The Crystal and Molecular Structure of $[(Pyridine)_2Cu(NO_3)_2]_2,C_5H_5N$: a Centrosymmetric Dimer with Bridging Nitrato-groups

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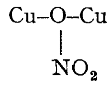
Summary The compound $[(py)_2Cu(NO_3)_2]_2,C_5H_5N$ is a centrosymmetric dimer of novel structure containing asymmetric bidentate nitrato-groups which also form bridges of the type Cu–O–Cu to effect dimerisation.


$Cu\text{–}\underset{NO_2}{\underset{|}{O}}\text{–}Cu$

CONSIDERABLE interest has been shown in the structure of inorganic nitrato-complexes, since the nitrato-groups can display a range of possible modes of co-ordination.[1] The far-i.r. spectrum of one such complex, of empirical formula $(py)_2Cu(NO_3)_2$ (py = pyridine), indicated the presence of asymmetric bidentate nitrato-groups, although the gross structure was not evident from this and other spectroscopic evidence.[2] This complex was originally isolated by the thermal decomposition of $(py)_4Cu(NO_3)_2$,[3] a process which does not yield material immediately suitable for an X-ray structure determination. Crystals may be obtained, however, either by recrystallisation of the thermal decomposition product from chloroform containing a slight excess of pyridine, or by the alternative synthetic method of stoicheiometric addition of pyridine to an ethanolic solution of anhydrous copper nitrate followed by recrystallisation as before. The far-i.r. spectra of the material resulting from all three processes are identical, but, because of their superior quality, crystals from the latter alternative reaction were used for our X-ray analysis.

The compound crystallises in the monoclinic system, space group $P2_1/c$, with two (dimeric) units of $[(py)_2Cu(NO_3)_2]_2,(py)$ (*i.e.* a maximum of two free pyridine molecules of crystallisation may be accommodated) in a unit cell of dimensions $a = 9{\cdot}79$, $b = 10{\cdot}89$, $c = 16{\cdot}15$ Å, $\beta = 98{\cdot}10°$. The structure was solved by Patterson and Fourier methods using some 2300 independent reflexions recorded by Weissenberg photographic techniques. Refinement on the basis of space group $P2_1/c$ has proceeded satisfactorily by

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full-matrix and block-diagonal least-squares calculations and R is currently 0·104. In space group $P2_1/c$, the two free pyridine molecules are constrained to lie at crystallographic centres of inversion, a result which may arise from statistical disorder of these free pyridine molecules to produce a centrosymmetric "average." In addition, our original choice of space group $P2_1/c$ was confirmed by a trial refinement using the non-centrosymmetric space group Pc.

The structure analysis has revealed the centrosymmetric dimeric molecule illustrated in the Figure, in which each copper atom is directly co-ordinated by two asymmetric bidentate nitrato-groups, and dimerisation is effected through the oxygen atoms O(4) and O′(4) of two (centrosymmetrically-related) nitrato-groups. In addition, each copper atom occupies a position in which it is surrounded by seven neighbouring atoms [O(1), O(2), O(4), O(5), O′(4), N(3), N(4) *etc.*].

The general geometric features of our structure are remarkably similar to those found in the $[\mathrm{Ni}(\beta\text{-picoline})_2(\mathrm{NO}_2)_2]_3,\mathrm{C}_6\mathrm{H}_6$ trimeric nitrito-complex described recently by Rogers and his co-workers,[4] in that the two copper atoms and four nitrato-groups of the dimer are essentially coplanar, and the four co-ordinated pyridine rings have a spatial relationship similar to that reported for the β-picoline units in the nickel complex. Another noteworthy feature is the inclusion of aromatic molecules of crystallisation in crystals of both the copper and nickel complexes.

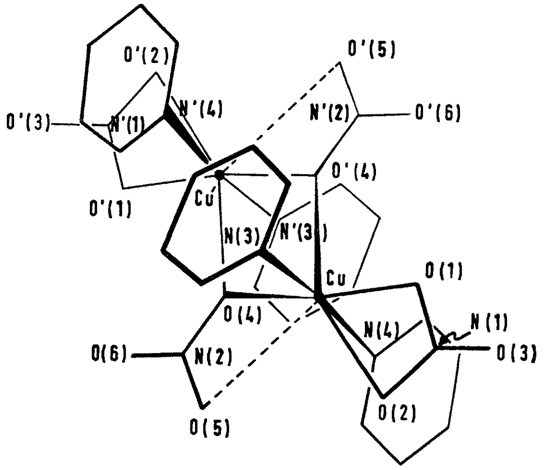

FIGURE. *A view down* b *of one dimeric unit.*

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