U—O5	2.369 (7)	N···O1	2.908 (12)
U—O7	1.779 (6)	N···O4^{iv}	2.851 (12)
U—O8	1.771 (7)	N···O5	2.875 (10)
Se1—O1	1.688 (6)	N···O7^{v}	2.874 (11)
Se1—O2	1.700 (7)		
O1—Se1—O2	99.1 (3)	O4—Se2—O5	102.4 (3)
O1—Se1—O3	101.2 (3)	O4—Se2—O6	98.2 (4)
O2—Se1—O3	99.2 (3)	O5—Se2—O6	95.7 (3)

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $1-x, -y, 1-z$; (v) $2-x, -y, 1-z$.

Because of the high absorption, both ψ-scan (North, Phillips & Mathews, 1968) and spherical absorption corrections were applied (*International Tables for X-ray Crystallography*, 1967, Vol. II, Table 5.3.6B). For the ψ-scan correction $T_{\max}$ was 0.999 and $T_{\min}$ was 0.779, and for the spherical correction $T_{\max}$ was 0.190 and $T_{\min}$ was 0.165. The maximum and minimum residual electron densities in the final difference Fourier map are located near the U atom at distances less than 0.7 Å.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to solve structure: *MULTAN*11/82 (direct methods) (Main *et al.*, 1982). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1138). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetracaesium Ytterbium Heptachloride with Partly Disordered Chloride Ions

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Abstract

The structure of the title compound, Cs_4YbCl_7, consists of layers of composition Cs_2YbCl_6 containing isolated $YbCl_6^{3-}$ octahedra, separated from each other by layers of composition Cs_2Cl containing sixfold disordered Cl ions. Similarities and differences with the cubic elpasolite structure and some of its distortional variants are discussed. The compound decomposes at *ca.* 520 K into the neighbouring phases CsCl and Cs_3YbCl_6.

Comment

In the CsCl/$LnCl_3$ systems, decreasing Ln ionic radii are associated with an increasing number of compounds and structural modifications. Recently, we found a new distortional variant of the cubic elpasolite structure for Cs_3NdCl_6 (Reuter & Frenzen, 1995) and have since shown that this low-temperature phase occurs for all lanthanides from Nd to Yb (Reuter, Roffe & Seifert, 1996). Apart from the 3:1, 2:1 and 1:2 compounds, an enneachloride $Cs_3Ln_2Cl_9$ exists for Ln = Ho, Tm, Yb and Lu (Meyer & Schönemund, 1980). During the course of our studies of the preparation of anhydrous compounds in these systems from aqueous solution, we found a new phase, Cs_4LnCl_7, for Ln = Ho, Er, Yb and Y. These compounds were not observed when preparation from melts was attempted, since they decompose above 520 K into CsCl and Cs_3LnCl_6, as shown by differential scanning calorimetry (DSC) and X-ray powder diffraction measurements. Because of their low decomposition temperatures, the compounds cannot be prepared by annealing the neighbouring phases CsCl and Cs_3LnCl_6 just below this temperature, even for months. This paper presents the crystal structure of the title compound, Cs_4YbCl_7.

The structure contains isolated, nearly regular $YbCl_6^{3-}$ octahedra [Yb—Cl1 2.594 (4) Å, Cl1—Yb1—Cl1 180, 88.96 (12), 91.04 (12)°]. All octahedra are oriented in the same way. They are arranged parallel to the *ab* plane showing a threefold axis of symmetry in projection along the *c* axis and a twofold axis in projection normal to this plane. Regarding the octahedra as isolated entities, they are cubic close packed. Thus, the stacking period of the octahedra layers is three.

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One half of the caesium ions (Cs1) are incorporated into the octahedra layers, which are separated by layers containing the other half of the caesium ions (Cs2) and the remaining chloride ion (Cl2), which is sixfold disordered (Wyckoff notation 18*h*, site occupancy 1/6). The stacking sequence of the octahedra layers is illustrated in Fig. 1.

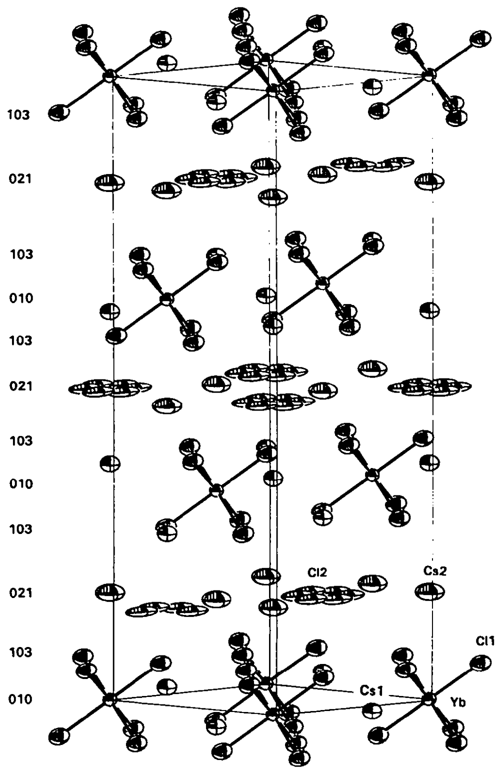

Fig. 1. A view of the structure in the [110] direction. Displacement ellipsoids are plotted at the 70% probability level.

The coordination sphere of Cs1 is formed by six coplanar Cl1 ions [Cs1—Cl1 3.843 (2) Å], which form a plane parallel to the *ab* plane, three Cl1 ions below this plane [Cs1—Cl1 3.534 (4) Å] and one disordered Cl2 site [Cs1—Cl2 3.41 (4) Å] above this plane. Cs1 is shifted 0.37 Å from the centre of the plane towards the three Cl1 ions closest to it (Fig. 2). The idealized coordination sphere of Cs2 is a triply capped trigonal prism, with three Cl1 ions at a distance of 3.584 (4) Å, three Cl1 ions at 3.665 (4) Å and three Cl2 ions at 3.37 (3) Å. This is the shortest distance to any position of the disordered Cl2 atom (Fig. 3). The distance to the idealized position (0,0,1/2) of Cl2 would be 4.417 Å, too long for a Cs···Cl contact. To accomplish its coordination sphere every Cs2 ion uses another position of the six disordered Cl2 ions, as shown in Fig. 4. Because of the disorder, the coordination sphere cannot be completed and the Cs2 ions will move statistically to one of the nearest Cl2 ions, resulting in large displacement parameters for Cs2 in the *ab* plane.

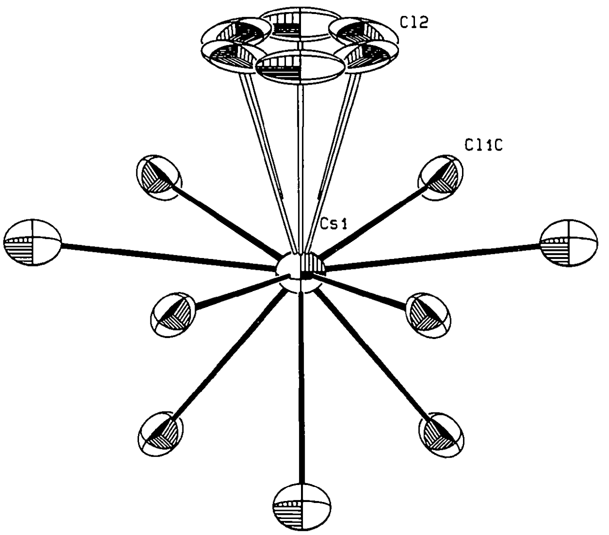

Fig. 2. *ZORTEP* (Zsolnai, 1994) plot of the coordination sphere of Cs1. Displacement ellipsoids are plotted at the 70% probability level.

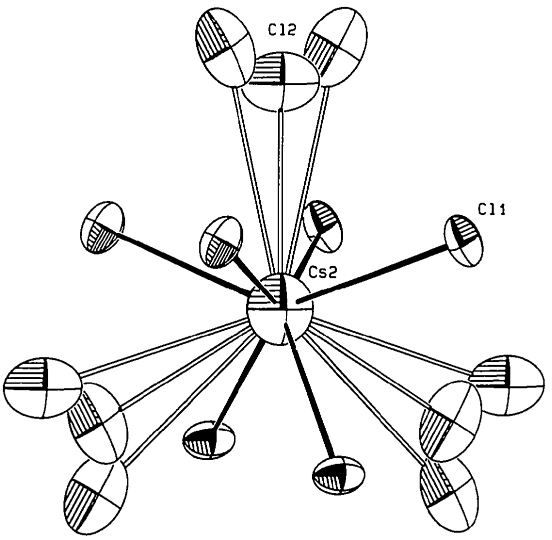

Fig. 3. *ZORTEP* (Zsolnai, 1994) plot of the coordination sphere of Cs2. Displacement ellipsoids are plotted at the 70% probability level.

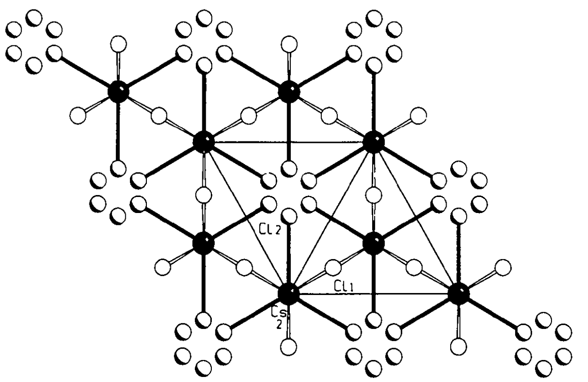

Fig. 4. A section of the structure parallel to the *ab* plane from $z = 0.05$ to $z = 0.28$.

The description of structures containing isolated octahedra using the notation of 'layers of close-packed octahedra' was first elaborated by Benachenhou, Mairesse & Nowogrocki (1986). They showed that cubic elpasolite and its distortional variants are distinguished by the arrangement of the octahedra within the layers and the stacking sequence of these layers, regardless of the nature of the alkali metal ions. Furthermore, they pointed out relationships between the elpasolite family and other compounds containing isolated octahedra. In contrast to these structures, the octahedra layers in the structure of the title compound are separated by layers of caesium and chloride ions, which means that the alkali ions play an important role here.

A second way of recognizing structural differences within the elpasolite family was discussed by Mattfeld & Meyer (1992). Proceeding from A_2BMX_6, where A and X are cubic close packed and B and M partially occupy the octahedral holes, they define close packed AX_3 layers separated by layers containing only B or M. This notation of the structure is dependent on the level of occupancy of the layers by the different ions. 103, for example, defines a layer containing $1 \times A$, $0 \times B/0 \times M$ and $3 \times X$. This notation defines the stacking sequence of the cubic elpasolite as –103,010,103,010–. In distortional variants, 'packets' of other compositions are inserted. Thus, the Cs_3BiCl_6 type and the Cs_3NdCl_6 type have the stacking sequence –103,010,103,202,012,202–. Within the framework of this description, the present structure may be expressed as $Cs1_2Cs2(Cs2Cl2)YbCl1_6$ or, more generally, as $A_2B(BX)MX_6$. The stacking sequence of the layers along the c axis is thus –103,010,103,021–, as illustrated in Fig. 1.

The volume of one formula unit of Cs_4YbCl_7 is 443.7 Å^3, compared to 416.59 Å^3 [347.51 (Reuter, Roffe & Seifert, 1996) + 70.08 Å^3] for the decomposition products Cs_3YbCl_6 and CsCl. The lower density of title compound expresses itself in an increased mobility in the (021) layers, which manifests itself in the larger displacement parameters of Cs2 and the disorder of Cl2.

Experimental

The compound was precipitated from a saturated solution at 345 K by oversaturating with gaseous HCl. The solution was composed of Cs and Yb in the molar ratio 4:1 (Yb_2O_3: 99.9% from Fa. Roth, Karlsruhe; CsCl: p.A. from Fa. Merck, Darmstadt) in hydrochloric acid. After filtration, the compound was dried at 370 K. The molar ratio of Cs:Yb:Cl was found to be 4:1:7 by chemical analysis (Yb: titration with edta; Cs: gravimetrically as tetraphenylborate; Cl: potentiometric titration with AgCl). The absence of the neighbouring phases Cs_3YbCl_6 and CsCl as impurities in the CsCl/$YbCl_3$ system was proved by X-ray powder diffraction. Measurements with a thermal balance (Stanton Redcroft) showed that the compound did not contain crystal water.

Crystal data

Cs_4YbCl_7
$M_r = 952.83$
Trigonal
$R\bar{3}m$
$a = 7.646 (4)$ Å
$c = 26.290 (10)$ Å
$V = 1331.0 (11)$ Å^3
$Z = 3$
$D_x = 3.566$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10–16°$
$\mu = 14.372$ mm^{-1}
$T = 293 (2)$ K
Platelet
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scans (Fair, 1990)
$T_{\min} = 0.64$, $T_{\max} = 0.99$
2852 measured reflections
298 independent reflections
293 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0488$
$\theta_{\max} = 23.98°$
$h = -8 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = -30 \rightarrow 30$
3 standard reflections
frequency: 120 min
intensity decay: 0.94%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0395$
$wR(F^2) = 0.0921$
$S = 1.270$
298 reflections
21 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 51.0048P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.747$ e Å^{-3}
$\Delta\rho_{\min} = -1.867$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic and anisotropic 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	0	0	0.0254 (4)
Cs1	0	0	0.37692 (6)	0.0474 (6)
Cs2	0	0	0.17229 (8)	0.0914 (10)
Cl1	0.1585 (3)	$2x$	−0.05800 (14)	0.0481 (10)
Cl2†	0.412 (3)	$2x$	0.1664 (15)	0.089 (16)

	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
Yb	0.0267 (5)	0.0134 (3)	0	0.0267 (5)	0	0.0228 (7)
Cs1	0.0536 (8)	0.0268 (4)	0	0.0536 (8)	0	0.0348 (9)
Cs2	0.1192 (15)	0.0596 (7)	0	0.1192 (15)	0	0.0357 (11)
Cl1	0.062 (2)	0.0168 (10)	0.0035 (8)	0.034 (2)	0.007 (2)	0.039 (2)
Cl2	0.149 (35)	0.041 (10)	0.004 (9)	0.083 (19)	0.008 (18)	0.014 (7)

† Site occupancy = 0.17.

The diffractometer found a rhombohedral cell [hexagonal setting: $a = 7.646 (4)$, $c = 26.29 (1)$ Å]. Analysis of the extinction conditions led to the space group $R\bar{3}m$ ($Z = 3$). Solution with direct methods, subsequent difference Fourier syntheses and full-matrix least-squares refinement led to the R values given above. As the displacement parameters of one independent Cs atom and the non-bonded Cl atom are strongly anisotropic and also too high, refinement of the site occupancies was attempted. However, this influenced neither the displacement parameters nor the R values. In an attempt to resolve the sixfold disorder, the structure was recalculated based on a triplet of a monoclinic unit cell (a = 9.814, b = 7.634, c = 12.445 Å, β = 108.14°, Z = 2) in space group $I2/m$ (t subgroup of $R\bar{3}m$). The transformation matrix is $-\frac{1}{3},\frac{1}{3},\frac{1}{3}/1,1,0/-\frac{1}{6},\frac{1}{6},-\frac{1}{3}$ and the matrix of threefold rotation (twinning element) is 0,1,0/−1,−1,0/0,0,1. However, the refinement did not stabilize and one Cl ion of the $YbCl_6$ octahedron showed strongly anisotropic displacement parameters. A further attempt involved refinement as an inversion twin in the space group Im. Anisotropic refinement gave $R1$ = 0.036 for 1274 reflections with $I < 2\sigma(I)$ and $wR2$(all data) = 0.092. The ratio of the triplets was 34(21 + 13):32(30 + 2):34(5 + 29), with the ratios of inversion twins in parentheses. However, the displacement parameters became even more anisotropic and the $YbCl_6$ octahedron showed an elongation that we could not rationalize. Furthermore, the R values are no better than in the rhombohedral model. We therefore believe that disorder rather than twinning gives a correct model of the structure.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *PROCESS*, *PSISCAN* and *PSICALC* in *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1994), *SCHAKAL92* (Keller, 1993). Software used to prepare material for publication: *SHELXL93*.

We thank Professor H.-J. Seifert for support and dedicate this paper to him on the occasion of his last 'first fine day'.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: JZ1121). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$Sr_4Ga_3Mo_{26}O_{48}$ Containing Mo_7 Clusters and Infinite Mo_7–Mo_{10}–Mo_7 Chains

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Abstract

The crystal structure of the strontium gallium molybdate $Sr_4Ga_3Mo_{26}O_{48}$ is characterized by quasi-isolated monocapped octahedral Mo_7 clusters and infinite Mo chains arranged in layers parallel to the ac plane of the monoclinic unit cell. The repeat unit of the chains is the tricluster Mo_{24} chain fragment consisting of one Mo_{10} and two Mo_7 clusters. The Mo—Mo distances range between 2.584 (1) and 2.786 (1) Å in the Mo_7 clusters and between 2.5963 (9) and 2.938 (1) Å in the chains. The shortest Mo—Mo distance between Mo_7 clusters is 3.1575 (9) Å and between Mo_7 clusters and the chains is 3.171 (1) Å, which excludes any direct Mo—Mo interactions. The Mo—O distances range from 1.922 (6) to 2.163 (6) Å, as usually observed in reduced Mo oxides. The four crystallographically independent Sr^{2+} ions have coordination numbers of 11 or 12 with an environment in each case based upon a distorted cuboctahedron. The Sr—O distances range from 2.495 (6) to 3.105 (5) Å. The Ga^{3+} ions are approximately tetrahedrally or octahedrally coordinated by O atoms. The Ga—O distances vary between 1.902 (6) and 2.059 (6) Å for the octahedral sites, and between 1.830 (5) and 1.873 (6) Å for the tetrahedral site.

Comment

Over the last two decades, numerous reduced molybdenum oxides have been synthesized by solid-state reaction and fused-salt electrolysis. Most of these compounds contain clusters, sheets or infinite chains of Mo atoms with strong metal–metal bonds. Until now, only sheets based on Mo_3 triangles were known, while infinite chains can be based on digonal Mo_2 groups, Mo_4 rhomboids or on octahedral Mo_6 clusters. Although the latter cluster has only been obtained in the unique compound $Ca_{16.5}Mo_{13.5}O_{40}$ (Lindblom & Strandberg, 1989) so far, it also constitutes the basic building block of larger clusters such as Mo_{4n+2} (n = 2, 3, 4 and 5) (Hibble, Cheetham, Bogle, Wakerley & Cox, 1988; Mattausch, Simon & Peters, 1986; Dronskowski & Simon, 1989; Schimek & McCarley, 1994) by sharing its *trans* edges. The final stage of this process of condensa-

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