Crystal Structures of the Isomorphous Perchlorate Hexahydrates of Some Trivalent Metal Ions (M=La, Tb, Er, Tl)

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The crystal structures of the isomorphous compounds $M(ClO_4)_3 \cdot 6H_2O$, where M=La, Tb, Er, Tl, have been determined from single-crystal X-ray diffraction data collected at room temperature on an automatic Syntex $P2_1$ four-circle diffractometer using graphite monochromatized $MoK\alpha$-radiation. The cubic unit cells contain four formula weights and the space group is $Fm3m$ (No. 225). The metal ions are octahedrally coordinated by water molecules with $M-O$ distances (corrected for thermal motion) of 2.48(2) Å for La, 2.35(3) Å for Tb, 2.25(2) Å for Er and 2.23(2) Å for Tl. Some of the perchlorate groups show rotational disorder.

Information on the structures of solvated metal ions can often be obtained from investigations of their perchlorate solutions because of the small tendency of the perchlorate ion to form complexes. Also in solid perchlorates, the coordination of solvent molecules around a metal ion is often unaffected by the anion which does not enter the first coordination sphere. In order to compare the hydration of some three-valent metal ions in their solid perchlorates with that in their solutions, the crystal structures of some isomorphous perchlorates, $M(ClO_4)_3 \cdot 6H_2O$, with M representing La, Tb, Er or Tl, have been determined. X-Ray scattering investigations of metal ion hydration in the corresponding perchlorate solutions will be reported separately.

EXPERIMENTAL

Crystals were prepared by slow evaporation in a desiccator of slightly acid aqueous solutions of the perchlorates. In some cases, this was done below room temperature. The colourless, irregularly shaped crystals are deliquescent and quickly transform into a saturated solution when taken out of the mother liquor. Complete separation of the mother liquor is, therefore, not possible and accurate analysis data are difficult to obtain. Values reported in the literature give six water molecules for the thallium compound[1] and from 5.4 to 7 for the corresponding lanthanum compound.[1,2] For the isomorphous praseodymium perchlorate values from 7 to 3 have been reported.[2,3] The water content was not, however, directly determined but was obtained as a difference.

For the data collection, which was performed at room temperature with $MoK\alpha$-radiation ($\lambda = 0.7107$ Å), a crystal with a maximum dimension not exceeding ~ 0.3 mm was enclosed in a glass capillary. The crystal data are summarized in Table 1. Included are also results for the isomorphous yttrium compound which has the same unit cell dimensions as the erbium perchlorate. Isomorphous crystals were also prepared for samarium. The yttrium and the samarium compounds were not, however, investigated further. Previously, powder photographs of the corresponding perchlorates of praseodymium and neodymium have been indexed on the basis of a cubic unit cell with $a = 12.12$ and 12.09 Å, respectively.[3]

The ω scan technique with variable scan speed (from 0.5 to 29° min^{-1}) was used. Four check reflections were measured after every 50th reflection. Their intensities decreased slightly (about 0 to 5 %) during the data collections but no correction for this effect was applied.

Because of the irregular shape of the crystals, a Gaussian absorption correction could not be applied. A semi-empirical correction[4] was done but did not seem to improve the data, and usually led to slightly higher R values than those obtained with the uncorrected data. For that reason, and since the correction did not lead to significant changes in

Table 1. Crystal data.

Parameter	La	Tb	Y	Er	Tl
$a\,(\text{Å})$	12.173(5)	11.926(5)	11.900(6)	11.900(7)	11.482(9)
$D_m\,(\text{g cm}^{-3})$	–	–	–	–	2.7
$D_x\,(\text{g cm}^{-3})$	2.01	2.21	1.95	2.26	2.68
$\mu(\text{Mo}K\alpha)\,(\text{cm}^{-1})$	29.3	48.2	41.3	57.2	113.7

the parameter values, the following calculations and results refer to intensity data not corrected for absorption. For the data reduction and all other calculations, the Syntex XTL programmes were used.[5] Anomalous dispersion corrections were included for all atoms. The least-squares refinements were based on a minimization of $\Sigma w\{|F_o|-|F_c|\}^2$ including reflections with $|F_o|>3.92\sigma(F_o)$. The weighting function was $w=\{\sigma^2(F_o)+(0.04\ F_o)^2\}^{-1}$ which gave a satisfactory error distribution according to a weight analysis.

Information on the data collections and refinements is summarized in Table 2.

STRUCTURE DETERMINATION AND REFINEMENT

From Weissenberg and precession photographs, the Laue symmetry was found to be $m3m$, which was confirmed by the diffractometer data. Accurate values for the unit cell dimensions (Table 1) were determined for each crystal by a least-squares refinement using at least 10 selected reflections accurately centered on the diffractometer. Each unit cell was found to contain four formula weight.

Only reflections with hkl all odd or all even were present which leads to three possible space groups: the centrosymmetric $Fm3m$ (No. 225) and the non-centrosymmetric $F\bar{4}3m$ (No. 216), and $F432$ (No. 209).

In all of the possible space groups, the metal atoms could only be placed in the 4(a) position (0,0,0). The Patterson functions led unambiguously to positions for all the 12 Cl atoms in the unit cell and also to positions for the six oxygen atoms octahedrally surrounding each metal atom (Table 3). These positions are the same in all the three possible space groups and correspond to a centrosymmetric arrangement.

In the centrosymmetric space group $Fm3m$, the 4(b) position, occupied by the Cl1 atom (Table 3), does not have tetrahedral symmetry. The same applies to the non-centrosymmetric $F432$. The oxygens of the Cl1 perchlorate group would conform to these space group symmetries only if they were equally distributed over two different positions, that is, if they occupied the 32(f) position (x,x,x).

In the non-centrosymmetric $F\bar{4}3m$, the symmetry around the Cl1 position, 4(b), is tetrahedral and the

Table 2. Data collection and refinement.

	La	Tb	Er	Tl
Number of reflections collected	619	1084	510	592
Number of unique reflections $(I>1.96\ \sigma)$	87	98	83	96
Zero weight reflections $(I<1.96\sigma)$	24	8	22	–
Final R-value (%) incl. zero-weight reflections	7.0 7.4	6.0 6.3	4.4 5.4	3.2 3.2
Final R_w-value (%) incl. zero-weight reflections	10.6 10.8	7.0 7.1	5.9 6.2	4.0 4.0
Final S value	2.4	1.6	1.2	1.0

Table 3. Final fractional atomic positional parameters and mean square amplitudes of vibration in $Å^2$. Estimated standard deviations in the last digit are given in parentheses. The expression used for the anisotropic thermal parameters is $\exp[-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{12}hka^*b^* + ...)]$.

	La	Tb	Er	Tl
M in 4(a): (0,0,0)				
$U_{11}=U_{22}=U_{33}$	0.1405(24)	0.0996(12)	0.0962(15)	0.0463(6)
$U_{12}=U_{13}=U_{23}$	0	0	0	0
O in 24(e): (0,0,z)				
z	0.189(2)	0.186(2)	0.181(2)	0.189(1)
$U_{11}=U_{22}$	0.549(56)	0.408(38)	0.323(24)	0.186(14)
U_{33}	0.092(14)	0.081(13)	0.069(12)	0.041(7)
$U_{12}=U_{13}=U_{23}$	0	0	0	0
Cl1 in 4(b): ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$)				
$U_{11}=U_{22}=U_{33}$	0.123(4)	0.092(3)	0.090(4)	0.055(2)
$U_{12}=U_{13}=U_{23}$	0	0	0	0
O1 in 32(f): (x,x,x) (occupancy = 0.5)				
x	0.435(2)	0.431(2)	0.433(2)	0.428(2)
$U_{11}=U_{22}=U_{33}$	0.21(2)	0.18(2)	0.19(2)	0.13(1)
$U_{12}=U_{13}=U_{23}$	$-0.04(2)$	$-0.05(1)$	$-0.05(1)$	$-0.03(1)$
Cl2 in 8(c): ($\frac{1}{4},\frac{1}{4},\frac{1}{4}$)				
$U_{11}=U_{22}=U_{33}$	0.46(6)	0.38(5)	0.42(8)	0.131(6)
$U_{12}=U_{13}=U_{23}$	0	0	0	0
O2 in 32(f): (x,x,x) (occupancy = 0.4)				
x	0.18	0.18	0.18	0.17(1)
U	0.9	0.6(5)	1.2(4)	0.6(2)
O2A in 48(g): ($\frac{1}{4},\frac{1}{4},z$) (occupancy = 0.4)				
z	0.145	0.131(9)	0.146(10)	0.123(6)
U	0.46(5)	0.43(8)	0.37(3)	0.20(3)

oxygens of the Cl1 perchlorate group can have an ordered position, *i.e.* in 16(e): (x,x,x).

Difference maps and least-squares refinements, not including the oxygens of the $ClO_4(2)$ groups, calculated for these two different assumptions, showed that for both alternatives, the oxygen atoms of the $ClO_4(2)$ units were disordered, apparently corresponding to a rotation of these perchlorate groups. Peaks in the difference maps which could be related to these oxygens, seemed slightly more extended along the directions of the unit cell axes (corresponding to the position 48(g): 1/4,1/4,x in *Fm3m*), possibly indicating a preferred orientation of the rotating perchlorate groups with

Cl−O bonds along these directions. As an approximate model for the disordered ClO_4 groups, the oxygens were assumed to be distributed over the axial (1/4,1/4,x) and the diagonal (x,x,x) positions in the unit cell.

Refinements of the structures according to the noncentrosymmetric $F\bar{4}3m$ did not give any significant differences in bond lengths compared to those obtained for the centrosymmetric *Fm3m* and did not lead to *R* values which, according to statistical tests, represented significant improvements. Neither did the difference maps calculated for the two alternative arrangements give any clear indication for one or the other. The available positions in space

Table 4. Interatomic distances in Å and angles in degrees. Estimated standard deviations in the last digit are given in parentheses. The distances are corrected for thermal motion.[a] The non-corrected distances and angles are given in italics.

	La	Tb	Er	Tl
M−O	2.48(3)	2.35(3)	2.25(2)	2.23(2)
	2.30(3)	*2.21(3)*	*2.15(2)*	*2.17(2)*
O−O	3.52(4)	3.34(4)	3.21(3)	3.16(3)
	3.25(4)	*3.13(3)*	*3.05(2)*	*3.07(2)*
O−O1	3.23(3)	3.20(3)	3.27(3)	3.03(3)
	3.21(3)	*3.15(2)*	*3.21(2)*	*2.98(2)*
Cl1−O1	−	−	−	−
	1.38(1)	*1.43(1)*	*1.37(1)*	*1.43(1)*
Cl2−O2	− − − − − − − − − − − − −		*∼1.44* − − − − − − − − − − − − −	
M−O−O1	*159.4(7)*	*158.3(7)*	*159.6(6)*	*156.9(5)*

[a] See Ref. 16. "Riding" motion was assumed for the M−O distances and independent motion for the oxygen−oxygen distances.

group $F432$ lead to the same arrangement as that in $Fm3m$.

The results given in Tables 2 to 4 have been obtained assuming the space group symmetry to be $Fm3m$, that is a centrosymmetric arrangement with the oxygens of the Cl1 perchlorate group equally distributed over two alternative positions related by the 4-fold rotation axis along $[1\,0\,0]$.

In the final refinement cycles, all parameter shifts were less than 1 % of the corresponding standard deviations. In most refinements, the oxygens of the Cl2 perchlorate groups, assumed to be rotationally disordered, were kept at fixed positions at a Cl−O distance of about 1.4 Å. In the final difference maps all peaks were below 0.5 e Å^{-3} (for the Tl compound 0.7 e Å^{-3}). No evidence was found for the presence of more water molecules in the unit cells than those corresponding to the formula $M(ClO_4)_3 \cdot 6H_2O$. For the Tl compound, with its smaller unit cell, the presence of additional water molecules is ruled out also by the limited space available. Hydrogen atoms could not be located.

Final positional and thermal parameters for the four structures are given in Table 3. Bond lengths are given in Table 4.

DISCUSSION

The structures are built up from octahedrally coordinated metal ions, $M(H_2O)_6^{3+}$, and perchlorate groups, ClO_4^-, (Fig. 1). Although the building blocks are not spherical, the structures can be described as a cubic close-packed arrangement of $M(H_2O)_6^{3+}$ ions with the perchlorate groups occupying all available octahedral (Cl1) and tetrahedral (Cl2) holes.

The $M(H_2O)_6$ and the $ClO_4(1)$ groups alternate along the four-fold symmetry axes which relate the two alternative positions for the Cl1 perchlorate oxygens. The lengths of the unit cell edges in the structures should thus be primarily determined by the lengths of the M−O bonds. This is approximately true for the lanthanides where the shortening of the a axes from La to Er (Table 1) corresponds to the shortening of the Ln−O bonds (Table 4). For Tl, however, with a Tl−O bond length approximately equal to that of Er−O the axis is considerably shorter. This is caused by a shortening of the contact distances, O1−O, between the perchlorate oxygens and the water molecules (Table 4) indicating stronger interactions between these oxygens in the Tl compound than in those of the lanthanides. Probably, this can be ascribed to hydrogen bonding and be related to the higher value for the electronegativity of Tl^{3+} than of Ln^{3+}.[6]
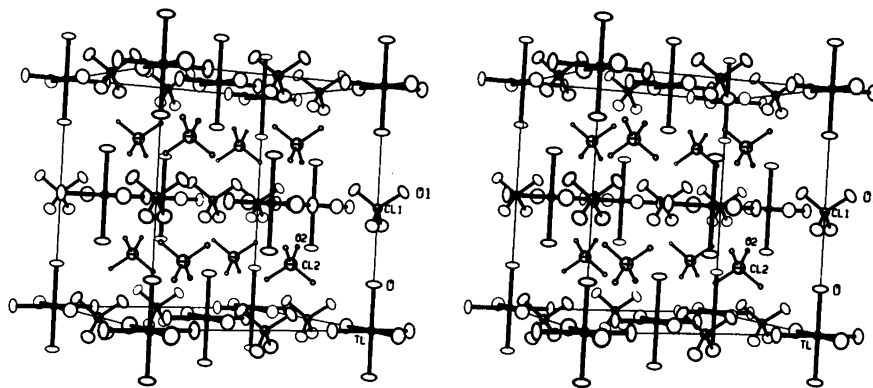
Fig. 1. A stereoscopic view of the cubic unit cell of $Tl(ClO_4)_3 \cdot 6H_2O$. For clarity, the ClO_4 groups are shown in ordered positions (*cf.* comments in the text).

The $ClO_4(2)$ groups are not in close contact with the $M(H_2O)_6$ octahedra. The space available for these perchlorate groups is sufficient for allowing rotational disorder and also for small displacements of the Cl2 atoms from their positions in $8(c)$ (Table 3), expecially when the $ClO_4(1)$ groups can also take up alternative positions. Perchlorate groups often occur as disordered in crystal structures and several examples can be found in the literature.[7] The disorder is probably least in the thallium perchlorate as judged from the calculated electron density maps where the peaks corresponding to the $16(e)$: (x,x,x) positions for the oxygen atoms of $ClO_4(2)$ are more marked than for the other structures (Fig. 1). It is also indicated by the much smaller values for the thermal parameters for the thallium compound (Table 3).

It is generally assumed that the hydration numbers of the lanthanide ions are higher than six, probably between eight and ten.[8] Commonly cited evidence for this are the crystal structures of neodymium bromate, $Nd(H_2O)_9(BrO_3)_3$,[9a] and ethylsulfate, $Nd(H_2O)_9(C_2H_5SO_4)_3$,[9b] in which the neodymium ion is coordinated by nine water molecules forming a tricapped trigonal prism with $Nd-O$ distance of about 2.5 Å. X-Ray scattering measurements on aqueous chloride solutions have given similar coordination numbers and bond lengths of 2.58 Å for La,[10] 2.41 Å for Tb,[11] and 2.37 Å for Er.[11] Preliminary results[12] from X-ray scattering measurements on aqueous perchlorate solutions lead to approximately the same $Ln-H_2O$ distances: 2.59 Å for $La-O$, and 2.36 Å for $Er-O$,

but indicate that the distances to the water molecules surrounding the metal ions in the solutions are not all equal. A coordination number of six throughout the series, as found here for the solid perchlorates, is thus unexpected. The $Ln-O$ bond lengths in the crystal structures, after correction for thermal motion, are about 0.1 Å shorter than those cited above. The difference is of the order of magnitude expected for a change in coordination number from eight to six.[8]

For the thallium(III) ion, a coordination number of six is the expected value. Suggestions have been made that two of these six water molecules may be more closely bonded than the others,[13,14] but this is not supported by the present structure determination and also is not consistent with results of X-ray scattering measurements on aqueous perchlorate solutions.[15] The $Tl-O$ bond length of 2.23(2) Å found in the crystals does not differ significantly from that found from the solution scattering measurements 2.235(5) Å.

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