Crystal and Molecular Structures of Two Crystalline Modifications of $(\alpha\text{-picoline})_2Cu(NO_3)_2$

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Summary We have found that the complex $(\alpha\text{-pic})_2Cu(NO_3)_2$ (α-pic = α-picoline) exists in two crystalline forms; the crystal-structure analysis of one form has already been reported, and we now report the results of a structure analysis of the second form: the overall geometries of the two molecules are similar, although there are detailed differences in bond lengths, probably arising from the different packing environments.

THE complex $(\alpha\text{-pic})_2Cu(NO_3)_2$ is found in two crystalline forms depending on the temperature to which the crystallising liquid[1] is heated prior to cooling. If the solution of the complex is simply warmed before cooling, crystals of form (I) result, and we have already reported the crystal and molecular structure of this species.[2] However, if the solution is allowed to boil for several minutes, on cooling form (II) crystals are obtained. The latter form is the subject of this three-dimensional *X*-ray analysis.

$(\alpha\text{-pic})_2Cu(NO_3)_2$ form (II), crystallises in the monoclinic system, space group $P2_1/c$, with four units of $(\alpha\text{-pic})_2Cu(NO_3)_2$ in a cell of dimensions $a = 8{\cdot}57$, $b = 14{\cdot}39$, $c = 14{\cdot}20$ Å, $\beta = 119{\cdot}5°$. The structure was solved by Patterson and Fourier methods using 1335 independent reflexions recorded by Weissenberg photographic techniques. Refinement of positional and anisotropic least-squares calculations, using the block-diagonal approximation, has proceeded satisfactorily, and R is currently 0·09.

A remarkable feature of the existence of these two polymorphs is the close similarity of the unit-cell dimensions in each case, and the identity of the space group $P2_1/c$. Indeed, X-ray diffraction photographs of the two forms differ only in the distribution of intensities, the spacings being virtually identical. However, the packing arrangements within these similar unit cells are quite different. The molecular packing of form (I) is shown in Figure 1, and we reported earlier[2] that this packing bears a spatial relationship to the molecular structure of the dimer $[(py)_2Cu(NO_3)_2, 0{\cdot}5(py)]_2$. Figure 2 shows the molecular packing of form (II); it is obvious that not only are the two packing arrangements quite different, but also that the significant spatial arrangement in form (I) does not apply in form (II).

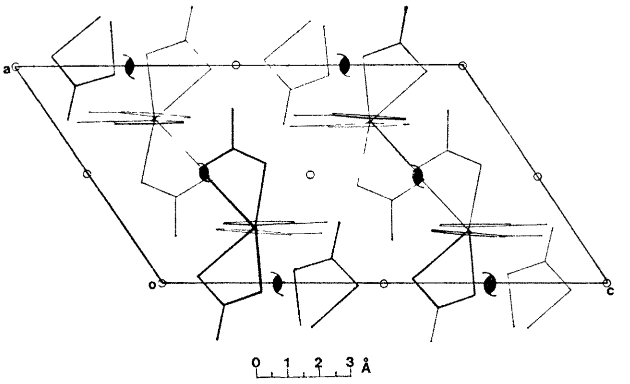

FIGURE 1. *The molecular packing of form* (I) *viewed along the* b-*axis.*

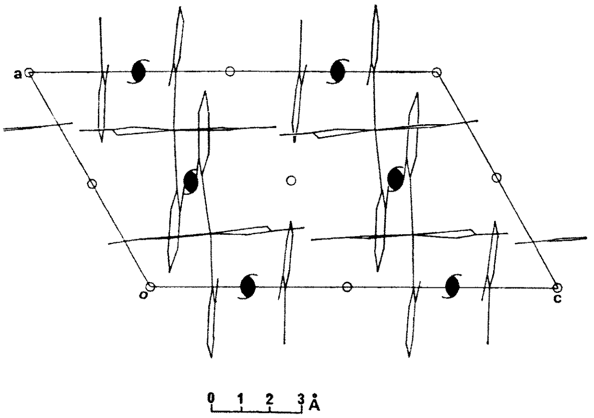

FIGURE 2. *The molecular packing of form* (II) *viewed along the* b-*axis.*

In both crystalline forms, the molecular structures possess similar stereochemistries, the significance of which has already been discussed.[2] There are, however, several detailed differences in the two molecules (Figure 3) which may arise from packing effects. In particular, whereas the nitrate groups in form (I) were not equivalent, in form (II) they are identical within the limits of experimental accuracy [Cu–O(1) = 2·517(8), Cu–O(2) = 2·551(7) Å]. Moreover, although the dihedral angles between the two nitrate groups in the two molecules are identical (*ca.* 6°), the angles between the aromatic planes of the α-picoline moieties are not. In form (I) the angle between the aromatic planes is *ca.* 7°, but in form (II), the corresponding angle is almost 13°.

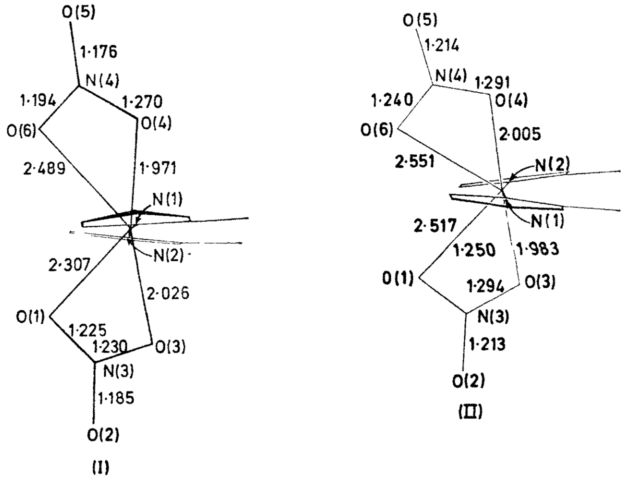

FIGURE 3. *Comparison of the molecular geometries of the two forms of* $(\alpha\text{-pic})_2Cu(NO_3)_2$.

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[1] B. J. Hathaway, personal communication.

[2] A. F. Cameron, R. H. Nuttall, and D. W. Taylor, *Chem. Comm.*, 1970, 865.