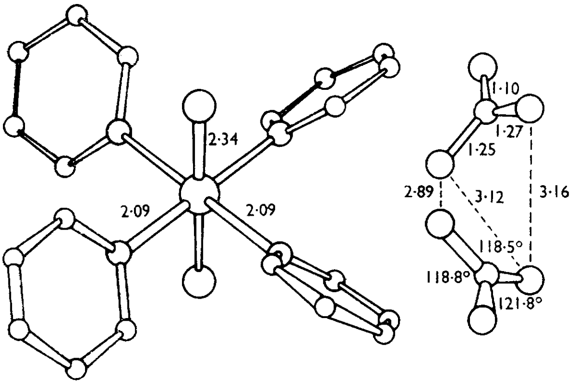
The Structure of the Hydrogen Dinitrate Ion

By G. C. DOBINSON, R. MASON, and D. R. RUSSELL

(*Departments of Chemistry, University of Sheffield and University of Leicester*)

AN adduct of nitric acid with *trans*-dibromotetrapyridinerhodium(III) bromide was first[1] formulated as *trans*-[Rh py$_4$Br$_2$](NO$_3$),HNO$_3$. The stoicheiometry of this complex was confirmed more recently[2] but reformulated as *trans*-[Rh py$_4$Br$_2$]-(O$_2$NO·H·ONO$_2$). The presence of the hydrogen dinitrate ion in this and related complexes was evidenced by several methods; infrared data were interpreted by postulating the presence of the symmetrical hydrogen bonded species (O$_2$N-O-H-O-NO$_2$)$^-$ ion with a probable O-H · · · O bond length of *ca.* 2·50 Å.



FIGURE

A single crystal analysis of *trans*-[Rh py_4Cl_2]-NO_3,HNO_3 has now been completed to the point where the reliability index for 846 independent reflexions is 0·093. The crystals are orthorhombic with a = 7·54 Å, b = 21·65 Å, c = 14·83 Å, Z = 4. The refinement analysis has converged satisfactorily on the basis of the space group *Pbcn*, the complex possessing exact C_2 symmetry in the crystal. The molecular stereochemistry is shown in the Figure, the mean e.s.d.s in the bond lengths being Rh–Cl 0·01 Å, Rh–N 0·02 Å, N–O 0·05 Å and O · · · O 0·04 Å.

The analysis confirms the presence of the hydrogen dinitrate anion. Two nitrate groups are related by a crystallographic two-fold axis so that four oxygen atoms lie at the corners of a slightly distorted tetrahedron. The mean oxygen–oxygen distance is 3·06 Å and individual values do not deviate from this result by more than four standard deviations. The Debye parameters for the nitrate group atoms show that it is undergoing large librational motions; as yet, the bond lengths given in the Figure have not been corrected for the systematic errors in atomic co-ordinates introduced by such vibrations since an adequate determination of translational and librational vibration parameters has not been completed.

The position of the hydrogen atom of the ($O{\cdot}NO_2 \cdots H \cdots O_2N{\cdot}O$) anion is difficult to infer. In a perfectly ordered structure, it must lie on the crystallographic (and molecular) C_2 axis and presumably, since all the oxygen–oxygen contacts are essentially equivalent, close to the centre of gravity of the distorted tetrahedron. Alternatively, the hydrogen could be statically or dynamically disordered between several sites of approximately equal potential energy. It is clear, however, that the anomalous infrared spectrum of the complex is not due to the presence of a short, symmetrical hydrogen bond but rather is consequent upon the pseudo-tetrahedral environment of the hydrogen atom. The present structure is also noteworthy in connection with the observation of the $(H_5O_2)^+$ ion in *trans*-[Co en_2Cl_2]Cl,HCl,$2H_2O$.[3]

There is nothing unusual about the co-ordination of the rhodium(III) ion; the pyridine ligands are oriented in a propeller-like way about the Cl–Rh–Cl bond axis.

(*Received, December* 1*st*, 1966; *Com.* 945.)

---

[1] P. Poulenc, *Ann. Chim.* (*France*), 1935, **4**, 647.
[2] R. D. Gillard and R. Ugo, *J. Chem. Soc.* (*A*), 1966, 549.
[3] A. Nakahara, Y. Saito, and H. Kuroya, *Bull. Chem. Soc., Japan*, 1952, **25**, 331.