Bond-valence calculations (Brown & Wu, 1976) gave only 1·54 v.u. (valence units) for the O(24) atom, but 1·87 to 2·04 v.u. for all the other O atoms in the title compound. The comparable values in the phosphate compound are 1·61 and 1·85 to 2·09 v.u. So one has to assume that the H atom is bonded to the O(24) atom. The short distance O(24)···O(24) indicates that between these two atoms there exists a symmetrically restricted hydrogen bond (either symmetrically linear with the H atom at $\bar{1}$ or only apparently symmetrical). Therefore the crystal chemical formula of the little compound is $Na_5Cu_3(AsO_4)_2(AsO_4HAsO_4)$. In the arsenate compound the distance O(24)···O(24) = 2·427 (4) Å is larger than the equivalent distance O(24)···O(24) = 2·388 (7) Å in the phosphate compound. Resulting from these short hydrogen bonds, the bond lengths P(2)—O(24) and As(2)—O(24) are 1·559 and 1·709 Å. These values are only 0·023 and 0·021 Å larger than the average X(2)—O distances. In particular, the X(2)—O(24) bonds are still comparatively short for an X—OH bond. Ferraris & Ivaldi (1984) gave average X—OH distances of 1·581 Å for X = P and 1·731 Å for X = As in $(HXO_4)^{2-}$ groups.

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Structure of Hydroxylammonium Nitrate (HAN) and the Deuterium Homolog

BY A. L. RHEINGOLD, J. T. CRONIN AND T. B. BRILL*

Department of Chemistry, University of Delaware, Newark, DE 19716, USA

AND F. K. ROSS*

Research Reactor, University of Missouri, Columbia, MO 65211, USA

Abstract. HAN, $[NH_3OH]NO_3$, $M_r = 96·04$, monoclinic, $P2_1/c$, $a = 4·816$ (1), $b = 6·800$ (1), $c = 10·728$ (1) Å, $\beta = 99·35$ (1)°, $V = 346·7$ (1) Å^3, $Z = 4$, $D_x = 1·841$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71073$ Å, $\mu = 1·86$ cm^{-1}, $F(000) = 200$, $T = 296$ K, $R_F = 0·032$ for 836 unique reflections. HAN-d_4, $[ND_3OD]NO_3$, $M_r = 100·07$, monoclinic, $P2_1/c$, $a = 4·8165$ (8), $b = 6·8007$ (9), $c = 10·7298$ (13) Å, $\beta = 99·303$ (11)°, $V = 346·84$ (8) Å^3, $Z = 4$, $D_x = 1·916$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71073$ Å, $\mu = 1·86$ cm^{-1}, $F(000) = 200$, $T = 296$ K, $R_F = 0·0411$ for 1073 unique reflections. HAN and HAN-d_4 are isostructural. All of the H atoms are involved in hydrogen bonding with one being bifurcated. The shortest heavy-atom interionic distance is O···O at 2·796 (1) Å.

Introduction. Hydroxylammonium nitrate (HAN) is an oxidizer and a chemical propellant when it is combined with an alkylammonium nitrate fuel in an aqueous solution (Klein, 1985). HAN dissolves in water in a stoichiometry up to about six HAN molecules to one H_2O molecule. The interionic distances are of interest in interpreting the IR spectra and as a starting point for modeling the solution (Fifer, 1984;

Cronin & Brill, 1986). Despite being a simple salt of low molecular weight, its crystal structure has not been determined. In this paper the structures of both [NH$_3$OH]NO$_3$ and [ND$_3$OD]NO$_3$ are reported.

Experimental. Crystals for the HAN-d_4 determination at the University of Delaware were cleaved in an anhydrous environment from larger ones provided by R. A. Fifer (BRL, Aberdeen Proving Ground, Maryland). Crystals for the HAN determination at the University of Missouri were prepared by vacuum dehydration at 343 K of the commercially available 2·8 M solution (Southwestern Analytical Chemicals, Austin, Texas). Cleaved sample rounded by rolling between sheets of filter paper. Parenthetical values for HAN-d_4. Crystal approximately 0·3 mm sphere (0·3 × 0·3 × 0·4 mm) in sealed glass capillary, Enraf–Nonius CAD-4 (Nicolet R3) diffractometer, graphite monochromator, Mo $K\alpha$, 24 reflections (27 < 2θ < 33°) used to refine orientation matrix, empirical absorption correction ranging from 0 to 3·3% (no absorption correction), 3613 (1398) reflections collected, $\theta/2\theta$ scan for 2 < 2θ < 60° (4 < 2θ < 65°), −6 ≤ h ≤ 6, −9 ≤ k ≤ 9, −14 ≤ l ≤ 14 (−7 ≤ h ≤ 7, 0 ≤ k ≤ 10, 0 ≤ l ≤ 16); R_{int} = 0·013 (0·027), 1163 (1248) unique, 836 (1073) observed reflections [F_o ≥ 2·5$\sigma(F_o)$], 72 parameters. Structure of HAN determined by full-matrix least squares using $MULTAN$ from Enraf–Nonius SDP (Frenz, 1980); structure of HAN-d_4 by blocked-cascade procedure using direct methods $SOLV$ from $SHELXTL$ (Sheldrick, 1983). R_F = 0·032 (0·0411), wR_F = 0·043 (0·0437) [w^{-1} = $\sigma^2(F_o)$ + gF_o^2, g = 0·0008, $\sigma(F_o)$ from counting statistics]. Non-H atoms anisotropic. H(O) atoms located from difference maps and refined isotropically. Final GOF 2·015 (1·485). Max. peak 0·28 (0·22) e Å^{-3}, min. peak −0·24 (−0·24) e Å^{-3} in final $\Delta\rho$ map. This is approximately one half of the height of the last H atom located [H(4)]. $(\Delta/\sigma)_{max}$ = 0·07 (0·05). A large secondary-extinction correction was required F^* = F_c/[1·0 + 0·002$x(F_c)^2$/sin(2θ)]$^{0.25}$; x refined to 4·3 × 10^{-3} (9·9 × 10^{-4}) in final run. All form factors from International Tables for X-ray Crystallography (1974).

Discussion. Table 1 lists the atomic coordinates of HAN and HAN-d_4, while Table 2 gives the intramolecular bond distances and angles, and Table 3 gives selected interionic heavy-atom distances that involve hydrogen bonding.† HAN and HAN-d_4 are isostructural and have remarkably similar crystal parameters, bond distances and angles. The structural

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43568 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atom coordinates* (× 10^4) *and temperature factors* (Å^2 × 10^3)

	x	y	z	U_{iso}
HAN-d_4				
O(1)	−528 (2)	−2054 (1)	6137 (1)	33 (1)*
O(2)	3194 (2)	−2132 (1)	5233 (1)	34 (1)*
O(3)	−772 (2)	−3198 (2)	4238 (1)	44 (1)*
O(4)	5347 (2)	397 (1)	7214 (1)	33 (1)*
N(1)	613 (2)	−2457 (1)	5193 (1)	25 (1)*
N(2)	3595 (2)	−360 (1)	8014 (1)	28 (1)*
D(1)	2142 (39)	−920 (25)	7563 (14)	39 (4)
D(2)	4631 (40)	−1108 (27)	8525 (15)	47 (4)
D(3)	2956 (40)	570 (26)	8464 (16)	49 (5)
D(4)	5000 (38)	−244 (26)	6606 (15)	45 (5)
HAN				
O(1)	−527 (2)	−2052 (1)	6139 (1)	33 (1)*
O(2)	3185 (2)	−2125 (1)	5233 (1)	34 (1)*
O(3)	−779 (2)	−3197 (1)	4241 (1)	44 (1)*
O(4)	5352 (2)	396 (1)	7213 (1)	33 (1)*
N(1)	610 (2)	−2454 (1)	5193 (1)	25 (1)*
N(2)	3592 (2)	−361 (1)	8014 (1)	28 (1)*
H(1)	2075 (29)	−950 (21)	7563 (11)	41 (4)
H(2)	4655 (30)	−1157 (3)	8546 (12)	53 (4)
H(3)	2935 (32)	631 (22)	8426 (11)	52 (4)
H(4)	4994 (30)	−235 (23)	6545 (11)	52 (4)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond distances* (Å) *and angles* (°)

	HAN-d_4	HAN
O(1)–N(1)	1·259 (1)	1·259 (1)
O(3)–N(1)	1·235 (1)	1·234 (1)
O(4)–D(4)	0·780 (17)	0·829 (12)
N(2)–D(2)	0·849 (17)	0·886 (13)
O(2)–N(1)	1·256 (1)	1·254 (1)
O(4)–N(2)	1·395 (1)	1·399 (1)
N(2)–D(1)	0·872 (17)	0·902 (12)
N(2)–D(3)	0·881 (18)	0·892 (12)
O(1)–N(1)–O(2)	119·5 (1)	119·4 (1)
O(2)–N(1)–O(3)	119·9 (1)	120·1 (1)
O(4)–N(2)–D(2)	105·5 (13)	106·0 (7)
O(4)–N(2)–D(3)	111·9 (12)	109·0 (7)
D(2)–N(2)–D(3)	107·2 (16)	110·9 (9)
N(2)–O(4)–D(4)	103·9 (14)	106·2 (8)
O(1)–N(1)–O(3)	120·6 (1)	120·5 (1)
O(4)–N(2)–D(1)	109·3 (11)	110·6 (7)
D(1)–N(2)–D(2)	115·6 (16)	114·0 (11)
D(1)–N(2)–D(3)	107·3 (17)	106·3 (11)

Table 3. *Shortest heavy-atom interionic distances* (Å)

Transformations are those to create the second atom.

	HAN-d_4	HAN
	x, y, z	
O(1)···N(2)	2·834 (1)	2·830 (1)
O(2)···O(4)	2·800 (1)	2·796 (1)
	$x, -\frac{1}{2}-y, \frac{1}{2}+z$	
O(3)···N(2)	2·829 (1)	2·833 (1)
O(2)···N(2)	2·961 (1)	2·963 (1)
	$-x, \frac{1}{2}+y, \frac{3}{2}-z$	
O(1)···N(2)	2·916 (1)	2·916 (1)
	$1+x, \frac{1}{2}-y, \frac{1}{2}+z$	
O(3)···N(2)	2·983 (1)	2·981 (1)

Fig. 1. Stereoscopic view of the unit cell along the b axis.

Fig. 2. The local environment of NO_3^- ions surrounding the $[NH_3OH]^+$ ion showing the hydrogen-bonding interactions.

consequences of deuteration of HAN are thus rather small. As shown in Fig. 1, the crystals at room temperature are devoid of water of crystallization despite the strong affinity that HAN and H_2O have for one another.

The local environment of the NH_3OH^+ ion is shown in Fig. 2. All of the H atoms take part in hydrogen bonding, with H(2) being bifurcated between O(2) and O(3). This distribution is consistent with the H to NO_3^- stoichiometry and the tendency for all H atoms in salts such as HAN to be involved in hydrogen bonding (Olovsson & Jönsson, 1976). The interionic O$\cdots$O and O$\cdots$N distances correspond to O—H and N—H bond distances of about 0·96 and 1·03 Å, respectively (Olovsson & Jönsson, 1976). As expected, however, the distances refined from diffraction data are about 0·2 Å shorter than this because of the scattering model used for the H atoms. Within the nitrate anion the N—O bond distances differ slightly despite the fact that all of the O atoms are involved in significant hydrogen-bonding interactions.
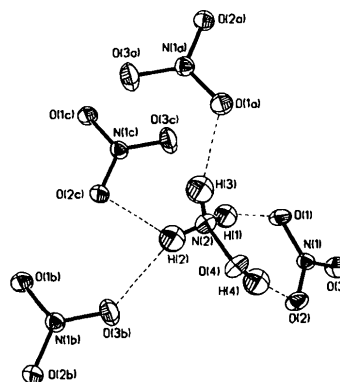
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Synthèse et Structure du Niobouranate de Césium: CsNbUO6

PAR MADELEINE GASPERIN

Laboratoire de Minéralogie–Cristallographie associé au CNRS, Université P. et M. Curie, 4 place Jussieu, 75252 Paris CEDEX 05, France

Abstract. $M_r = 559·85$, monoclinic, $P2_1/c$, $a = 7·430$ (1), $b = 8·700$ (1), $c = 10·668$ (2) Å, $\beta = 105·08$ (1)°, $V = 665·8$ (3) Å^3, $Z = 4$, $D_x = 5·58$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0·7107$ Å, $\mu(Mo\ K\alpha) = 30·1$ mm^{-1}, $F(000) = 944$, room temperature, $R(F) = 0·052$, $wR = 0·065$ for 2974 independent reflexions. The UO_7 and NbO_5 polyhedra are similar to those of $KNbUO_6$ and $RbNbUO_6$, with a nearly collinear uranyl group normal to the plane of five secondary bonds around U^{6+}. These polyhedra are also linked in