The Molecular Structure of Bis(pyridine *N*-oxide)copper(II) Nitrate

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ALTHOUGH crystal structures of several copper(II) compounds are known, they still attract our attention because copper(II) may have either four, six, or five ligands forming a tetrahedron, square, octahedron, or tetragonal pyramid with varying degrees of distortion.[1,2]

The crystals of bis(pyridine *N*-oxide)copper(II) nitrate are monoclinic with $a = 11{\cdot}280$, $b = 14{\cdot}862$, $c = 8{\cdot}005$ Å, $\beta = 95{\cdot}50°$; the space group is $P2_1/n$. The unit cell contains four formula units of $Cu(C_5H_5NO)_2(NO_3)_2$; Ni-filtered Cu radiation was used. The molecular structure was solved by Patterson projections and three-dimensional electron density syntheses, followed by least-squares refinement using isotropic temperature factors. The *R*-value is 11·6%, 1624 independent non-zero structure factors being used. The estimated standard deviations of bond lengths are ±0·007 Å for Cu–O, ±0·013 Å in NO_3 groupings, and ±0·016 Å in C_5H_5NO groupings.

The molecule is dimeric. It is composed of two centrosymmetrically related complex monomers and defined by formula $[Cu(C_5H_5NO)_2(NO_3)_2]_2$, (See Figure). The copper atom has a distorted tetragonal pyramidal environment of five oxygen atoms. Short and nearly coplanar bonds (mean value is 1·96 Å) are directed to O(1), O(2), O(3), and O(6) atoms which belong to two NO_3 and two C_5H_5NO groupings. The fifth (long) bond (2·44 Å) is approximately perpendicular to the O(1), O(2), O(3), O(6) plane and directed to the oxygen atom O(1′). Thus dimeric species exist where two copper atoms (Cu and Cu′) share two oxygen atoms

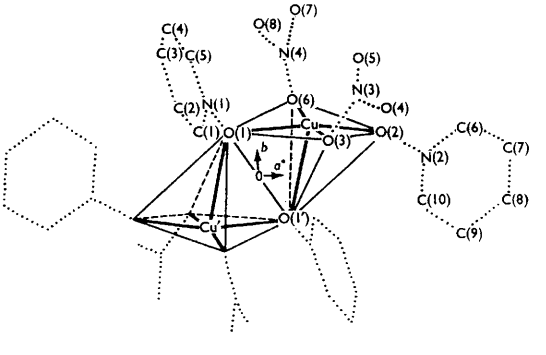

FIGURE. *Projection of the* $[Cu(C_5H_5NO)_2(NO_3)_2]_2$ *molecule along* (001). *Atoms in* NO_3 *and* C_5H_5NO *groupings are connected by dotted lines, the polyhedra of copper atoms by full and broken lines, and the copper–oxygen bonds by heavy full lines*

[O(1) and O(1′)]—double bridges—and the metal atoms are five co-ordinated. Copper(II) usually completes its co-ordination number to six. In the case of this structure two oxygen atoms [O(5)and O(7)] and two nitrogen atoms [N(3) and N(4)] from two NO_3 groups of the same monomer are on the opposite side of pyramidal apex. These copper–oxygen distances are much longer (the mean value is 2·80 Å) suggesting a 4 + 1 than 4 + 1 + 2 co-ordination of copper.

The distances in NO_3 and C_5H_5NO groups do not deviate significantly from the values obtained previously.[3,4] Their angles indicate that the both groups are planar within experimental error.

TABLE

Interatomic distances and angles within copper polyhedra

A B C	Distances (Å) A–B	A–C	Angles (degrees) A–B–C
O(1)–Cu–O(3)	1·98	2·84	92·1
O(6)–Cu–O(1)	1·95	2·79	90·2
O(3)–Cu–O(2)	1·96	2·88	93·8
O(2)–Cu–O(6)	1·94	2·64	85·6
O(1′)–Cu–O(1)	2·44	2·79	89·0
O(2)–Cu–O(1′)		3·10	89·4
O(3)–Cu–O(1′)		3·31	96·7
O(6)–Cu–O(1′)		3·16	90·2

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[3] "International Tables for *X*-ray Crystallography", 1962, Vol. III, Kynoch Press: Birmingham.
[4] "Interatomic Distances," *Chem. Soc. Special Publ.*, 1965, No. 18.