Structure of Caesium Hydrogen Bis(dibromoacetate)

By T. Głowiak, V. Videnova, J. Baran and H. Ratajczak

Institute of Chemistry, University of Wrocław, 50–383 Wrocław, Joliot-Curie 14, *Poland*

Abstract. $CsH(C_2HBr_2O_2)_2$, $C_4H_3Br_4O_4^-.Cs^+$, FW = 467·6, triclinic, $P\bar{1}$, $a = 11·496$ (4), $b = 7·848$ (3), $c = 6·791$ (3) Å, $\alpha = 90·49$ (5), $\beta = 102·35$ (5), $\gamma = 97·78$ (5)°, $V = 592·5$ Å³, $Z = 2$, $\mu = 17·40$ mm⁻¹, Mo $K\alpha$ radiation, $D_c = 3·189$ Mg m⁻³. The final $R = 0·084$ for 1774 reflections with $I \geq 1·96\sigma(I)$. The crystal is built up from Cs^+ cations and hydrogen bis(dibromoacetate) anions. The two dibromoacetate residues are linked by a non-symmetric hydrogen bond with $O(2)\cdots O(4) = 2·50$ (2) Å.

Introduction. A great deal of interest has been shown recently in the study of the properties of strong hydrogen bonds. Strong hydrogen bonds appear in crystals of the acid salts of acetic and halogenoacetic acids. In our laboratory a systematic study has been undertaken of the crystal structure and vibrational properties of $M(+1)$ hydrogen bis(dibromoacetates) and hydrogen bis(tribromoacetates) ($M = K^+$, Rb^+, Cs^+ and NH_4^+). In this paper the crystal structure of the title compound is presented.

$CsH(Br_2CHCOO)_2$ $[CsH(dba)_2]$ crystals were obtained by the slow evaporation of a solution containing caesium and dibromoacetic acid in stoichiometric ratio. Thin colourless rhombohedral plates were grown.

The unit-cell dimensions and intensity data were measured with a Syntex $P2_1$ four-circle diffractometer with a graphite monochromator and Mo $K\alpha$ radiation. Measurements were made on a single crystal approximately $0·12 \times 0·15 \times 0·11$ mm. Intensities of 2298 reflections were collected using the θ–2θ scan technique to $2\theta = 60°$. From the total collection, 1774 reflections with $I \geq 1·96\sigma(I)$ were retained for further calculation. The data were corrected for Lorentz and polarization factors, but not for absorption. The structure was solved by the heavy-atom technique. No attempt was made to locate the H atoms. The function minimized during refinement was $\sum w(|F_c| - |F_o|)^2$ with $w = 1/\sigma^2(F)$. The least-squares refinement was carried out by the full-matrix method with anisotropic temperature factors. B_{eq} values varied between 2·43 and 5·45 Å² (Table 1). The refinement gave $R_1 = 0·084$ and $R_2 = 0·074$. The structure factors were calculated with the neutral atomic scattering factors

taken from *International Tables for X-ray Crystallography* (1974). Calculations were performed on a Nova 1200 computer with Syntex *XTL* structure determination programs, except for the last few least-squares-refinement cycles which were performed with the XRAY 70 program system (Stewart, Kundell & Baldwin, 1970). The final atomic coordinates and their standard deviations are listed in Table 1.*

Discussion. Fig. 1 shows the crystal structure of $CsH(dba)_2$ in ac and ab projections. In the crystal there are well defined $[Br_2CHCOOHOOCHBr_2]^-$ dimeric anions. The two dba residues are not equivalent and their dimensions differ (Table 2). In residue dbaI comprising $C(1)$, $C(2)$, $O(1)$, and $O(2)$ there are C=O and C—O bonds. The C—O and C=O distances differ by 0·091 Å and the C—C—O angle is smaller than C—C=O by 8·2°. In the other residue, dbaII, comprising $C(3)$, $C(4)$, $O(3)$, and $O(4)$, the C—O distances differ by only 0·041 Å and the C—C—O angles by only 1·9°. These small differences may be questionable and so the dbaII residues seem to have the

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35355 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *with e.s.d.'s in parentheses and* B_{eq} (Å²) *for* $CsH(Br_2CHCOO)_2$

	x	y	z	B_{eq}
Cs	5552 (1)	2487 (1)	2626 (1)	2·98
Br(1)	2541 (2)	3667 (3)	9495 (3)	3·96
Br(2)	1893 (2)	3819 (3)	4769 (3)	4·56
O(1)	3886 (12)	1050 (17)	5611 (19)	3·37
O(2)	4684 (11)	3354 (17)	7685 (22)	4·18
C(1)	3803 (17)	2238 (23)	6703 (29)	2·62
C(2)	2546 (16)	2488 (25)	7005 (24)	2·86
Br(3)	8922 (2)	1745 (3)	6168 (3)	4·41
Br(4)	9289 (2)	2009 (4)	10907 (3)	5·45
O(3)	6414 (12)	430 (17)	9337 (21)	5·22
O(4)	6707 (11)	2684 (16)	7415 (18)	3·04
C(3)	7031 (16)	1390 (24)	8406 (25)	2·43
C(4)	8276 (15)	947 (24)	8429 (25)	2·62

structure with the COO⁻ group. Nevertheless, in the infrared spectra we did not observe the bands arising from the COO⁻-group vibrations (Videnova, 1979). The C—C distances [C(1)—C(2) 1·54 (3) Å and C(3)—C(4) 1·52 (3) Å] do not differ significantly from the corresponding bonds in the previously investigated acid salts of acetic acid (Speakman & Mills, 1961; Currie, 1972) and halogenoacetic acids (Macdonald, Speakman & Hadži, 1972; Golič & Speakman, 1965; Ichikawa, 1972, 1974; Leban, 1974; Golič & Lazarini, 1974, 1975). These distances are shorter than the corresponding distance in the potassium [1·57 (4) Å; Baran, Videnova, Głowiak & Ratajczak, 1979] and rubidium [1·60 (3) Å; Videnova, Baran, Głowiak & Ratajczak, 1980] hydrogen bis(dibromoacetates). The C and O atoms of each residue are virtually coplanar.

Fig. 1. Projections of the crystal structure of caesium hydrogen bis(dibromoacetate) on (a) the ac, and (b) the ab planes.

Table 2. *Interatomic distances* (Å) *and angles* (°) *in the dibromoacetate residues*

dbaI		dbaII	
C(1)—O(1)	1·21 (2)	C(3)—O(3)	1·24 (2)
C(1)—O(2)	1·30 (2)	C(3)—O(4)	1·28 (2)
C(1)—C(2)	1·54 (3)	C(3)—C(4)	1·52 (3)
C(2)—Br(1)	1·92 (2)	C(4)—Br(3)	1·92 (2)
C(2)—Br(2)	1·93 (2)	C(4)—Br(4)	1·94 (2)
O(1)—C(1)—O(2)	126·5 (1·8)	O(3)—C(3)—O(4)	126·2 (1·7)
O(1)—C(1)—C(2)	118·4 (1·7)	O(3)—C(3)—C(4)	116·0 (1·6)
O(2)—C(1)—C(2)	115·1 (1·6)	O(4)—C(3)—C(4)	117·9 (1·6)
C(1)—C(2)—Br(2)	104·9 (1·2)	C(3)—C(4)—Br(4)	105·5 (1·2)
C(1)—C(2)—Br(1)	114·7 (1·2)	C(3)—C(4)—Br(3)	114·3 (1·2)
Br(1)—C(2)—Br(2)	109·4 (1·0)	Br(3)—C(4)—Br(4)	109·8 (1·0)

The planes through the C and O atoms are $-0·0249X + 0·6234Y - 0·7815Z + 2·5756 = 0$ and $-0·1161X - 0·5571Y - 0·8223Z + 5·8374 = 0$ respectively for the dbaI and dbaII residues. The angle between the planes through dbaI and dbaII is 72·6 (1·5)°.

The two dba residues are linked by a non-symmetric hydrogen bond, with a distance of 2·50 (2) Å between O(2) and O(4). The O···O distance is one of the longest in the acid salts of a halogenoacetic acid so far known. According to the results obtained, the $CsH(Br_2CHCOO)_2$ crystal can be referred to the pseudo-A-type acid salts in the Speakman (1972) classification. The diffraction data are supported by the vibrational properties of this crystal. In the infrared spectra a broad, strong band at ~1000 ± 100 cm⁻¹ is observed. This band is connected with the v_a(OHO) stretching vibrations of the hydrogen bonds. The detailed vibrational properties (the infrared polarized spectra and Raman spectra) will be presented in a following paper.

There are no other unusual non-bonded inter-molecular contacts in the structure, the shortest being O(1)—C(3) [3·22 (2) Å] and O(3)—C(1) [3·45 (2) Å]. The Cs⁺ ion makes contact with eight O and three Br atoms. The Cs—O and Cs—Br distances, which are all shorter than 4·0 Å, are shown in Fig. 1(b).

References

BARAN, J., VIDENOVA, V., GŁOWIAK, T. & RATAJCZAK, H. (1979). *Acta Cryst.* B35, 2722–2723.
CURRIE, M. (1972). *J. Chem. Soc. Perkin Trans.* 2, pp. 832–835.
GOLIČ, L. & LAZARINI, F. (1974). *Cryst. Struct. Commun.* 3, 645–648.
GOLIČ, L. & LAZARINI, F. (1975). *Cryst. Struct. Commun.* 4, 487–490.
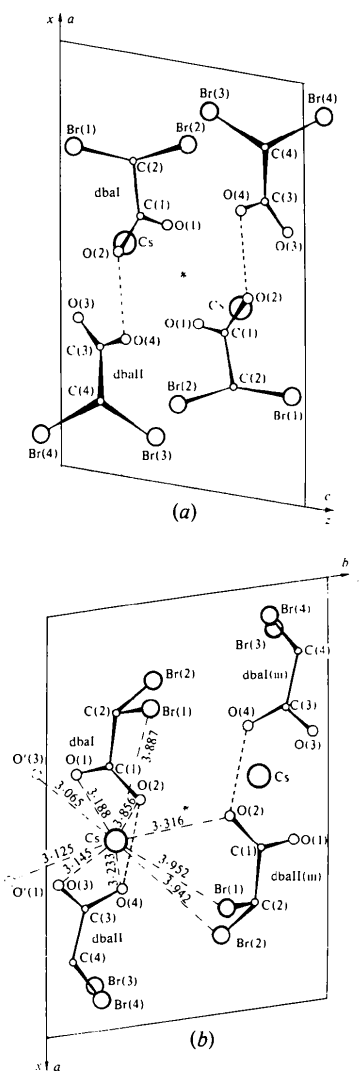GOLIČ, L. & SPEAKMAN, J. C. (1965). *J. Chem. Soc.* pp. 2530–2542.

ICHIKAWA, M. (1972). *Acta Cryst.* B28, 755–760.
ICHIKAWA, M. (1974). *Acta Cryst.* B30, 651–655.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
LEBAN, I. (1974). *Cryst. Struct. Commun.* 3, 245–248.
MACDONALD, A. L., SPEAKMAN, J. C. & HADŽI, D. (1972). *J. Chem. Soc. Perkin Trans.* 2, pp. 825–832.
SPEAKMAN, J. C. (1972). *Struct. Bonding (Berlin)*, 12, 141–199.

SPEAKMAN, J. C. & MILLS, H. H. (1961). *J. Chem. Soc.* pp. 1164–1175.
STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.
VIDENOVA, V. (1979). PhD Thesis, Univ. of Wrocław, Poland.
VIDENOVA, V., BARAN, J., GLOWIAK, T. & RATAJCZAK, H. (1980). *Acta Cryst.* B36, 459–461.

Magnesium (+)-Malate Pentahydrate

BY W. VAN HAVERE AND A. T. H. LENSTRA

University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium

Abstract. $Mg(C_4H_4O_5).5H_2O$, $P2_12_12_1$, $a = 5.923$ (3), $b = 11.340$ (2), $c = 15.397$ (3) Å, $Z = 4$, $d_{calc} = 1.583$ Mg m^{-3}. The conformation of the $^-OOC-C-C-COO^-$ chain is *gauche*. Mg^{2+} is coordinated by a slightly distorted octahedron of O atoms. The title compound is compared with cobalt(II) and zinc malate trihydrate; these latter salts are expected to be isomorphous with magnesium malate trihydrate. In the trihydrates the malic acid moiety behaves as a tridentate ligand to the metal, whereas in the title compound it behaves as a bidentate ligand with one COO^- group coordinated by water molecules and not by a Mg^{2+} ion.

Introduction. The crystals of $Mg(C_4H_4O_5).5H_2O$ were grown by slow evaporation of an aqueous solution at room temperature. Reflections up to $\theta = 30°$ were measured on an Enraf–Nonius CAD-4 diffractometer using Zr-filtered Mo radiation. An ω/θ scan with a 6:1 speed ratio was applied. The scan angle was given by $0.6° + 0.35°$ tan θ and the aperture of the detection unit was set to $(1.0 + 1.0$ tan $\theta)$ mm. From the systematic extinctions the space group $P2_12_12_1$ was inferred. In view of the crystal size $(0.25 \times 0.20 \times 0.15$ mm) and the linear absorption coefficient $(\mu = 0.222$ mm^{-1}) no absorption correction was applied.

The structure was solved using *MULTAN* (Germain, Main & Woolfson, 1971); the most likely E map with 200 terms showed all non-hydrogen atoms. A subsequent difference electron density map revealed the positions of the H atoms.

From a total of 1772 reflections, 1241 with $I > 2\sigma(I)$ were used in the refinement employing the Gauss–Seidel block method (Sparks, 1974), in which each

reflection was given a weight based on counting statistics. During the refinement the Debye–Waller temperature factor of the H atoms was kept fixed at 3.0 Å^2 ($B_{Wilson} = 2.6$ Å^2). After refinement of the isotropic extinction parameter (Zachariasen, 1963), $r = 0.54 \times 10^{-8}$ m, the R value converged to 0.027. R is defined by $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ for observed reflections only. The maximum noise level in the final difference Fourier map is 0.30 e Å^{-3}.

Refined parameters are listed in Table 1 and the numbering of the atoms is illustrated in Fig. 1.*

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35376 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
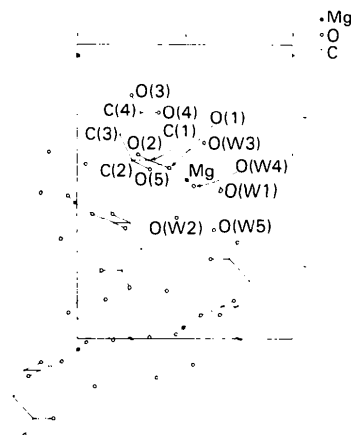

Fig. 1. Crystal packing of Mg (+)-malate pentahydrate projected on to the *yz* plane. The octahedral coordination of Mg is shown by dotted lines.