# **178.** *The Stereochemistry of Quadricovalent Atoms: Copper and Silver.*

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

Earlier work (*e.g.*, Cox, Wardlaw, and Webster, J., 1935, 1475; Cox and Webster, *ibid.*, p. 731; Cox, Sharratt, Wardlaw, and Webster, this vol., p. 129) has shown that many quadricovalent complexes of *bivalent* platinum, palladium, nickel, and copper possess a planar configuration, and that this configuration is maintained even when considerable changes are made in the nature of the co-ordinated groups. On the other hand, it appears that a change in the principal valency of the metal leads to a change in the spatial distribution of its bonds, since trimethylplatinic chloride (Cox and Webster, *Z. Krist.*, 1935, **90**, 561) and nickel carbonyl (Brockway and Cross, *J. Chem. Physics*, 1935, **3**, 828) both possess a tetrahedral configuration. We have further investigated the dependence of configuration on valency, and it is now shown that, in sharp contrast to the planar derivatives of bivalent copper, the four attached groups in quadricovalent cuprous complexes are disposed tetrahedrally about the metal atom; similarly, silver is found to be planar when bivalent and tetrahedral when univalent.

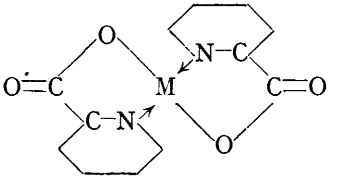
Anhydrous quadricovalent derivatives of bivalent silver suitable for $X$-ray studies are difficult to prepare; we have found, however, that the argentic derivative of picolinic acid (I) possesses a planar configuration. This result is based on the high birefringence of the compound, and on its isomorphism with the corresponding copper derivative. The birefringence (> 0·26) shows that the two picolinic acid residues in each complex must be coplanar (or very nearly so); with a tetrahedral distribution of the silver bonds the two picolinic acid groups would lie in two planes at right angles, and the birefringence would be very low. The crystals of both the copper and the silver derivative are too small for single-crystal *X*-ray examination, but the isomorphism has been established by microscopic investigation and by *X*-ray powder photographs. The results of the latter are given in Table I, where the principal spacings (*d*) and the corresponding approximate intensities (*I*) are given for each substance.

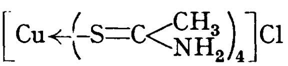
TABLE I.

| Silver picolinate. | | | | Copper picolinate. | | | |
|---|---|---|---|---|---|---|---|
| *d* (A.). | *I*. | *d* (A.). | *I*. | *d* (A.). | *I*. | *d* (A.). | *I*. |
| 8·57 | m. | 2·43 | m. | 8·46 | m. | 2·42 | m. |
| 6·73 | v.s. | 2·32 | m. | 7·01 | v.s. | 2·32 | m.w. |
| — | — | 2·23 | m. | 4·79 | m.w. | 2·23 | m. |
| 4·28 | m. | 2·08 | w. | 4·31 | s. | — | — |
| 3·96 | m.s. | 1·97 | m.w. | — | — | 1·96 | m.w. |
| 3·70 | m.s. | 1·86 | m.s. | 3·79 | s. | 1·89 | m.w. |
| 3·29 | v.w. | 1·75 | m.w. | 3·27 | m.w. | 1·76 | v.w. |
| 3·20 | v.s. | 1·68 | w. | 3·20 | v.s. | 1·70 | v.w. |
| 3·09 | m. | 1·60 | m.w. | — | — | 1·60 | m. |
| 2·86 | w. | 1·54 | v.w. | — | — | — | — |
| 2·73 | w. | 1·49 | w. | — | — | 1·49 | v.w. |
| 2·57 | m. | | | 2·57 | m.s. | | |

The configuration of the copper compound has been determined by an *X*-ray examination of single crystals of the dihydrate, in which the quadricovalent complex is found definitely to have a planar *trans*-structure. Both the *X*-ray data and the readiness with which the hydrate loses water to form the anhydrous compound indicate that the water molecules in the former are not co-ordinated to the copper atom, and that therefore the complex has the same configuration (*i.e.*, planar *trans*) in the anhydrous salt as in the hydrate. This is confirmed by the similarity of the optical data, both forms having very high birefringence.

(I.)





$$\left[\mathrm{Cu} \leftarrow \left(\mathrm{S{=}C}\genfrac{}{}{0pt}{}{\mathrm{CH_3}}{\mathrm{NH_2}}\right)_4\right]\mathrm{Cl}$$

(II.)

It is noteworthy that a second form of copper picolinate, having different crystalline structure and chemical properties, may be obtained by using alcoholic solutions in the preparation; detailed examination was not feasible on account of the microcrystalline nature of this form, but the high birefringence suggests a planar structure, and it is possible that this form is the *cis*-isomeride, since polymerisation is highly improbable.

In sharp contrast to the planar bivalent compounds, we find that quadricovalent argentous and cuprous derivatives possess a tetrahedral distribution of valencies. The only previous evidence on the configuration of compounds of this type has been that of Hein and Regler, who in a preliminary note (*Naturwiss.*, 1935, **23**, 320) claimed to have effected a partial resolution of an argentous derivative of 8-hydroxyquinoline, but full details have not yet been published. In the present paper the results are given of detailed *X*-ray studies of potassium cuprocyanide, $K_3[Cu(CN)_4]$, tetrakisthioacetamide-cuprous chloride (II), and *tetrakisthioacetamide-argentous chloride.* In each of these compounds a tetrahedral valency distribution has been found.

Potassium cuprocyanide forms large rhombohedral crystals which, in view of their strong pyroelectric properties and the absence of vertical planes of symmetry (as shown by Laue photographs), must be assigned to the trapezohedral class ($D_3$). *X*-Ray examination shows that there are two molecules in the rhombohedral unit cell, so that each complex ion $[Cu(CN)_4]$ possesses three-fold axial symmetry. This indicates a tetrahedral disposition of the Cu–CN bonds, one being parallel to the trigonal axis. The low birefringence is in agreement with the tetrahedral arrangement. Since the crystals are somewhat unstable, no attempt has been made to fix atomic positions, but the absence or weakness of the odd orders of {100} and {111} suggests a pseudo-body-centred arrangement of the copper atoms. We have not succeeded in preparing the corresponding silver compound.

It is noteworthy that the complex ion $[Cu(CN)_4]'''$ has exactly the same number of electrons, and presumably the same electronic distribution, as the neutral complex $[Ni(CO)_4]$ which has also been shown to be tetrahedral (Brockway and Cross, *loc. cit.*).

Tetrakisthioacetamide-cuprous chloride forms tetragonal crystals which Laue photographs and the absence of pyroelectric effects (by the liquid-air test) show to belong to the alternating ($C'_4$) class. Since the body-centred cell is found to contain two molecules, each complex ion possesses alternating tetragonal symmetry. This symmetry is consistent with either a planar or a tetrahedral distribution of the four Cu–S bonds, and the tetrahedral configuration has in this case been established by intensity measurements. Symmetry considerations fix the copper atoms at (000) and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ in the structure, and there are two possibilities for the positions of the chlorine ions, *viz.*, (*a*) $(0\frac{1}{2}\frac{1}{4})$ and $(\frac{1}{2}0\frac{3}{4})$ or (*b*) $(00\frac{1}{2})$ and $(\frac{1}{2}\frac{1}{2}0)$. The remaining atoms lie on general positions. With a planar distribution of sulphur atoms either (*a*) or (*b*) is possible for the chlorine ions, whereas on account of the relatively short length of the *c*-axis (5·52 A.) only (*a*) is possible with a tetrahedral configuration.

A preliminary survey of the intensities, assisted by interatomic distances known from previous work, enables the range of permissible structures to be restricted very considerably. Thus, it is found possible to account for the *relative* intensities of the orders of (001) by means of a structure in which the sulphur atoms are all coplanar with the copper atom, provided that the chlorine ions are situated in the positions (*b*); on the other hand, to account for the weakness of the odd orders of (110), the chlorine ions must be in the positions (*a*). The mutually contradictory nature of these results excludes the planar configuration completely; measurement of *absolute* intensities [by standardisation against the (400) rock-salt reflection], however, not only furnishes further convincing evidence against the planar arrangement, but enables the details of the tetrahedral structure to be found with reasonable precision. The following table gives a comparison of the experimental structure factors for {001} (col. 2) with the theoretical figures for the best possible planar arrangement (col. 3) and for the tetrahedral structure finally adopted (col. 4). It is clear that the planar structure is impossible.

| *hkl.* | *F* (obs.). | *F* (planar). | *F* (tetrahedral). |
|---|---|---|---|
| 002 | 64 | 126 | 76 |
| 004 | 70 | 134 | 82 |
| 006 | 28 | 70 | 32 |

The final tetrahedral structure is shown projected on (001) in the figure; Table II shows the comparison between the observed absolute *F*'s for {*hk*0} planes and those calculated from this structure. It will be seen that the general agreement is very good, the only considerable divergence being in the case of the (400) reflection. We are unable to account for this discrepancy, which, however, in view of the excellence of the remaining results, cannot be regarded as requiring more than minor adjustments of the atomic positions.

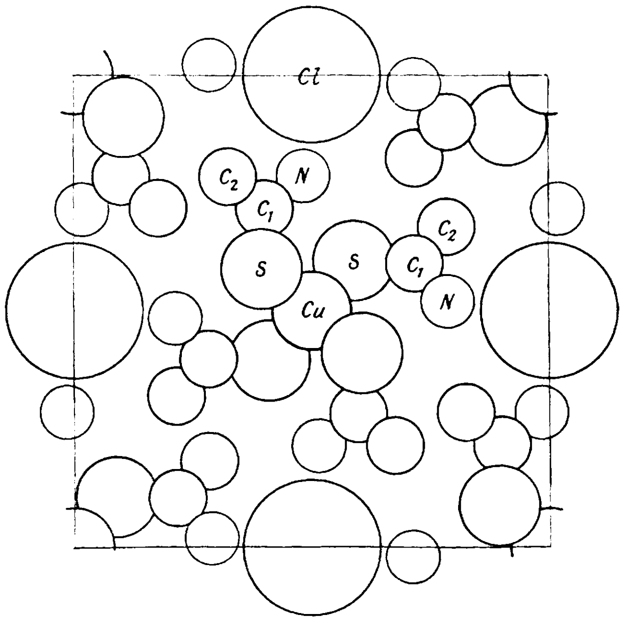
TABLE II.

| *hkl.* | *F* (obs.). | *F* (calc.). | *hkl.* | *F* (obs.). | *F* (calc.). | *hkl.* | *F* (obs.). | *F* (calc.). |
|---|---|---|---|---|---|---|---|---|
| 110 | 54 | 89 | 550 | 30 | 38 | 400 | $<12$ | 49 |
| 220 | 40 | 65 | 660 | 68 | 87 | 600 | $<14$ | 10 |
| 330 | 31 | 39 | 770 | 31 | 39 | 800 | 81 | 68 |
| 440 | 81 | 113 | 200 | 50 | 67 | | | |

The tendency for the observed structure factors to be low is probably to be accounted for by the formation on the crystals of a superficial layer of cuprous chloride which would increase their absorption coefficient, possibly by as much as 10%. The following table gives the co-ordinates of the atoms in one of the four thioacetamide groups attached to the copper atom at (000); the co-ordinates of the three atoms in the other three thioacetamide groups of the same complex corresponding to an atom at ($xyz$) in the first group are ($\bar{x}\bar{y}z$), ($y\bar{x}\bar{z}$), and ($\bar{y}x\bar{z}$). The co-ordinates of the second complex in the unit cell are derived by a translation of ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$). As previously mentioned, the co-ordinates of

| | | | |
|---|---|---|---|
| S .................. | (0·106 0·088 0·219) | $C_2$.................. | (0·177 0·285 0·415) |
| $C_1$.................. | (0·100 0·216 0·256) | N .................. | (0·016 0·285 0·138) |

the chlorine ions are ($0\frac{1}{2}\frac{1}{4}$) and ($\frac{1}{2}0\frac{3}{4}$). Each chlorine is surrounded approximately tetrahedrally by four amino-groups. The principal interatomic distances in the complex are Cu–S = 2·10 A., S–C = 1·60 A., C–C = 1·54 A., and C–N = 1·48 A. Other distances are $NH_2$ . . . . Cl = 3·40 A. and $CH_3$ . . . . $CH_3$ = 3·55 A.



Tetrakisthioacetamide-argentous chloride is fully isomorphous with the copper derivative, its structure differing only in the metal–sulphur distance (Ag–S = 2·20 A.). The following table shows the agreement between some observed and calculated structure factors [in this case relative, $F$(440) being taken as standard].

| *hkl.* | $F$ (obs.). | $F$ (calc.). | *hkl.* | $F$ (obs.). | $F$ (calc.). | *hkl.* | $F$ (obs.). | $F$ (calc.). |
|---|---|---|---|---|---|---|---|---|
| 110 | 130 | 130 | 550 | 71 | 56 | 400 | 24 | 71 |
| 220 | 87 | 105 | 660 | 81 | 81 | 600 | 45 | 33 |
| 330 | 35 | 67 | 200 | 96 | 100 | 800 | 112 | 90 |
| 440 | 160 | 160 | | | | | | |

A detailed Fourier analysis of these two substances will be published later.

## EXPERIMENTAL.

*Potassium Cuprocyanide.*—Freshly precipitated cuprous cyanide was dissolved in a slight excess of concentrated aqueous potassium cyanide, and the solution evaporated in a desiccator over phosphoric oxide. Large colourless crystals of the double cyanide separated [Found: Cu, 22·38; CN, 35·0. Calc. for $K_3Cu(CN)_4$: Cu, 22·31; CN, 36·5%].

*Tetrakisthioacetamide-cuprous Chloride* (II).—This was prepared according to the method of

Kurnakow (*Ber.*, 1894, **27**, 46), by boiling together aqueous solutions of cupric chloride (1·5 g.; 10 c.c.) and thioacetamide (3 g.; 10 c.c.). After removal of the black precipitate initially formed, the solution was set aside, and colourless crystals of the required compound separated [Found: Cu, 15·91; N, 14·18. Calc. for $CuCl(C_2H_5NS)_4$: Cu, 15·93; N, 14·03%]. This compound dissolves readily in alcohol, but is insoluble in other organic solvents; the aqueous solution decomposes on heating, with separation of copper sulphide.

*Tetrakisthioacetamide-argentous Chloride* (as II).—To an aqueous solution of silver nitrate (1·5 g.; 10 c.c.) was added a slight excess of aqueous thioacetamide (3 g.; 10 c.c.), followed by about 10 c.c. of 10% ammonium chloride; the mixture was heated nearly to boiling, and filtered. Colourless needles of the *silver* derivative separated on standing [Found: Ag, 24·22; Cl, 8·12. $AgCl(C_2H_5NS)_4$ requires Ag, 24·31; Cl, 8·00%].

Picolinic acid and potassium picolinate were prepared by oxidation of α-picoline by means of potassium permanganate as described by Weidel (*Ber.*, 1879, **12**, 1992).

*Argentic Picolinate.*—This compound was prepared by Barbieri's method (*Atti R. Accad. Lincei*, 1933, **17**, 1078): an aqueous solution of silver nitrate (1·7 g.; 50 c.c.) was added to picolinic acid (3·7 g.) in 50 c.c. of water, the precipitate redissolved by sodium carbonate (2·5 g.), and treated with a solution of ammonium persulphate (1·7 g.; 60 c.c.), orange-red needles of the argentic compound separating [Found: Ag, 30·54; N, 8·1. Calc. for $Ag(C_6H_4O_2N)_2$: Ag, 30·66; N, 7·9%].

*α-Cupric Picolinate.*—An aqueous solution of potassium picolinate (7·0 g.; 20 c.c.) was added to a hot aqueous copper acetate solution (4 g.; 50 c.c.), and on cooling deep-blue crystals of cupric picolinate dihydrate were obtained [Found: Cu, 18·55. Calc. for $Cu(C_6H_4O_2N)_2,2H_2O$: Cu, 18·50%]. When dried at 110° for a few hours it lost its water of crystallisation and left the anhydrous substance as a lavender-blue powder [Found: Cu, 20·62; N, 9·1. Calc. for $Cu(C_6H_4O_2N)_2$: Cu, 20·66; N, 9·1%]. The anhydrous compound melts at 298° (decomp.); it is slightly soluble in alcohol, readily soluble in phenol giving a deep-blue solution, but insoluble in other organic media. When shaken with excess of warm alcoholic thiourea, a turquoise-blue *compound* is formed [Found: Cu, 14·10; N, 18·3. $Cu(C_6H_4O_2N)_2,2CS(NH_2)_2$ requires Cu, 13·83; N, 18·1%].

The molecular weight of the picolinate was determined cryoscopically in phenol (constant = 7·27° per 1000 g.) (*M*, calc., = 307·6):

| | | |
|---|---|---|
| *c* (g./1000 g.) | 6·735 | 5·901 |
| Δ*t* | 0·163° | 0·138° |
| *M* | 300·2 | 310·3 |

*β-Cupric Picolinate.*—Solutions of copper acetate (2 g.; 25 c.c.) and potassium picolinate (3·5 g.; 10 c.c.) in absolute alcohol were mixed and kept. From the deep-blue solution a microcrystalline precipitate rapidly separated [Found: Cu, 20·56; N, 8·9. $Cu(C_6H_4O_2N)_2$ requires Cu, 20·66; N, 9·1%], m. p. 285° (decomp.); it is slightly soluble in alcohol, and in water gives the dihydrate. The molecular weight of this form of cupric picolinate could not be determined, since in the only solvent available (*viz.*, phenol) reversion to the α-form occurred (identified by the thiourea reaction). Treated with excess thiourea in absolute alcohol, it afforded a powder-blue *compound* [Found: Cu, 16·41; N, 14·9. $Cu(C_6H_4O_2N)_2,CS(NH_2)_2$ requires Cu, 16·56; N, 14·6%].

*Nickel Picolinate.*—A hot concentrated aqueous solution of picolinic acid was neutralised with nickel carbonate and filtered. On cooling, *nickel picolinate tetrahydrate* separated in small blue prisms [Found: Ni, 15·56. $Ni(C_6H_4O_2N)_2,4H_2O$ requires Ni, 15·66%]. When dried at 105°, it lost $2H_2O$, leaving the dihydrate, which became anhydrous after drying for 6 hours at 140°. When alcoholic solutions were used, the product had a very variable composition, and a second modification could not be obtained.

*Platinous Picolinate.*—Hot aqueous solutions of picolinic acid (1·6 g.; 5 c.c.) and potassium chloroplatinite (2 g.; 15 c.c.) were mixed; after a few minutes the platinum derivative separated as pale yellow microscopic needles [Found: Pt, 44·43; N, 6·3. Calc. for $Pt(C_6H_4O_2N)_2$: Pt, 44·42; N, 6·4%]. This is almost insoluble in water and organic solvents except phenol. When warmed on the water-bath with aqueous ethylenediamine, it slowly dissolved, and the product, after acidification with hydrochloric acid, gave the violet plato-salt $[Pt\,en_2][PtCl_4]$ with potassium chloroplatinite (Found: Pt, 59·69. Calc.: Pt, 59·82%), indicating that the picolinate groups are in *trans*-positions.

*Palladous Picolinate.*—Addition of aqueous picolinic acid to potassium chloropalladite immediately gave a cream-coloured precipitate of the *palladium* compound [Found: Pd, 30·41; N, 7·8. $Pd(C_6H_4O_2N)_2$ requires Pd, 30·42; N, 8·0%]. This compound closely resembles the platinum compound in its solubility, and *X*-ray powder photographs show that the two are isomorphous but quite unlike either the silver or the copper derivative. It dissolved in aqueous ethylenediamine and treatment as above afforded the plato-salt $[Pd\,en_2][PtCl_4]$ as pink needles (Found: Pt + Pd, 53·56. Calc.: Pt + Pd, 53·56%).

## *Crystallographic and* X-*Ray Results.*

All *X*-ray measurements were made with copper-$K_\alpha$ radiation upon single crystals unless otherwise stated. Refractive indices (determined by immersion methods) are for sodium light.

*Potassium Cuprocyanide.*—Occurs in colourless rhombohedral crystals exhibiting the form {110} and occasionally {100} very small. The crystals are strongly pyroelectric. The cell dimension is $a = 8·00$ A. and $\alpha = 77° 32'$. The number ($n$) of molecules in the unit cell is 2, whence $d$(calc.) = 2·06 g./c.c. (obs. 2·07).

There are no halvings, and Laue photographs show $D_{3d}$ symmetry. The space-group is therefore $R32$ ($D_3^7$), and each complex ion has a three-fold axis of symmetry. The cyanide groups must therefore be arranged tetrahedrally around the copper atom, or have the very improbable distribution of three in a plane and the fourth at right angles.

Refractive indices: $\omega = 1·552 \pm 0·003$ and $\varepsilon = 1·544 \pm 0·003$. These figures differ considerably from the earlier values of Grailich (1858; see Groth, I, 317).

*Tetrakisthioacetamide-cuprous Chloride.*—The crystals of this substance are colourless tetragonal combinations of $a$\{100\}, $m$\{110\}, and $r$\{101\}, elongated parallel to the $c$-axis. The cell dimensions are $a = 12·43$ and $c = 5·52$ A.; $n = 2$; $d$(calc.) = 1·56 g./c.c. (obs. 1·56).

Abnormal spacings: $\{hkl\}$ absent when $h + k + l$ is odd.

The crystals are non-pyroelectric and Laue photographs show $C_{4h}$ symmetry. The space-group is therefore $I\bar{4}$ ($C_4'^2$) and each complex ion has a four-fold alternating axis of symmetry, which is compatible with either a planar or a tetrahedral distribution of copper valencies. Refractive indices: $\omega = 1·775 \pm 0·005$ and $\varepsilon = 1·755 \pm 0·005$.

*Tetrakisthioacetamide-argentous Chloride.*—This compound crystallises in thin colourless needles exhibiting the same forms as the copper derivative, with which it is isomorphous. The cell dimensions are $a = 12·59$ and $c = 5·37$ A.; $n = 2$; $d$(calc.) = 1·67 g./c.c. (obs. 1·69).

Abnormal spacings: $\{hkl\}$ absent when $h + k + l$ is odd. The space-group is $I\bar{4}$ and the complex ion has a four-fold alternating axis of symmetry.

*α-Cupric Picolinate.—Dihydrate.* This substance crystallises in very thin, blue, six-sided, triclinic plates. The cell dimensions are $a = 7·80$, $b = 10·75$, $c = 5·10$, $d_{010} = 8·87$ A. and $\beta = 108° 40'$; $\alpha$ and $\gamma$ were not determined; $n = 1$; $d$(calc.) = 1·71 g./c.c. (obs. 1·71).

The crystals are not pyroelectric; they are therefore pinakoidal, so that the molecules are centro-symmetrical, *i.e.*, the picolinate groups are in *trans*-planar positions. The possibility of an octahedral arrangement, in which the water molecules are co-ordinated to the copper atom, is excluded by the shortness of the [$c$] axis (5·10 A.); the ease with which this substance loses its water also renders co-ordination improbable.

Refractive indices: $\alpha < 1·50$, $\gamma > 1·76$.

*Anhydrous salt.* This powder retains the form of the original dihydrate crystals. Refractive indices: $\alpha \leqslant 1·54$, $\gamma \geqslant 1·76$.

*β-Cupric Picolinate.*—Occurs in small blue needles showing straight extinction. Refractive indices: $\alpha \leqslant 1·56$, $\gamma \geqslant 1·78$.

*Argentic Picolinate.*—Small needles showing inclined extinction. Powder photographs show that this compound is isomorphous with the anhydrous α-cupric picolinate and Table I gives the principal lattice spacings of the two compounds. Refractive indices: $\alpha \leqslant 1·50$, $\gamma \geqslant 1·76$.

*Intensity Measurements.*—Absolute integrated intensities of the reflections from the tetrakisthioacetamide-cuprous chloride were obtained by direct comparison with the (400) reflection from a rock-salt crystal the cube face of which had been specially ground as recommended by Bragg and West (*Z. Krist.*, 1928, **69**, 122), who record accurate measurements of the absolute intensity of this reflection ($\rho = 0·98 \times 10^{-4}$ for Mo-$K_\alpha$). Large crystals were used, the incident *X*-ray beam being defined by narrow vertical slits. The two reflections were recorded on the same photograph, and the stronger reduced by means of absorbing screens of aluminium foil until approximately equal in intensity to the weaker. An accurate comparison of the photographic blackness of the resulting spots was then obtained photometrically. The reduction due to the known thickness of aluminium foil could be calculated accurately, and hence the intensities for the copper compound obtained with reasonable precision.

To obtain uniform exposures, the $X$-ray tube (a Metalix tube with half-wave rectification) was run under as steady conditions as possible, the actual exposure being determined by a prepayment meter of the ordinary type in the primary circuit of the H.T. transformer. Careful and repeated tests showed that this procedure could be relied upon to give $X$-ray exposures reproducible within less than 5%. No allowance for extinction has been made. The experimental structure factors ($F$) are then calculated from the observed absolute integrated intensities $\rho$ by means of the formula

$$\rho = \frac{1}{2\mu}\left[\frac{Ne^2F}{mc^2}\right]^2 . \lambda^3 . \frac{1 + \cos^2 2\theta}{2 \sin 2\theta}$$

where $\mu$ is the linear absorption coefficient of the crystal for $X$-rays of wave-length $\lambda$, and the other constants have their usual significance. The atomic scattering factors of James and Brindley (*Z. Krist.*, **1931**, **78**, 470) have been used in calculating the $F$ values for the proposed structure.

## SUMMARY.

By $X$-ray methods the picolinic acid derivatives of bivalent copper and silver are found to possess a planar structure, but potassium cuprocyanide and the tetrakisthioacetamide derivatives of cuprous and argentous chlorides are shown to exhibit tetrahedral configurations. The structures of the last two compounds are worked out in detail.

The importance of the principal valency of a metal atom in determining the configuration of its quadricovalent derivatives is emphasised.

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