Acta Cryst. (1979). B35, 2722–2723

The Structure of Potassium Hydrogen Bis(dibromoacetate)

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

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

(*Received* 17 *May* 1979; *accepted* 31 *July* 1979)

Abstract. $KH(C_2HBr_2O_2)_2$, $K^+.C_4H_3Br_4O_4^-$, FW 473·8, orthorhombic, *Pbcn*, $a = 20·716\ (5)$, $b = 7·102\ (3)$, $c = 7·744\ (3)$ Å, $V = 1139·3$ Å^3, $Z = 4$, $\mu = 15·30$ mm^{-1}, Mo $K\alpha$, $D_c = 2·76$ Mg m^{-3}. The structure was refined to $R = 0·078$ for 590 reflections with $I \geq 1·92\sigma(I)$. The bis(dibromoacetate) anions and K^+ cations form layers parallel to (100). The two dibromoacetate residues are linked through a symmetric $\bar{1}$ hydrogen bond with O···O = 2·44 (3) Å.

Introduction. In our laboratory a systematic study has been undertaken of the crystal structures and vibrational properties of acid salts of dibromoacetic acid. In this paper the crystal structure of the title compound is presented.

Crystals were prepared by addition of aqueous potassium carbonate to dibromoacetic acid solution in the stoichiometric ratio (pH = 1) followed by slow evaporation, whereupon colourless thin plates were formed.

Cell dimensions and intensities were measured on a Syntex $P2_1$ four-circle diffractometer with a graphite monochromator and Mo $K\alpha$ radiation. The lattice parameters and orientation matrix were obtained by least squares from 15 reflections. Intensities of 1296 reflections were collected by the θ–2θ scan technique to $2\theta = 60°$. 590 reflections were accepted for further calculations $[I \geq 1·92\sigma(I)]$. The intensity of a standard reflection was measured every 15 reflections and showed no significant change. The data were corrected for Lorentz and polarization factors, but not for absorption.

Table 1. *Atomic coordinates* (×10^4) *with e.s.d.'s in parentheses*

	x	*y*	*z*
K	5000 (0)	3688 (19)	2500 (0)
Br(1)	1373 (1)	1171 (6)	1204 (4)
Br(2)	2029 (1)	3588 (7)	4139 (4)
O(1)	0479 (10)	5079 (32)	4086 (31)
O(2)	0472 (11)	1963 (31)	4218 (27)
C(1)	0672 (13)	3414 (45)	3729 (36)
C(2)	1277 (13)	3465 (48)	2522 (41)

Symmetry code

(i) $0·0 + x, 0·0 + y, 0·0 + z$
(ii) $0·5 - x, 0·5 + y, 0·0 + z$
(iii) $0·0 + x, 0·0 - y, 0·5 + z$
(iv) $0·5 - x, 0·5 - y, 0·5 + z$
(v) $0·0 - x, 0·0 - y, 0·0 - z$
(vi) $-0·5 + x, -0·5 - y, 0·0 - z$
(vii) $0·0 - x, 0·0 + y, -0·5 - z$
(viii) $-0·5 + x, -0·5 + y, -0·5 - z$

The structure was solved by the heavy-atom technique. The positions of all the non-hydrogen atoms were found from Patterson and difference maps. H atoms were ignored. The refinement gave $R_1 = 0·078$ and $R_2 = 0·088$. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All calculations were carried out on the Nova minicomputer with programs supplied by Syntex. The final atomic coordinates are listed in Table 1.*

Discussion. In the crystal there are well defined dimeric anions $H(Br_2CHCOO)_2^-$ which are in the (*b*) positions of $\bar{1}$ symmetry and make layers parallel to (100), Fig. 1. In the layer the anions are connected by K^+ cations, which are on a twofold axis [(*c*) position]. The K^+ cations make contact with four O(2) and four O(1) atoms. The K^+···O(1) distances are all >3·0 Å and K^+···O(2) distances all <3·0 Å, Table 2. Two neighbouring layers are in contact through Br atoms. The distances between the closest Br atoms in adjacent layers are >4·0 Å, *i.e.* they are greater than twice the ionic radius of a Br^- ion. Therefore the interactions between neighbouring layers are very weak. This explains the presence of a cleavage plane parallel to (100).

Two crystallographically equivalent dibromoacetate residues are bonded by a strong symmetric ($\bar{1}$) hydrogen bond with O(1)···O(1)^v = 2·44 (3) Å. The C and O atoms of the dimeric anions are virtually coplanar, Table 3, the maximum deviation being <1σ. In each residue the C—O distances [1·28 (4) and 1·17 (4) Å] differ by 0·1 Å and the C—C—O angles [129·2 (3)° and 110·9 (3)°] by 18·3°, Table 4. The C—C distances do not differ significantly from the corresponding bonds in other acid salts of acetic acid (Speakman & Mills, 1961; Currie, 1972) and halo-

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34651 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0567-7408/79/112722-02$01.00

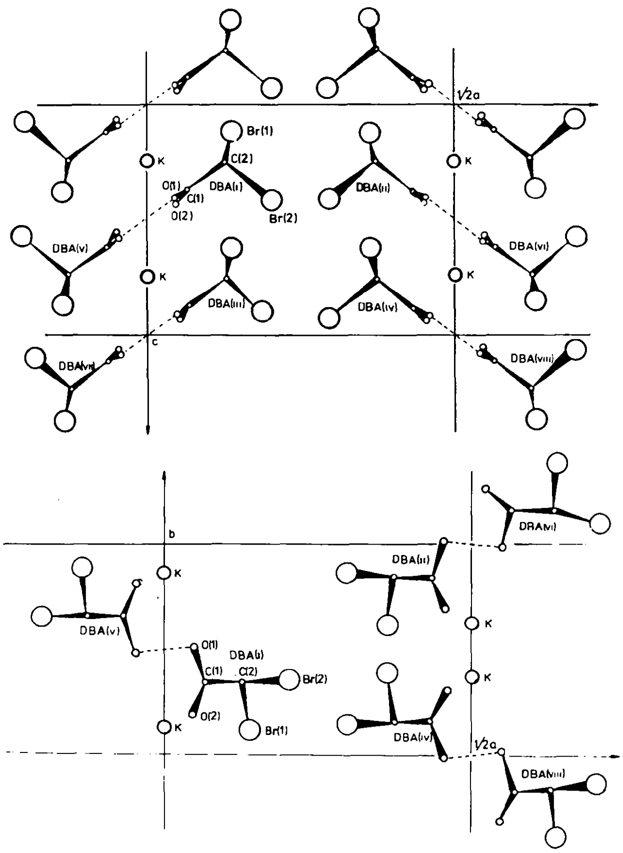

Fig. 1. Projection of the crystal structure of $KH(Br_2CHCOO)_2$ (*a*) on the *ac* plane and (*b*) on the *ab* plane.

Table 2. *The environment of a potassium cation*

K–O(1)^a	3·01 (3) Å
K–O(1)^b	3·01 (3)
K–O(2)^c	2·85 (3)
K O(2)^d	2·85 (3)
K–O(2)^e	2·76 (2)
K–O(2)^f	2·76 (2)
K–O(1)^e	3·89 (3)
K–O(1)^f	3·89 (3)

Symmetry code

(*a*)	0·5 – *x*,	–0·5 + *y*,	0·0 + *z*
(*b*)	0·5 + *x*,	–0·5 + *y*,	0·5 – *z*
(*c*)	0·5 – *x*,	0·5 + *y*,	0·0 + *z*
(*d*)	0·5 + *x*,	0·5 + *y*,	0·5 – *z*
(*e*)	0·5 – *x*,	0·5 – *y*,	–0·5 – *z*
(*f*)	0·5 + *x*,	0·5 – *y*,	1·0 – *z*

genoacetic acids (Macdonald, Speakman & Hadži, 1972; Golič & Speakman, 1965; Ichikawa, 1972, 1974; Leban, 1974; Golič & Lazarini, 1974, 1975). The C–Br distances [1·93 (3), 2·00 (3) Å] are greater than those in caesium hydrogen bis(dibromoacetate) (Głowiak, Videnova, Baran & Ratajczak, 1980).

According to our results the potassium hydrogen bis(dibromoacetate) crystal can be referred to as an *A*-type acid salt in the Speakman (1972) classification. The diffraction data are supported by the vibrational properties of this crystal. In the infrared spectrum a broad and very strong band at 870 cm^{-1} is observed. This band is connected with the ν_a OHO stretching vibrations of hydrogen bonds. The detailed vibrational properties will be presented in a subsequent paper.

Table 3. *Molecular plane for* $KH(Br_2CHCOO)_2$

Plane through C(1),C(2),O(1),O(2)

$$-0{\cdot}6057X - 0{\cdot}0329Y - 0{\cdot}7950Z + 3{\cdot}2333 = 0$$

Distances of atoms from the plane (Å)

Br(1)	0·741 (4)
Br(2)	–1·945 (4)
K	–4·6662 (4)

Table 4. *Interatomic distances* (Å) *and angles* (°) *in the dibromoacetate residue*

C(1)–O(1)	1·28 (4)	O(1)–C(1)–O(2)	129·2 (3)
C(1)–O(2)	1·17 (4)	O(1)–C(1)–C(2)	110·9 (3)
C(1)–C(2)	1·57 (4)	O(2)–C(1)–C(2)	119·7 (3)
C(2)–Br(1)	1·93 (3)	C(1)–C(2)–Br(1)	112·2 (2)
C(2)–Br(2)	2·00 (3)	C(1)–C(2)–Br(2)	104·4 (2)
Br(1)–Br(2)	3·156 (6)	Br(2)–C(2)–Br(1)	106·7 (1)

The authors thank the Polish Academy of Sciences for support (MR-I-9).

References

Currie, M. (1972). *J. Chem. Soc. Perkin Trans.* 2, pp. 832–835.

Głowiak, T., Videnova, V., Baran, J. & Ratajczak, H. (1980). *Acta Cryst.* To be published.

Golič, L. & Lazarini, F. (1974). *Cryst. Struct. Commun.* **3**, 645–649.

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.* B**28**, 755–760.

Ichikawa, M. (1974). *Acta Cryst.* B**30**, 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.