

the shorter (Cotton & Kraihanzel, 1962; Cotton, Darensbourg, Klein & Kolthammer, 1982). There are four carbonyl groups in (1). The Mo—C lengths for the mutually *cis* CO groups (*trans* to the bidentate phosphine ligand) are shorter than that of the mutually *trans* one [1.993 (5), 1.976 (5) vs 2.022 (5), 2.038 (5) Å]. But the two mutually *cis* CO groups in (1) have larger Mo—C distances than in (2) [1.948 (4) Å]. This trend which is also found in Mo(CO)<sub>4</sub>(dppp) (Ueng & Hwang, 1991) and Mo(CO)<sub>2</sub>(dppp)<sub>2</sub> (Chow, Wang, Sheu & Peng, 1986) [1.968 (5) vs 1.913 (8), 1.938 (9) Å] may be attributed to the presence of only two stronger  $\pi$ -acceptor CO ligands in the latter compound instead of four in the former. The bite angle,  $\angle$ P—Mo—P, of (1) is slightly smaller than that of (2) [78.56 (4) vs 79.85 (3) Å]. This order does not coincide the fact that  $\angle$ P—Mo—P in Mo(CO)<sub>4</sub>(dppp) is larger than that in Mo(CO)<sub>2</sub>(dppe)<sub>2</sub> [89.74 (4) vs 85.55 (8), 86.76 (8) Å]. The ranges of the P—C bond lengths [1.814 (5) to 1.851 (3) Å] and the C—C bond lengths in the phenyl groups [1.366 (8) to 1.402 (5)] for both title compounds are reasonable. From the C=C bond lengths [1.332 (7); 1.316 (5) Å] and the  $\angle$ P—C—C bond angles [119.8 (4), 120.6 (4); 119.9 (2), 121.7 (3)°] of the chelate rings, it is obvious that the distortions of the C=C double bonds are negligible when the bidentate ligands are coordinated to the central metal atom.

Neither title compound has intermolecular contacts of structural significance. Compound (1) has pseudo mirror molecular symmetry through Mo, the middle point of C1—C2 and the two *trans* carbonyl groups. Compound (2) has a crystallographic two-fold axis that coincides with the bisector of  $\angle$ C3—Mo—C3 at [0, *y*,  $\frac{1}{4}$ ]. The dihedral angles

between the two phenyl groups at P1 for (1) and (2) are comparable [101.0 (2) vs 95.6 (2)°], and so are those at P2 [76.9 (2) vs 73.2 (2)°].

The fact that compound (1) and Mo(CO)<sub>4</sub>(dppe) have similar bite angles [78.56 (4); 80.2 (1)°] and have the same Mo—P bond lengths [2.501 (1), 2.494 (1); 2.500 (2), 2.495 (2) Å] suggests that there may be no significant difference from any major electronic effect between *cis*-vpp and dppe ligands.

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## Structure of Sodium Hydrogen Glutarate Dihydrate

BY ALISTAIR L. MACDONALD, PAUL MORRISON AND ALISTAIR MURRAY

*Chemistry Department, Clydebank High School, Shelley Drive, Clydebank G81 3EJ, Scotland*

AND ANDREW A. FREER

*Chemistry Department, University of Glasgow, Glasgow G12 8QQ, Scotland*

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**Abstract.** C<sub>5</sub>H<sub>7</sub>O<sub>4</sub><sup>-</sup>.Na<sup>+</sup>.2H<sub>2</sub>O, *M<sub>r</sub>* = 190.1, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 5.371 (1), *b* = 13.367 (1), *c* = 11.587 (1) Å,  $\beta$  = 93.72 (1)°, *V* = 830.0 Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>*

= 1.52 (by flotation in heptane/iodobutane), *D<sub>x</sub>* = 1.527 g cm<sup>-3</sup>,  $\lambda$ (Cu *K* $\alpha$ ) = 1.5418 Å,  $\mu$  = 16.1 cm<sup>-1</sup>, *F*(000) = 400, *T* = 293 K, *R* = 0.034 for 1602 unique

Table 1. Fractional atomic coordinates with e.s.d.'s in parentheses and isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}}$
Na	0.73358 (10)	0.06766 (4)	0.43584 (5)	0.031
O(1)	0.6057 (2)	0.3268 (1)	0.2979 (1)	0.042
O(2)	0.4719 (2)	0.2196 (1)	0.4267 (1)	0.037
O(3)	-0.0323 (2)	0.4050 (1)	0.7760 (1)	0.041
O(4)	-0.0608 (3)	0.2525 (1)	0.7026 (1)	0.051
O(W1)	1.1181 (2)	0.1074 (1)	0.5487 (1)	0.034
O(W2)	0.6278 (2)	0.0201 (1)	0.6316 (1)	0.033
C(1)	0.4633 (2)	0.3011 (1)	0.3783 (1)	0.027
C(2)	0.2802 (3)	0.3832 (1)	0.4052 (1)	0.034
C(3)	0.0996 (3)	0.3603 (1)	0.4971 (1)	0.030
C(4)	0.2200 (3)	0.3629 (1)	0.6205 (1)	0.036
C(5)	0.0291 (3)	0.3411 (1)	0.7074 (1)	0.030

Table 2. Bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) in the glutarate residues and contact distances around the  $\text{Na}^+$  ion with e.s.d.'s in parentheses

O(1)—C(1)	1.289 (2)	O(2)—C(1)	1.225 (2)
O(3)—C(5)	1.227 (2)	O(4)—C(5)	1.278 (2)
C(1)—C(2)	1.519 (2)	C(2)—C(3)	1.518 (3)
C(3)—C(4)	1.530 (2)	C(4)—C(5)	1.511 (3)
Na $\cdots$ O(W2 <sup>m</sup> )	2.357 (2)	Na $\cdots$ O(3 <sup>m</sup> )	2.334 (2)
Na $\cdots$ O(W1)	2.431 (1)	Na $\cdots$ O(W1')	2.475 (1)
Na $\cdots$ O(W2)	2.458 (1)	Na $\cdots$ O(2)	2.469 (1)
Na $\cdots$ Na <sup>m</sup>	3.502 (1)	Na $\cdots$ Na <sup>i</sup>	3.622 (1)
O(1)—C(1)—O(2)	124.1 (2)	O(1)—C(1)—C(2)	112.2 (2)
O(2)—C(1)—C(2)	123.6 (2)	C(1)—C(2)—C(3)	116.7 (2)
C(2)—C(3)—C(4)	113.6 (2)	C(3)—C(4)—C(5)	110.7 (2)
O(3)—C(5)—O(4)	123.8 (2)	O(3)—C(5)—O(4)	121.3 (2)
O(4)—C(5)—C(4)	114.9 (2)	O(1) $\cdots$ H(11) $\cdots$ O(4)	169 (3)

Symmetry code: (i)  $2-x, -y, 1-z$ ; (ii)  $1+x, \frac{1}{2}-y, -\frac{1}{2}+z$ ; (iii)  $1-x, -y, 1-z$ .

observed reflections. The structure contains very short formally asymmetric hydrogen bonds [O $\cdots$ O 2.410 (2), O—H 1.07 (4), H $\cdots$ O 1.35 (4)  $\text{\AA}$ ] which link glutaric acid residues into infinite chains. Six-coordinate  $\text{Na}^+$  ions linked by water molecules are arranged in columns parallel to **a**. An unusual feature of the structure is that neither of the O atoms involved in the short hydrogen bond is coordinated to the  $\text{Na}^+$  ion.

**Introduction.** Acid salts ( $MH_2Y$ ) of dibasic carboxylic acids ( $H_2Y$ ) with  $M$  a monovalent cation have been classified (Speakman, 1972) as type  $A_2$  when the hydrogen bond linking the acid residues is formally symmetric and as type  $B_2$  when there is no such symmetry requirement. In type  $A_2$  salts the hydrogen bond is usually much shorter than in type  $B_2$  salts and it has been suggested (Speakman, 1972) that the symmetry plays a part in shortening the bond. As part of our systematic investigation of the acid salts of glutaric acid (Macdonald & Speakman, 1971, 1972; Macdonald, Murray & Freer, 1988), we report

here the structural analysis of sodium hydrogen glutarate dihydrate.

**Experimental.** Sodium hydrogen glutarate dihydrate was made by dissolving 1.32 g (0.01 mol) of glutaric acid and 0.4 g (0.01 mol) of sodium hydroxide in water and mixing. Large crystals were obtained on standing. (Attempts to make the anhydrous compound using ethanol as solvent failed to yield suitable crystals.) Crystal size  $0.9 \times 0.5 \times 0.4$  mm. Cell dimensions were derived by least-squares treatment of the  $\theta$  values of 25 reflections measured on an Enraf-Nonius CAD-4 diffractometer with Cu  $K\alpha$  radiation.) 2 standard reflections showed no variation. 1896 independent observed intensities were collected in the range  $\theta < 75^\circ$ ,  $\omega/2\theta$  scan, and of these 1602 satisfied the criterion  $I \geq 3.0\sigma(I)$ ,  $0 \leq h \leq 6$ ,  $0 \leq k \leq 16$ ,  $-14 \leq l \leq 14$ . The crystal structure was solved using the direct phasing procedure *MITHRIL* (Gilmore, 1984). Preliminary least-squares adjustment of the coordinates of the C, O and Na atoms followed by difference Fourier synthesis enabled the location of all the H-atom positions. Refinement with anisotropic thermal parameters for the C, O and Na atoms and H atoms isotropic (154 parameters) converged at  $R = 0.034$ ,  $wR = 0.065$  with weights  $w \propto 1/\sigma^2(F_o)$ .  $\Delta_{\text{max}}/\sigma$  for non-H atoms = 0.57 and 0.60 for H atoms.  $S = 14.4$ . Max. and min. heights in the final difference Fourier synthesis were 0.18 and  $-0.26 \text{ e \AA}^{-3}$ . Fourier, least-squares and geometry calculations were performed with the *GX* system of programs (Mallinson & Muir, 1985). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol.

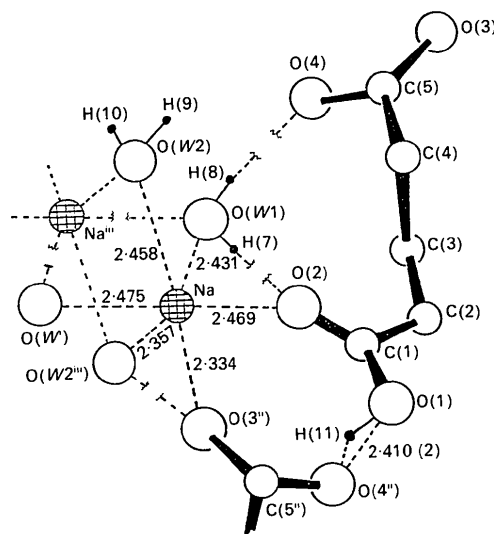


Fig. 1. View of part of the structure of sodium hydrogen glutarate dihydrate approximately perpendicular to the  $bc$  plane showing the atom-numbering scheme and interatomic distances ( $\text{\AA}$ ).

IV). Atomic coordinates are given in Table 1.\* Bond lengths and bond angles are listed in Table 2. The main details of the structure are shown in Fig. 1.

**Discussion.** The structure contains columns of water-bridged  $\text{Na}^+$  ions arranged parallel to **a** and centred at  $0, \frac{1}{2}, 0$  and  $0, 0, \frac{1}{2}$ . Within the columns, centrosymmetric pairs of  $\text{Na}^+$  ions are bridged by two water molecules; the symmetry-independent water molecules link alternate pairs of bridged  $\text{Na}^+$  ions along the columns with  $\text{Na}^+\cdots\text{O}$  in the range 2.357 (2)–2.475 (1) Å. The glutarate residue is hydrogen bonded to one of the bridging water molecules [ $\text{O}(W1)\text{—H}\cdots\text{O}$  2.844 (2) and 2.865 (2) Å] such that opposite ends of each residue join to the same water molecule forming ten-membered rings (Fig. 1). In addition, the carbonyl O atoms of each glutarate residue bond to two different  $\text{Na}^+$  ions [ $\text{Na}^+\cdots\text{O}(3)$  2.334 (2) and  $\text{Na}^+\cdots\text{O}(2)$  2.469 (1) Å] rendering

\* 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 53578 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

each  $\text{Na}^+$  ion six-coordinate. Adjacent  $\text{Na}^+\text{—H}_2\text{O}$  columns are linked through glutarate residues both by these  $\text{Na}^+\cdots\text{O}$  (carbonyl) contacts and by hydrogen bonds to the  $\text{O}(W2)$  water molecules [ $\text{O}(1)\cdots\text{H—O}(W2)$  2.819 (2),  $\text{O}(3)\cdots\text{H—O}(W2)$  2.816 (2) Å]. The glutarate residues [ $\text{—O}_2\text{C}(\text{CH}_2)_3\text{CO}_2\text{H}$ ] are linked into infinite chains along **c** by very short asymmetric hydrogen bonds [ $\text{O}(1)\cdots\text{O}(4)$  2.410 (2),  $\text{O}(1)\text{—H}(11)$  1.07 (4),  $\text{H}(11)\cdots\text{O}(4)$  1.35 (4) Å]. This is the shortest intermolecular hydrogen bond so far reported in acid salts and is amongst the shortest  $\text{O—H}\cdots\text{O}$  bonds yet found. It is all the more remarkable that the bond appears to be asymmetric.

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## Structure of a 4:1 Adduct of Cadmium(II) Chloride with 15-Crown-5 Ether

BY ALAN HAZELL AND RITA GRØNBÆK HAZELL

*Institute of Chemistry, Aarhus University, DK-8000 Århus C, Denmark*

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**Abstract.** Cadmium(II) chloride–1,4,7,10,13-pentaoxacyclopentadecane–water 4/1/1,  $\text{C}_{10}\text{H}_{20}\text{Cd}_4\text{Cl}_8\text{O}_5\cdot\text{H}_2\text{O}$ ,  $M_r = 971.55$ , orthorhombic, *Pnma*,  $a = 10.224$  (2),  $b = 11.353$  (2),  $c = 25.146$  (6) Å,  $V = 2919$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.211$  Mg m<sup>-3</sup>,  $\text{Mo } K\alpha$  ( $\lambda = 0.71073$  Å),  $\mu = 3.63$  mm<sup>-1</sup>,  $F(000) = 1832$ ,  $T = 295$  K,  $R(F) = 0.056$  for 1009 reflexions [ $I > 3\sigma(I)$ ] and 137 variables. The structure contains double chains built of  $\text{CdCl}_6$  and  $\text{CdCl}_5\text{H}_2\text{O}$  octahedra each sharing three edges. Adjacent unshared Cl atoms are linked by Cd atoms which are themselves coordinated to crown-ether molecules. Cd—Cl distances are 2.535 (7) to 2.586 (7) Å for Cl atoms which are shared between two Cd atoms and 2.629 (7) to 2.759 (6) Å for those shared by three.

**Introduction.** The dihalides of cadmium form a variety of complexes with 15-crown-5 ether (15C5) (Wulfsberg & Weiss, 1977; Hazell & Hazell, 1990).

During the recrystallization from ethanol of the 3:1 adduct of  $\text{CdCl}_2$  with 15C5, a batch of needle-shaped crystals with a different morphology from that of the 3:1 complex were obtained. These crystals have been studied by X-ray diffraction and shown to be a 4:1 adduct which also contained water.

**Experimental.**  $\text{Cd}_4\text{Cl}_8\cdot 15\text{C}_5\cdot\text{H}_2\text{O}$  was obtained from an ethanolic solution of 15C5 and  $\text{CdCl}_2$  which in spite of the addition of triethyl orthoformate was not completely dry. The crystals were needles elongated in the **b** direction and bounded by {101} and {001}. A crystal,  $0.05 \times 0.14 \times 0.31$  mm, was mounted on a Huber diffractometer. Cell dimensions were determined from the setting angles of 30 reflexions with  $15 < 2\theta < 27^\circ$  measured with  $\text{Mo } K\alpha$  radiation at  $2\theta, \omega, \chi, \varphi$ ;  $-2\theta, -\omega, \chi, \varphi$ ;  $2\theta, \omega, 180 + \chi, \varphi$  and  $-2\theta, -\omega, 180 + \chi, \varphi$ . Intensities were measured out to  $(\sin\theta/\lambda)_{\text{max}} = 0.595$  Å<sup>-1</sup> using an  $\omega$ - $2\theta$  scan and