Acta Cryst. (1950). **3**, 405

The Crystal Structure of Hexammine-cobaltic Hexachlorothalliate, $Co(NH_3)_6TlCl_6$, and Hexammine-cobaltic Hexabromothalliate, $Co(NH_3)_6TlBr_6$

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(*Received* 10 *March* 1950)

The crystal structure of hexammine-cobaltic hexachlorothalliate (1) and hexammine-cobaltic hexabromothalliate (2) have been determined in detail. Both crystals are cubic and isomorphous with the space group T_h^6–$Pa3$. There are four formula units in each unit cell of dimensions $a = 11{\cdot}40$ kX. for (1) and $a = 11{\cdot}77$ kX. for (2). The structure is a new type and consists of octahedral complexes, $TlX_6{}^{-3}$ and $Co(NH_3)_6{}^{+3}$, which form a sodium-chloride type arrangement. Abnormally short interatomic distances between thallium and halogen atoms were found. The Pitzer–Hildebrand rule concerning the colour of compounds in relation to bond character holds in halogeno-thallium complexes.

Introduction

$Co(NH_3)_6TlCl_6$, hexammine-cobaltic hexachlorothalliate, was first prepared by Spacu & Pop (1940) by adding to a solution of potassium hexachlorothalliate a solution containing hexammine-cobaltic chloride. They found that the complex is selectively precipitated out, is practically insoluble in water and is very stable. For these reasons they recommended its use for the separation and quantitative determination of thallium. No crystallographic examination on this substance has yet been reported. It was found possible to prepare single crystals of this substance by the diffusion method (Miles, 1931). Two small beakers, the one containing a solution of thallic chloride and the other of hexammine-cobaltic chloride, were put side by side in a large beaker, and distilled water was introduced carefully into all of them along their walls until its level reached about 1 cm. above the two beakers. After several days, single crystals in cubes up to 0·5 mm. in each dimension grew on the upper part of the wall of the beaker containing thallium solution. The crystals are isotropic under the polarizing microscope and split easily parallel to the cube faces; density 2·599 g.cm.$^{-3}$, index of refraction for Na D line$\sim$1·76. The colour of the crystals, orange-red at room temperature, fades into pale yellow at liquid-air temperature and turns to dark red at about 250° C. These colour changes are reversible. The crystals decompose above 280° C.

We have prepared a new compound, an analogous bromo-complex, hexammine-cobaltic hexabromothalliate, $Co(NH_3)_6TlBr_6$, by a similar method. By contrast with the chloro-complex, it is somewhat soluble in water, and single crystals were easily obtained by the slow evaporation of a solution containing hexammine-cobaltic bromide and thallic bromide in equivalent proportion. Its properties are similar to those of the chloro-complex, except the greater solubility. It is reddish brown in colour at room temperature, orange red at liquid-air temperature, and dark reddish brown at 250° C. The crystals are stable up to 280° C. Density 3·401 g.cm.$^{-3}$, refractive index for Na D line$\sim$1·8.

In the following we shall designate the chloro- and bromo-complexes as (1) and (2).

Determination of the crystal structure

Laue photographs were taken with a beam normal to the cube faces. Both crystals showed hemi-tesseral symmetry, the departure from holo-tesseral symmetry being very small, especially for (1). Oscillation photographs were prepared using Mo $K\alpha$ and Co$K\alpha$ radiations. They gave for the unit-cube edges:

$$a = 11{\cdot}40 \text{ kX. for (1), and } a = 11{\cdot}77 \text{ kX. for (2).}$$

There are four formula units in each unit cell, the calculated densities being 2·577 g.cm.$^{-3}$ for (1) and 3·418 g.cm.$^{-3}$ for (2). All types of reflexions were present except *hk*0 with *h* odd, 0*kl* with *k* odd and *h*0*l* with *l* odd. These systematic reflexions are characteristic only for T_h^6–$Pa3$. The relative intensities of reflexions were visually estimated with calibration scales. They were corrected for polarization, Lorentz and absorption factors, using Cochran's chart (1948).

There are four thallium, four cobalt, twenty-four halogen and twenty-four nitrogen atoms in the unit cell. The positions of these atoms are uniquely determined by the symmetry of the space group T_h^6–$Pa3$ as follows:

$$\begin{array}{rl} 4\,\mathrm{Tl} & (a)\ 0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, 0;\ \searrow. \\ 4\,\mathrm{Co} & (b)\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2};\ \tfrac{1}{2}, 0, 0;\ \searrow. \\ \left.\begin{array}{r} 24\,X \\ 24\,\mathrm{N} \end{array}\right\} & (c)\ x, y, z \text{ etc., general positions.} \end{array}$$

The nearly holohedral symmetry of the Laue photographs and the general features of the oscillation photographs follow naturally from the above atomic arrangement when we consider the exceedingly large scattering power of thallium.

As a first approximation, the Fourier representation of electronic density projected upon (001) was synthesized using $F(hk0)$'s with h and k all even, the signs of which were known from the arrangement of the heavy atoms. From the projection so obtained we could assign approximate parameters for the halogen atoms. Those were also in good accord with the conclusion derived from the Patterson diagrams $P(x, y)$. By successive approximations, all six parameters were determined. For the determination of the halogen parameters, the bromo-complex was found to be more useful, while for the nitrogen parameters the chloro-complex gave more reliable results. The final atomic co-ordinates for the two compounds are given in Table 1.

Table 1. *Atomic co-ordinates*

		x	y	z
(1)	Cl	0·139	0·150	−0·075
	N	0·10	0·64	0·05
(2)	Br	0·139	0·151	−0·075
	N	0·09	0·64	0·04

The calculated and observed structure factors are compared in Table 2. The agreement for (1) is excellent. The parameter values are estimated accurately to ±0·003 for the chlorine and ±0·005 for the nitrogen atoms. Less satisfactory results were obtained for (2), but the bromine parameters could be determined with a considerable degree of accuracy, for any variation greater than ±0·002 disturbed the general agreement. The minor discrepancy, shown with an asterisk in Table 2, may perhaps arise from the deformation of the electronic clouds of bromine atoms as in the cases of tetrabromo- and tetraiodo-thalliate (Watanabé, Saito, Shiono & Atoji, 1950) or of cadmium iodide (Smirnova, Brager & Zhdanov, 1941). In the calculation of structure factors, the atomic f curves tabulated in the *International Tables* were used, except for nitrogen, for which an appropriate correction, due to the embedded hydrogen atoms, was made (7·1 and 4·5 for $\sin\theta/\lambda$ 0·1 and 0·2). A correction for the anomalous dispersion for the cobalt atom ($\Delta f = 2{\cdot}8$) was also taken into account (Hönl, 1933) in cases where calculated values were to be compared with the data obtained with Co $K\alpha$ radiation.

The electronic density projected upon (001) for (1) is shown in Fig. 1, where small peaks corresponding to nitrogen atoms are clearly seen, besides the exceedingly large one for the overlapping thallium and cobalt atoms and the medium ones for the chlorine atoms.

Discussion of the structure

The structure belongs to a new type, and its projection upon (001) and its schematic representation are shown in Figs. 2 and 3.

Table 2. *Observed and calculated structure factors*

$hk0$	$F_{\text{obs.}}$	$F_{\text{calc.}}$
(1) Hexammine-cobaltic hexachlorothalliate		
200	10·8	11·5
210	0·9	0·9
220	10·0	9·9
230	1·6	1·7
400	2·0	2·1
410	1·6	1·8
240	6·3	6·8
420	7·5	7·6
430	0	−0·3
250	0	0·4
440	10·0	10·6
600	7·7	7·9
610	1·0	0·8
260	8·1	8·0
620	8·7	8·7
450	3·3	−3·3
630	0·7	−0·6
460	6·6	6·7
640	8·5	8·3
270	1·6	−1·3
650	2·1	−2·0
800	6·6	7·3
810	1·8	−1·6
470	0	0·7
280	8·0	8·0
820	6·9	6·9
660	4·9	4·9
830	0	−0·1
480	6·6	6·6
840	6·7	6·6
670	1·3	1·3
290	0·9	−0·8
850	3·2	3·1
490	2·4	−2·1
10,0,0	2·9	2·9
680	3·6	3·6
860	6·2	6·3
10,1,0	2·0	−2·0
2,10,0	5·6	5·7
10,2,0	4·8	4·8
10,3,0	1·4	−1·2
870	0	−0·3
4,10,0	8·5	8·1
10,4,0	4·3	4·1
690	2·5	2·3
2,11,0	0	−0·3
10,5,0	1·7	2·1
880	4·2	4·3
6,10,0	5·6	5·6
10,6,0	6·6	6·4
4,11,0	0	−0·3
12,0,0	5·2	5·8
12,1,0	0	0·2
(2) Hexammine-cobaltic hexabromothalliate		
200	10·0	12·3
210	2·1	1·9
220	11·0	11·3
230	5·0	5·2
400	3·8	−3·7
410	3·9	3·9
240	5·6	5·7
420	7·2	7·3
430	1·6	−0·2
250*	1·3	2·9
440	12·5	14·0
600	8·8	9·1
610	2·9	2·9
260	8·5	9·3
620	10·2	10·3
450	7·2	−8·4
630	0	−1·0
460	5·8	5·8
640	6·8	8·8
270	3·1	−3·2
650*	2·9	−6·9
800	6·8	7·7
810	3·5	−3·2
470	0	0·6
280	9·3	9·6
820	6·3	7·2
660	3·0	2·7
830	1·2	0·8
480	7·0	7·1
840	6·9	7·2
670	1·7	2·2
290	2·2	−3·0
850	6·5	7·2
490	5·5	7·0
10,0,0	0	−1·0
680	1·0	1·0
860	6·2	5·8
10,1,0	4·7	−5·1
2,10,0	4·6	4·6
10,2,0	4·2	4·1
10,3,0	2·9	−3·2
870	1·7	−1·0
4,10,0	10·3	10·4
10,4,0	8·0	8·5
690	4·0	5·5
2,11,0	0	−0·3
10,5,0*	1·0	5·1
880	3·1	3·2
6,10,0	6·2	6·3
10,6,0	5·1	7·1
4,11,0	1·5	−0·3
12,0,0	7·4	7·3
12,1,0	0	−0·3
890	6·4	−6·5
2,12,0	1·8	1·7
12,2,0	5·5	5·7
10,7,0	0	−0·1

The structure may be considered to be composed of octahedral complex radicals, $Co(NH_3)_6^{+3}$ and TlX_6^{-3}, in the NaCl type arrangement. Among the complex salts having the composition AX_6BY_6, the structures hitherto determined all belong to the I-6_1 type, a typical example being $SnCl_6Ni(H_2O)_6$ (Pauling, 1930).

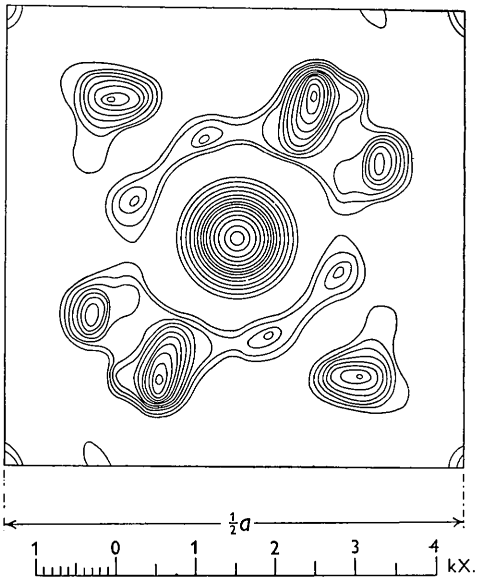

Fig. 1. Projection of electronic density of hexammine-cobaltic hexachlorothalliate on (001). The contour lines around the central part due to the overlapping of thallium and cobalt atoms are drawn with a spacing ten times larger than the rest. The medium peaks stand for chlorine and the smallest for nitrogen atoms.

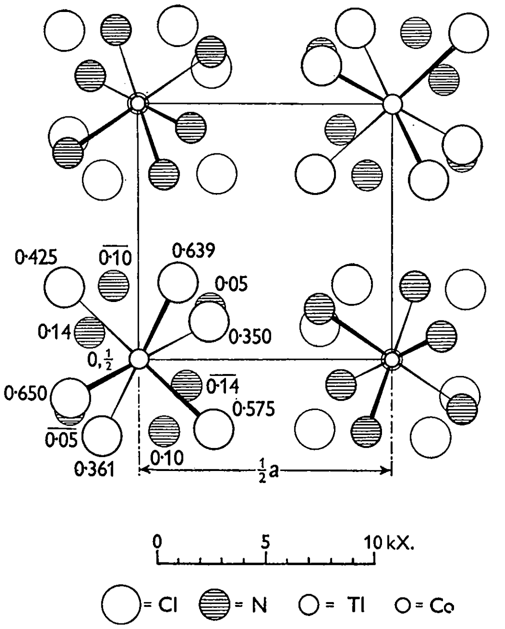

Fig. 2. Projection of the structure of hexammine-cobaltic hexachlorothalliate on (001). Figures give the height or depth of each atom expressed as a fraction of the unit translation.

The reason why $Co(NH_3)_6TlX_6$ assumes the arrangement of the NaCl type in contrast to the I-6_1 type (deformed CsCl type) is not yet clear. It can be shown, however, that this difference does not arise from the relative sizes of complex radicals, nor from the charges on the central atoms, but the structure may perhaps be determined chiefly by the interaction of the ligand molecules or ions.

The proper symmetries of thallium and cobalt atoms are C_{3i}–$\bar{3}$ and the complex radicals form nearly regular octahedra, as can be seen from the interatomic distances shown in Table 3. Each halogen atom is surrounded by six ammonia molecules and each ammonia molecule by six halogen atoms. Pauling's electrostatic valency rule is hence fulfilled satisfactorily.

Table 3. *Interatomic distances (in* kX.) *between neighbouring atoms*

Within a complex radical

	Co–N	Tl–Cl	Tl–Br	N–N	Cl–Cl	Br–Br
(1)	2·07	2·48	—	2·80	3·48	—
	—	—	—	2·98	3·54	—
(2)	2·02	—	2·58	2·80	—	3·61
	—	—	—	2·94	—	3·67

Between neighbouring groups

	Cl–N	Br–N
	3·30	3·44
	3·41	3·47
	3·43	3·62
	3·45	3·64
	3·53	3·67
	3·88	4·13
Mean value	3·50	3·66

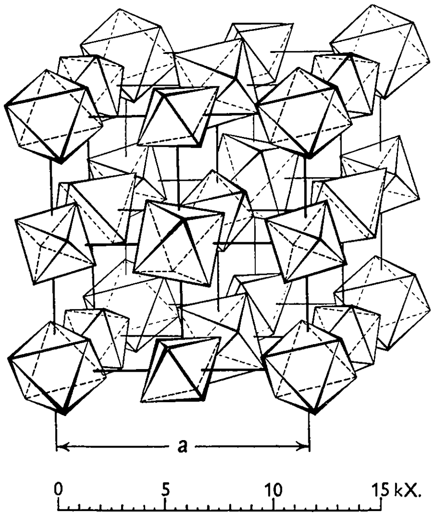

Fig. 3. Structure of hexammine-cobaltic hexachlorothalliate. Larger octahedra represent hexachlorothalliate ions $TlCl_6^{-3}$, smaller ones hexammine-cobaltic ions $Co(NH_3)_6^{+3}$.

The interatomic distances between thallium and halogen atoms are shorter than those hitherto reported (see Table 4) and much less than the sums of ionic radii. This shows the strong attraction between thallium and

Table 4. *The relations between colour and interatomic distance* Tl–*X* *in halogeno-thallium complexes*

Substance	$K_3TlCl_62H_2O$*	$Cs_2TlCl_5H_2O$†	$Co(NH_3)_6TlCl_6$	$r(Tl^{+3})+r(Cl^-)$‡
Tl–Cl	2·55 kX.	2·53 kX.	2·48 kX.	2·86 kX. (P) 2·76 kX. (G)
Colour	Colourless	Colourless	Orange red	—

Substance	$KTlBr_42H_2O$§	$Rb_3TlBr_6\frac{8}{7}H_2O$*	$CsTlBr_4$§	$Co(NH_3)TlBr_6$	$r(Tl^{+3})+r(Br^-)$‡
Tl–Br	2·75 kX.	2·70 kX.	2·65 kX.	2·58 kX.	3·01 kX. (P) 2·91 (G)
Colour	Pale yellow	Gold yellow	Yellow	Reddish brown	—

* Hoard & Goldstein (1935).
† Watanabé & Atoji (1950).
‡ (P) after Pauling; (G) after Goldschmidt.
§ Watanabé *et al.* (1950).

halogen atoms, and the large size and low polarizing power of the complex $Co(NH_3)_6{}^{+3}$ must be responsible for these short distances. The latter effect would be considerable in halogeno-thallium complexes, as both thallium and halogen atoms have large polarizabilities. In fact, this effect is clearly shown in Table 4. In caesium tetra-bromothalliate, $CsTlBr_4$, thallium and bromine atoms form a co-planar square, while in potassium tetrabromodiaquothalliate, $KTlBr_4(H_2O)_2$, two water molecules are, in addition, in contact with the central thallium atom, forming an octahedral complex (Wantanabé *et al.* 1950). As the octahedral and square bonds differ little in character, we may compare these complexes in the same scheme.

Though not sufficient and conclusive, we can see in the examples given in Table 4 the change of colour which may well accord with the Pitzer–Hildebrand rule concerning the colour of compounds in relation to bond character. The cleavage observed parallel to the cube faces would naturally be expected from the structure.

The authors would like to express their sincere thanks to Prof. I. Nitta for his continued encouragement, to Mr K. Osaki for his help in the structure determination and to R. Shiono and T. Yoshizaki for their assistance in preparing some of the specimens and the density determination. Their thanks are also due to the staff of the Kosaka mine who gave them a quantity of thallium for this investigation. This study was helped by the research grant given by the Ministry of Education.

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Acta Cryst. (1950). **3**, 408

Polymorphism of the Chlorites. I. Ordered Structures

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(*Received* 27 *March* 1950)

A variety of polymorphic forms has been found among single crystals of chlorites, consisting of ordered, partially ordered and disordered structures. Four different ordered structures have been analysed in detail. The reflexions are of two types: those with $k=3n$ are similar for all chlorites and confirm Pauling's structure of the chlorite layer and the *ac* projection of McMurchy's structure. Reflexions with $k\neq 3n$ show marked variations for the different ordered structures and degenerate into two-dimensional streaks for completely disordered structures. Four ordered structures are analysed in terms of three types of layer with displacements along the *a* and *b* axes, but a simpler description is given in terms of layers of a single type which are displaced along one of the three 'hexagonal' *a* axes by $-\frac{1}{3}a$, together, in some structures, with regularly occurring rotations of ±120° about the normal to the basal cleavage plane, which is the plane of the layers.

1. Introduction

The chlorites are a group of layer-lattice silicates of very variable composition (Orcel, 1927; Hallimond, 1939) which may be expressed approximately by the formula $X_mY_4O_{10}(OH)_8$, where *m* lies between 4 and 6, and *X* and *Y* stand for positive ions in octahedral and tetra-