The Crystal and Molecular Structure of (α-Picoline)$_2$Cu(NO$_3$)$_2$

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Summary The structure of (α-picoline)$_2$Cu(NO$_3$)$_2$ has been resolved by *X*-ray techniques, and proves to be monomeric as a result of the presence of the α-methyl groups.

ON the basis of spectroscopic measurements, it has been suggested that a number of nitrato-complexes possess structural features similar to those of (Me$_3$PO)$_2$Co(NO$_3$)$_2$.[1] In particular, far-i.r. studies[2] led to the conclusion that the complexes (α-pic)$_2$M(NO$_3$)$_2$ [M = Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}, (α-pic) = 2-methylpyridine] were of this type. We have therefore determined the structure of (α-pic)$_2$Cu(NO$_3$)$_2$ by three-dimensional *X*-ray techniques, in order not only to determine the relationship to the structure of (Me$_3$PO)$_2$-Co(NO$_3$)$_2$, but also to study the effect of steric hindrance by the α-methyl groups in comparison with the corresponding pyridine complex, [(py)$_2$Cu(NO$_3$)$_2$,0·5(py)]$_2$, which we have shown to be a centrosymmetric dimer with unusual bridging.[3]

Crystals of (α-pic)$_2$Cu(NO$_3$)$_2$ were prepared according to the method reported by Lever[4] followed by recrystallisation from 2,2-dimethoxypropane–ethanol mixtures. The compound crystallises in the monoclinic system, space group $P2_1/c$, with four units of (α-pic)$_2$Cu(NO$_3$)$_2$ in a cell of dimensions a = 8·31, b = 14·81, c = 14·14Å, β = 123·90°. The structure was solved by Patterson and Fourier methods using some 1197 independent reflexions recorded by Weissenberg photographic techniques. Initial refinement by full-matrix isotropic least-squares calculations has proceeded satisfactorily and R is currently 0·13.

Our *X*-ray analysis has revealed a distorted six-co-ordinate monomeric complex in which the copper atom is co-ordinated by two non-equivalent nitrato-groups which are both asymmetrically bidentate, and by two α-picoline ligands in a *trans*-configuration. These α-picoline moieties are spatially disposed such that the α-methyl groups are

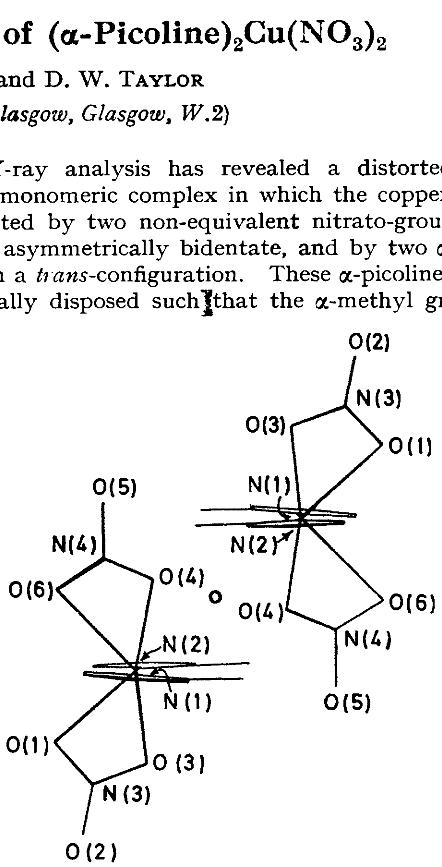

FIGURE. *A view down the* b *axis of the arrangement of two monomeric units about the crystallographic centre of symmetry.*

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cis to each other as in the corresponding chlorine complex,[5] the volume of space *trans* to this position being occupied by the two long-bonded oxygens (Figure). The α-methyl groups thus effectively block a site of possible co-ordination on the copper atom, and it is this site which is utilised to effect dimerisation in the corresponding pyridine complex.

When the packing arrangement of the crystal structure is considered, a relationship may also be seen to the dimeric pyridine complex. Centrosymmetrically-related monomers are aligned such that were it not for the blocking action of the *cis*-2-methyl groups in the present case, a relatively small reduction in the separation of the monomers would produce dimerisation similar to that observed for the pyridine complex.

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