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The Structure of Ammonium Oxalohydroxamate – a Monopropellant

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Abstract. $NH_4^+.C_2H_3N_2O_4^-$, $M_r = 137{\cdot}1$, triclinic, $P\bar{1}$, $a = 3{\cdot}952\,(1)$, $b = 6{\cdot}772\,(1)$, $c = 9{\cdot}993\,(1)$ Å, $\alpha = 98{\cdot}06\,(1)$, $\beta = 89{\cdot}96\,(1)$, $\gamma = 106{\cdot}96\,(1)°$. $V = 253{\cdot}06$ Å^3, $Z = 2$, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 15{\cdot}29\ \mathrm{cm^{-1}}$, $D_m = 1{\cdot}805$, $D_x = 1{\cdot}798\ \mathrm{g\,cm^{-3}}$, $F(000) = 144$, $T = 293$ K, $R = 0{\cdot}048$ for 795 observed reflections. The unit cell contains two independent centrosymmetric molecules, one centred at (0,0,0) and the other at (0·5, 0·0, 0·5). The presence of experimentally determined $>$N—H groups and the —C=O bond lengths of 1·248 (4) and 1·247 (4) Å indicate that the compound exists in the oxamic rather than the oximic form. Only one hydroxyl hydrogen is associated with each molecule. They are located at centres of inversion (0,0·5,0 and 0,0·5,0·5) and are shared between symmetry-related molecules *via* short symmetric H bonds with O···O = 2·454 (4), 2·457 (4) and all O—H = 1·23 Å.

Introduction. The crystal structure analysis of the title compound was carried out as part of our program of investigations on propellant formulations.

Experimental. The milky-white residue which resulted from isothermal heating of oxalohydroxamic acid (OXHA) at 368 K was cooled to room temperature. It was dissolved in water at 353 K, the solution was cooled to 323 K and the crystals separated out. Experimental conditions for data collection using a Nonius CAD-4 diffractometer are given in Table 1. Three check reflections ($1\bar{2}1$, $0\bar{1}\bar{2}$, 102) were monitored every 30 min. No decay was observed. Empirical absorption correction (North, Phillips & Mathews, 1968) was applied; minimum transmission 0·734, maximum transmission 0·898. Lorentz and polarization corrections were applied. The structure was solved in space group $P1$ by direct methods using *MULTAN*80 (Germain, Main & Woolfson, 1971). The centres of inversion for the two molecules were identified and the space group was reduced to $P\bar{1}$. The NH_4^+ ion was located from a difference Fourier map. The C, N and O atoms were refined anisotropically, H atoms, including those of the NH_4^+ ion, observed in difference Fourier maps were refined isotropically without constraints, using the program *SHELX*76 (Sheldrick, 1976). Full-matrix least-squares refinement on F. Final $R = 0{\cdot}048$ for 795 observed reflections $[|F| > 2\sigma(|F|)]$; $w = 1/\sigma^2(|F|)$; $wR = 0{\cdot}058$. In final cycle $\Delta/\sigma < 0{\cdot}03$. $\Delta\rho$ in final difference map within 0·71 and $-0{\cdot}39$ e Å^{-3}. Atomic scattering factors as supplied in *SHELX*76.

Table 1. *Experimental conditions*

Crystal size (mm)	0·08 × 0·15 × 0·5
Density	Flotation in $CHCl_3/CHBr_3$
Number and range of reflections used for lattice parameters	25 (12 to 34°θ, Cu $K\alpha$)
Scan method	$\omega/2\theta$
Range of *hkl* values	h −4 to 4, k −8 to 8, l 0 to 12
Number of unique reflections measured	822 with $\theta \leq 65°$
Number of observed reflections used in refinement $|F| > 2\sigma(|F|)$	795
Number of parameters refined	106
Final R, wR	0·048, 0·058

Discussion. Atomic coordinates and thermal parameters are given in Table 2, molecular geometry is given in Table 3.† A plot of the two independent centrosymmetric molecules with bond lengths and angles is shown in Fig. 1 and the packing diagram viewed down **a** is given in Fig. 2. Other examples of molecules containing independent centres of inversion are stil-

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† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44779 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 2. *Atomic coordinates and equivalent isotropic thermal parameters*

$$U_{eq} = \tfrac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	U_{eq}(Å^2)
O1*A*	−0·2645 (6)	0·3578 (3)	−0·0435 (2)	0·024 (1)
C*A*	−0·0555 (7)	0·0965 (4)	0·0261 (3)	0·015 (1)
N*A*	−0·1563 (7)	0·1797 (4)	−0·0716 (3)	0·018 (1)
O2*A*	−0·0450 (6)	0·1648 (3)	0·1492 (2)	0·023 (1)
O1*B*	1·1215 (5)	0·3571 (3)	−0·5435 (2)	0·023 (1)
C*B*	0·6517 (7)	0·0960 (4)	−0·4740 (3)	0·016 (1)
N*B*	0·8365 (6)	0·1801 (4)	−0·5714 (3)	0·018 (1)
O2*B*	0·7102 (5)	0·1648 (3)	−0·3511 (2)	0·023 (1)
N*W*	1·3878 (8)	0·5002 (5)	−0·2500 (3)	0·023 (1)

Table 3. *Molecular geometry*

(*a*) Bond lengths (Å) and angles (°) involving non-hydrogen atoms with e.s.d.'s in parentheses

O1*A*–N*A*	1·386 (4)	O1*B*–N*B*	1·379 (3)
N*A*–C*A*	1·310 (4)	N*B*–C*B*	1·310 (4)
C*A*–O2*A*	1·248 (4)	C*B*–O2*B*	1·247 (4)
C*A*–C*AS*	1·522 (5)	C*B*–C*BS*	1·517 (5)
O1*A*–N*A*–C*A*	120·8 (3)	O1*B*–N*B*–C*B*	121·1 (3)
N*A*–C*A*–O2*A*	125·3 (3)	N*B*–C*B*–O2*B*	124·8 (3)
N*A*–C*A*–C*AS*	112·5 (3)	N*B*–C*B*–C*BS*	112·8 (3)
O2*A*–C*A*–C*AS*	122·2 (3)	O2*B*–C*B*–C*BS*	122·4 (3)

Note: The atom C*AS* is related to C*A* through a centre of symmetry at 0·0, 0·0, 0·0.

The atom C*BS* is related to C*B* through a centre of symmetry at 0·5, 0·0, 0·5.

(*b*) Hydrogen-bond parameters

D–H···*A* or *D*···H···*A*	*D*–H(Å)* or *D*···H(Å)	*D*···*A* (Å)**	H···*A*(Å)*	*D*–H···*A*(°)* or *D*···H···*A*(°)	Symmetry of *A*
N*A*···O2*B*	0·83	2·825	2·10	146	$x-1, y, z$
N*B*···O2*A*	0·95	2·823	1·95	152	$x+1, y, z-1$
O1*A*···O1*A*	1·23	2·454	1·23	180	$-x, 1-y, -z$
O1*B*···O1*B*	1·23	2·457	1·23	180	$2-x, 1-y, -z-1$
N*W*···O1*B*	1·00	2·900	1·90	166	$x-1, y, 1+z$
N*W*···O2*A*	0·89	3·024	2·18	158	$1+x, y, z$
N*W*···O1*A*	0·93	2·900	1·98	170	$-x, 1-y, -z$
N*W*···O2*B*	0·83	3·027	2·23	161	$2-x, 1-y, -z$

D = Donor, *A* = Acceptor.
Mean e.s.d.'s are as * = 0·05 Å, ** = 0·004 Å and † = 5°.

bene, *trans*-azobenzene and potassium dithionate (Bunn, 1961, and references therein). The crystal structure of the non-ammoniated oxalohydroxamic acid (OXHA) has been reported (Lowe-Ma & Decker, 1986; Sameena Begum, Jain, Khetrapal & Shivaprakash, 1987). The presence of experimentally determined >N–H groups and the –C=O bond lengths of 1·248 (4) and 1·247 (4) Å indicate that the compound exists in the solid state in the oxamic rather than the oximic form. The C–N bond lengths, 1·310 (4) Å in both molecules, compare well with those observed in OXHA, 1·319 (1) Å. The torsion angles involving the N atom [O2*A*–C*A*–N*A*–O1*A* = −0·2 (5) and O2*B*–C*B*–N*B*–O1*B* = 0·4 (5)°] suggest that the N is closer to planarity than in OXHA, where the corresponding torsion angle is 4·9°.

The packing of the molecules is very different from that of OXHA, where the carboxyl O accepts a proton from a hydroxyl O atom. In the present structure the hydroxyl O of molecule *A* hydrogen bonds to the hydroxyl O of another molecule *A* related through a centre of inversion at (HSM1) 0,0·5,0 where there is a

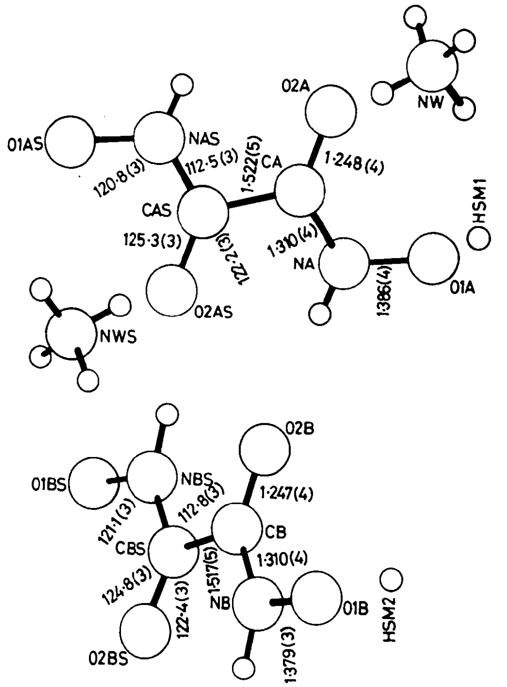

Fig. 1. Diagram of the two independent molecules. Bond lengths in Å; bond angles in degrees. Atoms with superscripts are related to atoms without superscripts by inversion ($-x, -y, -z$) for molecules *A* and by inversion ($1-x, -y, 1-z$) for molecule *B*.

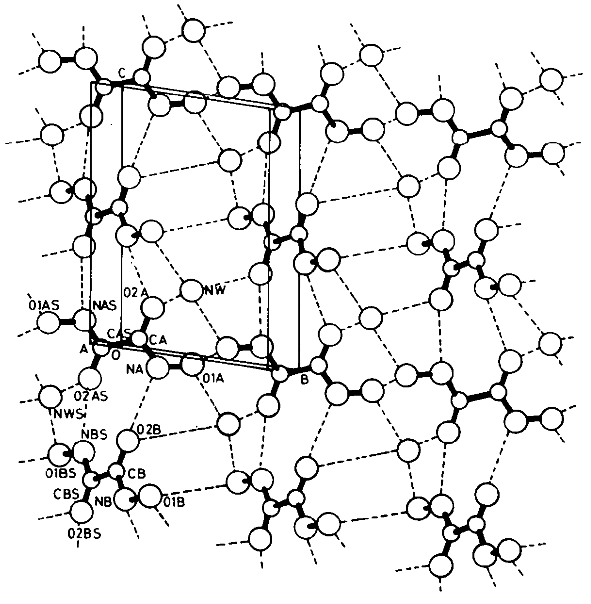

Fig. 2. Packing of the molecules viewed along a.

peak of height 0·71 e Å^{-3} in the difference Fourier map [O—H = 1·23, O···O = 2·454 (4) Å]. Similarly the hydroxyl groups of molecules *B* are H-bonded through an inversion centre (HSM2) at 0,0·5,0·5 with a peak of height 0·52 e Å^{-3} in the difference Fourier map [O···O = 2·457 (4), O—H = 1·23 Å] indicating the presence of symmetric hydrogen bonds (Table 3, Fig. 2). The hydroxyl H atoms are shared between molecules, and hence only one hydroxyl H is associated per molecule, the other protonating the ammonium group. Short O···O hydrogen bonds (~ 2·45 Å) have been observed in the crystal structure of acid salts of mono- and dicarboxylic acids (Speakman, 1972; Novak, 1974). The two independent molecules *A* and *B* have similar bond lengths, bond angles and torsion angles.

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Structure of 2-Methylnaphthimidazolium Chloride Dihydrate

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Abstract. $C_{12}H_{11}N_2^+.Cl^-.2H_2O$, $M_r = 254·72$, triclinic, $P\bar{1}$, $a = 7·326$ (2), $b = 9·634$ (3), $c = 10·927$ (2) Å, $\alpha = 62·42$ (2), $\beta = 74·77$ (2), $\gamma = 72·89$ (2)°, $V = 646·0$ (3) Å^3, $Z = 2$, $D_x = 1·309$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·46$ cm^{-1}, $T = 298$ K, $F(000) = 268$, final $R = 0·035$ for 1410 unique reflections. 2-Methylnaphthimidazolium chloride dihydrate was prepared by reacting 2,3-diaminonaphthalene with glacial acetic acid and hydrochloric acid. The composition of the compound was suggested by ^{1}H NMR spectra. Crystallographic analysis confirmed the complete structure. The cation is essentially planar excluding methyl H atoms. The planar rings have considerable aromatic character. The cations are linked by hydrogen-bonding bridges of the form N—H···Cl$^-$···H—O···H—O···H—N.

Introduction. There have been several reports of the structure of imidazole, including those by Martínez-Carrera (1966), Will (1969) and Craven, McMullan, Bell & Freeman (1977). The latter authors used neutron diffraction and data collected at 293 and 123 K. However, we are not aware of any reports of the structure of an imidazolium salt.

2-Methylnaphthimidazolium chloride dihydrate was synthesized as an intermediate as part of a program to prepare and characterize substituted naphthalenes as potential components of donor–acceptor complexes.

Experimental. 2,3-Diaminonaphthalene (0·5 g) was dissolved in glacial acetic acid (10 ml) and the reaction mixture was heated to the reflux temperature. Hydrochloric acid (37·5%, 3 ml) was added after 5 min and the reaction mixture was refluxed continuously for 1 h. The reaction solution was poured into a 100 ml beaker, covered and left standing at room temperature for 1–2 days. It yielded a crude product, which was filtered and dissolved in H_2O by heating to make a saturated solution. After filtering the hot saturated solution, a clear yellow solution was obtained. It gave yellowish needle-shaped crystals by slow evaporation of solvent at room temperature.

A transparent needle crystal with dimensions 0·58 × 0·18 × 0·25 mm was chosen for study by X-ray diffraction. A modified Picker FACS-1 diffractometer was used for data collection, with graphite-monochromated Mo $K\alpha$ radiation, $\theta/2\theta$ scan technique. Unit-cell parameters from 40 reflections, $27 < 2\theta < 37°$.

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