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X-ray Crystal Structures of Hexabromotellurates of Organic Ions.
I. Crystal Structure of the Hexabromotellurate of DL-α-Ammonio-*n*-butyric Acid

By Françoise Dahan and Odette Lefèbvre-Soubeyran

Laboratoire de Cristallochimie, CNRS, ER N° 63, Tour 44, 11 Quai Saint-Bernard, 75005-Paris, France

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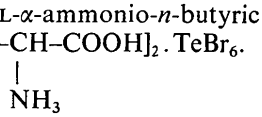
The structure of the hexabromotellurate of DL-α-ammonio-*n*-butyric acid has been determined by the heavy-atom method and refined by full-matrix least squares to a final R of 0·041 for 1049 independent reflexions. Crystals are monoclinic, space group $P2_1/c$, with $a=11\cdot443$ (4), $b=7\cdot881$ (3), $c=12\cdot886$ (4) Å, $\beta=112\cdot19$ (5)°, $Z=2$. The crystalline cohesion is controlled by N–H···Br and O–H···O hydrogen bonds and by intermolecular van der Waals forces.

Introduction

Gillespie & Nyholm (1957) predicted that hexacoordinated complexes of $\mathrm{Te^{IV}}$ and $\mathrm{Se^{IV}}$ should not possess a regular octahedral structure but rather one based on seven coordination with a lone pair of electrons occupying the seventh position. However, infrared and Raman spectroscopy (Adams & Morris, 1967), nuclear quadrupole resonance spectroscopy (Greenwood, 1970) and electronic spectra (Couch, Wilkins, Rossman & Gray, 1970) showed no distortion of $\mathrm{TeX_6^{2-}}$ octahedra (X = Cl or Br). The general conclusion made by Johnstone, Jones & Vasudev (1972) is that the Te atom employs essentially pure p orbitals in bonding, the $5s^2$ electrons being stereochemically inactive. Thus the $\mathrm{TeX_6^{2-}}$ ions are octahedral and have relatively long weak Te–X bonds when electronegativity of the ligand increases. No significant distortion of $\mathrm{TeBr_6^{2-}}$ octahedra was observed in the few X-ray structures reported, $\mathrm{K_2TeBr_6}$ (Brown, 1964), $\mathrm{(NH_4)_2TeBr_6}$ and $\mathrm{Cs_2TeBr_6}$ (Das & Brown, 1966).

Crystalline salts containing $\mathrm{TeBr_6^{2-}}$ anions, and cations of protonated amino acids or protonated amides, have been synthesized (Dobrowolski & Pastuszak, 1970; Bujewski & Dobrowolski, 1973). Professor Dobrowolski suggested an X-ray study of a compound of each kind in order to compare the regularity of the $\mathrm{TeBr_6^{2-}}$ ions and the influence of the different organic cations.

The structure described here is the hexabromotellurate of DL-α-ammonio-*n*-butyric acid



$$[\mathrm{CH_3{-}CH_2{-}\underset{\substack{|\\ NH_3}}{CH}{-}COOH}]_2\,.\,\mathrm{TeBr_6}.$$

Experimental

A single crystal 0·15 × 0·075 × 0·075 mm was selected for the X-ray investigation.

The intensities were collected on a CAD-3 Enraf-Nonius diffractometer in the θ–2θ scan mode. The range of each scan consisted of the base width of 1·0° at 2θ = 0° and an increment, Δ(2θ) = 0·5 tan θ°, to allow for spectral dispersion; background counts were taken at the extremes of the scan for a time equal to the time required for the scan itself. With Ni-filtered Cu $K\alpha$ radiation, 2022 reflexions up to $\theta = 66°$ were measured. Throughout the data collection, two reference reflexions were recorded after each sequence of 40 measured reflexions. The intensities of the standards remained constant to within ±2·5%.

With $I \leq 3\sigma(I)$, 973 reflexions were considered unobserved. Standard deviations $\sigma(I)$ were calculated from

$$\sigma(I) = \{I + I_1 + I_2 + [0{\cdot}02(I - I_1 - I_2)]^2\}^{1/2},$$

where I_1 and I_2 are the background and I the peak counts. The remaining 1049 reflexions were used in the structure determination. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Crystal data are given in Table 1.

Table 1. *Crystal data*

$(C_4H_{10}NO_2)_2TeBr_6$, M.W. 815
$F(000) = 752$
Space group $P2_1/c$
$a = 11{\cdot}443$ (4), $b = 7{\cdot}881$ (3), $c = 12{\cdot}886$ (4) Å
$\beta = 112{\cdot}19$ (5)°, $U = 1076$ Å^3, $Z = 2$
$D_m = 2{\cdot}52$, $D_c = 2{\cdot}516$ g cm^{-3}
$\mu = 262$ cm^{-1} [λ(Cu $K\alpha$) = 1·5418 Å]

Structure determination

The structure was solved by the heavy-atom method. The Te atom is at the origin in space group $P2_1/c$. A Fourier map phased on Te gave the three Br atoms of the asymmetric unit. From the subsequent Fourier synthesis all the non-hydrogen atoms were revealed.

Calculations were performed on an IBM 370/168 computer with a local version of *ORFLS* (Busing, Martin & Levy, 1962) for refinement and with NRC programs (Ahmed, Hall, Pippy & Huber, 1966) for geometrical calculations.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1962) for Te, Br$^-$, O, N and C and from Stewart, Davidson & Simpson (1965) for H. Correction for anomalous dispersion was carried out for Te ($\Delta f' = -0{\cdot}9$) and Br ($\Delta f' = -0{\cdot}9$) atoms.

Full-matrix least-squares calculations were used to refine the atomic coordinates and isotropic temperature factors of all non-hydrogen atoms. R fell to 0·108 and was reduced to 0·050 with anisotropic thermal parameters $[R = \sum w(||F_o| - |F_c||)/\sum w|F_o|]$.

All H atoms were located in a difference synthesis. The refinement of their coordinates (the isotropic thermal parameters were those of the atoms to which they are bonded) resulted in an R of 0·041. All reflexions were assigned unit weight. The final R_w was 0·045 $\{R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}\}$.

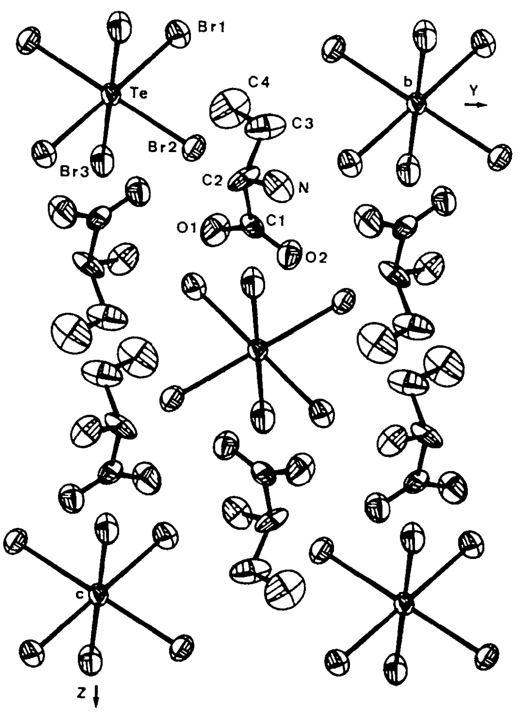


Fig. 1. *ORTEP* structure viewed along **a**. Thermal ellipsoids are at 50% probability.

Table 2. *Fractional atomic coordinates* (× 10^4) *and thermal parameters* (× 10^4)

$T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Estimated standard deviations (× 10^4) are in parentheses. B (in Å^2) is $\frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + 2\beta_{12}ab\cos\gamma + 2\beta_{13}ac\cos\beta + 2\beta_{23}bc\cos\alpha)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B
Te	0	0	0	67 (2)	86 (3)	46 (1)	0 (2)	11 (1)	3 (2)	2·69
Br(1)	1184 (2)	2137 (3)	−915 (2)	97 (2)	136 (4)	73 (2)	−10 (3)	35 (2)	9 (2)	3·90
Br(2)	−748 (2)	2756 (3)	823 (2)	100 (3)	123 (4)	63 (2)	11 (3)	24 (2)	−15 (2)	3·81
Br(3)	2088 (2)	−222 (3)	1879 (2)	98 (3)	120 (4)	72 (2)	−8 (3)	−7 (2)	6 (2)	4·39
O(1)	4612 (17)	3527 (22)	3855 (13)	134 (24)	202 (38)	72 (16)	48 (25)	0 (15)	−21 (19)	5·64
O(2)	3722 (15)	5964 (18)	4068 (13)	102 (20)	122 (29)	76 (15)	23 (20)	12 (14)	−6 (18)	4·38
N	1732 (16)	5532 (22)	2179 (15)	73 (21)	146 (36)	63 (15)	2 (22)	6 (14)	17 (19)	3·96
C(1)	3793 (19)	4729 (27)	3530 (17)	65 (23)	138 (44)	67 (18)	62 (28)	21 (16)	26 (24)	3·37
C(2)	2857 (19)	4483 (28)	2353 (15)	68 (23)	165 (45)	32 (15)	26 (26)	−17 (15)	−21 (20)	3·71
C(3)	3407 (25)	5068 (41)	1462 (19)	132 (34)	301 (71)	64 (20)	79 (47)	22 (21)	−22 (37)	6·14
C(4)	4393 (27)	3918 (47)	1373 (27)	109 (36)	396 (92)	132 (34)	13 (49)	62 (29)	−31 (47)	7·05

The final atomic and thermal parameters are listed in Tables 2 and 3.*

Description and discussion of the structure

Fig. 1. shows the *ORTEP* structure projection along **a** (Johnson, 1965) with the atomic numbering.

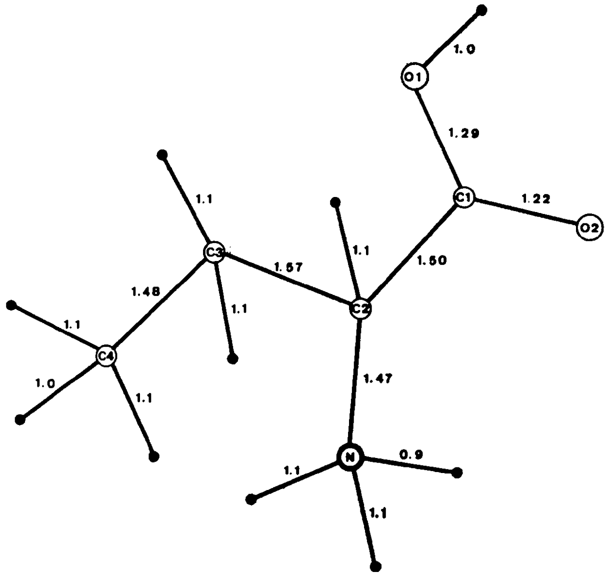


Fig. 2. Bond lengths (Å) in the DL-α-ammonio-*n*-butyric acid ion. $\bar{\sigma}$(C–O) = $\bar{\sigma}$(C–N) = $\bar{\sigma}$(C–C) = 0·03 Å; $\bar{\sigma}$(O–H) = $\bar{\sigma}$(N–H) = $\bar{\sigma}$(C–H) = 0·2 Å.

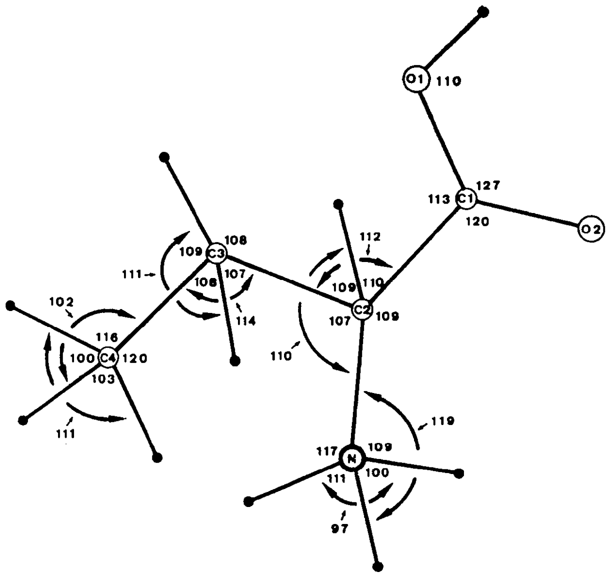


Fig. 3. Bond angles (°) in the DL-α-ammonio-*n*-butyric acid ion. The average e.s.d.'s are 2° for angles not involving H atoms and 13° for the others.

Table 3. *Fractional coordinates* (×10^3) *of the hydrogen atoms with e.s.d.'s* (×10^3) *in parentheses*

	x	*y*	*z*
H(O1)	516 (21)	369 (30)	466 (18)
H1(N)	134 (20)	550 (32)	284 (20)
H2(N)	99 (19)	557 (26)	136 (17)
H3(N)	195 (18)	657 (26)	225 (15)
H1(C3)	381 (21)	633 (31)	170 (18)
H2(C3)	262 (19)	510 (30)	65 (17)
H1(C4)	516 (25)	354 (33)	218 (21)
H2(C4)	391 (24)	278 (36)	115 (21)
H3(C4)	476 (23)	411 (34)	73 (19)
H(C2)	258 (18)	311 (29)	220 (18)

Hexabromotellurate anion

Interatomic distances and angles for the $TeBr_6^{2-}$ ion are listed in Table 4. Detailed examination of the individual values indicates a slight angular distortion of the octahedron. The Te–Br distances range from 2·689 to 2·695 Å, the Br–Br distances from 3·725 to 3·895 Å, the Br–Te–Br angles from 87·44 to 92·56°. The deviation from cubic symmetry is not large.

Table 4. *Interatomic distances* (Å) *and angles* (°) *for the* $TeBr_6^{2-}$ *ion with e.s.d.'s in parentheses*

ii denotes the centrosymmetric position $\bar{x},\bar{y},\bar{z}$.

Te–Br(1)	2·695 (3)	Te–Br (3)	2·689 (3)
Te–Br (2)	2·695 (3)	Mean Te–Br	2·693
Br(1)–Br(2)	3·725 (4)	Br(1)–Te–Br(2)	87·44 (8)
Br(1)–Br(3)	3·830 (3)	Br(1)–Te–Br(3)	90·68 (8)
Br(2)–Br(3)	3·815 (4)	Br(2)–Te–Br(3)	90·25 (8)
Br(1)–Br(2)^{ii}	3·895 (4)	Br(1)–Te–Br(2)^{ii}	92·56 (8)
Br(1)–Br(3)^{ii}	3·785 (4)	Br(1)–Te–Br(3)^{ii}	89·32 (8)
Br(2)–Br(3)^{ii}	3·799 (3)	Br(2)–Te–Br(3)^{ii}	89·75 (8)
Mean Br–Br	3·808	Mean Br–Te–Br	90·00

In K_2TeBr_6 (Brown, 1964) the mean Te–Br is 2·693 Å and the Br–Te–Br angles all lie within 0·3° of 90·0°. The $(NH_4)_2TeBr_6$ and Cs_2TeBr_6 structures (Das & Brown, 1966) present perfect regular $TeBr_6^{2-}$ octahedra by symmetry. Te–Br is 2·681 and 2·695 Å respectively. The mean Te–Br (2·693 Å) in this study is comparable with that found in the other structures. Te–Br bonds lie between covalent bonds, 2·66, and ionic bonds, 2·76, the octahedral Te^{IV} radius being 1·52, the covalent Br radius 1·14, and the ionic bond $Te^{4+}\cdots Br^-$ 2·76 Å (Pauling, 1960).

DL-α-*Ammonio-n-butyric acid*

Bond lengths and angles are shown in Figs. 2 and 3. They are in good agreement with those found by Ichikawa & Iitaka (1968) in DL-α-amino-*n*-butyric acid. The carboxyl group is planar within experimental error (Table 5).

Hydrogen bonding and crystal packing

The hydrogen bonds and angles are listed in Table 6, as are the Br···Br intermolecular distances less than 4·20 Å. The hydrogen-bonding scheme around N is shown in Fig. 4.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31863 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 5. *Equation of the mean plane of carboxyl group and deviations* (Å) *of atoms from this plane, with e.s.d.'s in parentheses*

The plane is represented by an equation of the type $lX+mY+nZ=P$, referred to an orthogonal system of axes, which has X along **a**, Y in the ab plane and Z along **c***.

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

$$0{\cdot}7884X+0{\cdot}5065Y-0{\cdot}3491Z=2{\cdot}4841$$

O(1)	−0·000 (19)	N†	−0·457 (19)
O(2)	−0·000 (17)	C(3)†	1·442 (30)
C(1)	0·001 (22)	C(4)†	1·944 (35)
C(2)	−0·000 (22)		

† Atoms not included in the calculation of the plane.

Table 6. *Hydrogen-bond distances* (Å) *and angles* (°)

Symmetry code

(i)	$x \quad y \quad z$	(v)	$x \quad 1+y \quad z$
(ii)	$-x \quad -y \quad -z$	(vi)	$-x \quad 1-y \quad -z$
(iii)	$-x \quad \frac{1}{2}+y \quad \frac{1}{2}-z$	(vii)	$x \quad \frac{1}{2}-y \quad z-\frac{1}{2}$
(iv)	$x \quad \frac{1}{2}-y \quad \frac{1}{2}+z$		

Atoms belong to molecule i unless otherwise specified.

O(1)–H(O1)···O(2)^{ii}	2·67 (2)	H(O1)···O(2)^{ii}	1·68 (16)
N—H1(N)···Br(1)^{iv}	3·47 (2)	H1(N)···Br(1)^{iv}	2·67 (17)
N—H1(N)···Br(2)^{iii}	3·63 (2)	H1(N)···Br(2)^{iii}	2·73 (18)
N—H2(N)···Br(2)	3·49 (2)	H2(N)···Br(2)	2·88 (18)
N—H2(N)···Br(1)^{vi}	3·61 (2)	H2(N)···Br(1)^{vi}	2·95 (19)
N—H3(N)···Br(3)^{v}	3·41 (2)	H3(N)···Br(3)^{v}	2·59 (17)

O(1)–H(O1)···O(2)^{ii}	170 (15)
N—H1(N)···Br(1)^{iv}	128 (12)
N—H1(N)···Br(2)^{iii}	138 (12)
N—H2(N)···Br(2)	116 (11)
N—H2(N)···Br(1)^{vi}	120 (11)
N—H3(N)···Br(3)^{v}	163 (15)

Intermolecular Br···Br distances (Å) less than 4·200 Å

Br(1)···Br(2)^{vi}	4·063 (4)	Br(1)···Br(3)^{vii}	4·158 (4)
Br(1)···Br(2)^{vii}	3·943 (3)	Br(2)···Br(3)^{iii}	4·134 (4)

The organic ions are linked by O–H···O hydrogen bonds around the centre of symmetry (O–H···O = 2·67 Å), as is usual for carboxylic acids.

Each Br atom is an acceptor of a H atom. Br(3) receives H3(N); Br(1) and Br(2) receive ½H1(N) and ½H2(N) respectively.

In this study we may conclude that the protonated amino acid has no significant influence on the regularity of the octahedron $TeBr_6^{2-}$. Stability is governed by the hydrogen-bond network and intermolecular Br···Br van der Waals contacts so that the packing of the molecules approaches close packing.

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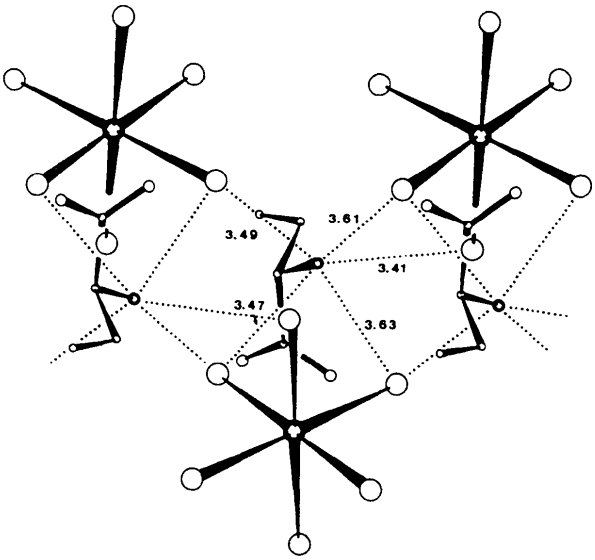

Fig. 4. Hydrogen-bond network around the N atom.

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