Structure of hexaaquadichloroyttrium(III) chloride

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groups around the Th atoms and the structure of the bridged chains parallel to [100].

The Th—O bond distances range from 2·35 (1) to 2·61 (1) Å with a mean of 2·45 (10) Å. The Th—O(water) distances are, on average, longer than the Th—O(sulfate) ones, the mean values being 2·59 (4) and 2·38 (3) Å respectively. This difference may perhaps be correlated with the relatively easy removal of water from the coordination sphere and/or with the fact that the waters occupy the equatorial positions.

The S—O bonds to coordinated oxygen are, as expected, longer than those to terminal oxygen. The mean values are 1·49 (1) and 1·46 (1) Å respectively.

The water molecules [represented by O(2), O(5), O(7), O(9), O(10), and O(15)] form hydrogen bonds among themselves and with the O atoms of the sulfate groups, though, without a neutron diffraction study, these hydrogen bonds cannot be positively located. The hydrogen-bond distances range from 2·56 to 2·88 Å and, as in the structure of Th-$(SO_4).8H_2O$ (Habash & Smith, 1983), some of them appear to be either disordered or bifurcated.

The sodium ions are each surrounded by six O atoms in the form of a distorted octahedron. The Na···O distances range from 2·29 to 2·65 Å with a mean of 2·45 Å.

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Structure of Hexaaquadichloroyttrium(III) Chloride

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Abstract. [$YCl_2(H_2O)_6$]Cl, $M_r = 303·356$, monoclinic, $P2/n$, $a = 7·8346$ (25), $b = 6·4729$ (26), $c = 9·5817$ (50) Å, $\beta = 93·768$ (35)°, $V = 484·86$ Å^3, $Z = 2$, $D_x = 2·0776$ g cm^{-3}, Mo $K\alpha$ ($\lambda = 0·71069$ Å), $\mu = 68·66$ cm^{-1}, $F(000) = 300$, room temperature, final $R = 0·0449$ for 940 unique observed reflexions. The yttrium is coordinated, as expected, by two chlorines and six water molecules in a square antiprismatic arrangement.

Introduction. In the course of attempts to prepare other yttrium compounds we obtained good crystals of [$YCl_2(H_2O)_6$]Cl. Although this compound is a member of a well known isomorphous series, its structure parameters have not previously been reported. Dicke & Crossthwaite (1956) have reported a β value of 92° for this compound.

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Experimental. Y_2O_3 was heated with excess solid NH_4Cl and the product (mostly YOCl) was dissolved in 2M HCl. Crystals were obtained on evaporation.

X-ray reflexion data from a small (approximately 0·2 × 0·2 × 0·4 mm) crystal were collected on a Nicolet *R3M* four-circle automatic diffractometer operating in the ω-scan mode and using Mo $K\alpha$ radiation. The unit-cell parameters were determined from a least-squares fit of the setting angles of 25 well centred and well distributed reflexions in the range $4 < \theta < 14°$. Reflexions in the range $3·5 < \theta < 55°$ and having h, k, and l in the ranges −10 to 10, 0 to 8, and 0 to 12, respectively, were surveyed. Two check reflexions were monitored every 50 reflexions and showed no evidence of decay. 1359 measurements were made giving 1307 unique reflexions, of which 940 were accepted as observed [$|F_o| > 3\sigma(F)$]. R_{int} was 0·0096. The structure was solved by Patterson and difference Fourier methods and refined by cascade blocked-diagonal least squares [function minimized $w(F_o - F_c)^2$] with weights $w =$

$1/[\sigma^2(F) + 0.00187F^2]$ (the weighting parameter was refined) to a final R of 0.0449 ($wR = 0.0552$) (74 refined parameters). Hydrogen positions were found from a low-θ difference Fourier map. The H atoms were then refined with 'soft' constraints applied to the O—H and H···H distances. These constraints were removed for the last refinement cycle in order to obtain meaningful e.s.d.'s. The (isotropic) hydrogen thermal parameters were each fixed at 1.2 times U_{eq} for the adjacent heavy atom. Because of the small size of the crystal no absorption correction was applied but an extinction correction of the form $F^* = F_c/[1 + 0.0002716F^2/(\sin 2\theta)]^{0.25}$ was found to be advantageous.

The shifts on the final cycle of refinement were all less than 0.1 of the corresponding e.s.d.'s; the final difference Fourier map showed density from -0.9 to $+0.6$ e Å^{-3} but there was no peak which could be interpreted as an atom. Analysis of variance against $\sin\theta$ and against $|F|$ showed no unusual features; neither did the normal probability plot. Atomic scattering factors, linear absorption coefficients, and f' and f'' values were taken from International Tables for X-ray Crystallography (1974). The SHELXTL suite of crystallographic programs (Sheldrick, 1983) was used throughout on a NOVA3 computer.

The atomic parameters are listed in Table 1, principal bond lengths and angles are in Table 2, and hydrogen bonds in Table 3.†

Discussion. The bond lengths are in line with expectation. The metal atom, which lies on the twofold axis, is eight-coordinated, by two chlorines and six water molecules, with approximate square-antiprism (D_{4d}) geometry. A fit of the M—L bonds to an idealized polyhedron gave a θ value of $57.39°$ (θ is the angle between the principal symmetry axis and a metal—ligand bond) and a σ of $4.08°$ (Smith, 1990). The best fit which could be obtained for a dodecahedron had a σ of $19.49°$.

It is instructive to compare this structure with those of other members of the series which have been reported. Determinations of atom coordinates have been reported for the isostructural compounds of neodymium (Habenschuss & Spedding, 1980a), samarium (Habenschuss & Spedding, 1980c), europium (Bel'sky & Struchkov, 1965; Lepert, Patrick & White, 1983), gadolinium (Marezio, Plettinger & Zachariasen, 1961; Habenschuss & Spedding, 1980d), and lutetium (Habenschuss & Spedding, 1980b). If the early determinations for the europium

† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52298 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atom coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Y(1)	2500	1556 (1)	2500	17 (1)
Cl(1)	2605 (1)	−1602 (2)	603 (1)	28 (1)
Cl(2)	7500	−3748 (2)	2500	30 (1)
O(1)	1071 (4)	2999 (5)	4362 (3)	29 (1)
O(2)	894 (4)	4247 (5)	1460 (3)	29 (1)
O(3)	−391 (4)	530 (5)	2181 (3)	29 (1)

Table 2. *Bond lengths* (Å) *and angles* (°)

Y(1)—Cl(1)	2.740 (1)	Y(1)—O(1)	2.360 (3)
Y(1)—O(2)	2.333 (3)	Y(1)—O(3)	2.361 (3)
Y(1)—Cl(1a)	2.740 (1)	Y(1)—O(1a)	2.360 (3)
Y(1)—O(2a)	2.333 (3)	Y(1)—O(3a)	2.361 (3)
Cl(1)—Y(1)—O(1)	146.4 (1)	Cl(1)—Y(1)—O(2)	108.2 (1)
O(1)—Y(1)—O(2)	76.0 (1)	Cl(1)—Y(1)—O(3)	77.0 (1)
O(1)—Y(1)—O(3)	73.2 (1)	O(2)—Y(1)—O(3)	70.7 (1)
Cl(1)—Y(1)—Cl(1a)	83.5	O(1)—Y(1)—Cl(1a)	76.0 (1)
O(2)—Y(1)—Cl(1a)	143.2 (1)	O(3)—Y(1)—Cl(1a)	78.8 (1)
Cl(1)—Y(1)—O(1a)	76.0 (1)	O(1)—Y(1)—O(1a)	133.4 (2)
O(2)—Y(1)—O(1a)	69.6 (1)	O(3)—Y(1)—O(1a)	120.8 (1)
Cl(1a)—Y(1)—O(1a)	146.4 (1)	Cl(1)—Y(1)—O(2a)	143.2 (1)
O(1)—Y(1)—O(2a)	69.6 (1)	O(2)—Y(1)—O(2a)	83.4 (2)
O(3)—Y(1)—O(2a)	138.7 (1)	Cl(1a)—Y(1)—O(2a)	108.2 (1)
O(1a)—Y(1)—O(2a)	76.0 (1)	Cl(1)—Y(1)—O(3a)	78.8 (1)
O(1)—Y(1)—O(3a)	120.8 (1)	O(2)—Y(1)—O(3a)	138.7 (1)
O(3)—Y(1)—O(3a)	147.3 (2)	Cl(1a)—Y(1)—O(3a)	77.0 (1)
O(1a)—Y(1)—O(3a)	73.2 (1)	O(2a)—Y(1)—O(3a)	70.7 (1)

Table 3. *Hydrogen bonds* (Å)

	H···X	O···X		H···X	O···X
O(1)—H(1)···Cl(2)	2.43	3.18	O(3)—H(5)···Cl(2)	2.51	3.25
O(2)—H(3)···Cl(1)	2.37	3.14	O(3)—H(6)···Cl(1)	2.40	3.16
O(2)—H(4)···Cl(2)	2.42	3.18			

H(2) does not appear to be involved in any hydrogen bonding.

gadolinium compounds are rejected as being less accurate (which they evidently are), the regular progression of structural parameters due to the lanthanide contraction can be readily observed, with yttrium in its expected position between gadolinium and lutetium. This is shown in Table 4, where the unit-cell volumes are listed but it could equally well have been shown from bond lengths, etc. It is remarkable that the θ values for all of these coordination polyhedra are the same to within $0.1°$. That is to say that the polyhedra, although of different sizes, all have exactly the same shape. As a check on the degree of stereochemical crowding, the sum of solid angles, S (Smith, 1975, 1981) is also given in the same table for each compound and these sums show a normal progression. For a fully triangulated polyhedron this result would have been less surprising, but the antiprism might have been expected either to have progressed to smaller θ with diminishing metal radius, or to have become more distorted, and neither of these is the case.

Table 4. *Structural parameters*

	$V(\text{Å}^3)$	S	$\theta(°)$
Nd	511·1	763	57·42 (4·22)
Sm	503·8	783	57·38 (4·18)
Eu	499·4	794	57·44 (4·28)
Gd	498·4	800	57·41 (4·28)
Y	484·9	836	57·38 (4·18)
Lu	479·3	855	57·47 (3·95)

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Structure of Silver(I) Barium Phosphoenolpyruvate Trihydrate

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Abstract. Barium silver 2-(phosphonooxy)propeno-ate trihydrate, $Ag^+.Ba^{2+}.C_3H_2O_6P^{3-}.3H_2O$, $M_r = 464\cdot3$, monoclinic, $P2_1/a$, $a = 6\cdot578$ (3), $b = 23\cdot811$ (9), $c = 6\cdot640$ (3) Å, $\beta = 90\cdot57$ (3)°, $V = 1035\cdot3$ (8) Å^3, $Z = 4$, $D_m = 2\cdot96$, $D_x = 2\cdot978$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 59\cdot1$ cm^{-1}, $F(000) = 864$, $T = 299$ (1) K, final $R = 0\cdot0274$ for 2144 nonzero reflections. The phosphate ester bond, $1\cdot662$ (4) Å, is comparable to the longest bonds of this type. The phosphate group is *trans* to the carboxylate group. The enolpyruvate system deviates slightly from planarity. Two Ag^+ ions are bridged by two carboxylate groups [Ag···Ag $2\cdot913$ (2) Å]. Each phosphoenolpyruvate trianion chelates through phosphate O and methylene C atoms to one Ag^+ ion and bridges two further Ag^+ ions through the carboxylate group, thereby forming polymeric chains along the a axis. One water molecule completes the Ag coordination sphere. The Ba^{2+} ions display ninefold coordination and are bridged by a water molecule and by two kinds of phosphate bridges along the a axis. The Ba^{2+} chains are connected to the Ag chains by phosphate, carboxylate and water oxygens. Only one O atom from the phosphate group does not coordinate to the metal ions but participates in four hydrogen bonds instead. All water H atoms are involved in hydrogen bonds.

Introduction. This work is a continuation of our investigations into organic phosphates and follows our earlier structural papers on the phosphoenolpyruvate (PEP) moiety (Weichsel & Lis 1990). The free energy of hydrolysis of PEP ($-58\cdot5$ kJ mol^{-1}) is the highest among naturally occurring phosphates (Lehninger, 1971) and the kinetics of PEP hydrolysis reactions depend strongly on the pH (Benkovic & Schray, 1968). From among four PEP forms the structures of the PEP acid (Weichsel, Lis & Kuczek, 1989), the PEP monoanion [monosodium salt (Katti, Hosur & Viswamitra, 1981), the monopotassium salt (Lis, 1987), the monocyclohexylammonium salts (Weichsel & Lis, 1989)] and the PEP dianion [bis(cyclohexylammonium) methanol solvate 1/0·5 (Weichsel & Lis, 1990)] have been described. Here we present the structure of the PEP trianion as a silver(I) barium trihydrate salt.

The isolation or purification of the PEP trianion by crystallization of a silver barium salt has been described by Baer & Fisher (1949). Quantitative analysis of our sample (Baer, 1952) suggested it was