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Crystal and Molecular Structure of Potassium Thallium(III) Bromide Dihydrate

JULIUS GLASER

Department of Inorganic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

The crystal structure of $KTlBr_4.2H_2O$ has been determined from single-crystal X-ray diffraction data collected at room temperature on a Syntex $P2_1$ four-circle diffractometer using graphite monochromatized Mo$K\alpha$-radiation.

The compound crystallizes in the cubic space group $Fm3c$ (No. 226). The cell parameters are: $a=18.657(7)$ Å and $Z=24$. The Tl atom is surrounded by four Br atoms forming a distinct, almost regularly tetrahedral $TlBr_4^-$ complex with a Tl–Br distance of 2.554(3) Å (corrected for thermal motion). This contradicts the results of a previous structure determination of this compound, where a square-planar $TlBr_4^-$ unit was claimed. The packing of the tetrahedra results in the formation of tunnels parallel to the three cubic axial directions. In these tunnels, disordered water molecules and potassium atoms are located.

The $KTlBr_4.2H_2O$ structure was refined to a conventional R-value of 4.0 % ($R_w=4.2$ %).

The sodium compound $NaTlBr_4.2H_2O$ is isomorphous with the potassium salt and has the unit cell edge $a=18.426(3)$ Å.

X-Ray diffraction investigations[1] of aqueous solutions of Tl^{3+} and Br^-, where the Br^- to Tl^{3+} mol ratio was varied, have been performed in order to determine the structural relationships between the different complexes formed. In the solutions where $4<Br^-/Tl^{3+}<5$ the experimental data could be explained by assuming formation of tetrahedral complexes, $TlBr_4^-$.

A number of different crystal structures containing the $TlBr_4^-$ ion have been reported. Thus, Hazell[2] reported it to be tetrahedral in Tl(I)Tl(III)Br_4, while Watanabe[3–5] found it to be square-planar in $KTlBr_4.2H_2O$ and the isomorphous compounds $NH_4TlBr_4.2H_2O$, $RbTlBr_4.H_2O$, $CsTlBr_4$ and $CsTlI_4$. The compounds NH_4TlI_4, $NH_4TlI_4.2H_2O$, $KTlI_4$, $KTlI_4.2H_2O$, $RbTlI_4.2H_2O$ and $CsTlI_4.2H_2O$ were also found[6] (by comparing the powder diffraction patterns) to be isomorphous with $KTlBr_4.2H_2O$. Raman and infrared spectra of some crystalline bromothallates[7] (among others $TlTlBr_4$, $CsTlBr_4$, $KTlBr_4$ and $RbTlBr_4.H_2O$) are consistent only with tetrahedral $TlBr_4^-$, not with square-planar, indicating that the early X-ray data[3–5] may be erroneous.

Thus, it seemed reasonable to reinvestigate the structure of $KTlBr_4.2H_2O$. This work is a part of a series of structure determinations of Tl(III)-compounds.

EXPERIMENTAL

Yellow, non-polarizing crystals were prepared by slow evaporation of an aqueous solution containing $TlBr_3$ and KBr in a ratio of about 1:3. The crystals were analyzed for Tl (bromatometric titration), Br (Volhard titration) and K (flame atomic absorption). The following results were obtained (H_2O by difference):

Analysis (%)	Tl	Br	K	H_2O
This work	33.0(5)	52.8(5)	6.8(5)	7(1)
Ref. 8	34.1	53.6	6.5	6.2
Calc. for $KTlBr_4.2H_2O$	34.11	53.35	6.52	6.01

$D_m=3.77$ g cm^{-3} (Ref. 3), $D_m=3.46$ g cm^{-3} (Ref. 8), $D_x=3.68$ g cm^{-3}, μ(Mo$K\alpha$)=309.8 cm^{-1}, $Z=24$. The crystal chosen for the data collection was cube-shaped and had the dimensions: $0.2\times0.2\times0.2$ mm. It was enclosed in a thin-walled glass capillary.

The lattice parameter $a=18.657(7)$ Å was determined and refined using 20 centered reflexions with $2\theta>20°$ by the standard method on the Syntex $P2_1$ four-circle diffractometer.[9] The ω-scan technique with variable scan speed (from 0.5°/min to 29.3°/min) was used. Three check reflexions were measured after every 100th reflexion. Their inten-

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sities decreased by about 5 % during the data collection. No correction for this effect was applied. One octant of the reciprocal lattice was measured out to $\sin\theta/\lambda = 0.59$ Å^{-1} (or $2\theta = 50°$), including 1774 reflexions. Of these, 265 reflexions were independent and 169 had a net intensity greater than $1.96\sigma(I)$ and were used in the calculations.

The following systematic extinctions were found:

hkl: $h+k=2n+1$, $k+l=2n+1$
hkl: $l=2n+1$

Thus, two space groups were possible: the centrosymmetric $Fm3c$ (No. 226) and the non-centrosymmetric $F\bar{4}3c$ (No. 219).

As the distribution of the normalized structure factors was closer to that expected for the centrosymmetric case, $Fm3c$ was assumed to be the correct choice. This assumption was then confirmed by the complete structure determination.

A semi-empirical absorption correction[10] was applied to the data. The correction factors varied from 1.00 to 0.52.

Further treatment of the structure factors was performed as previously, using computer programs and scattering factors from the same sources.[9] Anomalous dispersion corrections were included for all atoms.

STRUCTURE DETERMINATION AND REFINEMENT

A three-dimensional Patterson function was calculated. From this it was deduced that the Tl atom could be positioned either in 24(*c*) with tetrahedral symmetry or in 24(*d*) with octahedral symmetry.

The two possible Tl positions were treated as follows: Firstly, the scale factor and an isotropic temperature factor for Tl were refined, giving $R = 43$ % for both the 24(*c*) and 24(*d*). Secondly, Fourier maps were calculated. For 24(*c*), the presumed Br peaks had heights of about 21 eÅ^{-3}. Least squares refinement of Tl and Br with isotropic temperature factors gave $R = 11.7$ %.

For 24(*d*), the presumed Br peaks had heights of about 15 e Å^{-3}. Least squares refinement led to no decrease of the *R*-value. Therefore, the suggested octahedral $TlBr_4(H_2O)_2^-$ complex[3-5] was rejected and a tetrahedral $TlBr_4^-$-unit was assumed to be the correct one.

The subsequent Fourier map based on Tl and Br revealed the positions of eight potassium atoms (K1). An isotropic least squares refinement of the Tl, Br and K1 atoms led to an *R*-value of 10.5 % (6 parameters) and an anisotropic refinement to $R = 6.2$ % (10 parameters). In the following difference Fourier map the highest peaks had heights of 1.0 to 1.5 e Å^{-3}, and were positioned in groups of three at a distance of 1.2 Å from each other. As this might be caused by small deviations from a centrosymmetrical arrangement, the non-centrosymmetric space group, $F\bar{4}3c$, was tested. However, the Tl, Br and K1 atoms remained centrosymmetrically positioned and a least squares refinement gave no significant improvement in the *R*-value.

The following difference Fourier map was very similar to that calculated for the centrosymmetric space group.

Next, it was observed that there were eight very strong reflexions with low $\sin\theta/\lambda$ values, obviously suffering from secondary extinction. These were subsequently removed. This was justified by the fact that all the heavy atoms were already found and these strong reflexions could make it more difficult to locate the rest of the atoms. This procedure led to a decrease of the *R*-value from 6.2 % (see above) to 5.3 %. Neither the positional parameters nor the temperature factors changed significantly.

The low heights of the residual peaks made it reasonable to assume a disorder for all the water molecules and for the 16 remaining potassium atoms. The presence of large tunnels caused by the packing of the $TlBr_4^-$ tetrahedra seemed to allow this.

Least squares refinements (in the centrosymmetric $Fm3c$) including Tl, Br, K1 and all the oxygen atoms (statistically distributed over 192(*j*)) led to $R = 4.6$ % (14 parameters). The difference Fourier map revealed a region of increased electron density centered on (0.12,1/4,1/4). It had a sausage-like form, elongated parallel to the *x*-axis, indicating a large thermal movement of the remaining potassium atoms. A refinement including all the atoms (Tl and Br anisotropic, the light atoms isotropic, 16 K atoms in (0.12,1/4,1/4)) led to $R = 4.2$ % ($R_w = 4.6$ %, 16 parameters). As expected, the temperature factor for the K2 atoms reached a rather high value, namely $B = 35$ Å^2. The data were not sufficient to permit an anisotropic refinement of the light atoms. Nor could the occupancy factors of the oxygen and K2 atoms be refined, because of the strong correlation with the temperature factors.

In the subsequent difference Fourier map there were regions of increased electron density (0.6 e Å^{-3}) at (0.24,0.18,0.14). A least squares refinement with eight potassium atoms in (0.12,1/4,1/4) and eight in (0.24,0.18,0.14) gave reasonable temperature

factor values for the K atoms and $R=4.0\,\%$ ($R_w=4.2\,\%$, 20) parameters), which is a significant improvement according to the $\mathcal{R}$-test.[11] This model was therefore preferred. The final difference map showed a peak at (1/4,1/4,0) with a height of about 1.3 e $Å^{-3}$. No atom, however, could be refined in this position. Furthermore, when the final difference map was calculated using a limited set of data ($\sin\theta/\lambda<0.5$ $Å^{-1}$), the height of the peak decreased to 0.6–0.7 e $Å^{-3}$, indicating an accumulation of errors originating from the heavy atoms contributions (absorption, thermal movement). The remaining highest peaks (all lower than 1 e $Å^{-3}$) were in the vicinity of the heavy atoms, the rest of the map showing an essentially smooth background. It was not possible to locate the hydrogen atoms, obviously because of the disorder of the water molecules.

Least squares refinements. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$, where $w=1/\{\sigma^2(F_o)+(0.02\,F_o)^2\}$ and reflexions with $|F_o|>3.92\sigma(F_o)$ were included. This weighting scheme resulted in an S-value of 1.3. The parameter shifts in the last refinement cycle were all less than 1 % of the corresponding standard deviations.

Absorption correction. A test of the semi-empirical absorption correction was performed. A least squares refinement similar to that described above but without the absorption correction had no significant influence on the atomic parameters. Only the scale factor changed. The heights of the largest peaks in the final difference Fourier map were almost the same as for the corrected data. However, the R-value obtained without the correction increased to 4.6 % ($R_w=4.6$ %). The final parameter values, given in the Tables 1 and 2, were therefore calculated using the corrected data.

DISCUSSION

General. The structure comprises almost regular $TlBr_4^-$ tetrahedra with a Tl–Br distance of 2.554(3) Å[12] (non-corrected for the thermal movement: 2.534(3) Å), which can be compared with 2.51(3) Å in $TlTlBr_4$.[2]

The packing of the tetrahedra (Br–Br distances between adjacent tetrahedra are: $4\times4.048(3)$ Å and $2\times4.220(4)$ Å, mean value 4.105(3) Å), results in a tunnel structure, resembling that of some zeolites[13] (*cf.* Figs. 1 and 2). There are small cavities around (0,0,0) and the symmetry related positions with radii of about 1.8–1.9 Å. The K1 atoms positioned there thus have a lot of space available ($r_{K+}=1.33$ Å) and consequently a strong thermal movement is observed (*cf.* Table 1). The surroundings of the K1 atoms are almost regular icosahedra of the Br atoms. The icosahedra are connected to each other through the Tl atoms, forming a structure with three-dimensional tunnels (*cf.* Fig. 2). Within these, all the atoms (O, K2 and K3) are disordered. The type of disorder is somewhat different for the dif-

Table 1. Final fractional atomic positional parameters and isotropic mean square amplitudes of vibration in $Å^2$. Estimated standard deviations are given in parentheses.

Atom	Occupancy	Position	x	y	z	U
Tl	1.0	24(*c*)	1/4	0	0	
Br	1.0	96(*i*)	0	0.1117(1)	0.1728(1)	
K1	1.0	8(*b*)	0	0	0	0.114(8)
K2	1/24	192(*j*)	0.242(13)	0.181(5)	0.145(6)	0.10(5)
K3	1/6	48(*f*)	1.23(6)	1/4	1/4	0.21(4)
O	1/4	192(*j*)	0.195(5)	0.184(5)	0.150(2)	0.10(2)

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

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tl	0.0416(11)	0.0595(8)	0.0595	0	0	0
Br	0.090(2)	0.092(2)	0.077(2)	0	0	0.039(2)

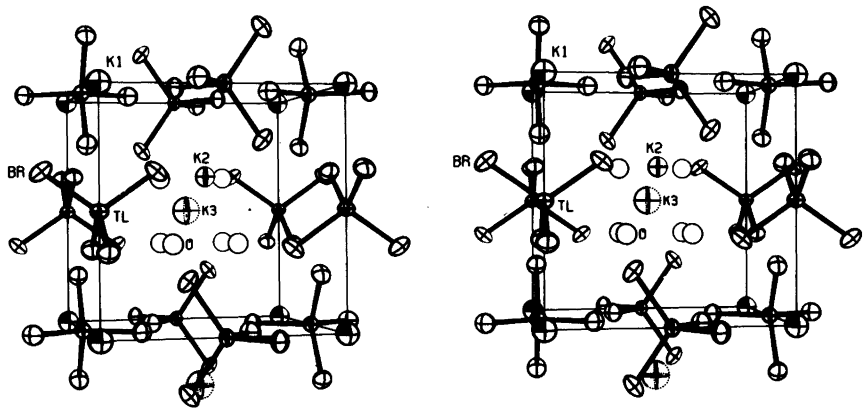

Fig. 1. A stereoscopic view of 1/8 of the unit cell (1/2 in each axial direction). Only one of the possible arrangements of the disordered atoms is represented. The oxygen atoms in the figure are placed in one idealized position (mean of the three possible positions) for clarity. The ellipsoids are drawn to enclose 30 % probability.

ferent atoms. Thus, the oxygen atoms are statistically distributed over six of the eight apex positions of a regular cube centered on (1/4, 1/4, 1/4), *i.e.* in the middle of the large cavities in the tunnels. Furthermore, there is a three-fold splitting of each of these apex positions, the distance between the alternative oxygen positions being 1.06(11) Å. The average distance between adjacent oxygen atoms is 2.84(12) Å, corresponding to idealized, non-split apex positions. All the angles O−O−O would then be 90°. The K2 atoms were placed in 192(*j*) with occupancy 1/24, giving a mean K−O distance of 2.7(2) Å, which is a reasonable value.

The positions of the K3 atoms, however, must be considered as a rough approximation. These were obtained as a result of an isotropic refinement, whereas in the difference map a high degree of anisotropy was observed (see above). These atoms occupy "tunnel sites" where the *x*-coordinate can range from −0.12 to −0.08 and from +0.08 to +0.12. The length of the site is thus 0.7−0.8 Å. Some distances and angles are given in Table 3. The distances between the ordered atoms were corrected for thermal motion [12] (Br atoms "riding" on Tl, the rest of the atoms having independent motion).

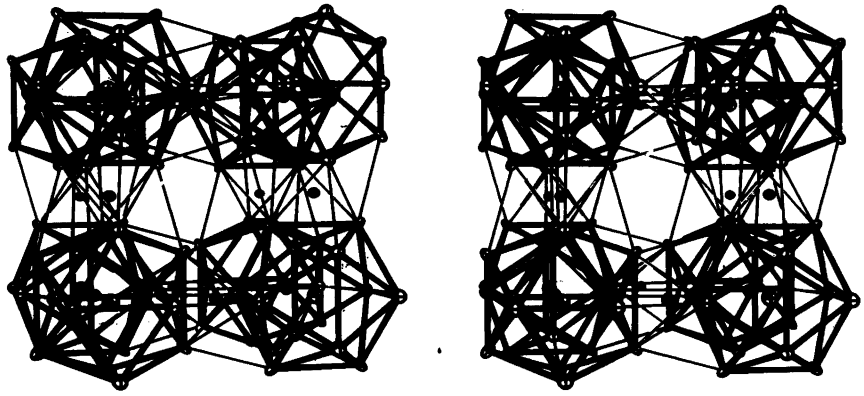

Fig. 2. A stereoscopic view of a selected part of the unit cell (0.43 in each axial direction), showing the tunnels in the structure. The atoms in the tunnels are omitted. Only the closest Br−Br interactions are shown: the icosahedra around K1 by filled lines, the remaining unfilled. The ellipsoids enclose 15 % probability.

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

	Corrected for thermal motion [12]	Non-corrected		
(a) Within the $TlBr_4$-tetrahedron				
Tl – Br	2.554(3)	2.534(3)	Br – Tl – Br	110.72(7)
Br – Br	4.210(5)	4.170(4)	Br – Tl – Br	108.85(7)
Br – Br	4.171(5)	4.122(3)		
(b) Between the $TlBr_4$-tetrahedra				
Br – Br	4.048(3)	4.005(3)		
Br – Br	4.220(4)	4.178(4)		
(c) Distances between the alternative positions of the disordered atoms				
O – O		1.06(11)		
K2 – K2		0.99(17)		
(d) Some other distances and angles				
K1 – Br	3.887(3)	3.839(3)	Br – K1 – Br	62.87(5)
			Br – K1 – Br	65.78(5)
			Br – K1 – Br	114.22(5)
			Br – K1 – Br	117.13(5)
			Br – K1 – Br	180.00(5)
O – O		2.74(13)		
O – O		3.00(10)		
O – O		3.16(11)		
K2 – O		2.57(16)		
K2 – O		2.79(16)		
K3 – O		2.60(9)		
O – Br		3.213(6)		
O – Br		3.528(9)		
K2 – Br		3.38(15)		
K3 – Br		3.74(7)		

The disorder in the structure leads to uncertainties in the location of some of the light atoms, but does not affect the parameters determined for the $TlBr_4^-$ complex. Possibly, an ordered arrangement would be found in $NH_4TlBr_4.2H_2O$, NH_4TlI_4, $NH_4TlI_4.2H_2O$. $KTlI_4$. $KTlI_4.2H_2O$. $RbTlBr_4.H_2O$. $RbTlI_4.2H_2O$. $CsTlBr_4$, $CsTlI_4$ or $CsTlI_4.2H_2O$. These structures were claimed [3-6] to be isomorphous with $KTlBr_4.2H_2O$, in spite of the fact that some of them have a lower water content.

The aim of this work was to establish the type of coordination of Tl(III) and to determine the distance between Tl and Br, and this purpose has been attained. The question of confirmation of the type of the disorder has been deferred to the future.

Test of electrical conductivity. It is well-known that many compounds with "tunnel structures" have a good ionic conducitivity. This fact may be of interest because of its possible use for storage of electrical energy in high capacity batteries. Ion mobility in the solid state may be due to the fact that there is a greater number of equivalent positions in the crystal structure than of charge-transporting ions. This means that an ion can jump between the various free sites, not necessarily caused by crystal defects but occurring naturally in disordered structures.

In $KTlBr_4.2H_2O$, the K3 ions (and possibly also K2) may have these properties. However, an attempt to measure the conductivity of a powder sample, made in cooperation with the solid electrolyte group at this department, was not successful. When pressure was applied to the crystals in order to make a powder tablet, the compound exploded,

probably according to the reaction

$$KTlBr_4.2H_2O(s) \rightarrow TlBr(s) + KBr(s) + 2H_2O(g) + Br_2(g)$$

and the attempt has not been repeated.

Probably, because of the high oxidizing power of Tl(III), the compound is not suitable as an ionic conductor for batteries. However, it is likely that large single crystals of $KTlBr_4.2H_2O$ can be obtained and that conductivity measurements can possibly lead to further understanding of the nature of ionic conductivity in solids, especially when the Na, K, Rb and Cs salts are compared.

In the potassium salt, the "bottleneck" of the tunnel has a radius of about 1.0 Å. Therefore, K^+ ions cannot pass through it and one can expect a higher conductivity in $NaTlBr_4.2H_2O$ (or $LiTlBr_4.2H_2O$ if it exists and is isomorphous).

$NaTlBr_4.2H_2O$. The crystals were obtained in the same way as the potassium compound. Powder diffraction photographs, together with a preliminary diffractometer data collection, showed that the compounds are isomorphous. The parameters obtained for $NaTlBr_4.2H_2O$ are: $a = 18.426(3)$ Å, $\mu = 318.2$ cm^{-1}, $3.6 < D_m < 4.0$ g cm^{-3}, $D_x = 3.71$ g cm^{-3}.

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REFERENCES

1. Glaser, J. *To be published.*
2. Hazell, A. C. *J. Chem. Soc.* (1963) 3459.
3. Watanabe, T., Saito, Y., Shiono, R. and Atoji, M. *Abstracts*, 1st Congress of the International Union of Crystallography, p. 30 (1948); *Struct. Rept. 11* (1947–48) 393.
4. Watanabe, T. and Atoji, M. *J. Am. Chem. Soc. 72* (1950) 3819.
5. Watanabe, T., Atoji, M. and Okazaki, Ch. *Acta Crystallogr. 3* (1950) 405.
6. Kashiwagi, H., Nakamura, D. and Kubo, M. *J. Chem. Phys. 71* (1967) 4443.
7. Spiro, T. G. *Inorg. Chem. 6* (1967) 569.
8. Garrote, M. del Pilar Cerezal *Acta Salmant. Cienc. 3* (1961) 127.
9. Glaser, J. *Acta Chem. Scand. 33* (1979) 789.
10. a. Kopfmann, G. and Huber, R. *Acta Crystallogr. A 24* (1968) 348; b. North, A. C. T., Phillips, D. C. and Scott Mathews, F. *Ibid.* 351.
11. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. IV.
12. a. Busing, W. R. and Levy, H. A. *Acta Crystallogr. 17* (1964) 142; b. Busing, W. R., Martin, K. O. and Levy, H. A. *Function and Error Program ORNL-TM-306*, Oak Ridge National Laboratory, Oak Ridge 1965 (thermal motion correction of interatomic distances).
13. Wells, A. F. *Structural Inorganic Chemistry*, Clarendon Press, Oxford 1975. (Fig. 23.25.)

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