A Novel Stereochemical Form for Bivalent Copper

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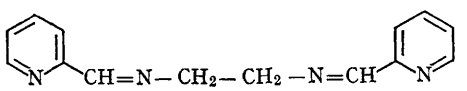
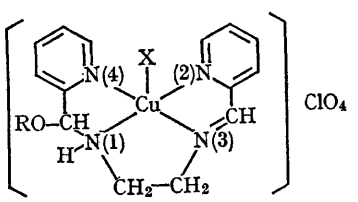
HARRIS and MCKENZIE[1] performed a series of reactions involving a Schiff base [prepared from two moles of pyridine aldehyde and one mole of ethylenediamine and denoted as BPE (I)] and copper(II) ions in alcohol solutions. Some of the compounds they isolated could be formulated as $[Cu(BPE + ROH)X]ClO_4$ (II) where it appeared that the copper environment was five co-ordinate and an alcohol molecule had added across one of the double bonds of the Schiff base.



(I)



(II)

We have determined the crystal structure of one of these compounds where R = CH_3 and X = Br. Crystal data: $C_{15}H_{18}O_5N_4ClBrCu$, $M = 513$, monoclinic, $a = 9{\cdot}30$, $b = 13{\cdot}14$, $c = 16{\cdot}03$ Å, $\beta = 98{\cdot}3°$, $U = 1959$ Å^3, $D_m = 1{\cdot}75$ (by flotation), $Z = 4$, $D_c = 1{\cdot}76$ g.cm.$^{-3}$, space group $P2_1/c$ (C_{2h}^5, No. 14), Cu-K_α radiation, single-crystal oscillation and equi-inclination Weissenberg photographs, $\mu = 57{\cdot}6$ cm.$^{-1}$.

The co-ordinates of the copper and bromine atoms were obtained from a three-dimensional Patterson synthesis using 2850 independent terms. The other atoms, except the hydrogen and the perchlorate oxygen atoms, were located in subsequent three-dimensional electron density distributions. For the calculation of structure factors, special provision was made for the rotating perchlorate ion.[2] The structure is being refined by the method of least squares, applying individual isotropic temperature factors. At present the *R*-value, based on observed reflections only, is 0·16.

The crystal consists of perchlorate anions and complex copper cations. As predicted the copper atom is bonded to five atoms. These are four nitrogen atoms and a bromine atom (Figure) all of which seem to be at normal covalent distances from the copper atom. There are however, significant differences between some of the copper–nitrogen interatomic distances; the Cu–N(3) and Cu–N(4) distances are 1·94 and 2·12 Å respectively,

each with an estimated standard deviation of 0·02 Å.

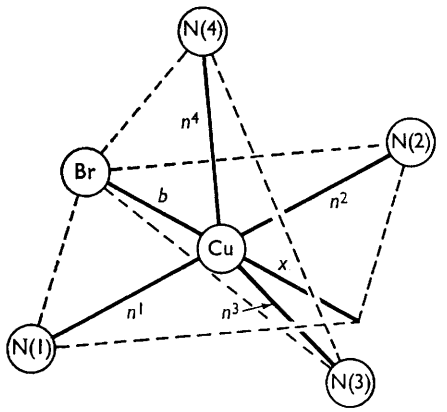


FIGURE. *Immediate environment of the copper atom in the* $[Cu(BPE + CH_3{\cdot}OH)Br]^+$ *ion.*

Lengths: $b = 2{\cdot}40$, $n^1 = 2{\cdot}04$, $n^2 = 2{\cdot}01$, $n^3 = 1{\cdot}94$, $n^4 = 2{\cdot}12$ Å

Angles: $n^1b = 90°$, $n^2b = 100°$, $n^2n^3 = 79°$, $n^1n^3 = 83°$, $n^4b = 102°$, $n^4n^2 = 100°$, $n^4n^3 = 112°$, $n^4n^1 = 80°$, $n^3b = 145°$, $n^1n^2 = 160°$, $xn^3 = 35°$

The stereochemistry of bivalent copper is usually such that the copper atom is surrounded by four atoms at normal covalent distances in a plane, with a fifth and sometimes a sixth atom at longer than normal covalent distances perpendicular to the plane. The five-covalent trigonal bipyramidal arrangement has been established also for copper(II) in the two ions $[Cu(bipyridyl)_2I]^+$,[3] and $[CuCl_5]^{3-}$.[4]

In the complex ion, $[Cu(BPE + CH_3{\cdot}OH)Br]^+$, the five atoms bonded to the copper atom are so disposed that they are neither square pyramidal nor trigonal bipyramidal in arrangement about the central metal atom. The configuration can be described as being intermediate between these two idealised forms.

Four atoms [Cu, Br, N(3), and N(4)] are coplanar as would be expected if the ion were trigonal bipyramidal in shape, the three donor atoms in the plane [Br, N(3), and N(4)] defining the corners of the trigonal plane. The three angles in the trigonal plane (102°, 112°, and 145°) however show considerable deviation from the expected value of 120°. The alternative square pyramidal description with the atom N(4) in the apical position shows that whilst the atoms Cu, Br, N(1), and N(2) are coplanar, the remaining nitrogen atom is displaced about 35° from the plane.

The structure of the $[Cu(BPE + CH_3{\cdot}OH)Br]^+$ ion bears a marked similarity to those observed for the complexes $[Ni(triarsine)Br_2]$[5] and [Pd(triphosphine)Br_2].[6] The structure determination also confirms the observation that an alcohol molecule has added across one of the double bonds of the Schiff base.

We thank Dr. B. Dawson for his calculations on the scattering factor curve of the perchlorate ion, Dr. J. C. B. White for considerable help with the computations and the use of his programmes, and Dr. E. D. McKenzie for providing the crystals.

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