233. *Complex-anion Formation by Tervalent Elements: The Structure of Cæsium Thallic Enneachloride.*

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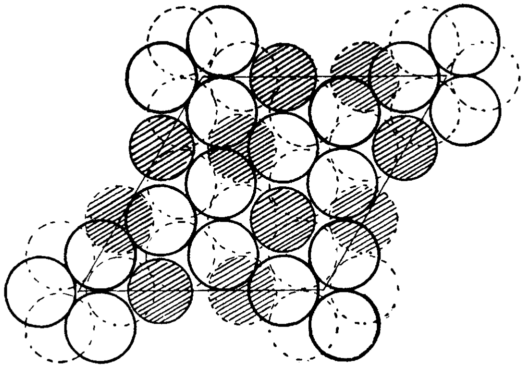
Cæsium thallic enneachloride, $Cs_3Tl_2Cl_9$, has been examined because compounds of similar formula are given by a number of tervalent elements and are often of greater stability than the complex chlorides of the simpler formula $A_3M^{III}Cl_6$ (A = univalent metal). Since this paper was first submitted, Hoard and Goldstein (*J. Chem. Physics*, **1935**, 199) have published a structure for this compound. Our conclusions are essentially the same as theirs.

Experimental.

The material, prepared according to Pratt (*Amer. J. Sci.*, 1895, **49**, 397) by adding a saturated aqueous solution of 2 g. of cæsium chloride to one of 5 g. of thallic chloride, was precipitated in the cold as hexagonal plates, which on recrystallisation gave prisms elongated along *c*. Prisms tabular on the basal plane were obtained from a solution containing 3 g. of cæsium chloride and 5 g. of thallic chloride [Found: Tl (as Tl_2CrO_4), 36·05; Cl (as AgCl), 27·95. Calc.: Tl, 36·22; Cl, 28·36%]. The density (pyknometer method) was 4·31 g./c.c. at 20°. According to Pratt (*loc. cit.*) the crystals are hexagonal with $a : c = 1 : 0{\cdot}8257$, and our crystals conform to his description. Oscillation photographs taken over 15° ranges with copper radiation gave the following translations : along the a axis 22·12, along a horizontal axis at 30° to the a axis 12·82 ($\approx 22{\cdot}12/\sqrt{3}$), along the c axis 18·27 Å. Photographs taken with crystals elongated along c rotating about the c axis appeared symmetrical about the equator, but the systematic absences suggested that the crystals might have a rhombohedral lattice obscured by twinning on the basal plane. The broken appearance of a number of spots on the strong fourth layer line also suggested the possibility of repeating twinning. All crystals of this kind examined gave equatorially symmetrical pictures, but some crystals of the tabular kind behaved differently. The first crystals used gave reflexions of similar spacings but of different intensities on the + 4 and − 4 layer lines, and similar results were observed for the + 2 and − 2 layer lines. The first and the fifth layer lines were almost entirely missing, while reflexions of similar spacing on the ± 3 and ± 6 layer lines which are permitted by the rhombohedral lattice had about equal intensities on the upper and lower lines. On the assumption that the crystal was twinned, two sets of reflexions due to the separate rhombohedral individuals could be distinguished, and, for corresponding indices, one set was found to be uniformly weaker than the other. Finally, a tabular crystal was obtained which was shown from a Laue photograph to be trigonal, and oscillation photographs from this showed the usual absences due to a rhombohedral Bravais lattice. Only on one photograph of very long exposure was there one very faint spot in disagreement with this, probably indicating that the crystal used was not completely one individual. The structure may therefore be referred to a hexagonal cell with the a axis at 30° to that of the original description having $a_0 = 12{\cdot}82$, $c_0 = 18{\cdot}27$ Å. and, from the density, $6{\cdot}03 \approx 6$ molecules per unit cell, or to a rhombohedral cell $a_0 = 9{\cdot}58$ Å., $\alpha = 83° \, 56'$ with two molecules per cell. The absences indicated that the space-group is $R3c$ or $R\bar{3}c$ (C_{3v}^{6} or D_{3d}^{6}). There was no pyroelectric effect or other evidence of polarity, but the twinning makes a definite decision impossible.

FIG. 1.



Close packing of Cl (*plain*) *and* Cs (*shaded*). *The atoms at height* (o) *are drawn heavily; those at height* ($\frac{1}{6}$) *are shown by broken circles.*

A structure was derived mainly from consideration of atomic sizes, and then modified to give better agreement with the observed intensities. It is evident from the space-group symmetry, the space available, and the almost complete absence of layer lines 1, 2, 5, and 7 for oscillation about the trigonal axis, that the structure consists basically of six closely packed layers of chlorine and cæsium ions parallel to the (0001) plane of the hexagonal cell. The smaller thallium must occupy spaces between the closely packed layers. On the assumption that the cæsium ions are to be kept as far as possible apart from each other, idealised co-ordinates are obtained with special values of the parameters in the following positions of the space-group $R\bar{3}c$ (Wyckoff, " Analytical Expression," 2nd Edn.) (the co-ordinates refer to the rhombohedral unit cell) : 6Cs (e) $u\bar{u}0$, etc., with $u = \frac{2}{3}$; 6Cl (e) with $u = \frac{1}{6}$; 12Cl (f), xyz, etc., with $x = \frac{1}{3}$, $y = \frac{1}{6}$, $z = 0$.

The sequence of layers is illustrated by the scale drawing (Fig. 1) and is that for hexagonal close packing of spheres, alternate layers being similar. The hexagonal close packing is revealed in the axial ratio, which may be written for Pratt's original setting (*loc. cit.*) as $2c : a = 1{\cdot}65 : 1$, the calculated axial ratio for close packing being 1·633 : 1. The idealised position for thallium is (*c*) *uuu*, etc., with $u = \frac{1}{12}$. Each thallium would then be half way between successive layers and equidistant from six chlorines, and one-third of the possible spaces between chlorine layers are without thallium atoms.

The ideal structure does not fit the observed intensities of reflexion, the chief discrepancies being that the relative intensities of orders from the basal plane (222, 444, and 666 in rhombohedral indices) are not correct, and the strongness of the fourth layer line relative to the second for oscillation about the trigonal axis is not explained. Some distortion of the structure is therefore necessary, and nearly complete agreement is obtained by a displacement of the thallium atoms alone to $u = \frac{1}{10}$ instead of $\frac{1}{12}$.

Hoard and Goldstein compared intensities observed from a twinned crystal, using only those reflexions which would be unaffected by the twinning. We find fairly good agreement (Table I) between intensities calculated by the formula $I \propto [(1 + \cos^2 2\theta)/2 \sin 2\theta]|S|^2$ and those observed from an untwinned crystal for all types of indices. These intensities are calculated for cæsium and chlorine in the ideal positions and thallium at $u = \frac{1}{10}$, with f values of Pauling and Sherman (*Z. Krist.*, 1932, **81**, 1). Corrections were applied to the calculated intensities according to Cox and Shaw (*Proc. Roy. Soc.*, 1930, *A*, **127**, 71). Our intensities cannot be compared directly with those of Hoard and Goldstein since these authors appear to have used *X*-radiation of wave-length different from ours.

TABLE I.

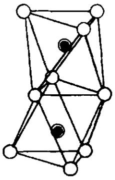
(Indices are rhombohedral.)

Indices.	*I*, calc.	*I*, obs.	Indices.	*I*, calc.	*I*, obs.	Indices.	*I*, calc.	*I*, obs.	Indices.	*I*, calc.	*I*, obs.
200	24	w	$25\bar{7}$	46	s	$3\bar{1}\bar{2}$	37	w	$\bar{1}\bar{3}2$	8	vw
400	69	m	$7\bar{8}1$	59	ms	$51\bar{3}$	80	m+	$2\bar{4}4$	3	vw
600	35	w	$6\bar{9}3$	82	s	$61\bar{4}$	9	vw	$32\bar{3}$	4·4	vw
800	1·8	nil	$5\bar{4}\bar{1}$	80	ms	$31\bar{1}$	356	vs	$21\bar{5}$	3·6	vw
202	175	ms	$\bar{3}\bar{4}7$	7	vw	$\bar{1}\bar{3}7$	40	w+	$9\bar{1}\bar{5}$	46	w+
303	0·6	nil	$1\bar{2}1$	515	vs	$32\bar{1}$	73	m	$43\bar{4}$	11	vw
404	5·5	vw	$2\bar{4}2$	380	vs	$42\bar{2}$	38	m−	$62\bar{5}$	6·7	vw
505	36	w+	$3\bar{6}3$	62	s	$52\bar{3}$	22	w	$72\bar{6}$	6	vw
606	79	m+	$4\bar{8}4$	123	s	$61\bar{3}$	18	w	$33\bar{2}$	44	m−
222	157	ms+	$20\bar{4}$	6	vw	$\bar{2}\bar{4}1$	0	nil	$43\bar{3}$	25	w
444	138	ms+	$0\bar{5}3$	3	vw	$21\bar{4}$	0	nil	121	376	s−
666	68	m	$40\bar{1}$	31	w	$43\bar{2}$	0	nil	$43\bar{1}$	95	m
$10\bar{1}$	129	m+	$50\bar{2}$	17	w	$32\bar{4}$	0	nil	$72\bar{3}$	32	w
$20\bar{2}$	0·3	nil	$10\bar{6}$	0	nil	$31\bar{3}$	0	nil	$82\bar{4}$	24	vw
$30\bar{3}$	189	s	103	119	m+	$1\bar{1}\bar{5}$	0	nil	$52\bar{1}$	0·2	nil
$40\bar{4}$	0·4	nil	$0\bar{6}2$	20	w	$1\bar{1}4$	54	m	$81\bar{3}$	26	w
$50\bar{5}$	8	vw	420	345	s	$2\bar{1}\bar{5}$	28	m−	$3\bar{2}5$	51	m
$60\bar{6}$	118	ms	$80\bar{2}$	57	m	$3\bar{1}\bar{6}$	17	m−	$72\bar{5}$	11	vw
$4\bar{1}\bar{3}$	17	w	102	123	m	$4\bar{2}\bar{6}$	14	w	$81\bar{5}$	11	vw
$42\bar{6}$	0·3	nil	$10\bar{5}$	32	w	321	422	s	$4\bar{1}\bar{7}$	12	vw
$5\bar{2}\bar{3}$	11	w	$41\bar{3}$	4·6	vw	$62\bar{2}$	95	ms	$1\bar{6}1$	21	vw

Oscillation photographs of long exposure about [111] show a few very weak reflexions on the first and fifth layer lines. The intensities calculated for these are all zero with the parameters given above, and it is evident that some further slight distortion of the structure is required. The interatomic distances given by these parameters are Tl–3Cl 2·8, Tl–3Cl 2·5, Cl–(8Cl + 4Cs) 3·7, Cs–12Cl 3·7 Å. Hoard and Goldstein suggest chlorine parameters slightly modified from the ideal in order to bring the interatomic distances more into agreement with expected values, mainly by shortening the edges of the shared face of the complex ion. These modifications are in themselves probable, and our observations of weak first and fifth layer line reflexions show that some such changes are necessary. The *X*-ray data obtainable are, however, not sufficient for accurate parameter determination.

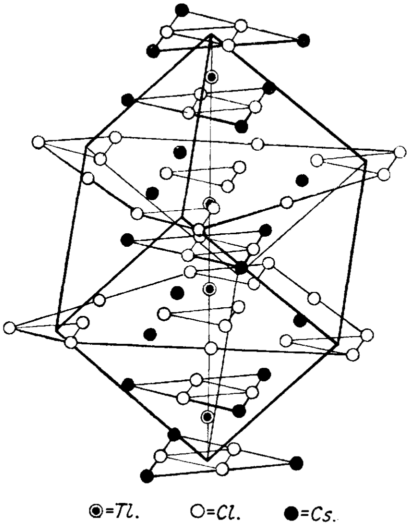
The structure contains the complex ion Tl_2Cl_9, consisting of two thallium atoms each surrounded by six chlorine atoms in the form of an octahedron, the two octahedra having one face in common. The thallium atoms are displaced from the centres of the octahedra away from each other, so that the Cl–Tl distance is less when the chlorine belongs to one octahedron than when it is shared between two. The complex ion is illustrated in Fig. 2, and a unit of the structure in Fig. 3. As in the structure of cæsium arsenic enneachloride (Hoard and Goldstein, *J. Chem. Physics*, **1935**, 116), cæsium has twelve chlorine neighbours. The great modifying influence of other circumstances on the co-ordination number observed compared with that expected from radius ratio alone is evident from the fact that cæsium and chlorine have now been found in crystal structures where the number of chlorine neighbours around cæsium is 6, as in the high-temperature form of cæsium chloride (Wagner and Lippert, *Z. physikal. Chem.*, **1933**, **21**, *B*, 471), 8 in ordinary cæsium chloride, 10 in tricæsium cobalt pentachloride (Powell and Wells, this vol., p. 359), and 12 in these two types of enneachloride. Each chlorine atom has four cæsium and eight chlorine neighbours in the close-packing positions. Two-thirds of them have one thallium and one-third have two thallium neighbours.

FIG. 2.



Tl_2Cl_9 *group.*

FIG. 3.



Atoms in the same layer perpendicular to the trigonal axis are enclosed by a line. Small triangles link chlorine atoms arranged in groups of three around trigonal axes.

If possible slight distortions are ignored, the structure has horizontal planes of symmetry apart from the thallium atoms, and the twinning may be brought about by these atoms entering some of the positions, between chlorine atoms, which should be unoccupied. One individual of the twin may be derived from the other either by reflexion across the basal plane or by a rotation of 60° about the trigonal axis.

DISCUSSION.

Tervalent metals in general give rise to a more complex series of halogeno-salts than do the bi- and quadri-valent metals. Compounds of the simple series A_3MHl_6, with the exception of the fluorides, are often exceedingly soluble, hygroscopic, and not recrystallisable from water. Other types formed are a limited number of formula $AMHl_4$; hydrated hexachlorides A_3MCl_6,xH_2O (x frequently 2); an extensive series of isomorphous compounds $A_2(MHl_5,H_2O)$, where M for a suitable cation and halogen may be Cr, Mo, In, Tl, V, Mn, Fe, Ti, Ru, or Rh; enneahalides $A_3M_2Hl_9$, examples being known when M is Mo, W, Tl, As, Sb, Bi, Fe, Al (?), and Cr; and other compounds of more complex formula.

This behaviour cannot be explained by assuming that it is impossible on account of unfavourable radius ratio to have, *e.g.*, six chlorine atoms around the tervalent metal atom to form the complex anion MCl_6, since six chlorine atoms are arranged round some of the smallest of these in the anhydrous trichlorides of iron and chromium, and probably for the other metals in the hydrated hexachlorides and in the enneachlorides, and even six of the larger bromine atoms may surround an iron atom in the compound of pyridinium bromide and ferric bromide $(PyH)_3Fe_2Br_9$. The widespread replacement of one chlorine or bromine atom to form the complex (MHl_5,H_2O) must be attributed to causes other than the smaller effective radius of the water molecule.

The complexity of these series is in part due to the instability of the resulting crystal structure of the simpler compounds A_3MCl_6, which results in the crystallisation of alternative compounds. The fluorides such as ammonium ferrifluoride, $(NH_4)_3FeF_6$, form an electrically stable and very compact structure of the anti-yttrofluorite type (Pauling, " Strukturbericht," p. 449). With increase in the size of the complex anion, it becomes increasingly difficult to form a compact structure of this type, since the arrangement of the octahedral groups produces gaps in the structure which are somewhat large compared with the cations which should occupy them, and similar difficulties may be anticipated with alternative structures. Increase in the radius of the cation will tend to stabilise the structure. In general agreement with these suggestions, it is found that the complex fluorides of tervalent metals usually have the formula A_3MF_6 and are stable. The extreme solubility and hygroscopic nature of the chlorides point to instability of the crystal lattice, and the increase of stability with increasing cation radius is shown by compounds containing the complex $(MoCl_6)^{3-}$, it being found (Bucknall, Carter, and Wardlaw, J., 1927, **512**) that the potassium and ammonium salts are extremely soluble in cold water, but the rubidium compound is almost insoluble and the cæsium compound quite so.

On this view the formation of the alternative series of salts is readily explicable. Water molecules in the hydrated salts will help to fill gaps in the structure, and a detailed investigation of the structure of these compounds should reveal why the water content is frequently two molecules. The formation of a bivalent complex anion by replacement of one halogen atom by water makes the compounds analogous to the series A_2MCl_6, with the possibility of a related structure for which a very large ratio of anion to cation radius is permissible. Formation of compounds of the enneachloride type is a particularly favourable way of obtaining compact structures, both the arsenic and the thallic compound being characteristically close packed.

The two types are respectively cubic and hexagonal close packed, and differ in the manner in which chlorine atoms are shared between two octahedra. In the thallium compound, two octahedron faces are shared and the complex anion $Tl_2Cl_9{}^{3-}$ may be distinguished in the structure. It does not follow that this ion will exist in solution, but Collenberg and Sandved (*Z. anorg. Chem.*, 1923, **130**, 1) have shown, from freezing-point depressions and conductivities of alkali tungsten enneachlorides, that a similar polynuclear complex * can exist in solution. In the arsenic compound, corners of octahedra are shared, and if a complex anion exists it is of the highly condensed type stretching throughout the crystal. It appears rather, according to Hoard and Goldstein (*loc. cit.*), that the arsenic trichloride molecule persists in the crystal and is built into the structure with cæsium and chlorine ions. The resemblance in formulæ of compounds of this type (which are presumably given only by elements such as arsenic, antimony, and bismuth that form stable trichloride molecules of pyramidal configuration) to the enneachlorides given by thallium, tungsten, and possibly other elements, is due to geometrical requirements of the structures rather than to chemical similarities of the elements.

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