25. *The Valency Angle of Bivalent Lead : The Crystal Structure of Ammonium, Rubidium, and Potassium Pentabromodiplumbites.*

By H. M. POWELL and H. S. TASKER.

COMPOUNDS of the type MB_2X_5, where M is an alkali metal or ammonium, B a bivalent metal, and X a halogen, are formed by the elements of group IVB and by mercury. The present work was begun with the object of determining the constitution of the compounds in which the bivalent element is lead. A preliminary X-ray survey of some of these substances showed that ammonium and rubidium lead bromides were most suitable for structure determination, and these compounds have been studied in detail. The corresponding potassium compound is shown to be isomorphous. The structures contain lead bromide molecules and therefore make possible a determination of the valency angle of bivalent lead.

The Structure of Ammonium Pentabromodiplumbite.—The substance was prepared by cooling an aqueous solution of the component salts in the proportions given by Wells and Johnstone (*Amer. J. Sci.*, 1893, **46**, 28). It forms tetragonal plates, tabular on (001), the plate edge being the [100] axis, and larger crystals show traces of a form (*h0l*). The crystals are optically uniaxial, have high refractive indices and show rather weak negative double refraction. The unit cell dimensions are $a = 8.39$, $c = 14.34$ A. These dimensions and the density determined by a pyknometer method give the number of molecules per unit cell as 3·77. The correct value should be 4 molecules per cell and the discrepancy is due to impurity of the material. The substance is obtained from very concentrated ammonium bromide solution and cannot be washed without decomposition ; it therefore always contains an excess of ammonium bromide. Different samples of the material were analysed, and the same samples used for density determination. The composition was found to be variable, high nitrogen content coinciding with high bromine results. From the analyses, the amount of excess ammonium bromide was calculated, and then from the known density of ammonium bromide and the density 5·46, calculated for the compound on the assumption of 4 molecules per cell, values for the density of the mixtures were obtained consistent with the observed ones (Table I). Analysis (1) was performed on the initial small sample made to check the method of preparation, and there was insufficient material for a density determination.

TABLE I.

	Pb (as PbCrO$_4$), %.	Br (as AgBr), %.	N (as N$_2$), %.	Density of mixture, calc.	Density, obs. (pyknometer), 22°/4°.
(1)		48·0	1·9	—	—
(2)		49·7	2·1	5·19	5·16
(3)	49·2	50·4	2·2	5·02	5·15
(Calc.)..................	49·8	48·1	1·7		

In (3) the calculation was made on the assumption that the bromine and nitrogen figures were correct, the lead value being regarded as the least reliable.

A complete series of 15° oscillation photographs from a plate 0·2 × 0·2 × 0·05 mm. about the a and c axes was taken with copper radiation. Indexed by the chart method, they showed the systematic absence of *h0l* spectra, and the absences corresponding to body-centring. Combined with the negative result of a liquid-air test for pyroelectricity, this gives the space group as $I4/mcm$. A complete structure based on this space group was deduced as follows.

In the cell there are 8Pb, 20Br, and 4NH$_4$, which may be arranged among the possible equivalent atomic positions as

(1) 8Pb + 16Br + 4Br + 4NH$_4$, (2) 8Pb + 8Br + 8Br + 4Br + 4NH$_4$, (3) 8Pb + 8Br + 4Br + 4Br + 4Br + 4NH$_4$, (4) 4Pb + 4Pb + 8Br + 8Br + 4Br + 4NH$_4$, or (5) 4Pb + 4Pb + 16Br + 4Br + 4NH$_4$. Arrangement (2) is excluded since if any two of the fourfold positions are occupied it is impossible to place the remaining atoms in three eightfold positions to give satisfactory interatomic distances. The intensities of 00*l* spectra show that the structure has a c axis parameter, and since the space occupied by atoms in fourfold positions in (3) and (4) makes it impossible for any other atom to enter an eightfold position with such a parameter, these two possibilities (3) and (4) are also re-

jected. In (5), 16Br would have to be in the 16-fold position with a c parameter, and any attempt to base a structure on this breaks down through impossible interatomic distances and incompatibility with observed intensities.

Arrangement (1) alone gives a satisfactory structure. Since three of the four 16-fold positions would require eight bromine atoms to be in one plane within an area of $8\cdot39 \times 8\cdot39$ A., which can only contain half the number, the only possible position for 16Br is $x, \frac{1}{2} + x, z$, etc. [position (l), " International Tables for Crystal Structure "]. When 16Br are given these co-ordinates, with x and z restricted so that no two bromines shall interpenetrate, the only dimensionally possible positions for the other atoms are at once fixed and the structure obtained has 16Br in (l) $x, \frac{1}{2} + x, z$, etc.; 8Pb in (h) $u, \frac{1}{2} + u, 0$, etc.; 4NH$_4$ in (a) 00$\frac{1}{4}$, etc., and 4Br in (b) 000, etc. The values found for the parameters are $x = 0\cdot163 \pm 0\cdot003$, $u = 0\cdot158 \pm 0\cdot002$, $z = 0\cdot363 \pm 0\cdot001$.

The 00l intensities are independent of x and u, and for these agreement is found if z or $\frac{1}{2} - z = 0\cdot363$ (Table II).

TABLE II.

Indices.	Intensity, calc.	Intensity, obs.	Indices.	Intensity, calc.	Intensity, obs.
002	380	vvs	00$\underline{12}$	7	m
004	15	m	00$\underline{14}$	48	s
006	180	vs	00$\underline{16}$	35	ms
008	150	vs	00$\underline{18}$	7	nil
00$\underline{10}$	9·5	m			

From contour diagrams showing the effect of simultaneous variation of x and u on the intensities of 20 spectra of the types h00, hh0, and hk0 which are independent of z, agreement is found with observation for $x = 0\cdot163$, $u = 0\cdot158$, or for the symmetrically related values of x and u (Table III).

TABLE III.

Indices.	I, calc.	I, obs.		Indices.	I, calc.	I, obs.		Indices.	I, calc.	I, obs.
200	52	s		440	27	nil	(ms)	640	11	m
400	83	s		550	0	nil	(nil)	370	29	ms
600	106	vs		660	46	m	(s)	820	2	vw
800	0·2	nil		310	119	vs		570	0·7	nil
$\underline{1000}$	56	m		420	31	m		910	16	m
$\overline{110}$	21	mw	(mw)	350	14	m		840	2·7	w
220	36	m	(s)	620	5	mw		930	34	s
330	120	s	(vs)	710	3·7	vvw		950	16	mw

In general, the observed intensities in the series hh0 are weaker than the calculated, but this is caused by the large absorption due to the crystal shape. Intensities obtained with a large crystal on which a face had been ground nearly parallel to (110) are given in parentheses above. The correct combination of the alternative values of parameters is obtained from hkl spectra. The intensities of these and others of type $h0l$ are shown in Table IV.

TABLE IV.

Indices.	I, calc.	I, obs.	Indices.	I, calc.	I, obs.	Indices.	I, calc.	I, obs.
112	1·5	nil	143	60	s	12$\underline{11}$	32	ms
211	30	m	404	0	nil	6$\underline{06}$	33	ms
114	3·5	w	127	1·3	nil	40$\underline{10}$	0·5	nil
123	178	vs	136	56	s	11$\underline{12}$	0	nil
202	4·5	mw	145	30	s	20$\underline{12}$	0	nil
222	12	m	208	7·6	m	6$\underline{08}$	45	ms
204	4	nil	523	56	s	40$\underline{12}$	0·3	nil
132	33	ms	129	14	m	60$\underline{10}$	4·7	w
125	67	s	352	3·2	m	20$\underline{14}$	4·1	w
116	2·8	vw	525	34	ms	40$\underline{14}$	11·3	m
323	5·6	vw	11$\underline{10}$	0	nil	42$\underline{14}$	3	w
206	8·2	m	6$\underline{02}$	15·5	m	60$\underline{12}$	10·2	w
402	9·4	w	408	14·3	m	100$\underline{2}$	11·4	mw
332	25	ms	604	3·9	vw	60$\underline{14}$	68	s
422	6·3	mw	20$\underline{10}$	0	nil			

All intensities were calculated by the formula

$$I \propto \frac{1 + \cos^2 2\theta}{\sin 2\theta} \cdot |S|^2$$

and corrected when necessary for position of the spot on the layer line. Observed intensities were estimated visually with the aid of a graduated scale.

Rubidium Pentabromodiplumbite.—A small quantity of this substance was prepared by the method of Wells and Johnstone (*loc. cit.*). It forms tetragonal crystals which have rather weak negative double refraction. The oscillation photographs of these crystals taken with copper radiation are almost superposable on the photographs from the ammonium compound taken over corresponding ranges of oscillation. They give for the cell dimensions $a = 8{\cdot}41$, $c = 14{\cdot}5$ A., and a density, calculated for 4 molecules per unit cell, 5·76. The space group is $I\,4/mcm$ and the atomic positions are the same as those for ammonium pentabromodiplumbite with rubidium replacing ammonium. Good agreement between observed and calculated intensities is obtained with 4Rb in (*a*) $00\frac{1}{4}$, etc.; 4Br in (*b*) 000, etc.; 8Pb in (*h*) $u, \frac{1}{2} + u, 0$, etc.; $u = 0{\cdot}158$; and 16Br in (*l*) $x, \frac{1}{2} + x, z$, etc., $x = 0{\cdot}163$, $z = 0{\cdot}365$ (Table V). The effect of substitution of rubidium for ammonium is shown especially in the 00*l* spectra which may be compared with the corresponding spectra in Table II.

TABLE V.

Indices.	I, calc.	I, obs.	Indices.	I, calc.	I, obs.	Indices.	I, calc.	I, obs.
002	280	vs	116	3·4	m	288	5·6	m
004	54	s	125	76·5	vs	279	1·5	m
006	117	s	127	1·5	vw	$27\overline{11}$	23	s
008	190	vs	129	11	m	$25\overline{11}$	17·2	s
$00\overline{10}$	6·7	w	$12\overline{11}$	34	s	$26\overline{10}$	0	nil
$00\overline{12}$	10	m	$22\overline{10}$	0	nil	228	15·2	s
$00\overline{14}$	31	ms	$14\overline{11}$	19·4	s	2412	3·3	w
$00\overline{16}$	50	ms	$24\overline{10}$	0·5	nil	$26\overline{12}$	0·9	nil
$00\overline{18}$	4	nil	198	34	ms			

Potassium Pentabromodiplumbite.—A quantity of this substance was prepared according to the directions of Wells (*Amer. J. Sci.*, 1893, **45**, 121). It forms tetragonal plates with the
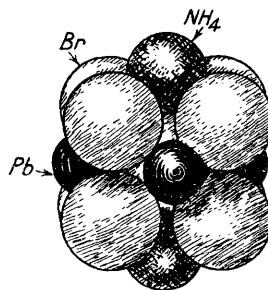
FIG. 1.
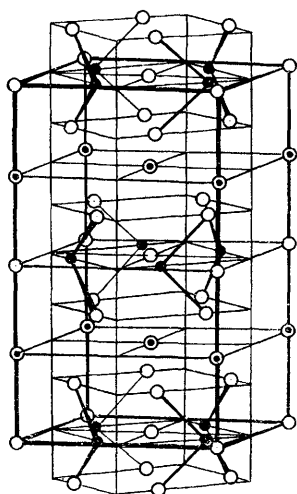
O = Br ◉ = NH₄ ● = Pb

Unit cell showing each lead atom linked to two bromines.

FIG. 2.

The packing of the atoms shown by use of ionic radii; the lead–bromine links by the interpenetration of the spheres.

[110] axis as plate edge. From oscillation photographs with copper radiation the unit cell dimensions were found to be $a = 8{\cdot}14$, $c = 14{\cdot}1$ A. The photographs are nearly superposable on the corresponding ones of the ammonium compound and the structure is clearly similar to that of the previous compounds.

Discussion of the Structure.—A complete unit cell is illustrated in Fig. 1, and the centre portion is further illustrated in Fig. 2, which is drawn to the same scale and shows the

essential character of the structure. It consists of vertical rows of alternate bromine and alkali (or ammonium) ions with lead bromide molecules arranged in groups of four around these rows. A list of near neighbours of the various atoms is given in Table VI.

TABLE VI.

	$NH_4Pb_2Br_5$.		$RbPb_2Br_5$.	
	Neighbours.	Distance, A.	Neighbours.	Distance, A.
Pb	$2Br_{II}$	$2\cdot89 \pm 0\cdot05$	$2Br_{II}$	$2\cdot89$
	$2Br_I$	$3\cdot16 \pm 0\cdot02$	$2Br_I$	$3\cdot17$
	$4Br_{II}$	$3\cdot35 \pm 0\cdot05$	$4Br_{II}$	$3\cdot39$
	$1Pb$	$3\cdot74 \pm 0\cdot05$	$1Pb$	$3\cdot76$
Br_I (at 000)	$4Pb$	$3\cdot16$	$4Pb$	$3\cdot17$
	$2NH_4$	$3\cdot59$	$2Rb$	$3\cdot62$
	$8Br_{II}$	$3\cdot70$	$8Br_{II}$	$3\cdot71$
Br_{II} at $(x, \frac{1}{2} + x, z)$	$1Pb$	$2\cdot89$	$1Pb$	$2\cdot89$
	$2Pb$	$3\cdot35$	$2Pb$	$3\cdot39$
	$2NH_4$	$3\cdot59$	$2Rb$	$3\cdot56$
	$2Br_I$	$3\cdot70$	$2Br_I$	$3\cdot71$
	$1Br_{II}$	$3\cdot93$	$1Br_{II}$	$3\cdot91$
NH_4 or Rb	$2Br_I$	$3\cdot59$	$2Br_I$	$3\cdot62$
	$8Br_{II}$	$3\cdot59$	$8Br_{II}$	$3\cdot56$

The ammonium or alkali-metal ion has for neighbours two bromine ions and eight bromines which are linked to lead. This co-ordination is similar to that found in the compound $Cs_3[CoCl_4]Cl$ (Powell and Wells, J., 1935, 359), where one of the cæsium ions has ten chlorine neighbours consisting of two chlorine ions and eight chlorines which are linked to cobalt. The distance between the positive and negative ions is in all cases slightly greater than it would be in the corresponding alkali (or ammonium) halide crystallising in an 8-co-ordination CsCl type of structure, but the distance of the positive ion from the other eight halogens does not obey a similar rule.

The bromine ions show a remarkable co-ordination, having no less than 14 other atoms in contact with them. This type of co-ordination, which may be seen in Fig 2, is made possible by the favourable ratios of the radii of the atoms involved. To obtain this arrangement the central bromine ion may first be regarded as at the centre of a cube in contact with 8 bromines at the corners. The cube is then flattened so that the 8 bromines, which originally are not touching, come into contact in four pairs. This leaves two spaces, at the centres of the upper and lower faces of the cube, large enough for the entry of ammonium ions into contact with the central bromine ion. When allowance is made for the shortening of the distances of each lead to two of its bromine neighbours the four smaller spaces on the sides of the flattened cube permit the approach of four lead atoms into contact with the central bromine.

Each lead has two close bromine neighbours at $2\cdot89 \pm 0\cdot05$ A. This distance is less than the sum of the ionic radii ($3\cdot16$, Pauling; or $3\cdot28$, Goldschmidt). It is also considerably less than the distance to the next set of neighbours at $3\cdot16$ A., which are two bromine ions of the vertical rows. The next four bromine neighbours at $3\cdot35$ A. are all closely attached to other lead atoms. A probable lead-to-bromine distance for a covalent link may be deduced from the mercury–bromine distance obtained from electron diffraction experiments with mercuric bromide vapour. Braune and Knoke (*Z. physikal. Chem.*, B, 1933, **23**, 163) give for this $2\cdot40$, and G. I. Jenkins (private communication) $2\cdot44$ A. From the latter value by addition of the difference of the atomic radii of lead and mercury the value $2\cdot63$ A. is obtained as a probable lead–bromine covalent distance. Whether our higher observed value corresponds to a covalent link or something intermediate between this and an ionic linkage, we may regard the structure as containing lead bromide molecules, since this accords best with the general characteristics of the structure. Thus the two nearest bromine neighbours of the lead atoms are much closer than the two which are known certainly to be ionised; and in agreement with this view there are few positive neighbours of the linked bromine atoms and no marked tendency for the lead atoms to keep widely apart.

The two bonds of the lead bromide molecule will be formed by the $6(p)^2$ electrons of the

lead atom, and according to the wave-mechanics treatment of the chemical bond by Pauling (*J. Amer. Chem. Soc.*, 1931, **53**, 1367), the angle between these bonds should be near to 90°. From the parameters found, the angle subtended at the centre of the lead by the two nearest bromine atoms is calculated to be $85\frac{1}{2}° \pm 2°$, a value in agreement with the prediction and providing confirmation of the essentially covalent character of the links. The bent form of the molecule is in contrast with the linear configurations found for the dimethyl-thallium ion (Powell and Crowfoot, *Z. Krist.*, 1934, **87**, 370) and the mercuric chloride molecule (Braekken, *ibid.*, **89**, 448), in both of which covalencies are formed by the $6(s)^2$ electrons.

DEPARTMENT OF MINERALOGY, UNIVERSITY MUSEUM, OXFORD.   [*Received, August 12th, 1936.*]