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# The Structure of Hexamethylenediammonium Bis(monohydrogen oxalate) Monohydrate, $C_6H_{18}N_2^{2+}.2C_2HO_4^-.H_2O$

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**Abstract.** $M_r = 314$, monoclinic, $P2/n$, $a = 11{\cdot}207$ (5), $b = 5{\cdot}690$ (1), $c = 12{\cdot}275$ (2) Å, $\beta = 105{\cdot}41$ (2)°, $V = 754{\cdot}6$ (4) Å$^3$, $Z = 2$, $D_m = 1{\cdot}36$, $D_x = 1{\cdot}38$ gcm$^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}3$ cm$^{-1}$, $F(000) = 336$, $T = 298$ K, $R = 0{\cdot}044$ for 1271 reflections. The crystal structure is stabilized by a network of hydrogen bonds involving all the H atoms of the ammonium and carboxylate groups, and the water molecule.

**Introduction.** Crystal structure determination of small biomolecules forms part of a continuing program in this laboratory. One class of such compounds is the polyamines. The structures of polymethylenediammonium compounds form interesting analogues of the polyamines. The crystal structures of these compounds in the form of carboxylates are being studied in this laboratory. These compounds form intermediates in Nylon manufacture.

**Experimental.** $D_m$ by flotation, transparent crystals (from aqueous solution), $0{\cdot}4 \times 0{\cdot}3 \times 0{\cdot}2$ mm, Enraf–Nonius CAD-4 diffractometer (at Indian Institute of Technology, Madras), cell parameters refined from angular positions of 21 strong accurately centred reflections, Lp correction, absorption ignored, 2348 reflections with $2\theta < 60°$, 1922 unique, 1271 observed reflections with $F_o \geq \sigma(F_o)$, solution using *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), anisotropic full-matrix refinement (Gantzel, Sparks & Trueblood, 1961) H (from $\Delta F$ synthesis) isotropic, final $R = 0{\cdot}044$, $R_w = 0{\cdot}044$, $w = 1/F_o^2$ if $|F_o| \geq |F_o|_{\min}$ and $w = 1/F_{o\,\min}^2$ if $|F_o| < |F_o|_{\min}$ with $|F_o|_{\min} = 15{\cdot}0$. Scattering factors for nonhydrogens from *International Tables for X-ray crystallography* (1974), for hydrogens from Stewart, Davidson & Simpson (1965).†

Table 1. *Atomic coordinates* (× 10$^4$) *and isotropic thermal parameters*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j B_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{\rm eq}$(Å$^2$) |
|---|---|---|---|---|
| C(1) | 6568 (2) | 493 (3) | −24 (2) | 2·2 |
| C(2) | 6207 (2) | −1971 (4) | −539 (2) | 2·4 |
| C(3) | 9955 (2) | −3445 (4) | 1607 (2) | 3·3 |
| C(4) | 10881 (2) | −1735 (5) | 1361 (2) | 3·7 |
| C(5) | 10331 (2) | 341 (4) | 606 (2) | 3·3 |
| O(1) | 6042 (2) | 2160 (3) | −624 (1) | 3·3 |
| O(2) | 7331 (2) | 643 (3) | 909 (1) | 3·3 |
| O(3) | 5493 (2) | −2215 (3) | −1454 (1) | 4·1 |
| O(4) | 6743 (1) | −3680 (3) | 128 (1) | 3·6 |
| N(1) | 9176 (2) | −2359 (4) | 2282 (2) | 2·8 |
| *W* | 7500 | 4127 (4) | 2500 | 2·6 |

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

| | | | |
|---|---|---|---|
| C(1)–C(2) | 1·547 (3) | N(1)–C(3) | 1·489 (4) |
| C(1)–O(1) | 1·249 (2) | C(3)–C(4) | 1·511 (4) |
| C(1)–O(2) | 1·237 (2) | C(4)–C(5) | 1·526 (4) |
| C(2)–O(3) | 1·202 (2) | C(5)–C(5′) | 1·526 (3) |
| C(2)–O(4) | 1·309 (2) | | |
| O(1)–C(1)–O(2) | 126·5 (2) | C(1)–C(2)–O(4) | 113·0 (2) |
| O(1)–C(1)–C(2) | 114·6 (2) | N(1)–C(3)–C(4) | 112·3 (3) |
| O(3)–C(2)–C(1) | 121·6 (2) | C(3)–C(4)–O(5) | 115·6 (3) |
| O(3)–C(2)–O(4) | 125·4 (2) | C(4)–C(5)–C(5′) | 114·1 (3) |
| O(2)–C(1)–C(2) | 118·9 (2) | | |

**Discussion.** Atomic coordinates are given in Table 1, bond lengths and angles in Table 2. The molecule is shown in Fig. 1.

As expected, the entire crystal structure is stabilized by a network of hydrogen bonds in which all the hydrogens of the ammonium and carboxylate groups and the water molecule take part. Both ammonium groups of hexamethylenediamine are protonated, while only one carboxyl group of the oxalic acid is deprotonated. The three protons of the $NH_3^+$ group are hydrogen bonded to two oxygen atoms of different carboxylate groups and to the water molecule with the expected approximate tetrahedral disposition. The water molecule is acceptor from two $NH_3^+$ groups and donor to two oxygens of two different carboxylate groups. In addition there is a strong O—H···O hydrogen bond (2·59 Å) involving the hydrogen of the carboxylate group (Table 3). The packing of the molecule is shown in Fig. 2, with the hydrogen bonds indicated by dashed lines.

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† Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bonds and angles involving H and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38456 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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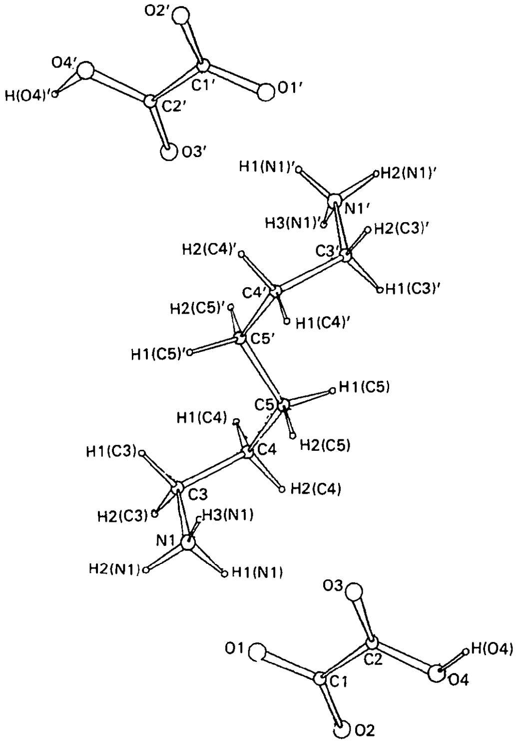

Fig. 1. Perspective view of the molecule.

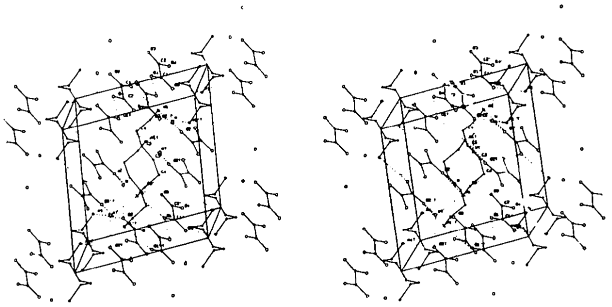

Fig. 2. Packing of the molecule in stereo using molecular plotting program (Radhakrishnan, 1982).

Table 3. *Hydrogen bonding: bond lengths* (Å) *and angles* (°)

| *D*–H···*A* | *D*–H | *D*···*A* | H···*A* | *D*–H···*A* |
|---|---|---|---|---|
| *W*–H(*W*)···O(2) | 0·86 (3) | 2·753 (2) | 1·91 (3) | 170 (2) |
| N(1)–H[1(N1)]···O(1) | 0·91 (3) | 2·853 (3) | 2·06 (3) | 144 (3) |
| N(1)–H[2(N1)]···*W** | 0·93 (3) | 2·805 (3) | 1·92 (3) | 159 (2) |
| N(1)–H[3(N1)]···O(2) | 0·91 (3) | 2·860 (3) | 1·96 (3) | 171 (3) |
| O(4)–H(O4)···O(1)* | 0·97 (4) | 2·586 (2) | 1·62 (4) | 170 (3) |

Symmetry code: (*) $x, y-1, z$.

The dihedral angle between the two COO planes of the hydrogen oxalate ion has been found to vary from 0° to as high as 12·9° [in $NaHC_2O_4.H_2O$, Tellgren & Olovsson (1971)] in various structures [see Table 3 of Thomas & Renne (1975)]. In the present structure this angle is 2·09 (3)°. The bond lengths and angles in the anion are in agreement with those found in similar structures [see Table 3 in Kuppers (1973) and Table 3 in Thomas & Renne (1975)]. The distance between the planes through two adjacent $C_2HO_4$ ions is 3·225 (2) Å. In the linear chain N(1)–C(3)–C(4)–C(5) the torsion angle around the bond C(3)–C(4) is −65·3 (3)°.

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