

Table 5. *Hydrogen bonds* $D-H \cdots A$

<i>D</i>	<i>H</i>	<i>A</i>	$D \cdots A$	$H \cdots A$	$\angle D-H \cdots A$
N(1)	H(10)	O(1 ⁱ)	2.806 Å	1.88 Å	161°
N(1)	H(11)	O(2 ⁱⁱ)	2.929	2.01	164
		O(3 ⁱⁱⁱ)	2.858	2.25	121
N(1)	H(12)	N(3 ⁱⁱⁱ)	2.886	1.96	178
N(2)	H(13)	O(2 ⁱ)	2.932	2.08	176
N(4)	H(14)	O(3 ^{iv})	2.696	1.82	171

Symmetry code

(i) $x, 1/2 + y, z$; (ii) $1 - x, 1 + y, -z$; (iii) $1 - x, 1 + y, 1 - z$;(iv) $1/2 - x, -1/2 + y, -z$.

(Freeman & Szymanski, 1967) belongs to the latter. The difference in the conformations may be attributed to the carnosine-Cu interaction. The χ_2^1 of His in the present peptide is -178.7° and that in methyl L-pyroglutamyl-L-histidinate (Cotrait & Allard, 1973) is -177.9° . The conformations of His in these peptides are, therefore, different from either the open or closed forms which are proposed by Kistenmacher, Hunt & Marsh (1972), χ_2^1 of the open and closed forms being very roughly -60 and $+60^\circ$ respectively. On the other hand, the conformation in the Cu complex is of the closed form ($\chi_2^1 = 53.1^\circ$).

The hydrogen-bond scheme is summarized in Table 5.

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Caesium Enneabromodibismuthate(III)

BY F. LAZARINI

Department of Chemistry, Faculty of Natural Sciences and Technology, University of Ljubljana, Murnikova 6, 61000 Ljubljana, Yugoslavia

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Abstract. $\text{Cs}_3\text{Bi}_2\text{Br}_9$; trigonal, $P3m1$; hexagonal axes; $a = 7.972$ (2), $c = 9.867$ (5) Å; $D_o = 4.65$ (2) g cm^{-3} , $Z = 1$, $D_c = 4.694$ g cm^{-3} ; $R = 0.058$ for 424 reflexions [$I > 3\sigma(I)$]. Cs and Br are in a cubic close-packed structure, with Bi in $1/6$ of the octahedral holes. The BiBr_6 octahedra share three *cis*-vertices with three other octahedra forming corrugated layers.

Introduction. This investigation is a part of a systematic study of bromo- and iodobismuthates(III) (Lazarini, 1977*a,b*). It is typical for $A_3B_2X_9$ structures (Wells, 1975) that *A* and *X* atoms are in either cubic or hexagonal closest packing with *B* atoms occupying $2/3$ of

the X_6 holes, *i.e.* $1/6$ of the total number of octahedral holes. Two different groups of structures are possible. In the first group of $A_3B_2X_9$ structures, with *A* and *X* atoms in hexagonal closest packing, complex $B_2X_9^{3-}$ ions are present, consisting of two BX_6 octahedra sharing a face. The representative examples of this group are: $\text{K}_3\text{W}_2\text{Cl}_9$ (Watson & Waser, 1958), with a strong bond between W atoms shifted to the bridging Cl atoms, a more symmetrical variant, $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ (Wessel & IJdo, 1957), $\text{Cs}_3\text{Bi}_2\text{I}_9$ (Lindqvist, 1968) with the same structure, and $\text{Cs}_3\text{Tl}_2\text{Cl}_9$ (Hoard & Goldstein, 1935*a*; Powell & Wells, 1935) with a more uniform spatial distribution of the complex anions. In the second

group of $A_3B_2X_9$ structures, with A and X atoms in cubic closest packing, corrugated layers are present, formed from octahedra sharing three vertices with three other octahedra. It was suggested in the older literature (Yamatera & Nakatsu, 1954) from powder diffraction data that $Cs_3Fe_2Cl_9$ and $Cs_3Sb_2Cl_9$ have this type of structure, but it was later concluded (Ginsberg & Robin, 1963), also on the evidence from powder diffraction photographs, that these compounds are isostructural with $Cs_3Cr_2Cl_9$. The title compound $Cs_3Bi_2Br_9$ definitely has such a layer structure. The structure of $Cs_3As_2Cl_9$ (Hoard & Goldstein, 1935*b*) is similar, but less symmetric; the $AsCl_6$ groups are distorted so that there are discrete $AsCl_3$ molecules embedded between Cs^+ and Cl^- ions. The structure of $Cs_3Bi_2Cl_9$, determined recently (Kihara & Sudo, 1974) consists of Cs and Cl atoms in nearly hexagonal closest packing and $BiCl_3$ molecules in a different orientation as compared with the $AsCl_3$ molecules in $Cs_3As_2Cl_9$.

Yellow crystals of $Cs_3Bi_2Br_9$ were grown by slow evaporation from an aqueous solution obtained by dissolving $Bi(OH)_3$ and Cs_2CO_3 (molar 4:3 ratio) in a dilute HBr solution. The formula was determined by standard chemical analytical methods (found: 27.11% Bi , 46.55% Br ; calculated: 27.21% Bi , 46.82% Br). A well developed crystal, selected for the intensity measurements, was characterized by the following planes (in parentheses are the distances from the crystal faces to an arbitrary origin inside the crystal): $\pm\{0\ 0\ 1\}$ (0.032 mm), $\pm\{0\ 1\ 0\}$ (0.113 mm), $\pm\{1\ -1\ 0\}$ (0.113 mm), $\{1\ 0\ 0\}$ (0.092 mm) and $\{-1\ 0\ 0\}$ (0.027 mm).

The intensity data were collected at 20 (1)°C with an Enraf-Nonius CAD-4 diffractometer. Experimental conditions: graphite-monochromatized $Mo\ K\alpha$ radiation ($\lambda = 0.71069\ \text{\AA}$), ω - 2θ scan, $\theta_{\min} = 1.0^\circ$, $\theta_{\max} = 27.5^\circ$, 2θ scan width ($^\circ$) $0.9 + 0.2 \tan \theta$, aperture (mm) $2.5 + 0.9 \tan \theta$, maximum scan time 20 s, background: $\frac{1}{4}$ of the scan time at each of the scan limits. A set of 2653 reflexions was recorded. After symmetry-related reflexions were averaged 507 independent reflexions remained (mean discrepancy on I : 11% for 2653 reflexions), and of these, 424 reflexions, having $I > 3\sigma(I)$ (calculations based on counting statistics), were used in the structure analysis. Corrections were applied for Lorentz and polarization effects

and for absorption [$\mu(Mo\ K\alpha) = 379.0\ \text{cm}^{-1}$]. The absorption corrections A^* , calculated with the measured crystal dimensions (Gaussian-grid method), range from 7.61 to 31.45.

The unit-cell parameters were obtained from a least-squares fit of the θ values of 15 reflexions measured on the four-circle diffractometer. The possible space groups, checked by Weissenberg, precession and cone-axis photographs, were (no systematic absences): $P\bar{3}m1$ (No. 164), $P31m$ (No. 162), $P31m$ (No. 157), $P3m1$ (No. 156), $P321$ (No. 150) and $P312$ (No. 149). However, only $P\bar{3}m1$, $P3m1$ and $P321$ had been implied by the Patterson function. $P\bar{3}m1$ was subsequently confirmed by successful refinement.

The positions of all atoms were determined from the three-dimensional Patterson function. The structure was then refined by full-matrix least-squares techniques with anisotropic thermal parameters and with anomalous dispersion correction for all atoms. The function minimized in the least-squares procedure was $\sum w(|F_o| - |F_c|)^2$. The weighting scheme applied was as follows:

$$|F_o| < 30: w_F = (|F_o|/30)^{1.5}, \\ \sin \theta < 0.2: w_S = (\sin \theta/0.2)^{-1},$$

$$30 < |F_o| \leq 80: w_F = 1.0, \\ 0.2 < \sin \theta \leq 0.4: w_S = 1.0,$$

$$|F_o| \geq 80: w_F = (80/|F_o|)^{2.1}, \\ \sin \theta \geq 0.4: w_S = (0.4/\sin \theta)^{1.8},$$

$$w = 0.1 w_F w_S.$$

An isotropic extinction parameter (Zachariasen, 1963; Larson, 1967) was also included in the final stage of the refinement ($g = 9.8 \times 10^{-4}$). Final R values are: $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.058$ and $R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2} = 0.061$ for 424 reflexions and 20 parameters.† The average parameter shift to error ratio was 0.1 in the final cycle. An attempt to refine the

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32728 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Final positional parameters ($\times 10^4$) and thermal parameters ($\times 10^4$) with standard deviations in parentheses

The anisotropic temperature factor is in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}k lb^*c^*)]$. W = Wyckoff position.

W	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	2(<i>d</i>)	$\frac{2}{3}$	$\frac{1}{3}$	1918 (1)	$=2U_{12}$	255 (6)	104 (2)	0	0
Cs(1)	1(<i>a</i>)	0	0	$=2U_{12}$	$=2U_{12}$	836 (31)	237 (8)	0	0
Cs(2)	2(<i>d</i>)	$\frac{2}{3}$	$\frac{1}{3}$	6669 (3)	$=2U_{12}$	523 (17)	251 (5)	0	0
Br(1)	3(<i>e</i>)	$\frac{1}{3}$	0	699 (21)	$=U_{11}$	654 (21)	492 (23)	$=-U_{23}$	155 (9)
Br(2)	6(<i>i</i>)	$=2y$	1676 (2)	$=2U_{12}$	544 (13)	562 (14)	173 (6)	$=2U_{23}$	100 (6)

structure in the acentric space groups $P3m1$ and $P321$ was unsuccessful (higher R values, unreasonable temperature factors for all atoms).

All calculations were performed on the CDC Cyber

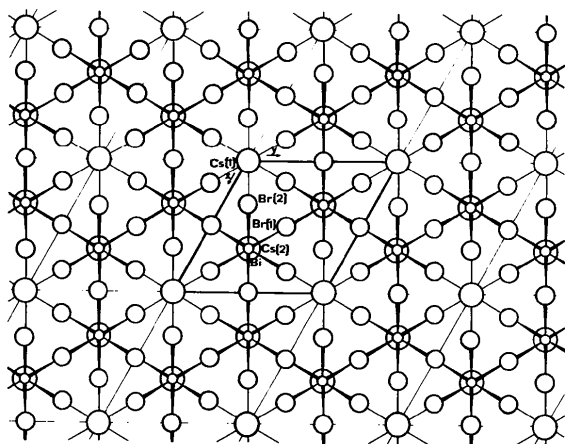


Fig. 1. The structure of $Cs_3Bi_2Br_9$ viewed along $[001]$.

72 computer of RRC Ljubljana with the XRAY 72 system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) adapted by Professor L. Golič. Atomic scattering factors for neutral atoms tabulated by Cromer & Mann (1968) and the values of $\Delta f'$ and $\Delta f''$ for the anomalous dispersion correction tabulated by Cromer & Liberman (1970) were applied.

The positional and thermal parameters are listed in Table 1. The structure in its c -axis projection and the atom-numbering system used are shown in Fig. 1. Some important interatomic distances and angles are given in Table 2.

Discussion. The Cs and Br atoms are in the cubic close-packed structure. The distances to the 12-coordinated atoms, given in Table 2, are all slightly longer than the sum of conventional ionic radii (Cs^+ 1.70 Å, Br^- 1.95 Å; Wells, 1975). The angles around the 12-coordinated atoms do not differ significantly from theoretical values (Table 3). The $BiBr_6$ octahedra share three *cis*-vertices with three other octahedra forming corrugated layers

Table 2. *Interatomic distances (Å) and angles (°) with standard deviations in parentheses*

$Bi^i-Br(1^{i,ii,iii})$	2.979 (1)	$Br(1^i)-Br(1^{ii,iii,vi,xxii})$	3.986 (1)
$Bi^i-Br(2^{i,ii,iii})$	2.713 (2)	$Br(1^i)-Br(2^{i,iii,x,xxiii})$	4.060 (3)
$Cs(1^i)-Br(1^{i,ii,iv,v,vi,vii})$	3.986 (1)	$Br(2^i)-Cs(1^i)$	4.071 (3)
$Cs(1^i)-Br(2^{i,v,vii,viii,ix,x})$	4.071 (3)	$Br(2^i)-Cs(2^i)$	3.959 (3)
$Cs(2^i)-Br(1^{xi,xii,xiii})$	4.012 (3)	$Br(2^i)-Cs(2^{xiv,xv})$	3.986 (2)
$Cs(2^i)-Br(2^{i,ii,iii})$	3.959 (3)	$Br(2^i)-Br(1^{i,ii})$	4.060 (3)
$Cs(2^i)-Br(2^{xiv,xv,xvi,xvii,xviii,xix})$	3.986 (2)	$Br(2^i)-Br(2^{ii,iii})$	3.964 (2)
$Br(1^i)-Cs(1^{i,xx})$	3.986 (1)	$Br(2^i)-Br(2^{v,vii})$	4.008 (2)
$Br(1^i)-Cs(2^{xiv,xxi})$	4.012 (3)	$Br(2^i)-Br(2^{xvii,xix})$	3.923 (3)
$Br(1^i)-Bi^i-Br(1^{ii,iii})$	83.97 (4)	$Br(2^i)-Bi^i-Br(2^{ii,iii})$	93.86 (7)
$Br(1^{ii})-Bi^i-Br(1^{iii})$	83.97 (4)	$Br(2^{ii})-Bi^i-Br(2^{iii})$	93.86 (7)
$Br(1^i)-Bi^i-Br(2^{i,iii})$	90.88 (5)	$Br(1^i)-Bi^i-Br(2^{ii})$	173.05 (6)
$Br(1^{ii})-Bi^i-Br(2^{i,ii})$	90.88 (5)	$Br(1^{ii})-Bi^i-Br(2^{iii})$	173.05 (6)
$Br(1^{iii})-Bi^i-Br(2^{ii,iii})$	90.88 (5)	$Br(1^{iii})-Bi^i-Br(2^i)$	173.05 (6)

Symmetry code

(i)	$x,$	$y,$	z	(ii)	$1-y,$	$x-y,$	z	(iii)	$1-x+y,$	$1-x,$	z
(iv)	$x-1,$	$y-1,$	z	(v)	$-y,$	$x-y,$	z	(vi)	$y-x,$	$1-x,$	z
(vii)	$y-x,$	$-x,$	z	(viii)	$-x,$	$-y,$	$-z$	(ix)	$y,$	$y-x,$	$-z$
(x)	$x-y,$	$x,$	$-z$	(xi)	$x,$	$y,$	$1+z$	(xii)	$1-y,$	$x-y,$	$1+z$
(xiii)	$1-x+y,$	$1-x,$	$1+z$	(xiv)	$1-x,$	$1-y,$	$1-z$	(xv)	$1-x,$	$-y,$	$1-z$
(xvi)	$1+y,$	$1-x+y,$	$1-z$	(xvii)	$y,$	$y-x,$	$1-z$	(xviii)	$1+x-y,$	$x,$	$1-z$
(xix)	$x-y,$	$x,$	$1-z$	(xx)	$1+x,$	$1+y,$	z	(xxi)	$x,$	$y,$	$z-1$
(xxii)	$1-y,$	$1+x-y,$	z	(xxiii)	$1-x,$	$1-y,$	$-z$				

Table 3. *The bond angles (°) around the 12-coordinated atoms*

Cs(1)	58.98 (3) to 60.51 (3)	90.00	119.49 (3) to 121.02 (3)	180.00
Cs(2)	59.18 (4) to 61.00 (3)	89.16 (4) to 90.84 (4)	119.25 (7) to 120.56 (7)	178.17 (8) to 179.68 (8)
Br(1)	58.44 (3) to 60.78 (3)	89.84 (1) to 90.15 (1)	119.22 (3) to 121.56 (3)	180.00
Br(2)	58.71 (4) to 60.78 (4)	89.84 (5) to 90.16 (5)	118.61 (7) to 121.49 (7)	178.27 (7) 180.00 (7)
Theoretical value	60.00	90.00	120.00	180.00

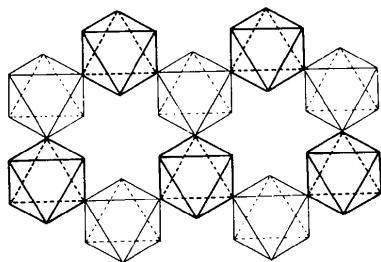


Fig. 2. A schematic representation of the corrugated Bi_2Br_9 layer.

(Fig. 2). Cs(1) lies inside the layer, Cs(2) outside the layer. The shorter Bi—Br (terminal) distances [2.713 (2) Å] and the longer Bi—Br (bridging) distances [2.979 (1) Å] are in reasonable agreement with the corresponding distances found in some other bromobismuthates(III): 2.65 to 2.88 Å and 3.02 to 3.13 Å in bispiperidinium pentabromobismuthate(III) (McPherson & Meyers, 1968), 2.64 Å and 2.97 to 3.27 Å in 2-picolinium tetrabromobismuthate(III) (Robertson, McPherson & Meyers, 1967) and 2.749 to 2.879 Å and 2.979 to 3.006 Å in potassium decabromodibismuthate(III) tetrahydrate (Lazarini, 1977a). The structure of $\text{Cs}_3\text{Bi}_2\text{I}_9$ is different (Lindqvist, 1968). Cs and I atoms are in the hexagonal close-packed structure with Bi atoms in pairs of adjacent octahedral holes, so that complex $\text{Bi}_2\text{I}_9^{3-}$ anions are present.

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Manganese(II) Propionate Dihydrate

By T. LIS

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

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Abstract. $\text{C}_6\text{H}_{14}\text{O}_6\text{Mn}$, monoclinic, $C2/c$, $a = 22.857(9)$, $b = 6.645(3)$, $c = 14.057(6)$ Å, $\beta = 114.28(3)^\circ$, $M_r = 237.12$, $V = 1946.2$ Å³, $Z = 8$, $D_m = 1.61$, $D_x = 1.618$ g cm⁻³, $\mu(\text{Mo } K\alpha, \lambda = 0.71069 \text{ Å}) = 14.2$ cm⁻¹. The Mn atoms are linked by a bridging system that contains three types of bridges: a bidentate $\text{C}_2\text{H}_5\text{COO}^-$ group, one O atom from a second propionate group and one water molecule, to give infinite, almost linear, chains parallel to **b**, with a

distorted octahedral Mn coordination and Mn—Mn distances of 3.350(1) Å. The compound shows a temperature-independent magnetic moment very close to the value 5.9 BM (78–295 K). The structure was refined to an R of 0.037 for 1537 diffractometer data.

Introduction. As part of our continuing study on the stereochemistry of Mn—carboxylate complexes (Lis & Jeżowska-Trzebiatowska, 1977; Lis, Matuszewski &

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