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$[Yb(H_2O)_8][Cd_3Cl_9(H_2O)]\cdot 6H_2O$

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The title compound, namely octaaquaytterbium(III) aquanonachlorotricadmate(II) hexahydrate, $[Yb(H_2O)_8][Cd_3Cl_9(H_2O)]\cdot 6H_2O$, was prepared by evaporation at 278 K from an aqueous solution of the ternary system $YbCl_3$–$CdCl_2$–H_2O and was characterized by elemental chemical analysis and by X-ray powder and single-crystal diffraction studies. The crystal structure can be viewed as being built from layers of double chains of $CdCl_6$ and $CdCl_5(H_2O)$ octahedra separated by antiprismatic $[Yb(H_2O)_8]^{3+}$ cations. The stabilization of the structure is ensured by O—H···O and O—H···Cl hydrogen bonds. A comparison with the structures of $SrCd_2Cl_6\cdot 8H_2O$ and $CeCd_4Cl_{11}\cdot 13H_2O$ is presented.

Comment

Investigations of hydrated rare-earth(III) chlorides are very important for understanding the physical (magnetic, optical) and structural properties of these compounds. The ternary systems ACl–$LnCl_3$–H_2O [where A is an alkali metal and Ln is a rare-earth(III) metal] have previously been investigated at various temperatures (Kost *et al.*, 1980; Shirai & Shevchuk, 1981; Lazorenko & Shevchuk, 1983; Shirai, 1986; Storozhenko *et al.*, 1987; Bunyakina *et al.*, 1991, 1992). However, all synthesized compounds were only characterized by powder X-ray diffraction, and no single-crystal structures have been reported. Interest in these hydrated alkali-metal/rare-earth(III) chlorides was mainly based on the change of the coordination number of the rare-earth ions and the parameters influencing these changes (Fink *et al.*, 1990; Reuter *et al.*, 1995; Reuter & Fenzen, 1995).

To the best of our knowledge, only a few examples of divalent metal halide (MX_2) rare-earth(III) halide (MX_3–H_2O) systems have been investigated. In the case of the $SrCl_2$–$CdCl_2$–H_2O and $CeCl_3$–$CdCl_2$–H_2O systems, the hydrated phases $SrCd_2Cl_6\cdot 8H_2O$ and $CeCd_4Cl_{11}\cdot 13H_2O$ have been isolated and their structures determined (Yahyaoui *et al.*, 2002, 2003). The room-temperature form of the first compound crystallizes in the $P\overline{1}$ triclinic system and is characterized by pseudo-monoclinic symmetry and the occurrence of twinning by twofold rotation around the c axis. $SrCd_2Cl_6\cdot 8H_2O$ undergoes a structural phase transition at 323 K, which is related to a change to higher symmetry and the disappearance of twinning. On the other hand, $CeCd_4Cl_{11}\cdot 13H_2O$ crystallizes in the monoclinic system with $P2_1$ symmetry. The replacement of strontium by cerium(III) cations leads to an increase of the symmetry, the disappearance of twinning phenomena and the preservation of the cation environments.

As part of our research, we have investigated the $YbCl_3$–$CdCl_2$–H_2O system in order to study further the influence of the substitution of strontium(III) and cerium(III) cations on the structural properties of the double chloride salts formed in these systems. We report here the results of a structural investigation of a new double-salt hydrate, *viz.* the title compound, (I). In contrast to $CeCd_4Cl_{11}\cdot 13H_2O$, the structural arrangement of (I) at room temperature is bidimensional (Fig. 1) and has an increased unit-cell volume. Two types of octahedra are present around the cadmium cations; atoms Cd2 and Cd3 are each coordinated to six Cl atoms, while atom Cd1 is surrounded by five Cl atoms and one O atom (Table 1). Six of these octahedra share edges, thus generating short double chains that are themselves connected through atom Cl5 to form layers parallel to the $(\overline{1}11)$ plane (Figs. 1 and 2). These layers of double octahedral chains around Cd atoms have not been observed previously in complex hydrated cadmium

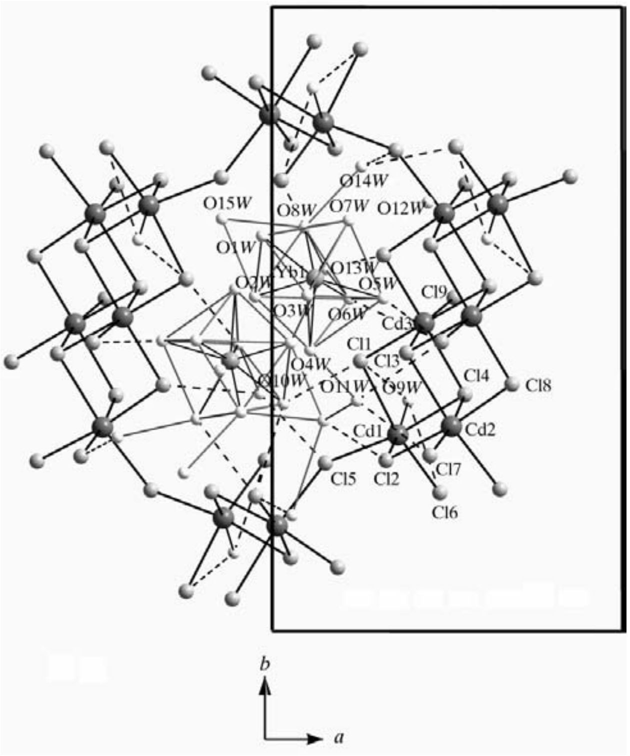

Figure 1
A projection of the structure of (I) on to the (001) plane. Hydrogen bonds are shown as dashed lines for O—H···Cl bonds and solid lines for O—H···O bonds.

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chlorides, and the structural arrangement in (I) differs from the infinite double chains of $CdCl_6$ octahedra found in $SrCd_2Cl_6{\cdot}8H_2O$ and $CeCd_4Cl_{11}{\cdot}13H_2$. The average Cd1—Cl, Cd2—Cl and Cd3—Cl distances in (I) are 2.626, 2.633 and 2.622 Å, respectively, and the Cd1—O distance is 2.322 (3) Å [*cf.* Cd—O = 2.374 (17) Å in $CeCd_4Cl_{11}{\cdot}13H_2O$].

Three types of water molecules are present in the crystal structure of (I); the first type corresponds to six water molecules not coordinated to cations (atoms O10*W*–O15*W*), the second corresponds to the water molecule (O9*W*) bonded to atom Cd1 and the last category contains the water molecules coordinating the ytterbium ions (atoms O1*W*–O8*W*). The ytterbium coordination sphere consists of eight water molecules at the corners of a distorted square antiprism, with an average Yb—O distance of 2.312 Å (Figs. 1 and 2, and Table 1). These square antiprisms are intercalated between the layers of cadmium octahedra. Compound (I) is the first known example of a complex hydrated cadmium chloride showing such a coordination environment, it having previously been observed only in $(CH_3NH_3)_3PrCl_6{\cdot}2H_2O$ (Runge *et al.*, 1990) and $(CH_3NH_3)_8[NdCl_6][NdCl_4(H_2O)_2]_2Cl_3$ (Runge *et al.*, 1991). The coordination number of the rare-earth(III) ion decreases from nine in $CeCd_4Cl_{11}{\cdot}13H_2O$ to eight in $YbCd_3Cl_9{\cdot}15H_2O$, in conjunction with a decrease of the rare-earth(III)–oxygen distance (*cf.* ⟨Ce—O⟩ = 2.542 Å).

A comparison can be made between the structures of (I) and $SrCd_2Cl_6{\cdot}8H_2O$. The triclinic Sr compound was found to be twinned, with a pseudo-monoclinic face-centered unit cell related to the triclinic unit-cell by the $100/001/1\overline{41}$ transformation matrix. In $SrCd_2Cl_6{\cdot}8H_2O$, pairs of Cd, Cl and O atoms are related by a *c*/2 pseudo-translation, whereas in (I), similar atoms are related by a true *b*/2 translation. The twin rotation axis parallel to *c* in the Sr compound is replaced by a real 2_1 axis parallel to *b* in the Yb compound.

A projection view of (I), illustrating the hydrogen bonding, is depicted in Fig. 1. The hydrogen bonds are of two types, namely O—H···Cl and O—H···O (Table 2). The O—H···Cl bonds appear between layers of cadmium octahedra and water molecules, with distances ranging from 3.130 (3) to 3.346 (4) Å. Atoms Cl6, Cl7 and Cl9 are each bonded to one Cd atom and establish the most hydrogen bonds; atom Cl9 forms four hydrogen bonds, and atoms Cl6 and Cl7 are each involved in three hydrogen bonds. Atoms Cl1, Cl2, Cl5 and Cl8 each bridge two Cd atoms and participate in fewer hydrogen bonds, *i.e.* one for atom Cl2 and two for atoms Cl1, Cl and Cl8. Atoms Cl3 and Cl4 are each bonded to three Cd atoms and, while atom Cl3 is not involved in any hydrogen bonds, atom Cl4 can be considered to be engaged in a weak hydrogen bond with one water molecule (O6*W*). O—H···O hydrogen bonds connect the water molecules surrounding the ytterbium ions to water molecules not coordinated to cations, and only atoms O1*W* and O5*W* are not involved in any hydrogen bonds. The associated O···O distances vary from 2.681 (4) to 3.202 (5) Å.

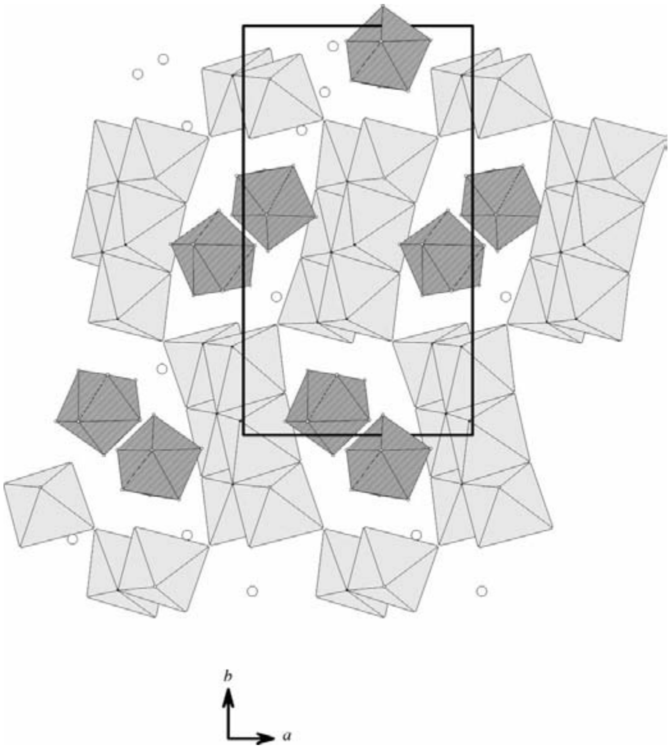

Figure 2
A polyhedral representation of (I), projected on to the (001) plane.

Experimental

Colorless single crystals of (I) were grown from a heated mixture (*T* = 363 K) of ytterbium oxide (Yb_2O_3, 0.9852 g) and cadmium chloride ($CdCl_2{\cdot}H_2O$, 1.14 g) in HCl solution (18 *M*) in a 1:4 molar ratio. This solution was allowed to evaporate slowly (at 278 K) to dryness and twinned needle-shaped crystals were obtained. Subsequently, several recrystallizations from acetone and methanol were performed, yielding colorless transparent parallelepiped-shaped single crystals. The hydrated double salt was characterized by X-ray powder diffraction, elemental chemical analysis and thermogravimetric studies in order to determine the water content. The formula was confirmed by density measurement and refinement of the crystal structure.

Crystal data

$[Yb(H_2O)_8][Cd_3Cl_9(H_2O)]{\cdot}6H_2O$
M_r = 1099.53
Monoclinic, $P2_1/n$
a = 12.2692 (12) Å
b = 20.057 (2) Å
c = 12.2820 (13) Å
β = 113.803 (11)°
V = 2765.3 (5) Å^3
Z = 4
D_x = 2.641 Mg m^{-3}
D_m = 2.611 Mg m^{-3}
D_m measured by picnometry
Mo *Kα* radiation
Cell parameters from 8000 reflections
θ = 2.7–28.1°
μ = 6.55 mm^{-1}
T = 293 (2) K
Parallelepiped, colorless
0.30 × 0.15 × 0.11 mm

Data collection

Stoe IPDS image-plate diffractometer
φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.234, T_{max} = 0.487
22 337 measured reflections
5583 independent reflections
5551 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 26.4°
h = −15 → 15
k = −25 → 25
l = −15 → 15
200 standard reflections
frequency: 4 min
intensity decay: 0.1%

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Table 1
Selected geometric parameters (Å, °).

O1*W*—Yb1	2.349 (3)	Cl3—Cd2	2.782 (1)
O2*W*—Yb1	2.279 (3)	Cl4—Cd2	2.652 (1)
O3*W*—Yb1	2.283 (3)	Cl4—Cd3	2.670 (1)
O4*W*—Yb1	2.308 (3)	Cl4—Cd1	2.737 (1)
O5*W*—Yb1	2.356 (3)	Cl5—Cd1	2.624 (1)
O6*W*—Yb1	2.312 (3)	Cl5—Cd2$^{\rm ii}$	2.629 (1)
O7*W*—Yb1	2.295 (3)	Cl6—Cd1	2.515 (1)
O8*W*—Yb1	2.311 (3)	Cl7—Cd2	2.519 (1)
O9*W*—Cd1	2.320 (3)	Cl8—Cd3$^{\rm i}$	2.577 (1)
Cl1—Cd3	2.596 (1)	Cl8—Cd2	2.602 (1)
Cl1—Cd1	2.684 (1)	Cl9—Cd3	2.577 (1)
Cl2—Cd1	2.568 (1)	Cd2—Cl5$^{\rm iii}$	2.629 (1)
Cl2—Cd2	2.613 (1)	Cd3—Cl8$^{\rm i}$	2.577 (1)
Cl3—Cd3	2.645 (1)	Cd3—Cl3$^{\rm i}$	2.665 (1)
Cl3—Cd3$^{\rm i}$	2.665 (1)		

O9*W*—Cd1—Cl2	170.47 (10)	Cl8$^{\rm i}$—Cd3—Cl3$^{\rm i}$	86.82 (3)
Cl6—Cd1—Cl5	95.45 (3)	Cl9—Cd3—Cl3$^{\rm i}$	87.13 (3)
Cl6—Cd1—Cl1	162.57 (4)	Cl1—Cd3—Cl3$^{\rm i}$	177.23 (3)
Cl5—Cd1—Cl1	87.48 (3)	Cl8$^{\rm i}$—Cd3—Cl4	177.83 (3)
O9*W*—Cd1—Cl4	90.53 (11)	O2*W*—Yb1—O3*W*	107.51 (13)
Cl7—Cd2—Cl8	91.50 (3)	O3*W*—Yb1—O7*W*	84.91 (13)
Cl7—Cd2—Cl2	89.80 (3)	O7*W*—Yb1—O4*W*	145.56 (12)
Cl8—Cd2—Cl2	173.50 (3)	O4*W*—Yb1—O8*W*	136.53 (11)
Cl2—Cd2—Cl3	89.63 (3)	O2*W*—Yb1—O6*W*	86.40 (12)
Cl5$^{\rm iii}$—Cd2—Cl3	171.06 (3)	O8*W*—Yb1—O6*W*	72.31 (10)
Cl8$^{\rm i}$—Cd3—Cl3	92.57 (3)	O7*W*—Yb1—O1*W*	74.99 (11)
Cl9—Cd3—Cl3	170.01 (3)	O4*W*—Yb1—O1*W*	120.97 (10)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H11···Cl7$^{\rm iv}$	0.91	2.27	3.130 (3)	159
O10*W*—H101···Cl5	0.90	2.30	3.188 (3)	170
O1*W*—H12···Cl1$^{\rm v}$	0.91	2.26	3.141 (3)	164
O2*W*—H21···O15*W*	0.89	2.22	2.893 (5)	132
O2*W*—H22···O13*W*$^{\rm vi}$	0.93	1.80	2.709 (4)	169
O3*W*—H31···Cl1	0.87	2.57	3.190 (3)	130
O3*W*—H32···O10*W*$^{\rm v}$	0.96	1.88	2.738 (4)	147
O4*W*—H41···O11*W*$^{\rm vii}$	0.96	1.77	2.730 (4)	176
O4*W*—H42···O10*W*	0.91	1.89	2.791 (4)	171
O5*W*—H51···Cl9	0.88	2.28	3.106 (3)	156
O5*W*—H52···Cl9$^{\rm viii}$	0.81	2.32	3.117 (3)	171
O6*W*—H61···Cl9$^{\rm viii}$	0.93	2.38	3.297 (3)	167
O6*W*—H62···O13*W*	0.78	1.96	2.713 (4)	161
O7*W*—H71···O12*W*	0.98	1.72	2.681 (4)	168
O7*W*—H72···Cl7$^{\rm iv}$	0.95	2.25	3.133 (3)	155
O8*W*—H81···O14*W*	0.83	1.91	2.731 (4)	170
O8*W*—H82···O15*W*	0.99	1.78	2.706 (4)	154
O9*W*—H91···O12*W*$^{\rm viii}$	0.95	1.83	2.773 (5)	168
O9*W*—H92···O5*W*	0.86	2.62	3.469 (5)	175
O10*W*—H102···Cl8$^{\rm ix}$	1.04	2.64	3.306 (3)	122
O11*W*—H111···Cl9$^{\rm i}$	0.78	2.57	3.309 (3)	159
O11*W*—H112···O14*W*$^{\rm x}$	0.91	1.91	2.808 (5)	168
O12*W*—H121···O15*W*$^{\rm xi}$	0.93	2.53	3.202 (5)	130
O12*W*—H121···Cl6$^{\rm viii}$	0.93	2.61	3.310 (3)	133
O12*W*—H122···Cl7$^{\rm i}$	0.88	2.31	3.171 (3)	166
O13*W*—H131···Cl8$^{\rm viii}$	0.82	2.34	3.153 (3)	171
O13*W*—H132···O8*W*	0.97	2.60	3.130 (4)	115
O13*W*—H132···Cl6$^{\rm xii}$	0.97	2.38	3.236 (3)	148
O14*W*—H141···Cl5$^{\rm xii}$	0.81	2.48	3.214 (3)	152
O14*W*—H142···Cl6$^{\rm viii}$	0.98	2.31	3.229 (3)	157
O15*W*—H151···O11*W*$^{\rm v}$	0.91	1.92	2.778 (5)	158
O15*W*—H152···Cl2$^{\rm v}$	0.85	2.50	3.346 (4)	179

Symmetry codes: (i) $-x, -y, -1-z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z$; (v) $1-x, -y, -z$; (vi) $1-x, -y, 1-z$; (vii) $x, y, 1+z$; (viii) $-x, -y, -z$; (ix) $1+x, y, 1+z$; (x) $\frac{1}{2}-x, y-\frac{1}{2}, -\frac{1}{2}-z$; (xi) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (xii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.064$
$S = 1.29$
5583 reflections
254 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0237P)^2 + 7.9527P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 1.30$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.37$ e Å^{-3}

All H atoms were found in difference Fourier maps but were introduced into the refinement as fixed contributors, with $U_{\rm iso}$ values fixed at 0.06 Å^2. The maximum electron-density residual peak is located 0.93 Å from the Yb atom and the largest hole is 0.90 Å from the same atom.

Data collection: *IPDS Software* (Stoe & Cie, 1996); cell refinement: *IPDS Software*; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1020). Services for accessing these data are described at the back of the journal.

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