2·70	m.s.	6·00	m.w.	2·70	m.w.
5·36	m.s.	2·53	v.w.	5·33	m.w.	2·51	m.w.
4·68	m.	2·32	m.	4·63	v.w.	2·32	m.
4·08	s.	2·09	m.	4·09	s.	2·08	m.
3·69	s.	1·87	m.	3·72	s.	1·86	m.
3·50	s.			3·52	m.		

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