162. *The Planar Structure of Quadricovalent Cupric Compounds.*

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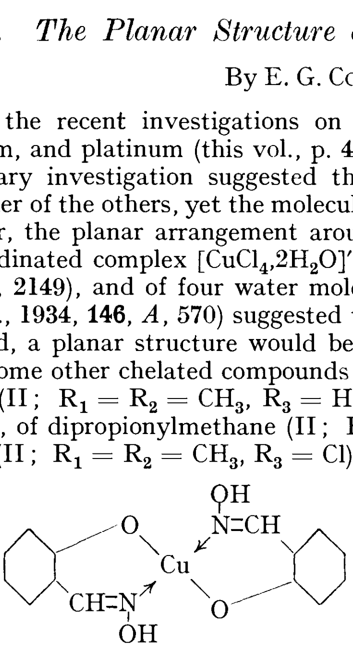
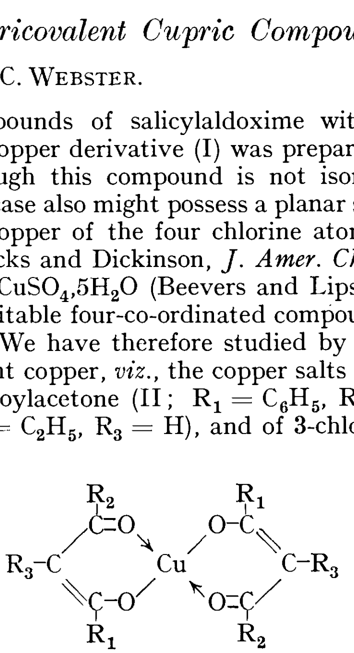
During the recent investigations on the compounds of salicylaldoxime with nickel, palladium, and platinum (this vol., p. 459), the copper derivative (I) was prepared, and a preliminary investigation suggested that, although this compound is not isomorphous with either of the others, yet the molecule in this case also might possess a planar structure. Moreover, the planar arrangement around the copper of the four chlorine atoms in the six-co-ordinated complex $[CuCl_4,2H_2O]''$ (Hendricks and Dickinson, *J. Amer. Chem. Soc.*, 1927, **49**, 2149), and of four water molecules in $CuSO_4,5H_2O$ (Beevers and Lipson, *Proc. Roy. Soc.*, 1934, **146**, *A*, 570) suggested that, if suitable four-co-ordinated compounds were examined, a planar structure would be found. We have therefore studied by means of *X*-rays some other chelated compounds of bivalent copper, *viz.*, the copper salts of acetylacetone (II; $R_1 = R_2 = CH_3$, $R_3 = H$), of benzoylacetone (II; $R_1 = C_6H_5$, $R_2 = CH_3$, $R_3 = H$), of dipropionylmethane (II; $R_1 = R_2 = C_2H_5$, $R_3 = H$), and of 3-chloroacetylacetone (II; $R_1 = R_2 = CH_3$, $R_3 = Cl$).

(I.)





(II.)

These investigations have definitely established that in the crystalline state these quadricovalent compounds of bivalent copper possess a planar structure. On account of the large number of parameters involved, a complete determination of the crystalline structure of any one of these compounds would be a very laborious undertaking; it has been possible, however, to demonstrate their planar configuration conclusively by means of (*a*) space-group considerations, (*b*) cell dimensions, and (*c*) optical properties. In view of the importance of these results, it is desirable to consider briefly the validity of the evidence under these heads.

(a) *Space-group Considerations.*—All the substances concerned (with the possible exception of the chloro-compound, which was not studied so thoroughly as the others) are monoclinic, and careful tests by means of liquid air (Martin, *Phil. Mag.*, 1931, **22**, 519) showed them to be non-pyroelectric, so that they belong to the prismatic class. The space-group was determined in each case by careful examination of numerous oscillation photographs taken with long exposures, special search being made for reflexions from such planes as the odd orders of (010), which were of particular importance in this respect. The compounds with acetylacetone and benzoylacetone gave identical results; the space-group was found to be C_{2h}^5 ($P2_1/n$), so that, since the cell contains only two molecules, each molecule must possess a centre of symmetry. In both these compounds, therefore, the copper atom and its four surrounding oxygen atoms are coplanar. It should be emphasised that in a case of this kind, where the symmetry is established by failure to find certain reflexions after careful search, although it is conceivable that still more exhaustive search might reveal very weak "forbidden" lines, yet the main conclusions would be unaffected, since such weak reflexions would merely indicate the very slightest divergence from perfect centro-symmetry. It may also be pointed out that the halvings for this particular space-group are different from those of any other in the monoclinic system; the results are independent of those of the pyroelectric tests, although the two are in agreement.

The salicylaldoxime derivative has the symmetry of the space-group C_{2h}^5 ($P2_1/n$) with four molecules in the cell, but an additional set of halvings indicates that the molecule of this compound also possesses a centre of symmetry. The space-group of the dipropionylmethane compound is C_{2h}^6 ($A2/a$), and as far as symmetry requirements are concerned, the molecule may have either a two-fold axis or a centre of symmetry; the former, however, is excluded by the cell dimensions.

(b) *Cell Dimensions.*—It is well established that the distance apart of carbon atoms in neighbouring molecules of crystalline organic compounds is approximately 3·7 Å.U. (see, *e.g.*, Robertson, Report of International Conference on Physics, 1934, II, 46, where the smallest carbon–carbon distance recorded is 3·4 Å.U.). From these values, a simple calculation shows that if, in the crystal of copper acetylacetonate, the disposition of the Cu–O bonds were tetrahedral, the distance apart of copper atoms in neighbouring molecules would probably be about 5·3 Å.U., and certainly not less than 4·8 Å.U. In the substituted acetylacetone compounds the distance would probably be somewhat greater. On the other hand, with a planar distribution of valencies, the distance apart of copper atoms in neighbouring molecules might be anything from about 3·7 Å.U. upwards, according to the arrangement of the molecules. Actually, for each of the four diketone compounds examined, one of the cell dimensions (which must be the distance apart of copper atoms in different molecules) is less than 4·8 Å.U.; this constitutes strong support for the conclusion drawn from the space-group results, *viz.*, that the molecules concerned are planar. As might be anticipated, the short axes of these substances are directions of very pronounced acicular growth.

(c) *Optical Properties.*—A molecule in which the two chelate groups are in planes at right angles (*i.e.*, in which the valencies of the central atom are tetrahedral) will possess a much smaller optical anisotropy than a molecule in which the chelate groups are coplanar; the latter alternative is therefore supported by the fact that at least two of the compounds studied have extremely high birefringence. It should be observed that, although the arrangement of highly anisotropic molecules in the crystal may be such as to produce low birefringence, yet no crystalline structure can give rise to high birefringence when the molecules themselves are not greatly anisotropic.

Since the compounds in which a planar distribution has been established appear to be in no way exceptional, it is reasonable to infer that the planar arrangement is normal for four-co-ordinated compounds of bivalent copper. This result, which confirms the view expressed by Werner, is not in accordance with the conclusions of Mills and Gotts (J., 1926, 3121), who obtained a strychnine salt of cupribenzoylpyruvic acid showing a small but definite mutarotation. These authors, however, were unable to remove the strychnine, and admit that the case for optical activity rests only on analogy with the behaviour of the brucine salt of the corresponding beryllium complex. Since there is no doubt as to the tetrahedral configuration of beryllium, it seems that this analogy is false, and that the observed results of Mills and Gotts were due to some cause other than a tetrahedral copper atom.

The present result is interesting also from a theoretical point of view. According to Pauling (*J. Amer. Chem. Soc.*, 1931, **53**, 1391), a planar configuration is to be expected when *s*, *p*, and *d* electrons are involved in the valency bonds; it is possible, therefore, that bivalent copper possesses a complete 3_3 sub-group of ten electrons, some being shared, instead of an incomplete group of nine as is usually supposed. This would involve one unpaired electron in the fourth principal quantum level, giving rise to a paramagnetic moment of the same order as that actually observed (Sugden, J., 1932, 161).

EXPERIMENTAL.

The *X*-ray investigations were carried out by means of single-crystal rotation and oscillation photographs, using $\mathrm{Cu}_{K\alpha}$ radiation, the probable accuracy of the cell dimensions being about $\frac{1}{2}\%$. Refractive indices were determined by immersion methods to 0·01.

Copper Disalicylaldoxime.—This was prepared by the addition of a slight excess of aqueous salicylaldoxime to a solution of cupric chloride made alkaline with caustic soda and then acidified with acetic acid. The dried product was recrystallised from chloroform (Found: Cu, 18·87; N, 8·4. Calc. for $\mathrm{CuC_{14}H_{12}O_4N_2}$: Cu, 18·94; N, 8·4%).

The molecular weight was determined by the cryoscopic method in naphthalene and the following results obtained (M = 336): for c = 3·336 and 1·914 g./1000 g., Δt = 0·070° and 0·040° respectively, whence M = 327, 329.

The crystals were found to be monoclinic holohedral combinations of $a\{100\}$, $p\{011\}$, $o\{111\}$, and $O\{11\bar{1}\}$; tabular on a. *X*-Ray measurements give a = 27·61, b = 6·00, c = 7·86 Å.U., β = 98° 13′. With four molecules to the unit cell, d(calc.) = 1·72 g./c.c. (Found: 1·72).

Abnormal spacings: $\{0k0\}$ absent when k is odd, all $\{h0l\}$ planes halved. These halvings are those of the space-group C_{2h}^5 ($P2_1/a$) [$\{010\}$ halved and $\{h0l\}$ halved for h odd] together with an additional halving [$\{h0l\}$ halved for l odd], indicating a further glide parallel to the c-axis. A consideration of the symmetry of this space-group shows that this additional halving (with four molecules in the cell) is only possible if each molecule possesses a centre of symmetry.

Optical properties: α = 1·55, β = 1·73, γ > 1·91, $\gamma - \alpha$ > 0·36. The plane of the optic axes is (010) and the acute bisectrix is nearly perpendicular to (100). Optic axial angle large; optic sign positive. These results indicate flat molecules arranged with their longest direction approximately parallel to the a-axis; the length of the latter is in good agreement with this.

Copper Acetylacetonate.—The crystals examined were from a highly purified specimen prepared by Morgan and co-workers. They are blue monoclinic needles with fractured ends (Found: Cu, 24·10; C, 45·9; H, 5·4. Calc. for $\mathrm{CuC_{10}H_{14}O_4}$: Cu, 24·30; C, 45·8; H, 5·4%).

Forms observed were $a\{100\}$, $r\{101\}$, and $R\{10\bar{1}\}$; pronounced elongation along [b]. From *X*-ray measurements: a = 11·24, b = 4·68, c = 10·24 Å.U., β = 92° 00′. With two molecules in the unit cell, d (calc.) = 1·58 g./c.c. (Found: 1·57).

Reflexions not occurring: $\{h0l\}$ when $h + l$ is odd, $\{0k0\}$ when k is odd. The space-group is therefore C_{2h}^5 ($P2_1/n$), and each molecule in the crystal has a centre of symmetry.

Refractive indices: α (parallel to [b]) = 1·59, $\gamma \geqslant$ 1·69.

Copper Benzoylacetonate.—Prepared by the addition of cupric acetate solution to an alcoholic solution of benzoylacetone and recrystallisation from hot alcohol (Found: C, 62·4; H, 4·4. Calc. for $\mathrm{CuC_{20}H_{18}O_4}$: C, 62·2; H, 4·7%).

The crystals are long needles with fractured ends, and were found to be monoclinic prisms elongated along [c]. Forms observed were $a\{100\}$ and $m\{110\}$. *X*-Ray measurements give a = 18·19, b = 10·44, c = 4·43 Å.U., β = 96° 58′. For two molecules in the cell, d (calc.) = 1·53 g./c.c. (Found: 1·53).

Reflexions not occurring: $\{h0l\}$ when $h + l$ is odd, $\{0k0\}$ when k is odd. Hence the space-group is C_{2h}^5 ($P2_1/n$), and the molecule has a centre of symmetry.

Refractive indices: α (inclined at 21° to [c]) = 1·57, γ > 1·78. These indices, in agreement with the *X*-ray results, indicate flat molecules more or less parallel to (001).

Copper Salt of Dipropionylmethane.—These crystals, also from a highly purified sample prepared by Morgan and co-workers, were deep blue monoclinic needles elongated along [b]; owing to the ends being fractured, the only forms observed were $a\{100\}$ and $c\{001\}$. *X*-Ray measurements give a = 19·44, b = 4·63, c = 16·72 Å.U., β = 89° 33′. Density calculated for two molecules per unit cell = 1·40 g./c.c. (Found: 1·39).

Abnormal spacings: $\{hkl\}$ absent when $k + l$ is odd, all $\{h0l\}$ halved. The space-group is therefore C_{2h}^6 ($A2/a$), whence the molecule may have either a two-fold axis or a centre of symmetry; the small value of [b], however, excludes the possibility of the former.

Birefringence greater than 0·07. Strong dichroism.

Copper 3-*Chloroacetylacetonate.*—Thin needles showing inclined extinction. Only the needle axis of this compound was measured, and found to be 4·78 Å.U. Birefringence greater than 0·10.

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