N1	0.9798 (7)	−0.1439 (4)	−0.0641 (7)	2.6 (1)
N2	1.2040 (8)	0.4858 (4)	0.5618 (8)	3.2 (1)
N3	0.9465 (9)	0.2929 (5)	0.7010 (9)	4.1 (2)
N4	0.5127 (8)	0.0817 (4)	0.7432 (8)	3.0 (1)
N5	0.4308 (8)	0.2556 (4)	0.0486 (8)	3.5 (2)
N6	1.3260 (8)	0.2585 (4)	0.5001 (8)	3.4 (2)

Table 2. *Selected geometric parameters (Å)*

Mo1—O1	1.712 (6)	Mo5—O16	1.709 (6)
Mo1—O2	1.714 (6)	Mo5—O17	1.815 (5)
Mo1—O8	1.915 (5)	Mo6—O17	2.042 (5)
Mo1—O9	2.350 (5)	Mo6—O18	1.701 (6)
Mo1—O12^{i}	1.910 (5)	Mo6—O19	1.719 (6)
Mo1—O13^{i}	2.207 (5)	Mo6—O25	1.896 (5)
Mo2—O3	1.712 (5)	Mo6—O26	2.213 (5)
Mo2—O4	1.698 (6)	Mo6—O29^{ii}	2.217 (5)
Mo2—O8	1.944 (5)	Mo7—O20	1.699 (5)
Mo2—O10	2.291 (5)	Mo7—O26	1.912 (5)
Mo2—O11	1.946 (5)	Mo7—O27	1.765 (5)
Mo2—O13^{i}	2.238 (5)	Mo7—O29^{ii}	2.121 (5)
Mo3—O5	1.700 (6)	Mo7—O30	1.935 (5)
Mo3—O9	1.764 (5)	Mo7—O30^{ii}	2.429 (5)
Mo3—O10	1.880 (5)	Mo8—O21	1.721 (5)
Mo3—O12	2.132 (5)	Mo8—O22	1.706 (5)
Mo3—O13	1.939 (5)	Mo8—O25	1.985 (5)
Mo3—O13^{i}	2.447 (5)	Mo8—O26	2.261 (5)
Mo4—O6	1.705 (6)	Mo8—O28	1.906 (5)
Mo4—O7	1.710 (6)	Mo8—O30^{ii}	2.253 (5)
Mo4—O10	2.205 (5)	Mo9—O23	1.711 (6)
Mo4—O11	1.905 (5)	Mo9—O24	1.706 (5)
Mo4—O12	2.190 (5)	Mo9—O27	2.320 (5)
Mo4—O14	2.040 (5)	Mo9—O28	1.954 (5)
Mo5—O14	1.824 (5)	Mo9—O29	1.919 (5)
Mo5—O15	1.733 (6)	Mo9—O30	2.254 (5)

Symmetry codes: (i) $2-x, -y, 1-z$; (ii) $2-x, 1-y, -z$.

Pairs of atoms further than 3.97 Å apart were assigned to be pairs of N atoms of ammonium ions, as distances between two N atoms should be longer than 3.7 Å (Seimons & Templeton, 1954).

All calculations were carried out using *TEXSAN* (Molecular Structure Corporation, 1989) software running on a MicroVAXII computer.

Lists of structure factors, anisotropic displacement parameters, hydrogen-bond distances and complete geometry have been deposited with the IUCr (Reference: OH1091). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Triperchloratoytterbium(III) Monohydrate, $Yb(ClO_4)_3.H_2O$

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Abstract

The crystal structure of triperchloratoytterbium(III) monohydrate, $Yb(ClO_4)_3.H_2O$, has been determined. In this coordination compound, bidentate and tridentate perchlorato groups form a channelled three-dimensional network. The eightfold coordination of ytterbium is completed by one strongly bound water molecule lying inside the channels.

Comment

In spite of its well known weak coordination behaviour, ClO_4^- can compete with more basic molecules or ions such as H_2O or OH^- in complexing small-sized and polarizing cations like the lanthanide ions Ln^{3+} (Huskowska, Legendziewicz, Schleid & Meyer, 1992). This is demonstrated well by the compounds $Nd_2(OH)_3(ClO_4)_3.5H_2O$ (Csöregh, Huskowska, Ertan, Legendziewicz & Kierkegaard, 1989) and $Pr_2(OH)_3H_2O(ClO_4)_3$ (Schleid, Meyer, Oczko & Legendziewicz, 1991), and particularly by the title compound, $Yb(ClO_4)_3.H_2O$.

The molecular structure of $Yb(ClO_4)_3.H_2O$ comprises bidentate and tridentate perchlorato groups that form catenated rings including six Yb atoms (Yb—Yb distances range from 5.77 to 5.92 Å). These rings are linked to each other exclusively through tridentate groups to form large channels along the *c* axis that contain water molecules. The bridging bidentate groups are slightly less distorted in this compound than in $Sb_2Cl_6(OH)O(ClO_4)$ (Belin, Chaabouni, Pascal & Potier, 1982) or in $Ti(ClO_4)_4$ (Fourati *et al.*, 1986) where ClO_4^- is not bridging but chelating. The tridentate groups compare well with those found in cobalt or nickel perchlorato complexes (Pascal, Potier, Jones, Roziere & Michalowicz, 1985) as well as in the praseodymium complex mentioned above, but are different from the 'pseudo' tridentate groups in $Cu(ClO_4)_2$ (Favier, Bargues, Pascal, Belin & Tillard-Charbonnel, 1994). The water molecules, tightly bonded to Yb atoms inside channels, are difficult to remove. Water can be removed either at high temperatures or at lower temperatures by using a strong dehydrating agent like Cl_2O_6 (Favier & Pascal, 1992).

The mean distance (2.79 Å) between the O atom of the water molecule (O_A) and the non-bonded O atoms of the perchlorato groups suggests the presence of hydrogen bonding. Owing to the presence of three crystallographically different perchlorato groups, the eight O atoms around the Yb atom are arranged at the vertices of a fairly distorted square antiprism. Yb—O distances [from 2.255 (8) to 2.493 (7) Å] are close to those expected from the effective ionic radii of Shannon and Prewitt (Huheey, 1978). The transition from monohydrated to anhydrous ytterbium perchlorate results in ninefold coordination of Yb, in which all perchlorato groups are tridentate as in other anhydrous lanthanide complexes (Favier & Pascal, 1992). Anhydrous $Ln(ClO_4)_3$, as well as the recently characterized compound $Yb(ReO_4)_3$ (Khrustalev, Varfolomeev, Shamrai, Struchkov & Pisarevskii, 1993), have hierarchical structures deriving from that of MCl_3 (M = U, Ln) (Morosin, 1968).

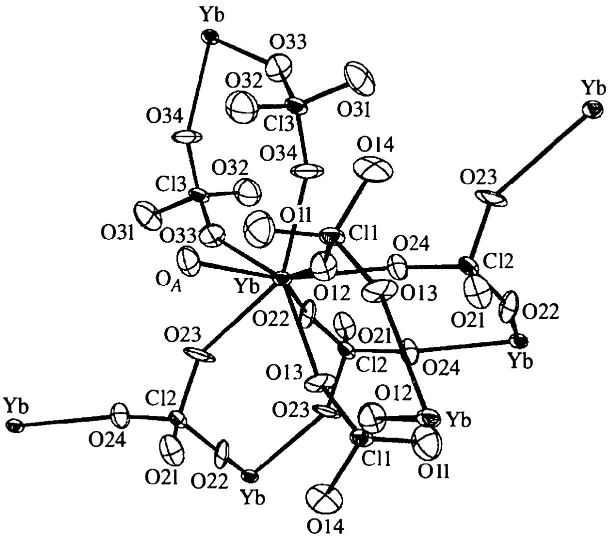

Fig. 1. The molecular structure of $Yb(ClO_4)_3.H_2O$ showing the ytterbium coordination shell of seven perchlorato groups and a water molecule (H atoms are not represented). 50% probability displacement ellipsoids are shown.

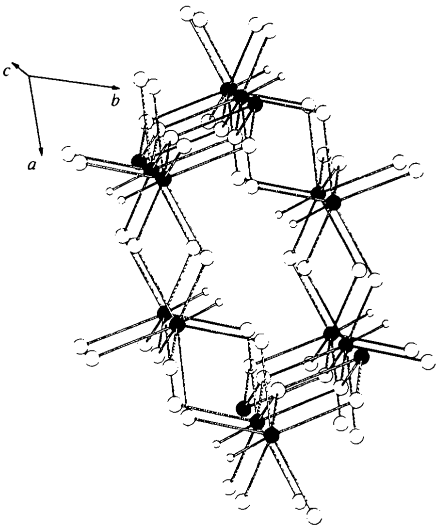

Fig. 2. Schematic packing in the $Yb(ClO_4)_3.H_2O$ structure. Black circles represent Yb atoms, small open circles represent water molecules, and large open circles represent perchlorato groups.

Experimental

In the first step, the polyhydrated ytterbium perchlorate was prepared by boiling ytterbium(III) oxide (99.9%) in a slight excess of perchloric acid (~ 1 *M*). The solution was concentrated until close to dryness and the white solid obtained by cooling at room temperature was stored in one of the two arms of a reactor sealed under vacuum (1.33 Pa). The arm containing $Yb(ClO_4)_3.nH_2O$ was heated to 443 K while the other was cooled to 93 K. After 12–24 h, a glassy solid and crystalline colourless needles were isolated in the warmed arm, while evaporated water (or oxonium perchlorate) was discarded in the cooled arm. The very hygroscopic crystals of $Yb(ClO_4)_3.H_2O$ were handled in a glove box filled with a purified argon atmosphere.

Crystal data

$Yb(ClO_4)_3.H_2O$
$M_r = 489.4$
Triclinic
$P\bar{1}$
$a = 9.473\ (4)$ Å
$b = 7.802\ (3)$ Å
$c = 6.755\ (2)$ Å
$\alpha = 78.14\ (2)^\circ$
$\beta = 75.58\ (2)^\circ$
$\gamma = 77.21\ (2)^\circ$
$V = 465.5$ Å^3
$Z = 2$
$D_x = 3.49$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9–20^\circ$
$\mu = 10.96$ mm^{-1}
$T = 298$ K
Wedge
0.13 × 0.10 × 0.08 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/θ scans

1398 observed reflections $[I > 3\sigma(I)]$
$R_{\rm int} = 0.0246$

Absorption correction: numerical (*SHELX76*; Sheldrick, 1976)
$T_{\min} = 0.361$, $T_{\max} = 0.635$
4488 measured reflections
1593 independent reflections
$\theta_{\max} = 25°$
$h = 0 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -16 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity decay: <0.6%

Refinement

Refinement on F
$R = 0.0313$
$wR = 0.0389$
$S = 0.84$
1347 reflections
154 parameters
H atoms not located
$w = 1/[\sigma^2(F) + 0.0014F^2]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.50$ e Å^{-3}
$\Delta\rho_{\min} = -2.69$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Mann (1968)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Yb	0.31022 (4)	0.32348 (5)	0.36213 (6)	0.0138 (3)
Cl1	0.3064 (2)	−0.1003 (3)	−0.2873 (3)	0.017 (2)
Cl2	0.5211 (2)	0.6796 (3)	0.2033 (3)	0.015 (2)
Cl3	−0.0091 (2)	0.3313 (3)	−0.2283 (3)	0.018 (2)
O11	0.231 (1)	0.816 (1)	−0.382 (1)	0.038 (7)
O12	0.3424 (8)	0.062 (1)	−0.421 (1)	0.028 (5)
O13	0.4464 (8)	0.787 (1)	−0.263 (1)	0.029 (6)
O14	0.2275 (9)	0.940 (1)	−0.093 (1)	0.040 (7)
O21	0.4651 (9)	0.8632 (9)	0.186 (1)	0.029 (6)
O22	0.4002 (8)	0.5853 (9)	0.233 (1)	0.027 (6)
O23	−0.3708 (8)	0.637 (1)	0.024 (1)	0.034 (6)
O24	−0.4072 (8)	0.6138 (9)	0.378 (1)	0.024 (6)
O31	0.017 (1)	0.280 (1)	−0.025 (1)	0.041 (7)
O32	−0.046 (1)	0.197 (1)	−0.305 (1)	0.044 (8)
O33	−0.1277 (8)	0.483 (1)	−0.223 (1)	0.036 (7)
O34	0.1188 (8)	0.394 (1)	−0.363 (1)	0.037 (7)
O_A	−0.1892 (9)	0.856 (1)	−0.270 (1)	0.0316 (6)

Table 2. *Geometric parameters (Å, °)*

Yb—$O_A^{\rm i}$	2.255 (8)	Cl2—O21	1.405 (7)
Yb—O13$^{\rm ii}$	2.257 (7)	Cl2—O23$^{\rm vi}$	1.425 (8)
Yb—O12$^{\rm iii}$	2.261 (7)	Cl2—O22	1.446 (8)
Yb—O33$^{\rm i}$	2.286 (8)	Cl2—O24$^{\rm vi}$	1.451 (7)
Yb—O34$^{\rm iii}$	2.307 (8)	Cl3—O32	1.407 (9)
Yb—O22	2.308 (7)	Cl3—O31	1.412 (8)
Yb—O24$^{\rm iv}$	2.352 (7)	Cl3—O33	1.438 (8)
Yb—O23$^{\rm i}$	2.493 (7)	Cl3—O34	1.439 (8)
Cl1—O11$^{\rm v}$	1.394 (9)	O_A· · ·O12$^{\rm vii}$	2.72 (1)
Cl1—O14$^{\rm v}$	1.398 (8)	O_A· · ·O23	2.84 (1)
Cl1—O13$^{\rm v}$	1.445 (7)	O_A· · ·O31$^{\rm i}$	2.79 (1)
Cl1—O12	1.451 (8)	O_A· · ·O33	2.81 (1)
O12—Yb—O23	125.9 (3)	O11—Cl1—O12	109.4 (5)
O12—Yb—O24	75.3 (2)	O11—Cl1—O13	109.4 (5)
O12—Yb—O33	139.9 (3)	O11—Cl1—O14	113.8 (5)
O12—Yb—O34	81.7 (3)	O12—Cl1—O13	106.1 (4)
O12—Yb—O_A	74.0 (3)	O12—Cl1—O14	109.2 (5)
O13—Yb—O22	80.1 (3)	O13—Cl1—O14	108.7 (5)
O13—Yb—O23	72.8 (3)	O21—Cl2—O22	109.0 (5)
O13—Yb—O24	78.2 (3)	O21—Cl2—O23	111.6 (5)
O13—Yb—O33	138.4 (3)	O21—Cl2—O24	112.3 (4)
O13—Yb—O34	145.7 (3)	O22—Cl2—O23	109.5 (5)
O13—Yb—O_A	105.8 (3)	O22—Cl2—O24	107.8 (4)
O22—Yb—O23	70.9 (3)	O23—Cl2—O24	106.6 (4)
O22—Yb—O24	73.0 (2)	O31—Cl3—O32	114.2 (5)
O22—Yb—O33	74.1 (3)	O31—Cl3—O33	107.0 (5)
O22—Yb—O34	104.0 (3)	O31—Cl3—O34	108.8 (5)
O22—Yb—O_A	139.9 (3)	O32—Cl3—O33	109.7 (5)
O23—Yb—O24	136.7 (2)	O32—Cl3—O34	110.7 (5)
O23—Yb—O33	68.2 (3)	O33—Cl3—O34	106.1 (5)
O23—Yb—O34	141.2 (3)	Yb—O12—Cl1	158.7 (5)
O23—Yb—O_A	73.2 (3)	Yb—O13—Cl1	155.6 (5)
O24—Yb—O33	122.6 (3)	Yb—O22—Cl2	147.2 (5)
O24—Yb—O34	70.8 (3)	Yb—O23—Cl2	145.9 (5)
O24—Yb—O_A	147.0 (2)	Yb—O24—Cl2	148.5 (4)
O33—Yb—O34	73.4 (3)	Yb—O33—Cl3	151.9 (5)
O33—Yb—O_A	76.5 (3)	Yb—O34—Cl3	142.1 (5)
O34—Yb—O_A	92.9 (3)		

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $1-x, 1-y, -z$; (iii) $x, y, 1+z$; (iv) $-x, 1-y, 1-z$; (v) $x, y-1, z$; (vi) $1+x, y, z$; (vii) $-x, 1-y, -1-z$.

H atoms of the solvating water molecule have not been taken into account for the structure refinement.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: own program. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Molecular graphics: *ORTEPII* (Johnson, 1976), *ATOMS* (Dowty, 1993).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1135). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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