stampede of contemporary chemical crystallography. It exposes one of the occasional mishaps but hardly disposes of the problems seen. They, in varying degrees, require separate reinvestigation and review.

Some will argue that the mishap was harmless: after all, the reported structure is essentially correct, as far as we know, except for the symmetry and the divergent lengths and angles. We can understand, but hardly agree.

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Disordered Structure of an $(O_2NO.H.ONO_2)^-$ Ion. A Neutron Diffraction Study of *trans*-Dichlorotetrakis(pyridine)rhodium(III) Hydrogendinitrate

BY JACQUES ROZIÈRE

Laboratoire des Acides Minéraux LA 79, Université des Sciences et Techniques du Languedoc, place Eugène Bataillon, 34060 Montpellier CEDEX, France

MOGENS S. LEHMANN

Institut Max Von Laue–Paul Langevin, avenue des Martyrs, 38042 Grenoble, France

AND JACQUELINE POTIER

Laboratoire des Acides Minéraux LA 79, Université des Sciences et Techniques du Languedoc, place Eugène Bataillon, 34060 Montpellier CEDEX, France

Abstract

Three dimensional single-crystal neutron diffraction data have been collected for *trans*-dichlorotetrakis-(pyridine)rhodium(III) hydrogendinitrate, $[Rh(C_5H_5N)_4Cl_2]H(NO_3)_2$, at 298 K. The unit cell is orthorhombic, space group *Pbcn* with four formula units. $a = 7.529$ (5), $b = 21.717$ (6), $c = 14.717$ (7) Å. The structure comprises $RhPy_4Cl_2^+$ cations and orientationally disordered symmetric $(O_2NO.H.ONO_2)^-$ anions. Contrary to earlier X-ray findings the hydrogen bond within the hydrogendinitrate ion is very short, 2·46 (2) Å. The structure was refined to a final *R* value of 0·031.

Introduction

Recently both neutron and X-ray diffraction studies have reported evidence for the hydrogendinitrate ion, $(O_2NO.H.ONO_2)^-$, in several crystals. Some controversy has surrounded the interpretation of hydrogen bonding in the hydrogendinitrate ion and it has been suggested that the ion exists in two forms. In tetraphenylarsonium hydrogendinitrate, the $H(NO_3)_2^-$ ions have been found with a planar conformation (Faithful & Wallwork, 1967). In caesium hydrogendinitrate, the anion is non-planar and the two nitrate groups lie in nearly orthogonal planes (Williams, Dowling, Gunde, Hadzi & Orel, 1976; Rozière, Rozière-Bories & Williams, 1976). In both salts, the nitrate groups are orientationally disordered and the hydrogendinitrate ions consist of two NO_3^- groups linked by a very short and possibly symmetric hydrogen bond of 2·43–2·47 Å.

Here we wish to report two other examples of the $H(NO_3)_2^-$ ion observed in *trans*-dichlorotetrakis-(pyridine)rhodium hydrogendinitrate.

Data

The crystals of $[Rh(C_5H_5N)_4Cl_2]H(NO_3)_2$ were prepared following the method of Gillard & Ugo (1966). The unit-cell parameters were established by the least-squares method from angular data recorded at 296 ± 1 K on an Enraf–Nonius four-circle CAD-4 diffractometer, for 25 resolved Mo $K\alpha_1$ reflections ($\lambda = 0.71069$ Å): $a = 7.529$ (5), $b = 21.717$ (6), $c = 14.717$ (7) Å, space group $Pbcn$, $Z = 4$, $D_c = 1.70$, $D_m = 1.78$ Mg m^{-3} (Gillard & Ugo, 1966).

Crystals suitable for neutron work were obtained by slow evaporation of a dichloromethane solution. The crystal used in this neutron diffraction study weighed 12 mg and was protected from moisture and nitric acid loss in a sealed silica-glass tube. 2240 reflections were measured at $\lambda = 1.175$ Å up to $2\theta = 88°$ with the $\theta–2\theta$ step-scan mode, using the diffractometer D15 at the Institute Laue–Langevin. Data reduction was carried out with the minimum $\sigma(I)/I$ method (Lehmann & Larsen, 1974) and the data were corrected for absorption effects and the Lorentz factor. The calculated linear absorption coefficient was 0.194 mm^{-1}. Averaging all equivalent data gave 1983 independent reflections.

Refinements

Although the molecular geometry was already known from a previous communication (Dobinson, Mason & Russel, 1967), the structure was redetermined using the neutron Patterson function. Disorder of the hydrogen-dinitrate ion, evidenced by two pairs of well resolved peaks for one O atom and the H atoms of a HNO_3 unit, was immediately recognized at the initial Fourier stage. The high thermal motion of the other atoms of the HNO_3 unit suggested that the anion was subject to a type of orientational disorder similar to that found in $CsH(NO_3)_2$ crystals (Rozière, Rozière-Bories & Williams, 1976). The refinement was continued with all the atoms of the hydrogendinitrate ion disordered in two closely spaced positions with occupancy factors respectively n and n'. Two groups were chosen so that the distances and angles within each group were physically reasonable.

The refinements proceeded rather well for all the atoms with fractional occupancy except the H atoms. Refinements with isotropic temperature factors for the two half-hydrogen atoms gave H coordinates inconsistent with the positions obtained from Fourier and difference Fourier maps and resulted in an unreasonably bent O—H—O group in one of the two $H(NO_3)_2^-$ units (OHO angle of 147°). This was caused by a very high correlation between the y positional parameters of the two sites of the H atoms which are located on the twofold rotation axis. The following constraint was

therefore introduced: the quantity refined was the deviation of the H atom position from the mid-point of the O$\cdots$O line. This deviation was assumed to be the same in the two $H(NO_3)_2^-$ units and appropriate constraints on the parameters and the derivatives were applied.

The structure was refined by full-matrix least-squares calculations, minimizing $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$, $\sigma^2(F) = \sigma^2_{count}(F)/4F^2 + (0.01F)^2$ including anisotropic temperature factors for all the atoms. In the final cycles of refinement, an isotropic extinction parameter (Coppens & Hamilton, 1970) was introduced.

The final agreement factors were: $R(F) = 0.060$; $R_w(F) = 0.031$; the goodness-of-fit, defined as $[\sum w(|F_o| - |F_c|)^2/(N - M)]^{1/2}$ where N and M are the numbers of observations and parameters respectively, was 1.29 for 1651 reflections with intensities greater than the standard deviation. The isotropic extinction parameter was 5.7 (3) $\times$ 10^4. Only the reflection $\bar{2}00$ which had an E value of 0.60 was severely affected by extinction. The final values of n and n' were the same [0.49 (1)] for the two $H(NO_3)_2^-$; the scattering lengths used in the refinements were taken from Bacon (1972).

Table 1. *Final positional parameters* ($\times 10^4$)

	x	y	z
Rh	0	1161 (1)	2500
Cl	2290 (2)	1159 (1)	1436 (1)
N(1)A	1323 (2)	495 (1)	3239 (1)
N(2)B	1310 (2)	1826 (1)	3227 (1)
C(2)A	1409 (3)	536 (1)	4144 (1)
C(6)A	2173 (3)	30 (1)	2834 (1)
C(3)A	2336 (3)	117 (1)	4664 (2)
C(5)A	3128 (3)	−402 (1)	3316 (2)
C(4)A	3218 (3)	−359 (1)	4249 (2)
C(2)B	3054 (2)	1786 (1)	3376 (1)
C(6)B	420 (3)	2311 (1)	3560 (1)
C(3)B	3969 (3)	2220 (1)	3872 (1)
C(5)B	1258 (3)	2763 (1)	4061 (1)
C(4)B	3052 (3)	2715 (1)	4229 (1)
H(2)A	696 (7)	908 (2)	4454 (3)
H(6)A	2078 (7)	11 (2)	2106 (3)
H(3)A	2345 (8)	173 (3)	5382 (3)
H(4)A	3936 (8)	−691 (2)	4637 (4)
H(5)A	3762 (8)	−778 (2)	2957 (4)
H(2)B	3737 (6)	1393 (2)	3084 (3)
H(6)B	−975 (6)	1332 (2)	3419 (3)
H(3)B	5387 (7)	2161 (2)	3962 (4)
H(5)B	464 (7)	3146 (2)	4300 (4)
H(4)B	3727 (8)	3059 (2)	4625 (4)
NA	3298 (28)	3620 (12)	1481 (18)
O(1)A	1909 (12)	3755 (5)	1204 (8)
O(2)A	3514 (14)	3260 (7)	2153 (11)
O(3)A	4420 (17)	3978 (6)	1299 (7)
HA	5000	3323 (11)	2500
NB	3282 (34)	3566 (10)	1536 (15)
O(1)B	2676 (15)	3420 (5)	791 (5)
O(2)B	4653 (18)	3884 (7)	1678 (7)
O(3)B	2856 (20)	3193 (9)	2100 (14)
HB	5000	3821 (0)	2500

The computer programs used were those listed by Rozière & Williams (1978).*

Atomic parameters are given in Table 1.

Discussion

The crystal structure is composed of *trans*-RhCl$_2$(Py)$_4^+$ cations and H(NO$_3$)$_2^-$ anions. A view of the cation is given in Fig. 1 and the numbering scheme is included together with interatomic distances and bond angles. The Rh atoms of the RhCl$_2$(Py)$_4^+$ ions are located on the twofold rotation axes which relate two pairs of pyridine groups and the Cl atoms.

An average value of 2·060 Å was determined for the two independent Rh—N(Py) distances which compare well with other Rh^{III}—N distances reported in the literature (Whuler, Brouty, Spinat & Herpin, 1976; Miyamae, Sato & Saito, 1977). On the assumption that chemically equivalent bonds are indeed equal in length, it appears that the derived standard deviations are underestimated by a factor of two. This is in agreement with results from comparisons using normal probability plots (Abrahams & Keve, 1971) among several determinations of the same molecular structure (Frey, Lehmann, Koetzle & Hamilton, 1973) where it was found that the e.s.d.'s were underestimated by a factor of 1·6. A similar difference in Rh—N distances, which

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* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34230 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
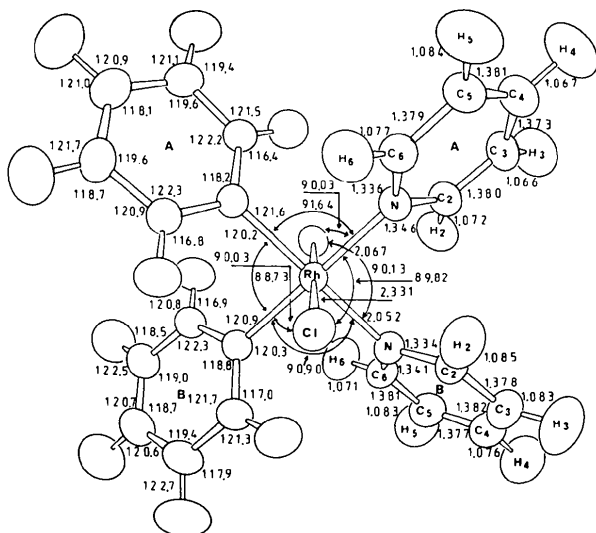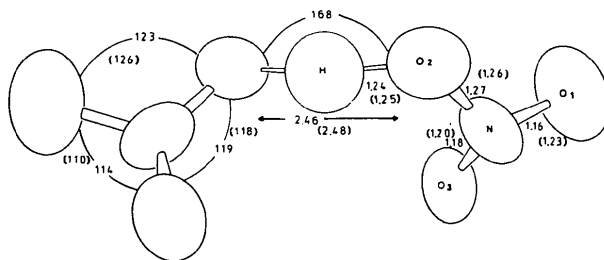

Fig. 2. The hydrogendinitrate ion. Values in parentheses are for H(NO$_3$)$_2^-$ (*B*). E.s.d. for O—H—O bonds is 0·02 Å, for OH bonds 0·01 Å, for N—O bonds 0·03 Å. Mean e.s.d. for bond angles is 2°. The dihedral angles between the planes of the two NO$_3^-$ groups in the hydrogendinitrate ions are respectively 96 (3)° for H(NO$_3$)$_2^-$ (*A*) and 91 (4)° for H(NO$_3$)$_2^-$ (*B*).

amounts to a bond-length difference of 5σ, was observed in a precise X-ray diffraction study of Rh(en)$_3^{3+}$ cations (Miyamae et al., 1977), so that it is still doubtful whether these distances ought to be identical.

In the pyridine groups, the four C—N bond distances have a mean value of 1·339 (3) Å and the eight C—C distances have an average value of 1·379 (1) Å; C—H distances appear quite normal with an average value of 1·076 (2) Å.

There is a disordered arrangement of the hydrogendinitrate ions in the structure. The double positions of the atoms appear to be occupied with equal probability [occupancy factors of 0·49 (1)]. Two hydrogen bonds are then possible linking two non-coplanar symmetry-related nitrate groups, with O···O distances of 2·461 (18) and 2·480 (18) Å and the H atoms located on the twofold symmetry axis. These distances are significantly shorter than previously reported in the X-ray study of Dobinson et al. (1967) (2·85 Å) which used a simpler model ignoring the orientational disorder. The hydrogen bonds are significantly bent, with an OHO angle of 167·5 (14)°.

Bond lengths and angles are reported in Fig. 2. The observed structure is of Speakman's type *A*, as is consistent with the infrared spectrum which indicates a very strong hydrogen bond (Gillard & Ugo, 1966).

It should be noted that, although the two H(NO$_3$)$_2^-$ units (*A* and *B*) have the same occupancy factor, they differ in some details of their geometries. It is also important to note that the thermal motion of the H atom is much higher in the *B* part than in the *A* part. It is not clear, however, whether these differences are produced by the correlation problem encountered in the refinement or arise from a real difference in the nature of the two hydrogendinitrate ions.

Fig. 1. The *trans*-dichlorotetrakis(pyridine)rhodium(III) cation. E.s.d. for Rh—N distances is 0·002 Å; Rh—Cl, 0·001 Å; C—N, 0·002 Å; C—C, 0·003 Å. Mean e.s.d. for bond angles is 0·08° around Rh and 0·2° in the pyridine rings.

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Etude Structurale et Energétique à l'Etat Cristallin d'un Composé Smectogène: Le Diheptyloxy-4,4′ Azoxybenzène

PAR M. COTRAIT ET P. MARSAU

Laboratoire de Cristallographie et de Physique Cristalline associé au CNRS, Université de Bordeaux I, 351 cours de la Libération, 33405 Talence, France
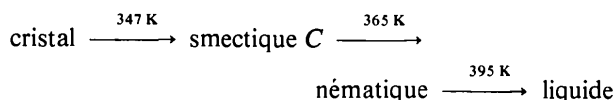
ET M. PESQUER

Laboratoire de Chimie Physique A, ERA n° 312 du CNRS, 351 cours de la Libération, 33405 Talence, France

Abstract

The crystal structure of a smectogenic compound: 4,4′-diheptyloxyazoxybenzene (HAOB), $C_{26}H_{38}N_2O_3$, has been established. It crystallizes in the space group $P\bar{1}$ with $a = 18.879$ (5), $b = 7.800$ (4), $c = 10.940$ (9) Å, $\alpha = 128.80$ (5), $\beta = 87.05$ (3) and $\gamma = 97.61$ (4)°. Neighboring molecules are antiparallel to each other and molecules related through the inversion center at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ form dimers, whose association energy has been found to be very high: 141.3 kJ. Dimers are aligned along a unique direction. Interactions in the crystal are of two types: between aliphatic chains and between an aliphatic chain and the central part of the molecule.

Introduction

Un certain nombre de structures cristallines de composés smectogènes ont été publiées à ce jour: les formes I et II du *p*-azoxybenzoate d'éthyle (Krigbaum & Barber, 1971; Krigbaum & Taga, 1974); le dérivé bis-*p*-butylanilino de l'acide téréphtalique ou TBBA (Doucet, Mornon, Chevalier & Lifchitz, 1977); le (méthoxy-benzylidèneamino-4′)-4 cinnamate d'éthyle ou MBACE

(Cotrait & Pesquer, 1977). Tous ces composés possèdent des chaînes aliphatiques relativement courtes. Nous avons choisi d'étudier un composé à chaîne plus longue: le diheptyloxy-4,4′ azoxybenzène, HAOB. Le composé dont la formule est représentée sur la Fig. 1, présente les transitions suivantes:

$$\text{cristal} \xrightarrow{347\,\text{K}} \text{smectique } C \xrightarrow{365\,\text{K}}$$

$$\text{nématique} \xrightarrow{395\,\text{K}} \text{liquide}$$

d'après les travaux de Chistyakov & Chaikowsky (1969).

Partie expérimentale

Des cristaux de HAOB nous ont été fournis par M le Professeur Ptak du Centre de Biophysique Moléculaire d'Orléans. Les données cristallines sont les suivantes: groupe spatial $P\bar{1}$ ($Z = 2$): $a = 18,879$ (5), $b = 7,800$ (4), $c = 10,940$ (9) Å, $\alpha = 128,80$ (5), $\beta = 87,05$ (3) et $\gamma = 97,61$ (4)°; $V = 1245$ Å³, $d = 1,14$ Mg m⁻³. Par suite de la décroissance rapide des intensités avec l'angle θ de Bragg, seules les réflexions avec $\theta < 50°$ (environ 2600) ont été collectées avec un diffracto-