

The Crystal and Molecular Structure of $(C_5H_5N)_3Zn(NO_3)_2$

By A. F. CAMERON* and D. W. TAYLOR

(Chemistry Department, University of Glasgow, Glasgow W.2)

and R. H. NUTTALL

(Chemistry Department, University of Strathclyde, Glasgow C.1)

Summary The structure of $(py)_3Zn(NO_3)_2$ has been resolved by a single-crystal X-ray analysis, and found to be monomeric, with a two-fold axis of symmetry which passes through the zinc atom and one C_5H_5N ring, the nitrate groups being equivalent, and asymmetrically bidentate.

PYRIDINE reacts with metal nitrates to form series of complexes of the type $(py)_nM(NO_3)_2$, where $n = 2, 3, 4$, or 6. Of particular interest are the tris- (C_5H_5N) derivatives, $(py)_3M(NO_3)_2$ which have been found for $M = Co^{II}$, Ni^{II} , Zn^{II} , and Cd^{II} . Haendler and his co-workers^{1,2} have shown by i.r. and conductance measurements that in these cases the pyridine and nitrate groups are all co-ordinated and, although unable to assign unequivocal molecular geometries, they suggested that the results were consistent with octahedral structures containing bridging nitrate groups. To investigate further the structures of such compounds and to resolve this problem, we have determined the crystal structure of $(py)_3Zn(NO_3)_2$ by three-dimensional X-ray techniques.

Crystals of $(py)_3Zn(NO_3)_2$ were prepared according to the method described by Ouellette and Haendler.² The compound crystallises in the monoclinic system, with four molecules in a unit cell of dimensions $a = 12.50$, $b = 9.40$, $c = 16.27$ Å, $\beta = 108.9^\circ$. The absences in the diffraction

patterns indicated the two possible space groups Cc and $C2/c$. Initially we assumed that the space group was Cc and solved the structure by Patterson and Fourier methods using some 1000 reflexions recorded by Weissenberg photographic techniques. The Zn atoms were, however, placed in the positions which would be imposed were the space group $C2/c$. The atomic positional and anisotropic thermal parameters were then subjected to two separate refinements to examine the effects of the different symmetry-constraints of the two possible space groups. The refinement in space group Cc , by block-diagonal least-squares calculations converged when R was 0.10 and revealed disturbing discrepancies in values of standard bond lengths. In particular, the C(3)—C(4) aromatic bond distance was 1.73 Å. On the other hand, the refinement in space group $C2/c$, which used full-matrix techniques, converged when R was 0.11, and the resulting molecular geometry revealed none of the anomalies produced by the previous refinement. We felt justified, therefore, in favouring the choice of space group $C2/c$, a result which constrains the molecule to possess two-fold symmetry.

Our X-ray analysis has therefore revealed a monomeric complex, possessing two-fold symmetry, in which the Zn atom is co-ordinated by three C_5H_5N molecules and by two equivalent nitrate groups. The nitrate groups are asymmetrically bidentate [$Zn-O(1) = 2.23 \pm 1$ Å, $Zn-O(2) = 2.41 \pm 1$ Å], and the overall arrangement of the C_5H_5N

and nitrate groups is such that the steric interactions are minimised (see Figure).

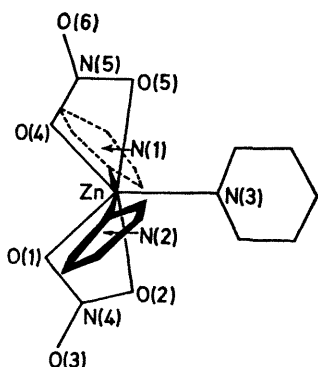


FIGURE.

The environment around the zinc atom may be compared with the molecular structures of $[(py)_2Cu(NO_3)_2, 0.5 py]_2$ ³ and $(2\text{-picoline})_2Cu(NO_3)_2$.⁴ In the present case the zinc atom is surrounded by four short-bonded atoms [O(2), O(5), N(1), and N(2)] in an approximately square-planar arrangement. The third C_5H_5N ring, constrained to lie along the two-fold axis, lies above the square-plane, whilst the two long-bonded oxygens [O(1) and O(4)] lie below the plane. The site of the axial C_5H_5N group is therefore in the same position as the dimer bridge in $[(py)_2Cu(NO_3)_2, 0.5py]_2$. Moreover, in $(2\text{-picoline})_2Cu(NO_3)_2$, it is this site which is blocked by the two α -methyl groups. The geometrical features which we have found in the two copper complexes are therefore repeated in the present zinc complex.

We thank the referee for pointing out a serious error which we had overlooked in the original manuscript.

(Received, October 9th, 1970; Com. 1734.)

¹ R. V. Biagetti and H. M. Haendler, *Inorg. Chem.*, 1966, 5, 383.

² T. J. Ouellette and H. M. Haendler, *Inorg. Chem.*, 1969, 8, 1777.

³ A. F. Cameron, K. P. Forrest, R. H. Nuttall, and D. W. Taylor, *Chem. Comm.*, 1970, 210.

⁴ A. F. Cameron, R. H. Nuttall, and D. W. Taylor, *Chem. Comm.*, 1970, 865.