

The Structure of Ammonium Hydrogen Oxydiacetate

BY HARALD HERBERTSSON*

Department of Engineering Materials, Technical University of Luleå, S-951 87 Luleå, Sweden

AND BRITT HEDMAN

Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

(Received 13 February 1981; accepted 19 June 1981)

Abstract. $\text{NH}_4^+ \cdot \text{C}_4\text{H}_5\text{O}_5^-$, $M_r = 151.1$, monoclinic, $I2/c$; $a = 10.1298$ (12), $b = 17.9857$ (15), $c = 7.0795$ (8) Å, $\beta = 91.286$ (12)°, $V = 1289.5$ Å³ at 295 K, $Z = 8$, $D_c = 1.557$ Mg m⁻³. The structure consists of infinite chains of hydrogen-bonded $\text{O}(\text{CH}_2\text{COO}^-)_2$ ions held together by NH_4^+ ions and was refined from 996 reflexions to $R = 0.041$. The oxydiacetate residue is bent and twisted around the ether oxygen and the distance between the hydrogen-bonded O atoms is 2.450 (2) Å. The two independent NH_4^+ ions are coordinated tetrahedrally by four O atoms with N–O distances from 2.891 (2) to 3.012 (2) Å. The shortest N–N distance is 3.558 (1) Å.

Introduction. The oxydiacetate residue has been investigated in the alkali hydrogen oxydiacetates (Herbertsson, 1976). In most compounds so far investigated the non-H atoms of the oxydiacetate ion are nearly coplanar. The ligand is planar in the isostructural Cs and Rb compounds (Albertsson, Grenthe & Herbertsson, 1973*b*) but twisted around the ether oxygen in the isostructural K and Na compounds (Albertsson, Grenthe & Herbertsson, 1973*a*). The structures contain infinite chains of oxydiacetate residues linked together by short hydrogen bonds [2.448 (12)–2.563 (2) Å]. The ligand is tridentate and the smaller the cation becomes, the larger the effect on the ligand. The ammonium ion with a radius close to that of Rb^+ should be a borderline case with respect to the planarity of the ligand. The aim of this investigation is to find out whether the non-H atoms of the oxydiacetate residue in ammonium hydrogen oxydiacetate are coplanar or not and to determine the nature of the hydrogen-bond system.

Colourless, short prismatic crystals of ammonium hydrogen oxydiacetate, AMHOXY, are formed when an aqueous solution containing equimolar amounts of NH_3 and oxydiacetic acid is evaporated slowly at room temperature. Elemental analyses were in good agreement with the values calculated for $\text{C}_4\text{H}_9\text{NO}_5$. Weissen-

berg photographs showed the crystals to be monoclinic with systematic absences hkl : $h + k + l = 2n + 1$ and $h0l$: $l = 2n + 1$ indicating space group $I2/c$ or Ic . The dimensions of the unit cell were determined from powder data collected with a Guinier–Hägg camera (Cu $K\alpha_1$ radiation, $\lambda = 1.54051$ Å, 295 K) with Al (cubic, $a = 4.04934$ Å) as an internal standard. A single crystal, $0.08 \times 0.10 \times 0.14$ mm, mounted along b was used for data collection on an automatic diffractometer of type CAD-4. Intensity data were measured at a take-off angle of 5° with Cu $K\alpha$ radiation. A graphite monochromator was used. The ω – 2θ scan technique was employed with a scan interval $\Delta\omega = 1.00^\circ + 0.15^\circ \tan \theta$. The background was measured for one quarter of the scan time at each end of the peak scan interval. All 1226 independent reflexions in the range $5^\circ < \theta < 70^\circ$ were measured. Of these reflexions, 230 with $I < 3\sigma_c(I)$ were considered insignificantly different from the background and excluded from the refinement. The values of $\sigma_c(I)$ were based on counting statistics. The reflexions 200 and 204 were selected as standards, and the intensity of one of them was recorded every hour. The fluctuation in the intensities of the standard reflexions was random and less than 5%. The reflexions were corrected for Lorentz, polarization and absorption effects [$\mu(\text{Cu } K\alpha) = 1.29$ mm⁻¹]. The transmission factor evaluated by numerical integration varied from 0.849 to 0.905.

The multi-solution tangent refinement method *MULTAN* (Germain, Main & Woolfson, 1971) was used for the structure determination. The systematic extinctions were consistent with two space groups, but the E statistics were decidedly in favour of the centrosymmetric space group $I2/c$ (non-standard setting of space group $C2/c$). In the subsequent full-matrix least-squares refinements it became evident that the data were affected by extinction, and it was necessary to give the 16 strongest reflexions zero weight at an early stage. With isotropic thermal parameters the refinements gave $R = 0.149$. The positions of the H atoms were found in a difference

* To whom correspondence should be addressed.

Fourier synthesis based on data with $(\sin \theta)/\lambda \leq 0.5 \text{ \AA}^{-1}$. An isotropic extinction parameter was introduced (Coppens & Hamilton, 1970) but could not quite compensate the F_o values for the four strongest reflexions, whereas a slight overcorrection was induced for most of the other strong reflexions. These four reflexions (200, 202, 002, 202) were therefore excluded from all remaining computations. With anisotropic temperature factors for the non-H atoms and isotropic temperature factors for the H atoms the refinements converged at $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.041$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.050$ with

$\sum w_i(|F_o| - |F_c|)^2$ being the function minimized. Weights, $w = 1/\sigma^2(F_o)$, were applied in which $\sigma^2(F_o)$ was modified to $\sigma^2(F_o) = \sigma^2(F_o) + (0.008F_o)^2$. In the final cycle the shifts in the parameters were $< 0.1 \sigma$. A final difference Fourier synthesis showed no peaks higher than 0.3 e \AA^{-3} . The refined value of the extinction parameter $g = 0.0069 (7) \times 10^4$ corresponds to a mosaic spread of $14'3''$ if the crystal is of type (I) and a domain size of $1.06 \times 10^{-5} \text{ mm}$ if it is of type (II). Scattering factors and real and imaginary dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). The positional parameters are given in Table 1.* The computations

Table 1. Atomic coordinates ($\times 10^5$ for N, O and C and $\times 10^4$ for H), and equivalent (non-H atoms) and isotropic thermal parameters with e.s.d.'s in parentheses

	x	y	z	$B_{eq}*/B(\text{\AA}^2)$
N(1)	0	37037 (13)	$\frac{1}{2}$	2.5 (3)
N(2)	0	60968 (14)	$\frac{1}{2}$	2.8 (4)
H(11)	521 (23)	3376 (15)	1718 (34)	2.4 (6)
H(12)	588 (21)	4027 (13)	3216 (30)	1.3 (4)
H(21)	570 (27)	5803 (17)	3231 (40)	3.6 (7)
H(22)	553 (27)	6403 (16)	1813 (38)	3.4 (7)
O(1)	25590 (11)	38080 (6)	375 (19)	2.6 (3)
O(2)	12120 (13)	25562 (7)	2642 (23)	3.6 (3)
O(3)	29683 (12)	18629 (7)	-3525 (20)	2.8 (3)
O(4)	14842 (12)	51439 (7)	-5462 (20)	2.9 (3)
O(5)	33315 (12)	57143 (7)	4429 (23)	3.2 (3)
C(1)	33047 (17)	31421 (10)	-566 (30)	2.2 (3)
C(2)	23836 (16)	24862 (10)	-379 (24)	2.2 (3)
C(3)	34084 (16)	44256 (10)	2483 (28)	2.5 (3)
C(4)	26367 (17)	51376 (10)	195 (25)	2.2 (3)
H(1)	3803 (23)	3137 (13)	-1229 (30)	1.3 (5)
H(2)	3930 (21)	3114 (12)	1112 (28)	0.8 (4)
H(3)	3840 (20)	4406 (12)	1557 (30)	0.8 (4)
H(4)	4100 (23)	4403 (12)	-744 (30)	1.3 (4)
H(5)	2809 (31)	6268 (17)	372 (44)	4.7 (8)

* B_{eq} according to Hamilton (1959).

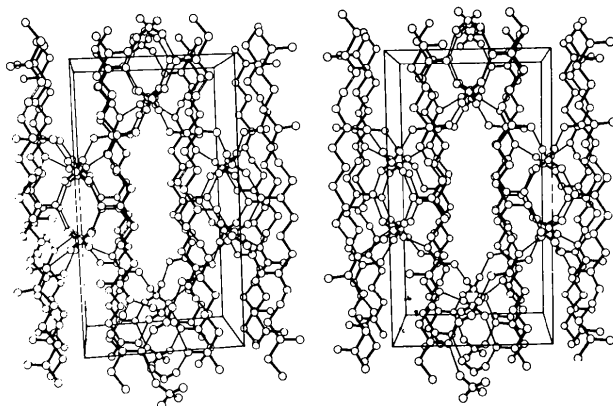


Fig. 1. A stereoscopic view of the structure of AMHOXY. The O—H...O bonds are drawn unfilled, and the H...O bonds from NH_4^+ are drawn with thin lines. The origin is at the rear, lower, left corner with a horizontal, b vertical and c out of the page. Figs. 1–3 were drawn using the program ORTEP II (Johnson, 1976).

* Lists of structure factors and anisotropic temperature factors including r.m.s. components along the principal axes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36231 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

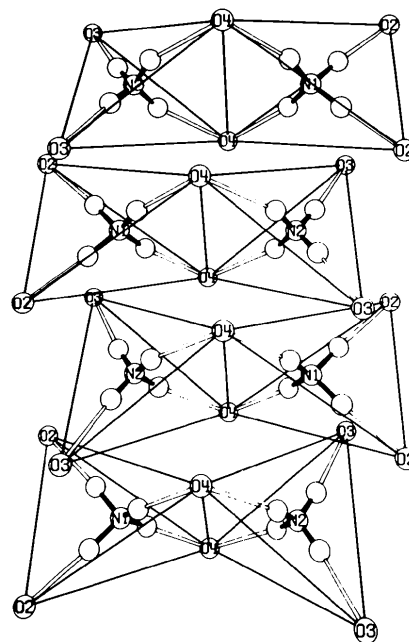


Fig. 2. The coordination around the NH_4^+ ions.

Table 2. Coordination distances (\AA) and angles ($^\circ$) in AMHOXY

2N(1)—O(2)	2.891 (2)	2N(2)—O(3)	2.929 (2)
2N(1)—O(4)	2.894 (2)	2N(2)—O(4)	3.012 (2)
2N(1)—H(11)—O(2)	166 (2)	2N(2)—H(21)—O(4)	161 (3)
2N(1)—H(12)—O(4)	167 (2)	2N(2)—H(22)—O(3)	167 (3)

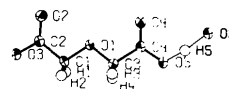


Fig. 3. The oxidiacetate ion and the hydrogen bond. Thermal ellipsoids are scaled to include 50% probability.

Table 3. Selected interatomic distances (Å) and angles (°)

E.s.d.'s of dihedral angles are $<2^\circ$. The superscript (i) refers to the symmetry code $\frac{1}{2} - x, \frac{1}{2} + y, z$.

(a) The ligand

O(1)—C(1)	1.418 (2)	C(1)—O(1)—C(3)	110.2 (1)
O(1)—C(3)	1.411 (2)	O(1)—C(1)—C(2)	109.3 (1)
C(1)—C(2)	1.504 (2)	O(1)—C(3)—C(4)	110.1 (1)
C(3)—C(4)	1.507 (2)	C(1)—C(2)—O(2)	121.9 (2)
C(2)—O(2)	1.217 (2)	C(1)—C(2)—O(3)	113.1 (1)
C(2)—O(3)	1.290 (2)	O(2)—C(2)—O(3)	125.0 (2)
C(4)—O(4)	1.226 (2)	C(3)—C(4)—O(4)	122.1 (2)
C(4)—O(5)	1.285 (2)	C(3)—C(4)—O(5)	112.4 (2)
O(2)—O(3)	2.224 (2)	O(4)—C(4)—O(5)	125.6 (2)
O(4)—O(5)	2.233 (2)	O(1)—C(1)—H(1)	109 (1)
O(1)—O(2)	2.640 (2)	O(1)—C(1)—H(2)	109 (1)
O(1)—O(4)	2.666 (2)	C(2)—C(1)—H(1)	109 (1)
O(1)—O(3)	3.534 (2)	C(2)—C(1)—H(2)	109 (1)
O(1)—O(5)	3.471 (2)	H(1)—C(1)—H(2)	111 (2)
C(1)—H(1)	0.98 (2)	O(1)—C(3)—H(3)	109 (1)
C(1)—H(2)	1.03 (2)	O(1)—C(3)—H(4)	109 (1)
C(3)—H(3)	1.02 (2)	C(4)—C(3)—H(3)	110 (1)
C(3)—H(4)	1.00 (2)	C(4)—C(3)—H(4)	109 (1)
		H(3)—C(3)—H(4)	110 (2)

(b) Dihedral angles

O(1)—C(1)—C(2)—O(2)	-8.6	C(2)—C(1)—O(1)—C(3)	173.0
O(1)—C(1)—C(2)—O(3)	172.0	C(1)—O(1)—C(3)—C(4)	170.5
O(1)—C(3)—C(4)—O(4)	9.9		
O(1)—C(3)—C(4)—O(5)	-171.4		

(c) The hydrogen bond

O(3)⋯O(5)	2.450 (2)	O(3)⋯H(5)—O(5)	171 (3)
O(3)⋯H(5)	1.33 (3)	C(2)—O(3)⋯H(5)	115 (1)
O(5)—H(5)	1.13 (3)	C(4)—O(5)—H(5)	117 (2)

(d) The ammonium ions

N(1)—H(11)	0.97 (2)	H(11)—N(1)	H(11)	105 (3)
N(1)—H(12)	0.97 (2)	H(11)—N(1)—H(12)		109 (2)
N(2)—H(21)	0.93 (3)	H(11)—N(1)—H(12)		114 (2)
N(2)—H(22)	0.93 (3)	H(12)—N(1)—H(12)		106 (3)
		H(21)—N(2)—H(21)		111 (4)
		H(21)—N(2)—H(22)		105 (2)
		H(21)—N(2)—H(22)		115 (2)
		H(22)—N(2)—H(22)		108 (3)

Table 4. Deviations (Å) from least-squares planes through the independent halves in the oxydiacetate ion (the points have been given individual weights based on the e.s.d.'s of the atomic coordinates)

Atoms defining planes: (I) O(1), C(1), C(2), O(2), O(3); (II) O(1), C(3), C(4), O(4), O(5). The angle between the planes is 28.9° .

Plane I		Plane II	
O(1)	-0.035 (2)	O(1)	-0.039 (2)
C(1)	0.101 (3)	C(3)	0.103 (2)
C(2)	0.020 (2)	C(4)	0.011 (2)
O(2)	0.017 (2)	O(4)	0.016 (2)
O(3)	-0.032 (2)	O(5)	-0.043 (2)

were carried out on the CD CYBER 172 computer in Umeå, with programs described by Antti (1976).

Discussion. The structure (Fig. 1) is composed of chains of oxydiacetate ions along **b**. The oxydiacetate residues are linked end-to-end by short hydrogen bonds into infinite chains forming layers parallel to the *ab* plane. The layers are held together by NH_4^+ ions stacked along **c**. This creates broad empty channels $3 \times 8 \text{ \AA}$ parallel to the *c* axis.

The coordination around the two independent NH_4^+ ions is fourfold, best described as tetrahedral (Fig. 2). The N—(H)—O distances, listed in Table 2, range between 2.891 (2) and 3.012 (2) Å, in agreement with values found for fourfold coordination. The shortest N—N distance is 3.558 (1) Å, and the polyhedra surrounding two adjacent NH_4^+ ions have one edge in common. Each NH_4^+ ion coordinates four different oxydiacetate ions. No chelate is formed and each ligand coordinates four NH_4^+ ions, one by O(2), one by O(3) and two by the O(4) atom.

The oxydiacetate ion is shown in Fig. 3 and its interatomic distances, angles, and dihedral angles are given in Table 3. The oxydiacetate ion is non-planar. It is bent and twisted around the ether oxygen and the angle between the ligand halves is 28.9° . The non-H atoms in each half of the ligand are almost coplanar and the deviations from the least-squares planes through the ligand halves are given in Table 4.

The hydrogen-bond system in AMHOXY has a very short O—H—O distance of 2.450 (2) Å. The hydrogen bond is shorter than in all the other mentioned alkali hydrogen oxydiacetates. It is very difficult to determine the position of the H atom in a hydrogen bond with X-ray methods. A neutron diffraction study is therefore planned in order to decide whether the hydrogen bond is asymmetric or symmetric.

References

- ALBERTSSON, J., GRENTHE, I. & HERBERTSSON, H. (1973a). *Acta Cryst.* **B29**, 1855–1860.
 ALBERTSSON, J., GRENTHE, I. & HERBERTSSON, H. (1973b). *Acta Cryst.* **B29**, 2839–2844.
 ANTTI, B.-M. (1976). *Acta Chem. Scand. Ser. A*, **30**, 24–30.
 COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71–83.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
 HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
 HERBERTSSON, H. (1976). *Structural Studies of Some Solid Dicarboxylic Acids and Their Alkali Hydrogen Salts*. Thesis, Stockholm, Sweden.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–98, 149. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.