Acta Cryst. (1976). B32, 2863

X-ray Crystal Structures of Hexabromotellurates of Organic Ions. II. Crystal Structure of the Monohydrate of the Hexabromotellurate of Protonated Disuccinamide

By Françoise Dahan and Odette Lefèbvre-Soubeyran

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

(*Received* 26 *March* 1976; *accepted* 30 *April* 1976)

The structure of the hexabromotellurate of protonated disuccinamide has been determined by Patterson and Fourier syntheses and refined by full-matrix least squares to a final R of 0·068 for 1121 independent non-zero reflexions. The crystals are monoclinic, space group $C2/c$, with $a=11\cdot092$ (4), $b=13\cdot997$ (5), $c=14\cdot916$ (5) Å, $\beta=105\cdot18$ (5)°, $Z=4$. The crystalline cohesion is governed by a hydrogen-bond network and intermolecular van der Waals forces.

The structure reported here is the hexabromotellurate of protonated disuccinamide $[(CONH_2)_2(CH_2)_2]_2H_2TeBr_6$. It will be compared with the hexabromotellurate of DL-α-ammonio-*n*-butyric acid (Dahan & Lefèbvre-Soubeyran, 1976).

Experimental

A single crystal 0·125 × 0·15 × 0·20 mm was selected for the X-ray investigation. The density was determined by flotation in a mixture of $CHCl_3$ and $CHBr_3$. The measured value, 2·56, is greater than that calculated, 2·500 g cm^{-3}. This was explained later by the presence of a water molecule, the crystals being very sensitive to hydrolysis (Bujewski & Dobrowolski, 1973).

The lattice constants were obtained from a least-squares analysis of the setting of 25 reflexions measured on a four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda=0\cdot7107$ Å).

The intensities were collected on a Philips PW1100 computer-controlled four-circle diffractometer in the ω-scan mode (scan width = 0·8°, scan speed = 0·02 s^{-1}) in the laboratory directed by Dr Pascard at the ICSN (Gif sur Yvette, France).

2141 reflexions up to $\theta=25°$ were measured. Throughout the data collection, three reference reflexions were recorded after each sequence of 66 measured reflexions. The intensities of the standards remained constant to within ±2·5%.

With $I\leq 3\sigma(I)$, 856 reflexions were omitted as unobserved. Standard deviations $\sigma(I)$ were calculated according to counting statistics. 88 other reflexions were absent owing to systematic extinction and 76 were redundant owing to space-group equivalence. The remaining 1121 reflexions were used in the structure determination. The data were corrected for Lorentz and polarization effects, but not for absorption.

The crystal data are given in Table 1.

Table 1. *Crystal data*

$(C_4H_8N_2O_2)_2H_2TeBr_6$, M.W. 841
$F(000)=1552$
Space group $C2/c$
$a=11\cdot092$ (4), $b=13\cdot997$ (5), $c=14\cdot916$ (5) Å
$\beta=105\cdot18$ (5)°, $U=2235$ Å^3, $Z=4$
$D_m=2\cdot56$, $D_c=2\cdot500$ g cm^{-3}
$\mu=127$ cm^{-1} [λ(Mo $K\alpha$) = 0·7107 Å]

Structure determination

The Te atom is in a special position. In space group $C2/c$, it was located from a Patterson function. A first Fourier map phased on its coordinates resulted in the location of the three Br atoms of the asymmetric unit. All the other non-hydrogen atoms appeared on a second Fourier synthesis.

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.

The 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. Corrections for anomalous dispersion were carried out for Te ($\Delta f'=-0\cdot5$) and Br ($\Delta f'=-0\cdot3$).

Full-matrix least-squares calculations were used to refine the atomic coordinates and isotropic temperature factors of all non-hydrogen atoms. R fell to 0·140 and was reduced to 0·089 by anisotropic refinement of Te and Br atoms. Attempts to refine the structure further with anisotropic temperature factors for the organic moiety resulted in one component of the thermal vibrations of several atoms going negative. This is possibly a result of the lack of correction for absorption.

At this stage, a difference synthesis showed a residual atom in the special position $0,y,\frac{1}{4}$. We introduced it as an O atom, presuming the presence of a water molecule in the crystal. The new calculated density is 2·554 g cm^{-3}, in better agreement with the measured value. R converged to 0·071.

On a new difference synthesis, the H atoms of the organic moiety were located. We could not locate the extra proton nor the H atoms of the water molecule. The H atoms found were introduced with the isotropic temperature factors of their atom of attachment. Their coordinates were not refined.

During the last cycles of refinement, the weighting scheme was $w=(0\cdot0037|F_o|^2-0\cdot2740|F_o|+10\cdot6)^{-1}$. The final $R=\sum w||F_o|-|F_c||/\sum w|F_o|=0\cdot068$, $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}=0\cdot080$.

Positional and thermal parameters are listed in Tables 2 and 3.*

Description and discussion of the structure

Fig. 1 shows the structure projection along **c**, with the atomic numbering.

Table 2. *Fractional atomic coordinates* ($\times 10^4$), *isotropic thermal parameters* (*in* Å^2), *and anisotropic temperature factors* ($\times 10^4$) *of the* $TeBr_6^{2-}$ *ion*

Estimated standard deviations are in parentheses.
$T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

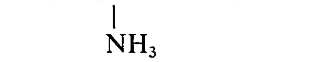
	x	y	z	B
Te	0	368 (1)	2500	1·74 (2)
Br(1)	1599 (2)	1668 (1)	2234 (2)	3·09 (3)
Br(2)	1568 (2)	−1097 (1)	2204 (2)	2·69 (3)
Br(3)	1217 (2)	418 (2)	4321 (1)	2·94 (3)
O(1)	3495 (15)	1614 (11)	−344 (11)	3·2 (3)
N(1)	4162 (18)	2987 (14)	396 (14)	3·1 (4)
C(1)	4374 (20)	2176 (15)	4 (16)	2·5 (4)
C(2)	5703 (21)	1963 (16)	19 (16)	2·7 (4)
C(3)	5875 (22)	1538 (17)	−895 (16)	2·9 (4)
C(4)	5422 (18)	557 (14)	−1135 (14)	2·0 (4)
N(4)	6107 (18)	−37 (14)	−1469 (14)	3·1 (4)
O(4)	4390 (14)	280 (11)	−1019 (10)	3·0 (3)
O(w)	0	6807 (21)	2500	4·9 (5)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Te	46 (1)	11 (1)	27 (1)	0	8 (1)	0
Br(1)	68 (2)	23 (1)	53 (2)	−11 (1)	17 (2)	7 (1)
Br(2)	59 (2)	19 (1)	47 (1)	5 (1)	15 (1)	−3 (1)
Br(3)	83 (2)	26 (1)	31 (1)	0 (1)	4 (1)	2 (1)

Table 3. *Fractional coordinates* ($\times 10^3$) *of the hydrogen atoms*

	x	y	z
H1(C2)	604	146	57
H2(C2)	620	264	14
H1(C3)	689	152	−81
H2(C3)	541	200	−145
H1(N1)	485	332	91
H2(N1)	334	344	29
H1(N4)	683	40	−137
H2(N4)	608	−74	−178

Hexabromotellurate anion

Interatomic distances and angles for the $TeBr_6^{2-}$ ion are listed in Table 4. Examination of the individual values shows an unexpected distortion of the octahedron. Te–Br(1) is a kind of covalent bond, 2·642, Te–Br(2) an ionic bond, 2·798, and Te–Br(3) intermediate, 2·699 Å, if we consider the theoretical values given by Pauling (1960). The mean Te–Br value, 2·713 Å, is a little larger than those found in  $(CH_3CH_2\underset{\displaystyle NH_3}{\underset{|}{C}}HCOOH)_2TeBr_6$ (Dahan & Lefèbvre-Soubeyran, 1976), 2·693; K_2TeBr_6 (Brown, 1964), 2·681; $(NH_4)_2TeBr_6$ and Cs_2TeBr_6 (Das & Brown, 1966), 2·695 Å.

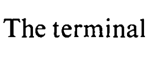
The greatest angular deviation from the ideal octahedron is 4·27°.

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

iii denotes the equivalent position $-x,y,\frac{1}{2}-z$.

Te—Br(1)	2·642 (3)	Te–Br (3)	2·699 (2)
Te—Br(2)	2·798 (3)	Mean Te–Br	2·713
Br(1)–Br(2)	3·870 (3)	Br(1)–Te–Br(2)	90·66 (8)
Br(1)–Br(3)	3·690 (3)	Br(1)–Te–Br(3)	87·41 (8)
Br(1)–Br(1)^{iii}	3·831 (4)	Br(1)–Te–Br(1)^{iii}	92·97 (8)
Br(1)–Br(3)^{iii}	3·796 (4)	Br(1)–Te–Br(3)^{iii}	90·57 (8)
Br(2)–Br(3)	3·907 (3)	Br(2)–Te–Br(3)	90·56 (8)
Br(2)–Br(2)^{iii}	3·807 (4)	Br(2)–Te–Br(2)^{iii}	85·73 (8)
Br(2)–Br(3)^{iii}	3·942 (3)	Br(2)–Te–Br(3)^{iii}	91·59 (8)
Mean Br–Br	3·835	Mean Br–Te–Br	89·93

Disuccinamide moiety

Bond lengths and angles are shown in Figs. 2 and 3. They are similar to those found in succinamide (Davies & Pasternak, 1956). The terminal groups  $-C-C\overset{\displaystyle N}{\underset{\displaystyle O}{\lessgtr}}$ are planar within experimental error (Table 5). The angle between the two planes is 20·7°.

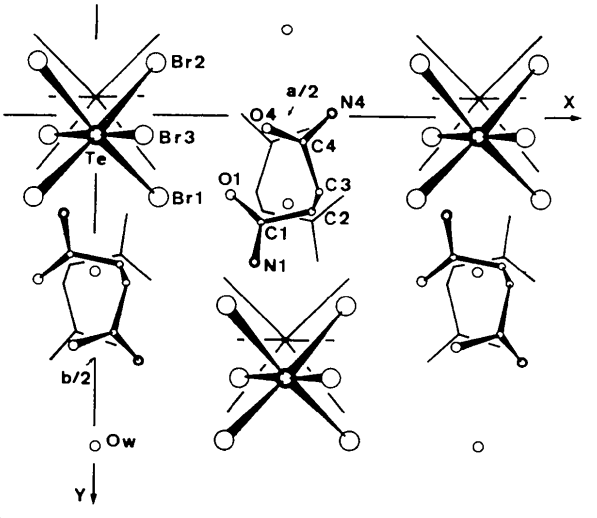


Fig. 1. The structure viewed along **c** with atomic numbering.

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31864 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 5. *Equations of the mean planes and deviations* (Å) *of atoms from these planes, with e.s.d.'s in parentheses*

The planes are represented by equations 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 1: C(1), C(2), N(1), O(1)
$0{\cdot}0949X+0{\cdot}4621Y-0{\cdot}8817Z=1{\cdot}8557$

Plane 2: C(3), C(4), N(4), O(4)
$-0{\cdot}2280X+0{\cdot}3095Y-0{\cdot}9232Z=0{\cdot}2726$

Plane 1		Plane 2	
C(1)	0·01 (2)	C(3)	−0·00 (3)
C(2)	−0·00 (2)	C(4)	0·01 (2)
N(1)	−0·00 (2)	N(4)	−0·00 (2)
O(1)	−0·00 (1)	O(4)	−0·00 (1)
C(3)†	0·91 (3)	C(1)†	−0·44 (2)
C(4)†	0·56 (2)	C(2)†	−0·88 (3)
N(4)†	0·69 (2)	N(1)†	−0·52 (2)
O(4)†	0·12 (1)	O(1)†	−0·04 (2)

† Atoms not included in the calculation of the planes.

Hydrogen bonding

The hydrogen bonds and angles are listed in Table 6, as are the Br$\cdots$Br and O$\cdots$Br intermolecular distances less than 4·2 Å.

The H atoms from N(4) are accepted by Br(2) [N(4)–H$\cdots$Br(2) = 3·44 Å] and by the water molecule [N(4)–H$\cdots$O(w) = 3·00 Å]. One H from N(1) is accepted by Br(2) [N(1)–H$\cdots$Br(2) = 3·50 Å], the other forms bifurcated hydrogen bonds with Br(3) and one of the terminal O atoms of the succinamide [N(1)–H$\cdots$Br(3) = 3·47, N(1)–H$\cdots$O(1) = 2·98 Å]. The water molecule has contacts with Br(2) [O(w)$\cdots$Br(2) = 3·50 Å] and Br(1) [O(w)$\cdots$Br(1) = 3·69 Å] which seem a little too long for O–H$\cdots$Br hydrogen bonds. Br(3) is involved in one hydrogen bond, Br(2) in two and Br(1) in none. Contrarily, in the hexabromotellurate of DL-α-ammonio-n-butyric acid (Dahan & Lefèbvre-Soubeyran, 1976) each Br atom is involved in one strong hydrogen bond. As expected, the electronegativity of Br increases with Te–Br distance.

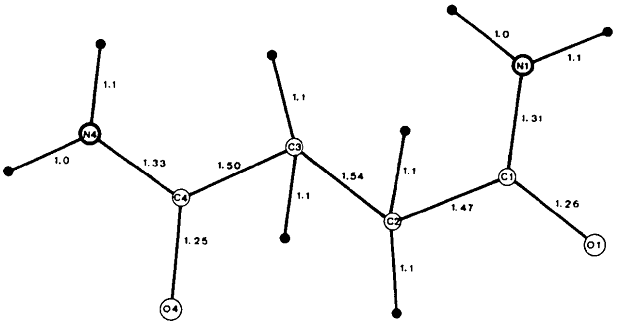


Fig. 2. Bond lengths (Å) in the disuccinamide. The average e.s.d.'s are 0·03 on C–O, C–N and C–C and 0·2 Å on C–H and N–H bonds.

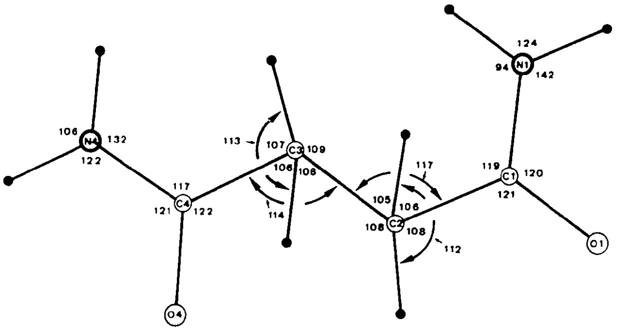


Fig. 3. Bond angles (°) in the disuccinamide. The average e.s.d.'s are 2° on the angles not involving H atoms and 13° on the others.

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

Symmetry code

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

Atoms belong to molecule i unless otherwise specified.

N(1)–H1(N1)$\cdots$Br(2)$^{\mathrm{v}}$	3·50	H1(N1)$\cdots$Br(2)$^{\mathrm{v}}$	2·47
N(1)–H2(N1)$\cdots$Br(3)$^{\mathrm{vii}}$	3·47	H2(N1)$\cdots$Br(3)$^{\mathrm{vii}}$	2·84
N(1)–H2(N1)$\cdots$O(1)$^{\mathrm{vi}}$	2·98	H2(N1)$\cdots$O(1)$^{\mathrm{vi}}$	2·06
N(4)–H1(N4)$\cdots$Br(2)$^{\mathrm{ii}}$	3·44	H1(N4)$\cdots$Br(2)$^{\mathrm{ii}}$	2·61
N(4)–H2(N4)$\cdots$O(w)$^{\mathrm{vi}}$	3·00	H2(N4)$\cdots$O(w)$^{\mathrm{vi}}$	2·04

N(1)–H1(N1)$\cdots$Br(2)$^{\mathrm{v}}$	173
N(1)–H2(N1)$\cdots$Br(3)$^{\mathrm{vii}}$	116
N(1)–H2(N1)$\cdots$O(1)$^{\mathrm{vi}}$	141
N(4)–H1(N4)$\cdots$Br(2)$^{\mathrm{ii}}$	142
N(4)–H2(N4)$\cdots$O(w)$^{\mathrm{vi}}$	147

Intermolecular distances (Å) less than 4·20 Å

O(w)$\cdots$Br(2)	3·50	O(w)$\cdots$Br(1)$^{\mathrm{v}}$	3·69
O(1)$\cdots$Br(1)$^{\mathrm{vi}}$	3·69	O(1)$\cdots$Br(2)$^{\mathrm{iv}}$	3·79
O(1)$\cdots$Br(3)$^{\mathrm{iv}}$	3·75	O(4)$\cdots$Br(2)$^{\mathrm{iv}}$	3·71
O(4)$\cdots$Br(3)$^{\mathrm{iv}}$	3·81		
Br(1)$\cdots$Br(2)$^{\mathrm{vii}}$	3·705	Br(3)$\cdots$Br(3)$^{\mathrm{ii}}$	3·953

It must be remembered that the H atom involved in the protonation of the succinamide has not been found. We may expect O- rather than N-protonation, knowing that the HNH angles about each N atom add up to 360°. There is a very short O(1)$\cdots$O(4) intramolecular distance, 2·45 Å. We may reasonably think that the proton is statistically divided between O(1) and O(4), linking them by a strong hydrogen bond.

The influence of the cation on general valence force field constants and mean amplitudes of vibration has been discussed (Srivastava, Dublish & Pandey, 1974). From the variation of the stretching force constants, the authors inferred that in the presence of organic cations the stiffness of the chemical bonds in anions generally increases with the size of the cations. In our study, the succinamide being a little larger than the amino acid, it is interesting to note the mean respective Te–Br values: 2·713 compared with 2·693 Å.

The hexabromotellurate of protonated disuccinamide is, to our knowledge, the first crystalline structure reported with a distorted TeBr_6^{2-} octahedron. Not only may the regularity of the octahedra in the two compounds be discussed but also the deviations of the structures from the cubic symmetry found with inorganic cations. With the amino acid, Te atoms are at the apex of an *A* face-centred monoclinic lattice. The contacts between Br atoms in different anions range from 3·943 to 4·134 Å, which are larger than van der Waals contacts. With the succinamide, Te atoms are 0·515 Å away from the apex of the *C* face-centred lattice. The van der Waals contacts between Br atoms in different $TeBr_6^{2-}$ ions are grouped into four short contacts of 3·705 and two longer contacts of 3·953 Å. A larger organic cation tends to distort the octahedra network but does not deform it fundamentally.

In the two structures, the cohesion is governed by hydrogen bonds and Br···Br intermolecular van der Waals contacts. The packing of the molecules approaches close packing, with the octahedra in contact, and the cavities occupied by the organic cations.

The authors thank Dr C. Stora for her interest in this work, Pr J. Dobrowolski for suggesting this study and supplying the samples and Dr J. Guilhem for the collection of the data.

References

AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). NRC Crystallographic Programs for the IBM/360 System. *Word List of Crystallographic Computer Programs*, p. 52. Utrecht: Oosthoek.

BROWN, I. D. (1964). *Canad. J. Chem.* **42**, 2758–2767.

BUJEWSKI, A. & DOBROWOLSKI, J. (1973). *Rocz. Chem.* **47**, 401–405.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak-Ridge National Laboratory Report ORNL-TM-305.

DAHAN, F. & LEFÈBVRE-SOUBEYRAN, O. (1976). B**32**, 2859–2862.

DAS, A. K. & BROWN, I. D. (1966). *Canad. J. Chem.* **44**, 939–943.

DAVIES, D. R. & PASTERNAK, R. A. (1956). *Acta Cryst.* **9**, 334–340.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–215. Birmingham: Kynoch Press.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., pp. 244–264. Ithaca: Cornell Univ. Press.

SRIVASTAVA, B. B., DUBLISH, A. K. & PANDEY, A. N. (1974). *Z. Naturforsch.* **29a**, 602–604.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1976). B**32**, 2866

The Crystal Structure of 2,5-Dimercaptothiadiazole

BY J. W. BATS*

Chemistry Department, State University of New York at Buffalo, Buffalo, New York 14214, *U.S.A.*

(*Received* 6 *April* 1976; *accepted* 25 *April* 1976)

The crystal structure of 2,5-dimercaptothiadiazole ($C_2H_2N_2S_3$) has been determined at room temperature. The compound has the space group $P2_1/c$, with $a=6{\cdot}225$ (1), $b=10{\cdot}593$ (3), $c=9{\cdot}248$ (3) Å and $\beta=113{\cdot}65$ (2)°. The compound crystallizes as thiadiazole-2-thiol-5-thione, as a result of proton transfer in one of the two S–H···N hydrogen bonds. Difference density maps based on atomic parameters from a conventional and a high-order X-ray refinement have been calculated and interpreted in terms of bonding effects in the molecule.

Introduction

With the improvement in accuracy of X-ray diffraction analyses, several studies have recently been concerned with the determination of electron densities in solids (see Coppens, 1976). In the field of the determination of the nature of the bonding of the sulfur atom, electron density studies have been applied to orthorhombic sulfur (Blessing, Cooper, Yang & Coppens, 1973), sulfamic acid (Bats, Coppens & Koetzle, 1977), and Na sulfanilate.$2H_2O$ (Bats, 1977).

As a continuation in this field, it seemed interesting to study 2,5-dimercaptothiadiazole, in which the sulfur atom is involved in some type of bonding not present in other compounds studied.

The present work is concerned with the determination of the structure of the title compound at room temperature (295 K), in order to investigate the suitability of the structure for electron density studies.

---

* Present address: Chemical Physics Laboratory, Twente University of Technology, P. O. Box 217, Enschede, The Netherlands.