

Crystal and Molecular Structure of Trisodiumhexachloro-thallium(III) Dodekahydrate, $\text{Na}_3\text{TlCl}_6 \cdot 12\text{H}_2\text{O}$

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The crystal structure has been determined from three-dimensional X-ray diffraction data collected at room temperature using a Syntex $P2_1$ four-circle diffractometer. The unit cell is trigonal, space group $R\bar{3}m$ (No. 166) with hexagonal cell parameters: $a=10.345(5)$, $c=18.007(5)$ Å and $Z=3$. The Tl atom is surrounded by 6 Cl atoms forming a slightly distorted octahedron with Tl–Cl distances of 2.593(3) Å (corrected for thermal motion). The two independent Na atoms are octahedrally surrounded by water molecules. The three Na-octahedra along the c -axis share faces.

There is a disorder in the structure: the Cl-atoms and one of the two independent water molecules have two possible positions. This may indicate the existence of two different unit cells of the space group $R\bar{3}$ (No. 148), the disorder leading to the apparent extra mirror plane of $R\bar{3}m$.

The structure was refined to a conventional R -value of 2.4 % for 391 independent reflexions. $R_w=3.0$ %.

In dilute aqueous solutions containing Tl^{3+} and Cl^- , emf, solubility and thermodynamic data^{1–3} show TlCl_4^- to be the highest complex formed. However, in concentrated aqueous solutions Raman measurements⁴ indicate the formation of at least one higher complex, probably TlCl_6^{3-} . In order to clarify whether this complex is really formed, and if so, to determine its structure, concentrated aqueous solutions of Tl^{3+} and Cl^- ($\text{Cl}^-/\text{Tl}^{3+} > 6$) have been subjected to X-ray diffraction studies.⁵

In order to facilitate the interpretation of the solution data, the present work was undertaken. It is part of a series of crystal structure determinations of Tl^{3+} compounds.

EXPERIMENTAL

Crystals were prepared by mixing concentrated aqueous solutions of TlCl_3 and NaCl to a mol ratio $\text{Cl}^-/\text{Tl}^{3+}$ greater than 6 and evaporating at room temperature. The TlCl_3 solution was prepared by oxidizing a suspension of TlCl in water with gaseous chlorine.

The transparent crystals became opaque when exposed to air. They were analyzed for Tl by bromatometric titration^{6,7} and for Cl by Volhard titration.⁶ The analysis gave Tl 28.8; Cl 31.5 (calc. for $\text{Na}_3\text{TlCl}_6 \cdot 12\text{H}_2\text{O}$: Tl 29.1; Cl 30.3). An irregular crystal, with approximate dimensions $0.09 \times 0.09 \times 0.09$ mm, enclosed in a thin-walled glass capillary, was used for the data collection. The lattice parameters were determined and refined from the setting angles of 25 centered reflexions by the standard method on a Syntex $P2_1$ four-circle diffractometer.

The trigonal diffraction symmetry, $\bar{3}m$, was found by axial photographs. Hexagonal axes were used: $a=10.345(5)$, $c=18.007(5)$ Å. $1.8 < D_m < 2.2$ g cm^{-3} (by flotation), $D_x=2.10$ g cm^{-3} , $Z=3$, $\mu=81.3$ cm^{-1} , $\lambda=0.71069$ Å. The ω -scan technique with variable scan speed (from $0.8^\circ \text{ min}^{-1}$ to $29.3^\circ \text{ min}^{-1}$) was used. Three check reflexions were measured after every 100th reflexion. Their intensities decreased gradually and were about 10 % lower at the end of the data collection. No correction for this effect was applied. 2075 reflexions were measured out to a $\sin \theta/\lambda$ value of 0.59 \AA^{-1} ($2\theta=50^\circ$). Of these, 392 reflexions were independent, and the 391 with intensities greater than $1.96\sigma(I)$ were used in the calculations.

A semi-empirical absorption correction was applied to the data.⁸ The largest variation in the correction factor was from 1 to 0.65. The data were further reduced to scaled F_o values as described previously,⁹ using computer programs and scattering factors from the same sources.⁹ Anomalous dispersion corrections were included for all atoms.

STRUCTURE DETERMINATION AND REFINEMENT

The diffraction symmetry was $\bar{3}m$. The hkl reflections were systematically absent for $-h+k+l \neq 3n$. Thus, three space groups were possible: $R\bar{3}m$ (No. 166), $R3m$ (No. 160) and $R32$ (No. 155). In all the space groups, the Tl atom could be placed at the origin.

The scale factor and an isotropic temperature factor for Tl were refined ($R=23.4\%$). The subsequent difference Fourier synthesis revealed all the sodium atoms (as the highest peaks) and double peaks of Cl.

As the distribution of the normalized structure factors was closer to that expected for the non-centrosymmetric case, and because the Cl atoms appeared as double peaks, the centrosymmetric space group seemed less likely. In the non-centrosymmetric $R3m$, the Cl atoms would be too close to each other. $R32$ was, therefore, assumed to be the correct space group.

Using least squares refinements and difference Fourier maps, all the non-hydrogen atoms could be located. The refinement gave the R -value 4.2% (based on 35 parameters).

However, one Cl–O distance equal to $2.70(2)$ Å was considerably shorter than the expected value, even if hydrogen bonding is assumed (Cl–O = 3.0 Å¹⁰). Obviously, in spite of the low R -value, the model was still not complete.

In the difference Fourier map, the highest peaks had a height of $1.2-1.3$ e Å⁻³ and were positioned $1.3-1.4$ Å from the Cl atoms. The error distribution among different classes of reflexions seemed to be

non-random. For example, the 40 reflexions with h, k and l all odd gave the R -value 6.7% , whereas the 59 reflexions with parity (even, even, odd) led to $R=2.8\%$.

A disorder was thus assumed. In the space group $R\bar{3}m$, a difference Fourier map based on Tl, Na1, Na2 and O1 atoms gave double peaks about 1.2 Å from each other for Cl and O2, indicating a partial occupancy of the 36-fold positions. Least-squares refinement of such a disordered structure with anisotropic thermal parameters gave $R=2.8\%$ ($R_w=3.6\%$, 32 parameters).

The following difference Fourier map showed several peaks of $0.4-0.5$ e Å⁻³. Their positions agreed very well with predicted hydrogen atoms and only a few of the highest peaks occurred in the neighbourhood of the Tl atom. Consequently, the hydrogen atoms were included in the refinements. The H3 atom could be expected to have two alternative positions, but in the difference map it appeared as a relatively broad region of increased electron density. It was, therefore, placed midway between the expected positions and refined in this way. Hence, all distances and angles which involve H3 have rather high standard deviations. The H3–O2 and H3–Cl distances are probably too long, whereas the angles O2–H3–Cl and H1–O2–H3 are probably too small. The refinement gave $R=2.4\%$ ($R_w=3.0\%$, 42 parameters), which was a significant improvement according to the \mathcal{R} -test.¹¹

The final parameters are given in Tables 1 and 2. The effect of the absorption correction was checked. The non-corrected data gave nearly the same final R -value, but the resulting background in the difference Fourier map increased, especially in the

Table 1. Final fractional atomic positional parameters and isotropic mean square amplitudes of vibration in Å². Estimated standard deviations are given in parentheses.

Atom	Occupancy	Position	x	y	z	U
Tl	1.0	3(<i>a</i>)	0	0	0	
Cl	0.5	36(<i>i</i>)	0.1112(2)	0.6149(3)	0.7514(1)	
Na1	1.0	6(<i>c</i>)	0	0	0.3199(2)	
Na2	1.0	3(<i>b</i>)	0	0	1/2	
O1	1.0	18(<i>h</i>)	0.4340(3)	0.5660	0.0776(3)	
O2	0.5	36(<i>i</i>)	0.4991(9)	0.6257(9)	0.4240(4)	
H1	1.0	18(<i>h</i>)	0.470(7)	0.530	0.411(6)	0.09(4)
H2	1.0	36(<i>i</i>)	0.534(7)	0.623(7)	0.074(4)	0.08(2)
H3 ^a	1.0	18(<i>h</i>)	0.405(13)	0.595	0.476(12)	0.30(13)

^a Cf. the comments in the text.

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

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tl	0.0298(3)	0.0298	0.0295(3)	0.0149	0	0
Cl	0.0377(10)	0.0578(13)	0.0537(13)	0.0241(10)	0.0120(9)	0.0058(10)
Na1	0.0443(15)	0.0443	0.0389(20)	0.0222	0	0
Na2	0.0555(23)	0.0555	0.0353(29)	0.0277	0	0
O1	0.0642(27)	0.0642	0.0576(29)	0.0427(32)	0.0005(11)	-0.0005
O2	0.0637(41)	0.0580(42)	0.0526(37)	0.0388(33)	0.0009(32)	0.0046(32)

neighbourhood of the heavy atoms. The only parameter which changed significantly was the scale factor.

The refinements were based on minimization of $\sum w\{|F_o| - |F_c|\}^2$ including reflexions with $|F_o| > 3.92\sigma(F_o)$. The weighting function used was $w = 1/[\sigma^2(F_o) + (0.03 \times F_o)^2]$ which gave a satisfactory error distribution according to a weight analysis and resulted in $S = \{\sum [w(F_o - F_c)]^2 / (n - m)\}^{1/2} = 0.9$, where n = number of reflexions and m = number of parameters. A total of 42 parameters were varied in the final refinements. The ratios of the shifts of the parameters to the standard deviations in the last cycle of the refinement were less than 0.01. The three-dimensional difference Fourier map was calculated and showed an essentially smooth background (less than $0.5 \text{ e}\text{\AA}^{-3}$). The occupancy factors for the two alternative positions of Cl and O2, which were assumed to be 50%–50%

in the preceding calculations, could be refined in the space group $R\bar{3}$ (660 independent reflexions). The refinement showed no significant deviation from this value. Similar refinement in $R3m$ or $R32$ was not meaningful, because any deviation from 50% would inevitably lead to too short distances in the structure. The non-centrosymmetric space group $R3$ did not give a significantly lower R -value, finally confirming the proper choice of the space group, *i.e.* $R\bar{3}m$.

DISCUSSION

General. The structure comprises almost regular octahedra of TiCl_6^{2-} and $\text{Na}(\text{H}_2\text{O})_6^+$ stacked in columns parallel to the z axis and kept together by hydrogen bonds (Figs. 1 and 2). Some interatomic distances are given in Table 3.

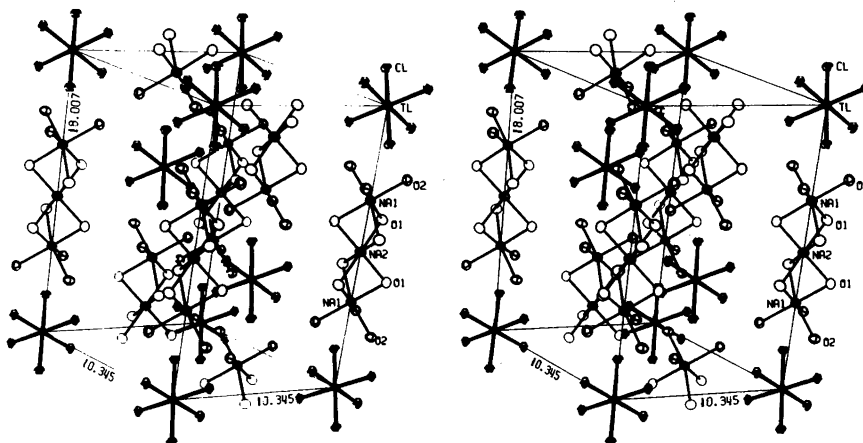


Fig. 1. A stereoscopic view of the hexagonal unit cell. The lengths of the unit cell edges are given in \AA . The a -edge is parallel to the observer's interocular line. The ellipsoids are drawn to enclose 30% probability. For clarity, hydrogen atoms are omitted and an ordered structure of space group $R\bar{3}$ is assumed.

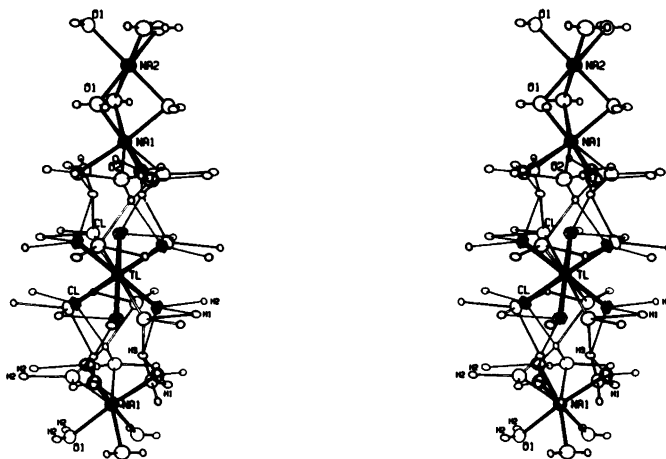


Fig. 2. A stereoscopic view of a selected part of the structure showing the nature of the disorder and the positions of the hydrogen atoms. The alternative positions of the pairs of the symmetry-related atoms are marked by unfilled bonds. The thermal ellipsoids enclose regions of 30 % probability (except for the hydrogen atoms, which have been given $B=1.0$ for clarity)

The Ti–Cl distance 2.582(3) Å can be compared with that assumed for $K_3TiCl_6 \cdot 2H_2O$ (2.55 Å),¹² with $Cs_3Ti_2Cl_9$ (3×2.66 Å and 3×2.54 Å)¹³ and with $Co(NH_3)_6TiCl_6$ (2.48 Å).¹⁴ These determinations are, however, all old and rather inaccurate.

The mean Na–O distance is 2.418(5) Å. This can be compared with that in $Na_2HAsO_4 \cdot 7H_2O$ (2.437(5) Å),¹⁵ $Na_2HPO_4 \cdot 7H_2O$ (2.418(5) Å)¹⁵ and $NaOH \cdot 3\frac{1}{2}H_2O$ (2.420(8) Å),¹⁶ which have somewhat distorted, but essentially similar arrangement around the sodium atoms. In the two water molecules, the angles (H–O–H) are 128(7) and 97(8)°, and all the O–H distances about 1.0 Å (except for the H3–O2 distance), which are close to the expected values.

Some bond distances and angles are given in Table 3. The distances have been corrected for thermal movement.¹⁷ 'Riding' motion was assumed for the Ti–Cl, Na–O and O–H distances. All the other distances were calculated for atoms moving independently.

Disorder. The two alternative sets of positions of Cl and O2 have equal probability with regard to the neighbouring atoms. This leads to a structure in which both the positions have equal occupancy, giving the disorder indicated in Fig. 2.

The disordered structure is more favourable than the more symmetrical packing of the Cl and the O2 atoms, which would occur if the atoms had just one position (half way between them).

Different explanations of the type of the disorder are possible: (1) The Cl and O2 atoms jump between the two possible positions (1.2 Å apart from each other). This would, however, require a simultaneous movement of Cl, O2 and H3 in a very definite way (random movement would lead to too short distances).

(2) Two different unit cells, *A* and *B*, space group $R\bar{3}$, with a possible meeting plane (0,0,1) at $z=1/6$ or $z=1/2$ or $z=5/6$. The *A* and *B* must not be ordered in any special way, e.g. *ABABAB*....., because this would merely lead to a doubled *c*-edge and an *AB* unit cell.

(3) Two different orders in the same unit cell: order *A* and order *B* (meeting plane as for (2)).

(4) Doubling of the *c*-axis. This possibility was checked by taking a several hours long axis photograph on the diffractometer. No additional reflexions were observed.

The 'averaging nature' of diffraction data does not permit a decision as to which alternative is the correct one. In Fig. 1, however, the 2nd alternative with a meeting plane at $z=0$ was assumed in order to clarify the picture.

Hydrogen bonding. Both the distance and angle requirements for the bonds are fulfilled by the disordered structure (cf. Table 3(d)), whereas an ordered structure with Cl and O2 in the averaged positions would not allow any hydrogen bonding, mainly because of the increase of the O–O and

Table 3. Interatomic distances in Å and angles in degrees. Estimated standard deviations are given in parentheses.

	Corrected for thermal motion ¹⁷	Non-corrected		
(a) Within the TiCl ₆ octahedron				
Ti—Cl	2.593(3)	2.582(3)	Cl—Ti—Cl	88.62(8)
Cl—Cl	3.637(4)	3.607(4)	Cl—Ti—Cl	91.38(8)
Cl—Cl	3.723(3)	3.696(3)	Cl—Ti—Cl	180.00(8)
(b) Within the Na1—O ₆ octahedron				
Na1—O1	2.444(5)	2.437(5)	O1—Na1—O1	79.7(1)
Na1—O2	2.411(8)	2.405(8)	O2—Na1—O2	89.9(3)
O1—O1	3.163(3)	3.124(3)	O1—Na1—O2	86.1(2)
O2—O2	3.430(14)	3.397(14)	O1—Na1—O2	106.0(2)
O1—O2	3.339(9)	3.305(9)	O1—Na1—O2	163.5(3)
(c) Within the Na2—O ₆ octahedron				
Na2—O1	2.418(4)	2.413(4)	O1—Na2—O1	80.7(1)
			O1—Na2—O1	99.3(1)
O1—O1	3.163(3)	3.124(3)	O1—Na2—O1	180.0(1)
(d) Hydrogen bonds				
			O2—O1—Cl	102.4(2)
			O1—O2—Cl	80.0(2)
			O1—O2—Cl	123.7(3)
O1—O2	3.020(11)	2.983(11)		
O1—H2	0.97(8)	0.90(8)	O1—H2—O2	126(6)
O2—H2	2.42(8)	2.36(8)		
O1—Cl	3.259(2)	3.226(2)		
O1—H2	0.97(8)	0.90(8)	O1—H2—Cl	140(6)
Cl—H2	2.44(8)	2.36(8)		
O2—Cl	2.998(7)	2.964(7)		
O2—H3 ^a	—	1.28(19)	O2—H3 ^a —Cl	104(8)
Cl—H3 ^a	—	2.38(19)		
O2—Cl	3.347(9)	3.316(9)		
O2—H1	1.13(3)	0.91(3)	O2—H1—Cl	159(7)
Cl—H1	2.57(3)	2.45(3)		
(e) Distances between the "disorder positions"				
Cl—Cl		1.227(4)		
O2—O2		1.292(13)		
(f) Some other distances				
Na1—Na2	3.273(4)	3.242(4)	H2—O1—H2	128(7)
			H1—O2—H3 ^a	97(8)

^a Cf. comments on H3 in the text.

Cl—O distances. In particular, the bond between Cl and O2 in the same 'column of octahedra' is very strong, 2.964(7) Å. This bond is probably the most important contribution to the stability of the disordered structure.

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