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Crystal and Molecular Structure of Thallium(III) Bromide Tetrahydrate and Thallium(III) Chloride Tetrahydrate, a Redetermination

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The crystal structures of the isomorphous compounds $TlBr_3.4H_2O$ and $TlCl_3.4H_2O$ have been determined from X-ray diffraction data collected at room temperature on a Syntex $P2_1$ four-circle diffractometer.

The compounds crystallize in the orthorhombic space group *Pcmn* (No. 62). The cell parameters are: $TlBr_3.4H_2O$: $a = 6.710(2)$, $b = 11.006(2)$, $c = 12.735(3)$ Å. $TlCl_3.4H_2O$: $a = 6.503(1)$, $b = 10.673(2)$, $c = 12.308(3)$ Å. $Z = 4$ for both compounds.

The Tl atom forms a slightly distorted trigonal bipyramidal complex with three X (= Br,Cl) atoms in the equatorial plane and two water molecules in the axial positions. The distances corrected for thermal motion are:

$TlBr_3.4H_2O$: Tl – Br = 2.516(3) and 2.514(2) Å; Tl – O = 2.602(16) and 2.515(15) Å.

$TlCl_3.4H_2O$: Tl – Cl = 2.395(6) and 2.387(5) Å; Tl – O = 2.511(16) and 2.428(15) Å.

The Tl atom is slightly off the plane of the X atoms, at a distance from the plane of 0.101(1) Å for $TlBr_3.4H_2O$ and 0.071(1) Å for $TlCl_3.4H_2O$. The structures were refined to conventional *R*-values of 5.2 % ($TlBr_3.4H_2O$) and 6.6 % ($TlCl_3.4H_2O$).

Several studies of chloride and bromide complexes of Tl^{3+} have revealed interesting properties of these species. They are among the most stable metal halide complexes.[1,2] The thermodynamic data[2,3] show a distinct break in the enthalpy change after the second complex, TlX_2^+, indicating interesting structural relationships between the different complexes. Thus, the first and second complexes could be linear, as in the isoelectronic Hg^{2+} complexes, further addition of halogen changing the geometry to tetrahedral and then again to octahedral in TlX_6^{3-}, if the latter is formed in solution.

In order to cast some light on these relationships, a series of X-ray diffraction experiments on Tl^{3+}-halides in aqueous solutions has been undertaken.[4] The present work is part of a series of crystal structure determinations of Tl^{3+} compounds. It was undertaken in order to study the changes in coordination of X-atoms around Tl^{3+} in the solid state and to obtain accurate interatomic distances in the different TlX_n^{3-n} complexes formed. The results could then be used for comparison and help in explaining the radial distribution curves obtained from the solution experiments.

The structure of $TlX_3.4H_2O$ crystals was investigated in 1956 by X-ray diffraction[5] (chloride and bromide) and in 1959 by the Tl NMR technique[6] (chloride). The X-ray results were obtained by Patterson and Fourier projections and geometrical considerations and showed a regular bipyramidal $TlX_3.2H_2O$ complex with the three X atoms and Tl in the equatorial plane. The positional parameters of the oxygens were not determined. The NMR investigation showed three thallium resonances claimed to be consistent with the presence of $Tl(H_2O)_x^{3+}$, $TlCl_4^-$ and $TlCl_6^{3-}$.

Obviously, the results[5,6] are contradictory. It was thus of interest to make an accurate determination of the coordination of Tl^{3+} in the compounds.

EXPERIMENTAL

The crystals were prepared by an overnight evaporation of concentrated aqueous solutions of

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$TlBr_3(TlCl_3)$ at 2 °C. The solutions were prepared by oxidizing a suspension of TlBr(TlCl) in water with bromine (chlorine) until all solid had dissolved. A stream of nitrogen was then passed through the solution in order to remove excess halogen. The subsequent chemical analysis showed that at least 99.9 % of the thallium was present as Tl^{3+}.

The shape of the crystals was irregular. They were enclosed in a glass capillary during the data collection.

The intensity data were collected with a computer-controlled Syntex $P2_1$ four-circle diffractometer using graphite monochromatized Mo$K\alpha$-radiation and a scintillation counter. The ω-scan mode was used for intensity data collection. The scan speed varied from 0.5°/min for weak reflexions up to 29.3°/min for strong reflexions.

All intensities were corrected for Lorentz and polarization effects.

After every 100th reflexion, three check reflexions were measured. Their intensities varied within ±5 % for the chloride and for the *hkl*-data of the bromide, whereas variations of ±15 % were measured for the $hk\bar{l}$-data of the bromide. No correction for this effect was applied. For the bromide, however, separate calculations were performed for each set of the data to check the influence of the intensity variations. There were no significant changes in the atomic parameters obtained from the two sets. As a consequence, both the sets for the bromide were used together in the following calculations (*cf.* Table 2).

A semi-empirical absorption correction[7] was applied to $TlBr_3.4H_2O$. The variation of the correction factor was from 1.0 to 0.31. The $TlCl_3.4H_2O$ data gave a lower *R*-value without the correction. When the *hkl* and $hk\bar{l}$ data for the bromide were compared it was clear that the intensities of equivalent reflexions were much closer to each other when corrected for absorption. However, as the correction for the bromide had no significant influence on either the atomic positional parameters or the temperature factors, the absorption correction data for the chloride were not remeasured and the final parameters were obtained from the non-corrected data. (It was thus assumed that the absorption effect does not influence the data for the chloride more than that for the bromide.)

The unit cell was found to be orthorhombic with $Z=4$ (Table 1). The cell dimensions were refined by the least squares procedure[8] using 12–14 reflexions with $2\theta > 30°$. The programs used for all calculations were supplied by Syntex (XTL version 2)[8] for a NOVA 32K computer with a disc memory unit. In addition, the plot program for crystal structure illustrations, ORTEP-II,[9] was used, and the interatomic distances were corrected for thermal motion by means of the ORFFE program.[10]

The scattering factors used for all atoms were calculated from analytical expressions for the neutral atoms.[11] Anomalous dispersion corrections were included for all atoms.[11]

Table 1. Crystal data.

Parameter	$TlBr_3.4H_2O$	$TlCl_3.4H_2O$
Crystal colour	yellow	colourless
Crystal dimensions (mm)	0.20 × 0.20 × 0.10	0.23 × 0.13 × 0.07
a (Å)	6.710(2)	6.503(1)
b (Å)	11.006(2)	10.673(2)
c (Å)	12.735(3)	12.308(3)
V (Å^3)	940.5(4)	854.3(3)
D_m (g/cm^3) (Ref. 5)	3.65	3.00
D_x (g/cm^3)	3.65	2.98
μ(Mo$K\alpha$) (cm^{-1})	307.4	199.2

STRUCTURE DETERMINATION AND REFINEMENT

From the systematic extinctions ($0kl$ for $l=2n+1$ and $hk0$ for $h+k=2n+1$) two space groups were possible, the centrosymmetric $Pcmn$, – (No. 62 non-standard setting) and the non-centrosymmetric $Pc2_1n$ – (No. 33 non-standard setting).

Both the three-dimensional Patterson function and the distribution of the normalized structure factors were consistent with the centrosymmetric space group – $Pcmn$, which was, accordingly, assumed to be the correct one. This assumption was then confirmed by the complete structure determination.

Table 2. Data collection and refinements.

	$TlBr_3.4H_2O$	$TlCl_3.4H_2O$
2θ max (°)	50	50
Collected reflexions	$hkl+hk\bar{l}$	hkl
Number of collected reflexions	987+864	808
Unique reflexions used in the refinements ($I>1.96\sigma$)	698	694
Final R-value (%)	5.2	6.6
Final R_w-value (%)	6.8	8.3
Final S-value	1.4	1.8

The structure was solved by means of the Patterson function and consecutive Fourier difference syntheses, followed by least-squares refinements.

In both the data sets there were 12 strong reflexions with low $(\sin\theta)/\lambda$ values, apparently suffering from secondary extinction effects. They were subsequently removed for $TlBr_3.4H_2O$, which improved the R-value. The atomic parameters were not significantly changed by this procedure. However, the background in the difference Fourier map increased slightly. The chloride data were not corrected for this effect; it was not regarded as justified because of the non-corrected absorption effects. The refinements were based on minimization of $\sum w\|F_o|-|F_c\|^2$ including reflexions with $|F_o|>4.0\sigma(F_o)$. The weighting function used was $w=1/[\sigma^2(F_o)+(0.04F_o)^2]$, which gave a satisfactory error distribution according to a weight analysis.

A total of 32 parameters (Tl and halogens anisotropic, oxygens isotropic) were varied in the final refinements. The ratios of the shifts of the parameters to the standard deviations were less than 0.01 in the last cycle of the refinement.

The final values are given in Tables 2, 3, 4, and 5. An anisotropic refinement of all non-hydrogen atoms gave no further improvement in the R-factor.

A three-dimensional Fourier difference map was calculated and showed regions of increased electron density (1.3–2.6 e $Å^{-3}$) at a distance of about 0.9–1.5 Å from the thallium atoms. This is probably caused by the absorption effect.

The remaining background contained a few peaks (less than 1.3 e $Å^{-3}$) in the vicinity of the halogen atoms, and only some peaks corresponded to any of the 32 possible H atoms. No hydrogen atoms were therefore included in the final refinement model.

Table 3. Final fractional atomic positional parameters and isotropic mean square amplitudes of vibration in $Å^2$. Estimated standard deviations are given in parentheses.

Compound	Atom	Position	x	y	z	U
$TlBr_3.4H_2O$	Tl	4(*c*)	0.8232(1)	1/4	0.2411(1)	
	Br1	4(*c*)	0.6697(4)	1/4	0.0619(2)	
	Br2	8(*d*)	0.9170(3)	0.4496(2)	0.3222(1)	
	O1	4(*c*)	0.167(2)	1/4	0.148(1)	0.034(4)
	O2	4(*c*)	0.477(2)	1/4	0.317(1)	0.030(4)
	O3	8(*d*)	0.358(2)	0.086(1)	0.471(1)	0.053(4)
$TlCl_3.4H_2O$	Tl	4(*c*)	0.8255(1)	1/4	0.2386(1)	
	Cl1	4(*c*)	0.6766(10)	1/4	0.0619(5)	
	Cl2	8(*d*)	0.9106(8)	0.4461(4)	0.3184(4)	
	O1	4(*c*)	0.169(29)	1/4	0.146(1)	0.038(4)
	O2	4(*c*)	0.480(2)	1/4	0.313(1)	0.032(4)
	O3	8(*d*)	0.347(2)	0.084(1)	0.469(1)	0.052(4)

Table 4. Final anisotropic thermal parameters ($Å^2$) with estimated standard deviations in parentheses. The expression used is $\exp[-2\pi^2(U_{11}h^2a^{*2}+\cdots+2U_{12}hka^*b^*+\cdots)]$.

Compound	Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$TlBr_3.4H_2O$	Tl	0.0320(6)	0.0298(5)	0.0284(5)	0	−0.0018(4)	0
	Br1	0.0408(15)	0.0836(21)	0.0290(13)	0	−0.0034(11)	0
	Br2	0.0450(10)	0.0300(9)	0.0486(10)	−0.0028(8)	0.0008(8)	−0.0022(8)
$TlCl_3.4H_2O$	Tl	0.0362(6)	0.0303(6)	0.0244(6)	0	−0.0008(4)	0
	Cl1	0.0456(38)	0.0887(63)	0.0228(25)	0	−0.0051(25)	0
	Cl2	0.0557(25)	0.0304(25)	0.0469(25)	−0.0051(25)	0.0013(25)	−0.0076(13)

Table 5. Interatomic distances in Å and angles in degrees. Estimated standard deviations are given in parentheses.

$TlBr_3.4H_2O$			$TlCl_3.4H_2O$		
	Corrected for thermal motion [10]	Non-corrected		Corrected for thermal motion	Non-corrected
Within the $TlX_3.2H_2O$ complex					
Tl – Br1	2.516(3)	2.504(3)	Tl – Cl1	2.395(6)	2.381(6)
Tl – Br2	2.514(2)	2.508(2)	Tl – Cl2	2.387(5)	2.377(5)
Tl – O1	2.602(16)	2.588(16)	Tl – O1	2.511(16)	2.510(16)
Tl – O2	2.515(15)	2.515(15)	Tl – O2	2.428(15)	2.423(15)
Br1 – Br2	4.332(3)	4.309(3)	Cl1 – Cl2	4.108(7)	4.082(7)
Br2 – Br2′	4.416(3)	4.394(2)	Cl2 – Cl2′	4.210(6)	4.186(6)
Br1 – O1	3.544(16)	3.552(16)	Cl1 – O1	3.394(17)	3.336(17)
Br1 – O2	3.517(16)	3.491(16)	Cl1 – O2	3.373(17)	3.339(17)
Br2 – O1	3.593(12)	3.538(12)	Cl2 – O1	3.446(14)	3.425(14)
Br2 – O2	3.702(12)	3.682(12)	Cl2 – O2	3.519(13)	3.495(13)
Br1 – Tl – Br2		118.6(1)	Cl1 – Tl – Cl2		118.2(2)
Br2 – Tl – Br2′		122.3(1)	Cl2 – Tl – Cl2′		123.4(2)
O1 – Tl – O2		175.4(4)	O1 – Tl – O2		175.0(4)
O1 – Tl – Br1		87.2(3)	O1 – Tl – Cl1		86.9(3)
O2 – Tl – Br1		88.2(3)	O2 – Tl – Cl1		88.1(3)
O1 – Tl – Br2		87.9(3)	O1 – Tl – Cl2		88.9(3)
O2 – Tl – Br2		94.3(3)	O2 – Tl – Cl2		93.5(3)
Br1 – Br2 – Br2		59.35(4)	Cl1 – Cl2 – Cl2		59.16(12)
Br2 – Br1 – Br2′		61.31(4)	Cl2 – Cl1 – Cl2′		61.68(12)
Hydrogen bond distances and angles					
O1 – O2	3.03(2)	2.98(2)	O1 – O2	2.91(2)	2.88(2)
O1 – O3	2.98(2)	2.90(2)	O1 – O3	2.84(2)	2.81(2)
O2 – O3	2.81(2)	2.78(2)	O2 – O3	2.78(2)	2.75(2)
O3 – O3	2.82(2)	2.78(2)	O3 – O3	2.82(2)	2.79(2)
O1···O2···O3		107.9(6)	O1···O2···O3		106.0(6)
O2···O1···O3		126.9(6)	O2···O1···O3		125.3(6)
O1···O3···O2		99.5(6)	O1···O3···O2		98.4(6)
O1···O3···O3		104.9(6)	O1···O3···O3		102.6(6)
O2···O3···O3		115.8(6)	O2···O3···O3		112.4(6)
Some other distances and angles					
Br2 – O3	3.564(13)	3.538(13)	Cl2 – O3	3.431(14)	3.402(14)
Br1 – Br2	3.831(3)	3.806(3)	Cl1 – Cl2	3.718(7)	3.698(7)
Br1 – Br2	4.020(2)	3.998(2)	Cl1 – Cl2	3.984(6)	3.960(6)
Br2 – Br2	4.003(2)	3.983(2)	Cl1 – Cl2	3.859(7)	3.839(7)
O1 – O3 – Br2		116.0(5)	O1 – O3 – Cl2		116.7(5)
O2 – O3 – Br2		86.1(4)	O2 – O3 – C12		86.8(4)
O3 – O3 – Br2		129.6(5)	O3 – O3 – Cl1		133.3(6)

DISCUSSION

The structures are built up of distinct $TlX_3.2H_2O$ complexes located on a mirror plane and two non-coordinated water molecules (*cf.* Fig. 1). For X = Br the triangle (Br2 – Br2′ – Br1) with Tl in the middle and 0.101(1) Å from the bromide plane and the O1 and O2 atoms situated 2.60(2) and 2.52(2) Å from the

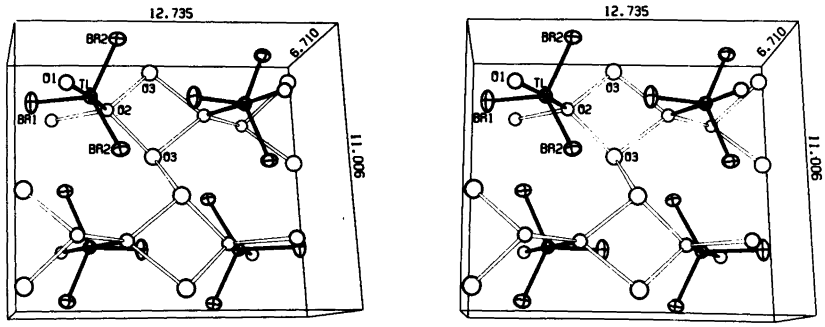

Fig. 1. A stereoscopic view of the orthorhombic unit cell. The lengths of the unit cell edges are given in Å. The *a*-edge is almost perpendicular to the plane of the paper. The ellipsoids are drawn to enclose 40 % probability. The unfilled bonds connect hydrogen-bonded oxygens.

Tl atom form a slightly distorted trigonal bipyramid [0.071(1), 2.51(2), 2.43(2) Å for the chloride]. The O3 water molecules complete the structures by filling the holes between the $TlX_3.2H_2O$ units.

Some interatomic distances and angles are given in Table 5. The distances were corrected for thermal movement,[10] assuming "riding" motion for the atoms bonded to Tl and independent motion for all the other atoms.

The deviation from 180° of the (O1 – Tl – O2)-angle in the bipyramid is probably caused by hydrogen bonding. The formation of such bonds is strongly indicated by short distances between O1 – O2, O1 – O3, O2 – O3, and O3 – O3 (2.78 – 3.03 Å). The proposed hydrogen bonding scheme (Fig. 1) assumes that each oxygen atom forms H-bonds with the three oxygen neighbours. The only proton not participating in hydrogen bonding is that belonging to O3 and pointing towards Br2: the distance Br2 – O3 = 3.56(1) Å [Cl2 – O3 = 3.43(1) Å] is too long.

The structure can thus be described as $TlX_3.2H_2O$ complexes held together by a three-dimensional network of hydrogen bonds. The hydrogen bonds between O1 and the three oxygen neighbours are about 0.10 – 0.15 Å shorter in the chloride than in the bromide. The O2 – O3 hydrogen bond is also somewhat shorter in the chloride. This fact may at least partially explain the difference in melting points of the compounds, which are: 25 – 30 °C for $TlBr_3.4H_2O$ and 37 °C for $TlCl_3.4H_2O$.

Tl^{3+} is isoelectronic with Hg^{2+}. Complexes HgX_3^- (X = Cl,Br,I) with flattened pyramidal configuration were found in $[N(CH_3)_4]HgBr_3$ [12] and in aqueous and DMSO solutions.[13] The trend of an increasing flattening of the HgX_3^- complexes in solution in the sequence I, Br, Cl observed in Ref. 13 is confirmed in the present work.

The present investigation is in agreement with Ref. 5. The NMR spectra of the chloride [6] led to erroneous conclusions probably caused by the experimental broadening of the lines.

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