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Hydrogen Bond Studies. CIII.* Monomethylammonium Hydrogen Oxalate: an X-ray Structure Determination

BY JOHN O. THOMAS

Institute of Chemistry, Uppsala University, Box 531, S-751 21 Uppsala, Sweden

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Abstract. Monoclinic, $P2_1/n$, $a=9.143$ (1), $b=8.248$ (1), $c=7.548$ (1) Å, $\beta=96.30$ (1)°, $V=565.72$ Å³ at 25°C, $\text{CH}_3\text{NH}_3\text{HC}_2\text{O}_4$, $Z=4$, $D_x=1.420$ g cm⁻³. Single-crystal four-circle diffractometer data. The HC_2O_4^- ions are linked by 2.515 (2) Å O–H...O bonds to form infinite chains along [101]. Transverse linkage between these chains is *via* a complex network of N–H...O bonds from the CH_3NH_3^+ cation. Dihedral twist between COO planes within the oxalate group is 1.1 (1)°.

Introduction. $\text{CH}_3\text{NH}_3\text{HC}_2\text{O}_4$ was prepared by bubbling air through a mixture of $\text{CH}_3\text{NH}_3\text{Cl}$ and excess NaOH, and slowly adding water. Crystallization ensued on passing the resulting gas (an air– CH_3NH_2 mixture) through a concentrated solution of oxalic acid in alcohol. Recrystallization from 80% ethanol gave flat rectangular crystals. The crystals sublime above 150°C and melt while decomposing at ~180°C. The crystal selected for data collection measured 0.30 × 0.22 × 0.08 mm. A preliminary film investigation indicated absences $h0l$ for $h+l$ odd and $0k0$ for k odd (β angle for $P2_1/c$ was ~126°). Cell parameters were refined from 34 θ values measured on a Guinier–Hägg XDC-700 powder camera calibrated with silicon. Intensity data were collected on a Stoe–Philips four-circle X-ray diffractometer with graphite monochromatized Mo $K\alpha$ radiation [for further details see Thomas (1972)]. In all, 1754 reflexions were measured out to $\sin \theta/\lambda=0.593$ Å⁻¹. After removal of systematic absences and averaging of hkl and $h\bar{k}l$ reflexions, 991 reflexions remained of which 728 were greater than 2σ and used in the refinements. An absorption correction ($\mu=1.43$ cm⁻¹) was made, making use of an explicit description of the crystal shape and size.

The structure was solved by direct methods following the iterative procedure programmed by Long (1965). Hydrogen atoms were subsequently located unambiguously in a difference synthesis. The weighting function used in the full-matrix least-squares refinement (based on F) was: $w=1/\sigma^2(F)$; where $\sigma^2(F)=\sigma^2(F^2)/4F^2$ and $\sigma^2(F^2)=\sigma_{\text{count}}^2(F^2)+(0.05F^2)^2$.

The refined value of g , the isotropic extinction parameter (Coppens & Hamilton, 1970), was 4630 (1770). Final $R(F)$ and $R_w(F)$ values were 0.044 and 0.056, respectively, for 102 refined parameters. Atomic scattering factors for C, N and O were those of Hanson, Herman, Lea & Skillman (1964), and for H those of Stewart, Davidson & Simpson (1965).

Final positional and thermal parameters are given in Tables 1 and 2.†

Discussion. Hydrogen oxalate ions exhibit a strong tendency to form infinite chains in crystal structures. The internal geometry of the ion would nevertheless appear to be readily distortable. The dihedral angle between the COO planes has been found to be as large as 12.9° [in $\text{NaHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$: Tellgren & Olovsson (1971)]; significant variations have also been found in the C–O lengths [see, for example, $\text{N}_2\text{H}_5\text{HC}_2\text{O}_4$ (Ahmed, Liminga & Olovsson, 1968), KHC_2O_4 (Einspahr, Marsh & Donohue, 1972) and $\text{LiHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (Thomas, 1972)]. The geometry of the HC_2O_4^- ion may thus be expected to respond sensitively to changes in the hydrogen-bond environment of the ion chain.

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31015 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* Part CII: *Acta Cryst.* **B31**, 1842–1846.

Table 1. Atomic coordinates ($\times 10^5$) for non-hydrogen atoms and ($\times 10^3$) hydrogen atoms

The isotropic temperature factors for the hydrogen atoms are also given.

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> (Å ²) |
|------|------------|------------|-------------|----------------------------|
| O(1) | 9215 (17) | 30463 (25) | 34334 (23) | |
| O(2) | 14195 (16) | 21366 (25) | 8034 (22) | |
| O(3) | 42949 (19) | 20051 (32) | 20724 (25) | |
| O(4) | 37272 (18) | 28641 (25) | 46765 (21) | |
| C(1) | 17582 (26) | 25635 (28) | 23867 (29) | |
| C(2) | 34169 (26) | 24440 (29) | 30305 (29) | |
| N | 31660 (26) | 3082 (31) | -13433 (30) | |
| C(3) | 21620 (38) | 40 (45) | -29554 (41) | |
| H(1) | 484 (4) | 281 (4) | 509 (4) | 6.3 (8) |
| H(2) | 399 (3) | 76 (4) | -159 (4) | 4.5 (7) |
| H(3) | 276 (3) | 97 (4) | -63 (4) | 3.8 (7) |
| H(4) | 340 (4) | -69 (5) | -64 (4) | 6.9 (9) |
| H(5) | 190 (3) | 97 (4) | -363 (4) | 5.9 (8) |
| H(6) | 133 (3) | -55 (4) | -272 (4) | 4.6 (7) |
| H(7) | 256 (4) | -62 (5) | -376 (6) | 7.3 (11) |

Here, and in the two papers which follow (Thomas & Pramatus, 1975; Thomas & Renne, 1975), the response to successive methyl substitution of an accompanying NH_4^+ cation is observed.

Two views of the structure are given in Figs. 1 and 2; bond distances and angles in Fig. 3. More extensive data relating to the hydrogen-bond scheme are given in Table 3. As might have been expected from the large number of potential hydrogen-bond donors and acceptors, the hydrogen-bond system is relatively complex. The HC_2O_4^- ions link by means of asymmetric $\text{O}-\text{H}\cdots\text{O}$ bonds of length 2.515 (2) Å to form chains along [101]. The dihedral angle between the COO planes within the ion is 1.1 (1)°, and the angle between the least-squares planes through the heavy atoms of successive ions in the chains is 39.0°. The chains are linked transversely in a three-dimensional network of hydrogen bonds from the CH_3NH_3^+ cation

Table 2. Anisotropic thermal parameters ($\times 10^4$)

The temperature factor is defined as: $\exp[-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$. The r.m.s. components of thermal displacement along the principal axes of the thermal vibration ellipsoids ($R_i \times 10^3$ Å) are also provided for the non-hydrogen atoms.

| | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} | R_1 | R_2 | R_3 |
|------|--------------|--------------|--------------|--------------|--------------|--------------|---------|---------|---------|
| O(1) | 62 (2) | 248 (5) | 145 (4) | 30 (2) | 0 (2) | -64 (3) | 154 (3) | 183 (3) | 310 (3) |
| O(2) | 59 (2) | 254 (4) | 110 (4) | 15 (2) | -18 (2) | -45 (3) | 138 (3) | 186 (3) | 303 (3) |
| O(3) | 66 (2) | 402 (6) | 169 (4) | 31 (3) | 4 (3) | -117 (4) | 160 (3) | 188 (3) | 392 (3) |
| O(4) | 56 (2) | 257 (5) | 117 (4) | 17 (2) | -12 (2) | -42 (3) | 142 (3) | 184 (3) | 305 (3) |
| C(1) | 56 (3) | 115 (5) | 97 (5) | 5 (3) | -5 (3) | -8 (3) | 145 (4) | 173 (4) | 202 (4) |
| C(2) | 53 (3) | 136 (5) | 97 (5) | 3 (3) | -1 (3) | -17 (4) | 145 (4) | 167 (4) | 220 (4) |
| N | 67 (3) | 136 (4) | 126 (4) | -7 (3) | 13 (3) | 4 (4) | 165 (4) | 189 (3) | 218 (4) |
| C(3) | 132 (4) | 181 (7) | 120 (5) | -37 (5) | -21 (4) | 10 (5) | 173 (5) | 219 (5) | 278 (5) |

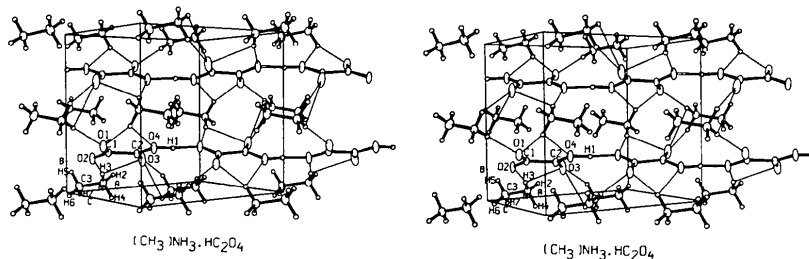


Fig. 1. A general stereoscopic view of the structure. The labelled atoms represent the chosen asymmetric unit. Thermal ellipsoids for the non-hydrogen atoms here and in Fig. 2 are drawn to include 20% probability.

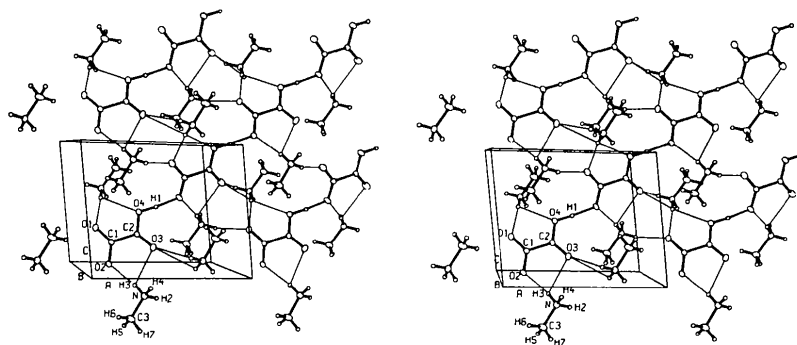


Fig. 2. A stereoscopic view of the structure showing more clearly the HC_2O_4^- ion chains which run along [101].

Table 3. Distances and angles associated with the hydrogen-bond scheme around the cation

The suffices imply the following symmetry operations: (a) $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (b) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (c) $1 - x, -y, -z$.

| N-H...O | N...O | N-H | H...O | \angle N-H...O |
|------------------------------|-------------|------------|------------|------------------|
| N-H(2)...O(1) _a | 2.883 (3) Å | 0.88 (3) Å | 2.02 (3) Å | 167 (3)° |
| N-H(3)...O(2) | 2.831 (3) | 0.88 (3) | 1.97 (3) | 166 (3) |
| N-H(3)...O(3) | 3.014 (3) | 0.88 (3) | 2.49 (3)* | 119 (2) |
| N-H(4)...O(1) _b | 2.932 (3) | 0.99 (3) | 2.00 (3) | 155 (3) |
| N-H(4)...O(4) _b | 3.020 (3) | 0.99 (3) | 2.46 (3)* | 115 (2) |
| { N-H(2)...O(3) _c | 3.100 (3) | 0.88 (3) | 2.81 (3)* | 101 (2) |
| { N-H(4)...O(3) _c | 3.100 (3) | 0.99 (3) | 2.70 (3)* | 105 (2) |

* See text.

(see Table 3 and Fig. 3). In the absence of neutron-diffraction determined proton positions, a precise description of the hydrogen-bond scheme is clearly open to speculation. Of the H...O contacts indicated by thin lines in Fig. 3, however, only H(2)...O(1), H(3)...O(2) and H(4)...O(1) are likely to fall within the currently accepted upper limit of 2.4 Å for a hydrogen-bond interaction distance (Olovsson & Jönsson, 1975). The other contacts merely represent weak electrostatic interactions.

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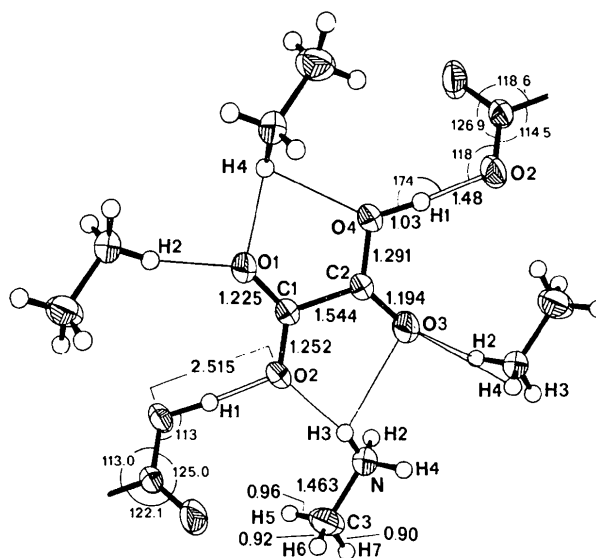


Fig. 3. Bond distances and angles in the structure. Thermal ellipsoids for the non-hydrogen atoms are drawn to include 50% probability. The average standard deviations are X-X: 0.003 Å, X-H: 0.03 Å, \angle X-X-X: 0.2°, \angle X-X-H (or \angle X-H-X): 2°.

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