THE INVESTIGATION BY ELECTRON DIFFRACTION OF SOME DIHALIDES OF CADMIUM, TIN AND LEAD.

By M. W. Lister and L. E. Sutton.

Received 25*th March*, 1941.

In extension of the work described in the previous paper we have examined a number of dihalides. Some are of a metal with a group valency of two, *viz.*, cadmium ; and some are of metals which display di-valency because of the operation of the " inert pair " effect, *viz.*, tin and lead.

The two classes of dihalide were expected to show a difference in valency angle, for although in the cadmium compounds this should be 180° as it is in the mercuric compounds,[1, 2, 3, 4, 5] in the others it

---

[1] Krishnamurti, *Ind. J. Physics*, 1930, **5**, 113.

[2] Braune and Engelbrecht, *Z. physikal. Chem.*, *B*, 1930, **10**, 1 ; *ibid.*, 1931, **11**, 409.

[3] Braune and Knoke, *ibid.*, 1933, **23**, 163.

[4] Braune and Linke, *ibid.*, 1935, **31**, 12.

[5] Gregg, Hampson, G. I. Jenkins, P. L. F. Jones, and Sutton, *Trans. Faraday Soc.*, 1937, **33**, 852.

would be expected to be nearer 90°, both from theory and from measurements on related compounds.[6] As will be explained in the experimental section, however, it was found impossible to determine the angle in the tin and lead compounds because of the effects of temperature on the diffraction pattern. Such effects have been considered theoretically by James,[7] and have been considered in the instance of tetranitromethane,[8] but appear not to have been previously observed for such simple compounds in electron diffraction experiments.

Experimental.

Preparation and Purification of Materials.

Stannous chloride.—Hydrated crystals of this substance were dehydrated by heating and finally distilling them in a stream of HCl.

Stannous bromide.—Tin was dissolved in aqueous HBr, and the solution evaporated to give crystals of the hydrated salt, which were treated in a manner similar to that for $SnCl_2$.

Stannous iodide.—SnI_2 was precipitated by the double decomposition of $SnCl_2$ (1 mol.), KI (2 mols.) in the presence of HCl (1 mol.) in hot strong aqueous solution. According to Freundler and Laurent [9] at temperatures above 50° C. the precipitate consists of anhydrous SnI_2. The product was filtered off, dried, and finally sublimed in a stream of CO_2 to prevent oxidation by air.

Plumbous chloride, bromide and iodide.—These were all prepared by precipitation by double decomposition in aqueous solution, and were recrystallised from water.

Cadmium chloride and bromide.—These were prepared by dissolving the oxide in HCl or HBr and evaporation to dryness. They were dried by heating and subsequent distillation in a Pyrex tube, a slow stream of N_2 being used to carry away the water, and finally to take the vapour of the distilling salt along the tube. Even though the dehydration was carried out in N_2 and not in HCl or HBr, there appeared to be very little hydrolysis.

Cadmium iodide.—A commercial (Kahlbaum) specimen was used.

Electron Diffraction.

The apparatus and general experimental technique employed were those described previously.[10]

Results.

Stannous chloride.—The plates obtained from this substance showed five rings, which were all fairly symmetrical, and fell fairly uniformly in intensity from the centre outwards. The s values ($= 4\pi \sin \frac{\theta}{2}/\lambda$) observed for the maxima and minima are given in Table I.

TABLE I.—STANNOUS CHLORIDE.

Max.	Min.	No. of Plates.	s_{obsd}.
1		6	3·28
	2	6	4·61
2		6	5·81
	3	6	7·09
3		6	8·48
	4	6	9·69
4		6	11·05
	5	5	12·19
5		6	13·45

The interpretation of the plates obtained from stannous chloride, bromide and iodide will be discussed together.

---

[6] Powell and Tasker, *J. Chem. Soc.*, 1937, 119.

[7] James, *Physikal. Z.*, 1932, **33**, 737.

[8] Stosick, *J. Amer. Chem. Soc.*, 1939, **61**, 1127.

[9] Freundler and Laurent, *Bull. Soc. chim.*, 1925 (4), **37**, 1133.

[10] Lister and Sutton, *Trans. Faraday Soc.*, 1939, **35**, 495.

Stannous bromide.—This compound gave plates with up to six rings, which were all symmetrical and whose intensities fell off fairly regularly from the centre. The observed values of *s* for the maxima and minima are given in Table II.

TABLE II.—STANNOUS BROMIDE.

Max.	Min.	No. of Plates.	$s_{\text{obsd.}}$	
1		13	3·20	
	2	6		4·46
2		14	5·49	
	3	6		6·85
3		14	8·03	
	4	6		9·41
4		13	10·46	
	5	9		11·86
5		9	12·99	
	6	—		—
6		1	15·34	

TABLE III.—STANNOUS IODIDE.

Max.	Min.	No. of Plates.	$s_{\text{obsd.}}$	
1		6	2·85	
	2	6		4·12
2		6	5·13	
	3	6		6·35
3		6	7·48	
	4	6		8·63
4		6	9·75	
	5	6		10·92
5		6	12·13	

Stannous iodide.—Five maxima were observed for stannous iodide. These were all symmetrical and regularly spaced, and fell off fairly regularly in intensity. The minima were also symmetrical and of steadily decreasing depth. The *s* values observed for the maxima and minima were :—

The first question which arises in the interpretation of these plates is the molecular formula of the diffracting vapour; that is, whether it is SnX_2 or Sn_2X_4. Biltz and Meyer's results for the vapour density of stannous chloride[11] indicate that at the temperature and pressure of diffraction there would be very little if any association. The pressure of the diffracting vapour is certainly not above 5 mm. of mercury, which is the vapour pressure in the oven found to give the best results, and will be very considerably below this when it has diffused through the capillary jet of the oven head into the high vacuum of the camera. To confirm this, however, theoretical curves for Sn_2X_4 were calculated, assuming the following models :—

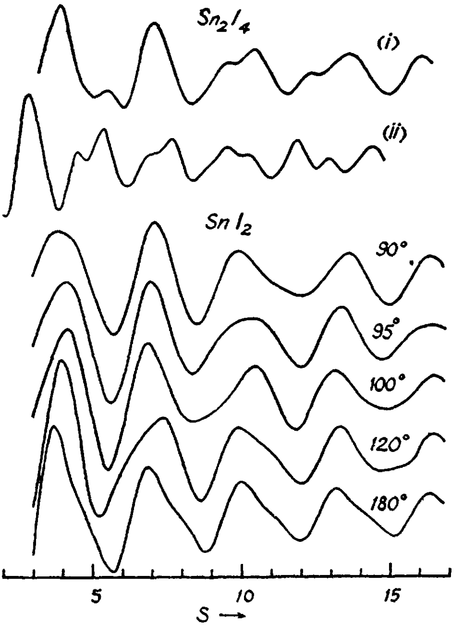
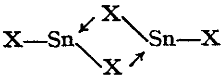


FIG. 1.—Theoretical intensity curves for various models of stannous iodide.

(i) A regular planar model of the form

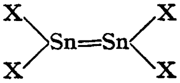


$$\mathrm{X{-}Sn}\begin{matrix}\swarrow \mathrm{X} \searrow \\ \searrow \mathrm{X} \nearrow\end{matrix}\mathrm{Sn{-}X}$$

---

[11] Biltz and Meyer, *Z. physikal. Chem.*, 1888, **2**, 184.

(ii) A regular planar model of the form



These curves are plotted in Fig. 1, and bear no resemblance to the appearance of the plate.

If, therefore, the molecular formulæ are taken as SnX_2, two independent variables must be determined in order to fix the structure: namely, the length of the Sn—X bond, and the tin valency angle. The procedure first adopted was to calculate curves for models with an arbitrary Sn—X distance of 2 A, and various X—Sn—X angles. Then for any curve an observed value can be calculated for the Sn—X distance from each maximum, and that model is finally chosen which shows the least average deviation amongst the Sn—X distances so obtained. This method can be most advantageously applied to stannous iodide, for here the halogen-halogen term which is dependent on the valency angle is most important relative to the tin-halogen term.

TABLE IV.—SnI_2.

Angle Max.	90°.	95°.	100°.	110°.	120°.	150°.	180°.
2	2·768	2·721	2·682	2·639	2·849	2·705	2·678
3	2·647	2·733	2·786	2·706	2·647	2·722	2·679
4	2·774	2·732	2·688	2·784	2·723	2·746	2·682
5	2·688	2·718	2·750	2·684	2·739	2·737	2·688
Mean	2·712	2·726	2·726	2·703	2·739	2·728	2·682 A
Average deviation	0·049	0·006	0·041	0·042	0·054	0·014	0·003

Fig. 1 shows the theoretical curves for stannous iodide for various angles. The Sn—I distances calculated from various models are given in Table IV.

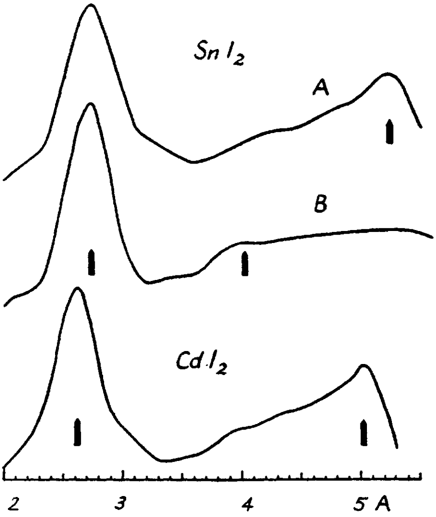


FIG. 2.—Radial distribution curves for stannous iodide and cadmium iodide.

Thus there are two angles, 95° and 180°, which give theoretical curves whose maxima fit the observed ones with an accuracy as great as is the accuracy of observation of the maxima. On quantitative grounds it is impossible to select one or other. The curve for 180° is, however, shaped like a saw edge, and a plate with such a curve would be almost identical with those obtained from cadmium iodide (*q.v.*), where the angle is 180°. On these latter plates the unsymmetrical nature of the maxima is most marked and quite unmistakeable; the stannous iodide plates show no such asymmetry, so that the model with an I—Sn—I angle of 180° can be rejected. This leaves the angle as 95°. A similar conclusion is reached from the radial distribution curves of the older kind[12] (Fig. 2, A and B). A shows the result when maxima only are taken into account; it indicates distances of 2·73 and 5·24 (shown by heavy arrows), *i.e.*, an angle of nearly 180°; while B shows the effect of including minima as well; it indicates an angle of 95°.

Minima of deviation at 95° and 180° were also found with the other stannous halides and with the plumbous halides, but, as we shall see later (p. 411), this proves not to be a convincing reason for thinking that the angle really is 95°.

Halogen.	$l_{\text{Sn—X}}$ in A.
Cl	2·42 ± 0·02
Br	2·55 ± 0·02
I	2·73 ± 0·02

However, our immediate need is to know what we may call the *apparent* configurations which will enable us to calculate the bond lengths accurately, and it will be shown that the 95° configurations are satisfactory for this purpose in all these dihalides. The bond lengths then obtained for the stannous halides are shown in table above.

Plumbous chloride.—This compound has a very unfavourable ratio of molecular to atomic scattering. Plates were obtained with four rings, which were symmetrical and fell off regularly from the centre. The *s* values observed for the maxima and minima are given in Table V.

The interpretation of the plates of the three plumbous halides examined will be discussed together.

TABLE V.—PLUMBOUS CHLORIDE.

Max.	Min.	No. of Plates.	$s_{\text{obsd.}}$
1		6	3·38
	2	5	4·51
2		6	5·69
	3	5	7·07
3		6	8·27
	4	2	9·40
4		3	10·82

Plumbous bromide.—The plates from this compound showed five symmetrical maxima, whose intensities fell off regularly from the centre. The *s* values observed for the maxima and minima are given in Table VI.

TABLE VII.—PLUMBOUS IODIDE.

Max.	Min.	No. of Plates.	$s_{\text{obsd.}}$
1		6	2·98
	2	6	4·02
2		6	5·05
	3	6	6·11
3		6	7·31
	4	6	8·48
4		6	9·55
	5	6	10·72
5		6	11·82
	6	6	12·87
6		5	13·96

TABLE VI.—PLUMBOUS BROMIDE.

Max.	Min.	No. of Plates.	$s_{\text{obsd.}}$
1		3	3·19
	2	4	4·35
2		4	5·45
	3	4	6·70
3		4	7·84
	4	4	9·17
4		4	10·19
	5	3	11·47
5		3	12·57

Plumbous iodide.—Six rings were obtained with this compound, all of which were symmetrical and of regularly decreasing intensity from the centre outwards, and were situated at the *s* values given in Table VII.

---

[12] Brockway, *Rev. Mod. Phys.*, 1936, 8, 231.

For an apparent angle of 95°, the bond-lengths calculated for the plumbous halides are the following :—

Halogen.	$l_{\text{Pb—X}}$ in A.
Cl	2·46(5) ± 0·02
Br	2·60 ± 0·03
I	2·79 ± 0·02

The Temperature Effect.

As was stated previously, if for any of the stannous or plumbous halides the average deviations of bond length are plotted against the assumed valency angle, sharp minima are obtained at 95° and 180°. The qualitative agreement between the appearance of the plates and the shape of the theoretical curves for 180° is not good when the halogen-halogen terms are relatively important, but neither is that with the 95° curves. Thus the 95° curve for stannous iodide gives the first and second maxima nearly equal intensities, and likewise the third and fourth, yet the intensities of the actual maxima fall off steadily ; furthermore, the quantitative fit of the minima is not very good.

Now, an angle of 95° makes the halogen-halogen distance nearly 1·5 times the metal-halogen distance, and hence the maxima of the theoretical curve approximate more closely than for any other angle except 180° to those of a simple sin sl/sl curve ; the maxima of the metal-halogen term coincide alternately with a maximum and a minimum of the halogen-halogen term.

All the observed maxima and minima would fit a sin sl/sl curve well ; *e.g.*, the *minima* for stannous iodide with such a curve give :—

Min.	2.	3.	4.	5.	Mean.	Av. Dev.
$l_{\text{Sn—I}}$	(2·65)	2·713	2·725	2·731	2·723	0·007 A.

whereas the values calculated from a 95° model show considerably more variation :—

Min.	2.	3.	4.	5.	Mean.	Av. Dev.
$l_{\text{Sn—I}}$	(2·728)	2·630	2·765	2·689	2·695	0·047 A.

An explanation which therefore appears possible is that the thermal vibration of the molecule makes the halogen-halogen terms less distinct and important than was anticipated. James [7] has shown that, for the diffraction of X-rays by vapours, if $\overline{\delta l_{\text{ij}}^2}$ is the mean square deviation of l_{ij} owing to vibration, then the coherent term in the theoretical expression for the diffracted intensity must be multiplied by $e^{-(\overline{\delta l_{\text{ij}}^2}\cdot s^2)/2}$. This same result should hold for electron diffraction.[12] In general it is found that the bending of two valencies relative to each other is easy compared with the stretching of a link, and so the importance of the halogen-halogen term will be decreased relative to the metal-halogen term. The force-constants of the stannous and plumbous halides are not known, but it is reasonable to suppose that they are about the same as those of the mercuric halides (for bending, 3×10^{-12} ergs/radian²/molecule ; for stretching, $2{\cdot}5 \,.\, 10^5$ dynes/cm./molecule ; see Braune and Engelbrecht [13]).

If it be further assumed that the deviations from the mean bond length, l, or mean angle, θ, follow a Boltzmann distribution, values of $\overline{\delta l^2}$ and $\overline{\delta\theta^2}$ may be very easily calculated. At 600° K, the temperature at which stannous iodide was volatilised, $\sqrt{\overline{\delta l_{\text{Sn—I}}^2}} = 0{\cdot}057$ A, and $\sqrt{\overline{\delta\theta^2}} = 6{\cdot}7°$. Now $l_{\text{I—I}} = 2l_{\text{Sn—I}} \sin \theta/2$, and provided that $\delta l_{\text{Sn—I}}$ and $\delta\theta$ are as likely to be positive as they are negative, *i.e.* provided that the potential energy

---

[13] Braune and Engelbrecht, *Z. physikal. Chem.*, *B*, 1932, **19**, 303.

functions of δl and $\delta\theta$ are symmetrical, as for simplicity we assume them to be, it can readily be shown that

$$\overline{\delta l^2_{I-I}} = 4 \sin^2 \theta/2\ \overline{\delta l^2_{Sn-I}} + l_{Sn-I} \cos^2 \theta/2\ \overline{\delta\theta^2}. \quad . \quad . \quad (1)$$

Hence, in the above example, taking $\theta = 90°$ and $l_{Sn-I} = 2{\cdot}73$ A, we find $\sqrt{\overline{\delta l^2_{I-I}}} = 0{\cdot}24$ A. The I—I term is thus clearly more sensitive to temperature effects than is the Sn—I term, and when the corresponding coefficients for a series of s values are calculated as in Part I of Table VIII, it is seen that beyond $s = 6$ the theoretical curve is almost a pure $\sin sl/sl$ curve. When $s = 16$ the ratio of the coefficients is no less than 1,041 : 1, so the I—I term has become of negligible importance.

TABLE VIII.

	Part I. SnI$_2$. $\theta = 90°$; $T = 600°$ K.		Part II. SnI$_2$. $\theta = 180°$; $T = 600°$ K.		Part III. HgI$_2$. $\theta = 180°$; $T = 400°$ K.	
s \ $\sqrt{\overline{\delta l^2_{ij}}}$	Sn—I 0·057.	I—I 0·24.	Sn—I 0·057.	I—I 0·12.	Hg—I 0·047.	I—I 0·10.
0	1·000	1·000	1·000	1·000	1·000	1·000
2	0·993	0·891	0·993	0·972	0·996	0·980
4	0·974	0·631	0·974	0·891	0·983	0·923
6	0·943	0·355	0·943	0·772	0·963	0·835
8	0·900	0·158	0·900	0·631	0·932	0·726
10	0·848	0·056	0·848	0·487	0·895	0·606
12	0·789	0·016	0·789	0·355	0·853	0·487
14	0·725	0·0035	0·725	0·244	0·805	0·375
16	0·656	0·00063	0·656	0·158	0·754	0·278
Ratio . .	1,041		4·14		2·71	

TABLE IX.—SnI$_2$.

$l_{Sn-I} = 2{\cdot}73$ A.
I—Sn—I = 95°.

$s_{calc.}$ (corrected for thermal effect).		$s_{calc.}/s_{obsd.}$
2·98		(1·046)
	4·07	0·988
5·12		0·998
	6·28	0·989
7·48		1·000
	8·63	1·000
9·77		1·002
	10·91	0·999
12·08		0·996
	Mean	0·997
	Average deviation	0·004

Thus final value of $l_{Sn-I} = 2{\cdot}722$ A.
Average deviation $= 0{\cdot}011$ A.

In Table IX the SnI distance is recalculated. The maxima and minima are those for a corrected theoretical curve with $l_{Sn-I} = 2{\cdot}73$ A and $\widehat{\text{I—Sn—I}} = 95°$; the ratios of $s_{calc.}/s_{obsd.}$ lead to a final value for $l_{Sn-I} = 2{\cdot}72$ A with an average deviation of 0·011 A and a probable error of about 0·02 A, *i.e.* to one hardly different from that given by a simple 95° model. Since the discrepancy should be greatest for this compound the 95° models are adequate for calculating bond-lengths in any other stannous halides or in the plumbous halides.

It can readily be shown that thermal vibration does not seriously affect the characteristic asymmetry of the maxima found in the simple theoretical curves for linear models of the di-iodides, since the M—I and the I—I terms are affected to more nearly the same degree by temperature. According to equation (1), for these molecules with $\theta = 180°$,

$$\overline{\delta l^2_{\mathrm{I-I}}} = 4\overline{\delta l^2_{\mathrm{M-I}}}, \qquad \text{whence } \sqrt{\overline{\delta l^2_{\mathrm{I-I}}}}$$

for stannous iodide at 600° K, with $\theta = 180°$, would be 0·114 A; but since this relation is derived by differential methods, whereas the changes in $l_{\mathrm{Sn-I}}$ and especially in θ are not infinitesimal, this value is not precise. If the effect of the former change be neglected it can be shown that the second alone would make $\sqrt{\overline{\delta l^2_{\mathrm{I-I}}}} = 0{\cdot}01$ A. A more exact treatment would not be warranted, in view of the other approximations made, and so calculations have been made for $\sqrt{\overline{\delta l^2_{\mathrm{I-I}}}} = 0{\cdot}12$ A in stannous iodide, and corresponding with 0·10 A (at 400° K) for mercuric iodide[5]; the results are given in Parts II and III of Table VIII. The importance of the I—I term is not seriously reduced for s values below about 14, and none of the rings for dihalides which we have observed fall beyond this point, owing to limitations imposed by the apparatus. Furthermore, although the absolute values of the coefficients at $s = 16$ are distinctly less than unity, the sixth maximum on the total intensity curve is then reached and, for a $\sin sl/sl$ curve, this has an intensity only one-fifth that of the first, so the extra decrease caused by the temperature effect, up to that point, is of little importance. Thus, for the range $s = 0$ to $s = 14$, with which our present work is concerned, temperature has little effect upon the theoretical curves for linear models of the dihalides, but it has a very marked effect upon those for right-angled models.

Maxima with the characteristic saw-tooth asymmetry were observed with mercuric iodide[5] but they were not for stannous iodide. We therefore conclude that although in the former the valency angle is probably 180°, in the latter it is certainly considerably less, although we cannot say within narrow limits what it is.

Cadmium chloride, bromide, and iodide.

The photographs from these substances all showed regularly spaced rings, which diminished steadily in intensity from the centre outwards. All the rings were unsymmetrical, rising more steeply on the inside, and the minima were correspondingly steeper on the outside. This asymmetry was least marked in the chloride, and most in the iodide, where the rings had the appearance of thin, intense maxima with weak shelves outside them. In the iodide this asymmetry was quite marked in the sixth ring, though the seventh was so weak as not to show it very clearly.

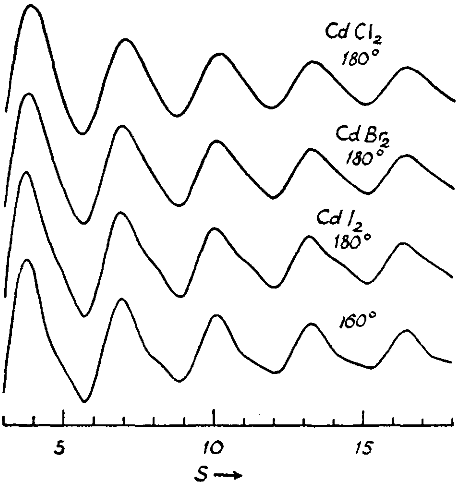


FIG. 3.—Theoretical intensity curves for cadmium halides.

These all agree with the theoretical curves for models with cadmium valency angles of 180° (Fig. 3). No other model produces the characteristic saw-tooth asymmetry of the maxima and the consequent nearness of each minimum to the subsequent maximum.

Assuming an angle of 180°, a value of the cadmium-halogen distance can be calculated from each maximum and minimum. However, owing to the St. John effect[12] all the maxima will be observed too far in and all the minima too far out. Hence all bond lengths calculated from the maxima will be too large and from the minima too small. The final value chosen for the bond length of each halide was therefore the mean of the means of the values from the maxima, and of the values from the minima.

The results for cadmium chloride are given in Table X. The theoretical s values, calculated from a model with an arbitrary Cd—Cl distance of 2 A, are given in the 4th and 9th columns. The results for cadmium bromide are given in Table XI, and for cadmium iodide in Table XII.

TABLE X.—$CdCl_2$.

Max.	Number of Photographs.	$s_{obsd.}$	$s_{calc.}$ for Cd—Cl = 2 A.	$l_{Cd—Cl}$	Min.	Number of Photographs.	$s_{obsd.}$	$s_{calc.}$ for Cd—Cl = 2 A.	$l_{Cd—Cl}$
1	6	3·56	3·78	(2·13)	2	6	5·03	5·54	2·205
2	6	6·27	6·96	2·220	3	6	7·83	8·68	2·233
3	6	9·01	10·10	2·243	4	6	10·52	11·12	2·248
4	6	11·72	13·26	2·261					
Mean				2·241					2·229
Average deviation				0·014					0·016

Mean Cd—Cl length from maxima = 2·241
Mean Cd—Cl length from minima = 2·229

Total mean : Cd—Cl = 2·235 A.

The radial distribution curve calculated from estimated intensities of maxima alone (Fig. 2) gives peaks at 2·61 and 5·02 A (heavy arrows) which, while still agreeing quite well with the SnI length derived above from maxima alone, indicates an I—Sn—I angle of about 160°. In order further to explore the possibility that the I—Cd—I angle is not

TABLE XI.—$CdBr_2$.

Max.	Number of Photographs.	$s_{obsd.}$	$s_{calc.}$ for Cd—Br = 2 A.	$l_{Cd—Br.}$	Min.	Number of Photographs.	$s_{obsd.}$	$s_{calc.}$ for Cd—Br = 2 A.	$l_{Cd—Br.}$
1	8	3·24	3·72	(2·30)	2	9	4·86	5·62	(2·31)
2	10	5·79	6·89	2·377	3	10	7·43	8·77	2·355
3	10	8·40	10·04	2·392	4	10	10·10	11·91	2·356
4	10	11·01	13·19	2·397	5	7	12·58	15·05	2·393
5	7	13·48	16·34	2·423	6	3	15·24	18·20	2·386
6	6	16·06	19·48	2·426	7	—	—	—	—
7	3	18·61	22·62	2·431					
Mean				2·407					2·372
Average deviation				0·019					0·017

Mean Cd—Br length from maxima = 2·407
Mean Cd—Br length from minima = 2·372

Total mean : Cd—Br = 2·390 A.

TABLE XII.—CdI_2.

Max.	Number of Photographs.	$s_{obsd.}$	$s_{calc.}$ for Cd—I = 2 A.	$l_{Cd—I.}$	Min.	Number of Photographs.	$s_{obsd.}$	$s_{calc.}$ for Cd—I = 2 A.	$l_{Cd—I.}$
1	12	3·02	3·68	(2·44)	2	12	4·56	5·67	(2·49)
2	12	5·35	6·85	2·559	3	12	6·96	8·81	2·531
3	12	7·83	9·99	2·552	4	12	9·41	11·96	2·542
4	12	10·23	13·14	2·570	5	12	11·79	15·10	2·563
5	12	12·64	16·29	2·577	6	4	14·25	18·26	2·563
6	6	15·00	19·43	2·590	7	—	—	—	—
7	5	17·44	22·57	2·580					
Mean				2·573					2·550
Average deviation				0·012					0·013

Mean Cd—I length from maxima = 2·573
Mean Cd—I length from minima = 2·550

Total mean : Cd—I = 2·562 A.

180°, but rather less, a curve (Fig. 3) was calculated for an angle of 160°. It shows that even at the fourth maximum the rings have lost much of their characteristic "saw tooth" appearance, which is visible even in the sixth ring on the plates. Further, a model of 160° would give less consistent Cd—I distances. The angle in cadmium iodide may be taken as > 160°, probably 180°, and the same applies with less certainty to the bromide and chloride. The results for the cadmium halides are summarised in Table opposite.

Halogen.	$l_{Cd—X}$ in A.	Angle.
Cl .	2·23(5) ± 0·03	180° ± 10°
Br .	2·39 ± 0·03	180° ± 10°
I .	2·56 ± 0·03	180° ± 10°

(See also Hasseland Strömme,[14] who report $l_{Cd—I}$ = 2·596 ± 0·02 A in cadmium iodide from four maxima, in good agreement with the result here given from maxima alone.)

Discussion.

The bond lengths found in the zinc and cadmium halides are less than the respective sums of the normal covalent radii assigned by Pauling and Huggins,[15] by 9·5, 8·8 and 8·9 % for chloride, bromide, and iodide respectively, and a possible explanation of this fact is that they have some degree of double-bond character (*cf.* mercuric halides [3, 5]).

No radii have been assigned to stannous tin or to plumbous lead, so no normal, single-bond lengths can be calculated for comparison with the observed ones; and consequently there is no obvious, direct means of deciding whether or not these bonds are abnormal. It is to compound to compound. It is true that the radii so calculated from the be noticed, however, that if values of the apparent radii for the metals in these states be calculated from the several halide bond lengths, by subtracting the normal halogen radii, they are found to be sensibly constant in the series for each element, as are the values for thallous thallium derived from the thallous halides. This fact suggests that these apparent radii are the actual covalent radii, for it would be expected that when contraction occurs the apparent radii would vary from contracted halides of certain elements vary very little; but it is then

TABLE XIII.

		Cl.	Br.	I.
Sn^{II}	l_{SnX}	2·42 ± 0·03	2·55 ± 0·02	2·73 ± 0·02
	Halogen radius	0·99	1·14	1·33
	Sn^{II} radius .	1·43	1·41	1·40
Pb^{II}	l_{PbX} . . .	2·46 ± 0·02	2·60 ± 0·03	2·79 ± 0·02
	Pb^{II} radius .	1·47	1·46	1·46
Tl^{I} .	l_{TlX} . . .	2·55†	2·68†	2·87†
	Tl^{I} radius .	1·56	1·54	1·54

† Grether.[16]

---

[14] Hassel and Strömme, *Z. physikal. Chem.*, *B*, 1938, **38**, 466.

[15] Pauling and Huggins, *Z. Krist.*, *A*, 1934, **87**, 205.

[16] Grether, *Ann. Physik*, 1936, **26**, 1.

found, as the examples in Table XIV show, that similar values for the element immediately above or below in their Groups show considerable variation.

TABLE XIV.

	Cl.	Br.	I.	Range.
Cd^{II} radius .	1·245	1·25	1·23	0·015
Hg^{II} radius .	1·35§	1·30§	1·28§	0·07
Ge^{IV} radius .	1·09*	1·15*	1·17*	0·08
Sn^{IV} radius .	1·31*	1·30*	1·31*	0·01
As^{III} radius .	1·17§	1·22§	1·25§	0·08
Sb^{III} radius .	1·38§	1·38§	1·42§	0·04

§ Gregg *et al.*[5] These values are preferred to those given by Braune and Knoke.[3]

* Lister and Sutton.[17]

Both the stannous and the plumbous series, however, give constant series of values.

A more positive indication that the bonds in the stannous and plumbous halides are not shortened is that the divalent radii calculated above are as great as the normal values for the tetravalent radii, being 1·41 and 1·46 A as compared with 1·40 and 1·46 respectively; yet, so far as is known, atoms have larger radii in their higher valency states than in their lower ones (*cf.* boron,[18] phosphorus [19]).

If the contractions observed in the cadmium and mercuric halides are correctly explained by the theory that they have some double-bond character, it is surprising that the bonds in the stannous, plumbous, and thallous compounds are normal; for the tin, lead, and thallium atoms have incomplete octets, and might therefore be expected to accept co-ordinate links from the halogen atoms, just as cadmium and mercury are supposed to do, especially since one such bond could be formed without splitting the *s* pairing, if the third *p* orbital were used (see later). This expectation is supported by the fact that both stannous and plumbous halides readily form complexes of the type $[MCl_3]^-$ just as the cadmium and mercuric halides do.

A further conclusion to be drawn from the constancy of the apparent radii is that the bonding orbitals used by the metal atoms are the same in all the halides. This is consistent with the view that the stannous and plumbous states exist stably because it is comparatively difficult to break the pairing of the *s* electrons in the valency group; for then it would be expected that the two bonds formed would utilise pure *p* orbitals (5*p* and 6*p* for tin and lead respectively). Should this surmise be correct, the predicted valency angle would be about 90°. As was explained in the experimental section, it is impossible to determine the valency angle in these compounds with any precision, but we can at least be certain that it is considerably less than 180°, and is therefore quite different from that found in the zinc, cadmium, and mercury compounds, as our view requires.

---

[17] Lister and Sutton, *preceding paper*.

[18] Lévy and Brockway, *J. Amer. Chem. Soc.*, 1937, **59**, 2085.

[19] Brockway and Beach, *ibid.*, 1938, **60**, 1836.

There is an interesting difference between the length which we find for the Pb—Br link in the free, gas-phase molecule, and that found by Powell and Tasker [6] in the molecule when it is incorporated into the complex crystal lattices of the double salts ammonium, potassium, or rubidium pentabromo-diplumbite. In these latter it is 2·89 ± 0·05 A, which is no less than 0·29 A greater than the distance which we observed and, as these authors pointed out, is intermediate between the values to be anticipated for a covalent and for a purely ionic bond.

Summary.

The structures of the chlorides, bromides and iodides of cadmium, and of divalent tin and lead have been examined by the electron diffraction method. It has been shown that the cadmium halides are probably linear molecules while the others certainly are not.

The bond lengths found were

$l_{\text{Cd—Cl}} = 2{\cdot}23(5) \pm 0{\cdot}03$ A, $l_{\text{Cd—Br}} = 2{\cdot}39 \pm 0{\cdot}03$ A,
$l_{\text{Cd—I}} = 2{\cdot}56 \pm 0{\cdot}03$ A;
$l_{\text{Sn—Cl}} = 2{\cdot}42 \pm 0{\cdot}02$ A, $l_{\text{Sn—Br}} = 2{\cdot}55 \pm 0{\cdot}02$ A,
$l_{\text{Sn—I}} = 2{\cdot}73 \pm 0{\cdot}02$ A;
$l_{\text{Pb—Cl}} = 2{\cdot}46(5) \pm 0{\cdot}02$ A, $l_{\text{Pb—Br}} = 2{\cdot}60 \pm 0{\cdot}03$ A,
$l_{\text{Pb—I}} = 2{\cdot}79 \pm 0{\cdot}02$ A.

The cadmium-halogen bond lengths are less than the sums of the appropriate Pauling-Huggins covalent radii, but those of the tin-halogen or lead-halogen bonds are close to the sums of the tetrahedral covalent radius for tin or lead and the appropriate halogen radius. The latter fact is interpreted as meaning that the covalencies in stannous and plumbous compounds involve only *p*-orbitals on the metal atom.

The authors wish to thank Mr. D. Ll. Hammick and Professor N. V. Sidgwick for their interest and advice, The Royal Society and Imperial Chemical Industries Ltd. for loan of apparatus, and the Department of Scientific and Industrial Research for a maintenance grant to one of them (M. W. L.).

The Dyson Perrins Laboratory,
Oxford.