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Crystal structure and thermal study of the new hydrated cadmium-cerium(III) chloride $CeCd_4Cl_{11} \cdot 13H_2O$

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Abstract

The new double-salt $CeCd_4Cl_{11} \cdot 13H_2O$ in the ternary system $CeCl_3$–$CdCl_2$–H_2O has been prepared from aqueous solution upon evaporation at 5°C and characterized based on elemental analysis, spectroscopic data, thermal studies and X-ray powder and single-crystal diffraction. $CeCd_4Cl_{11} \cdot 13H_2O$ crystallizes in the monoclinic space group $P2_1$ with $a = 7.667(2)$, $b = 17.351(3)$, $c = 11.970(2)$Å, $\beta = 101.61(3)^\circ$ and $Z = 2$. After refinement of the structure the reliability factor R in the final cycle is 0.064. The structure can be regarded as consisting of endless double chains of $CdCl_6$ and $CdOCl_5$ octahedra and isolated tricapped triangular prisms surrounding the cerium cations. Differential scanning calorimetry showed that the title compound exhibits five endothermic anomalies interpreted from thermogravimetry. A comparison with the structure of $SrCd_2Cl_6 \cdot 8H_2O$ is proposed.

Keywords: Rare earth(III) chloride; Crystal structure

1. Introduction

Investigations on hydrates of ternary systems of rare earth(III) chlorides are very important for understanding their structural and physical properties (magnetic, optic …). The ternary systems ACl–$LnCl_3$–H_2O (where A = Na, NH_4, K, Rb, Cs and Ln = La, Nd, Sm, Gd) have been investigated at various temperature by the group around *Shevchuk* [1–8]. Compounds that they prepared were characterized by X-ray powder patterns only and no crystal structure was reported. Thus, interest of other authors [9–11] in the structures of these hydrated alkali-metal–rare earth(III) chlorides was based on the change of the coordination number of the rare earth ions and the parameters influencing these changes.

However, much less is known about divalent metal halide(MX_2)–rare earth(III) halide(MX_3)–H_2O systems. In our previous work [12] by investigating $SrCl_2$–$CdCl_2$–H_2O ternary system, we have isolated the hydrated phase $SrCd_2Cl_6 \cdot 8H_2O$ and determined its structure. Room temperature phase of this compound has a triclinic structure with space group $P\bar{1}$ and characterized by a very persistent occurrence of twinning by pseudo-monoclinic symmetry and the twin element was found to be a two-fold axis [001]. $SrCd_2Cl_6 \cdot 8H_2O$ exhibits a structural phase transition at 323 K related to a higher symmetry accompanied by a disappearance of the twin. In the present study, our interest to the system $CeCl_3$–$CdCl_2$–H_2O, which has not previously been reported in the literature, is mainly based on the structure determi nation of the new hydrated double-salt $CeCd_4Cl_{11} \cdot 13H_2O$ in order to understand the influence of substitution of strontium cations by rare earth cations on the structural properties (symmetry changes, coordination of cations, structural framework…). We report here the synthesis of $CeCd_4Cl_{11} \cdot 13H_2O$ and X-ray diffraction measurements accompanied by thermogravimetric and calorimetric measurements.

2. Experimental details

Colorless single crystals of $CeCd_4Cl_{11} \cdot 13H_2O$ were grown from aqueous solution containing a mixture of cerium chloride $CeCl_3 \cdot 7H_2O$ and cadmium chloride $CdCl_2 \cdot H_2O$ in a molar ratio of $\frac{1}{2}$. This solution was allowed to evaporate slowly to dryness at 5°C. Several

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recrystallizations were performed in distilled water and methanol. Single crystals obtained are hygroscopic and needle shaped. The formula was determined by chemical elemental analysis and the water content was determined thermogravimetrically. Calorimetric measurements were performed between 293 and 573 K on a Mettler DSC calorimeter with a heating rate of $5\,K\,min^{-1}$ and a sensitivity of $200\,\mu V\,mW^{-1}$. TG and DTA measurements were performed with a SETARAM TGDTA92 instrument for temperatures ranging from 293 to 573 K (see Figs. 1 and 2). The details of the crystal data and X-ray measurements are given in Table 1. The structure was solved using the Patterson method with the SHELXS 97 program [14]. The refinement was carried out using anisotropic temperature factors for all the atoms (SHELXL 97 program) [15].

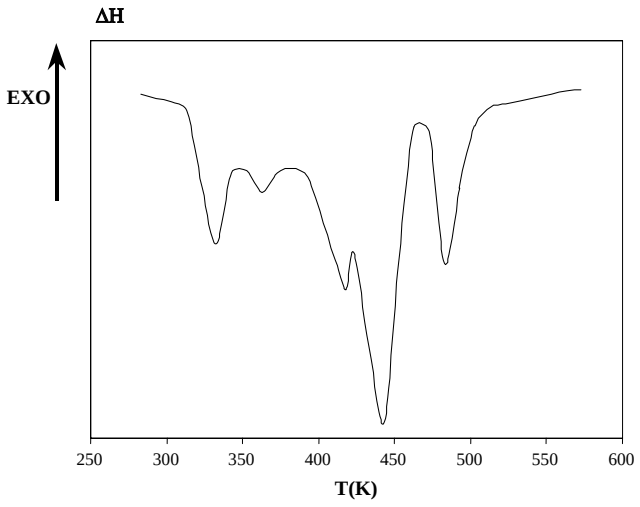

Fig. 1. DSC thermogram of $CeCd_4Cl_{11}\cdot 13H_2O$ in the temperature range 273–573 K.

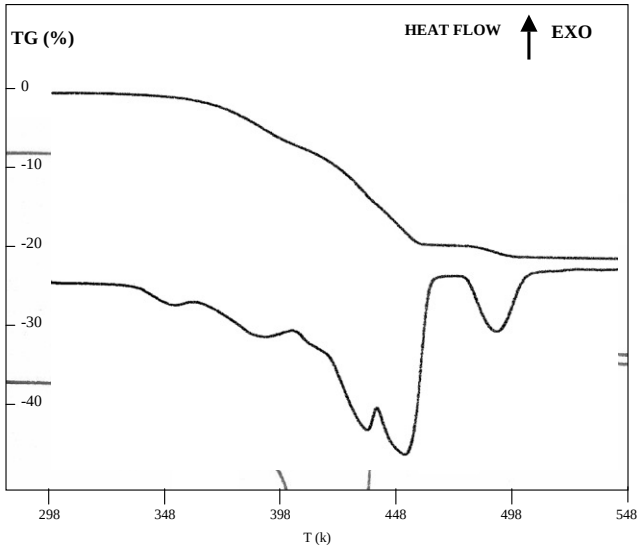

Fig. 2. TG and DTA thermogram of $CeCd_4Cl_{11}\cdot 13H_2O$ in the temperature range 273–573 K.

Table 1
Crystal data and summary of intensity data collection and structure refinement

Compound	$CeCd_4Cl_{11}\cdot 13H_2O$
Color/shape	Colorless/needles
Formula weight	1213.88
Space group	$P2_1$
Temperature (°C)	25
Cell constants[a]	
a (Å)	7.667(2)
b (Å)	17.351(3)
c (Å)	11.970(2)
α (deg)	90.00
β (deg)	101.61(3)
γ (deg)	90.00
Cell volume (Å^3)	1559.8(6)
Formula units/unit cell	2
D_{calc} ($g\,cm^{-1}$)	2.585
μ_{calc} (mm^{-1})	5.093
Crystal size	$(0.40\times 0.05\times 0.04)$ mm^3
Diffractometer	Xcalibur Oxford diffraction
Radiation, graphite monochromator λ (Å)	Mo$K\alpha$ (0,71071)
Detector	CCD camera
Measurement device method	Ω scan
2θ range (deg)	$6.28<2\theta<46.52$
Reflections measured	7887
Completeness to $2\theta = 46.52$	99.6%
Reflections unique	3281
Reflections observed $[F_o>4\sigma(F_o)]$[b]	2774
Absorption corrections	Semi-empirical [13]
T_{min}–T_{max}	0.418–0.804
Structure solution	SHELXS [14]
Computer programs[c]	SHELXL [15]
No. of parameters varied	264
No. of parameters restrained	1
Weights	$[\sigma^2(F_o^2)+(0.0799P)^2+1.6107P]^{-1}$ where $P=(F_o^2+2F_c^2)/3$
Goodness-of-fit	1.029
$R=\sum(\lvert F_o\rvert-\lvert F_c\rvert)/\sum\lvert F_o\rvert$	0.064
	0.140
$WR^2\left[\frac{\sum[w(\lvert F_o\rvert^2-\lvert F_c\rvert^2)]^2}{\sum[w(\lvert F_o\rvert^2)]^2}\right]^{1/2}$	0.17(6)
Absolute structure parameter [17]	

[a] Least-squares refinement of $(\sin\theta/\lambda)^2$ values for all measured reflections.
[b] Corrections : Lorentz-polarization.
[c] Neutral scattering factors and anomalous dispersion corrections.

3. Results and discussion

3.1. Crystal structure determination and description

At room temperature, $CeCd_4Cl_{11}\cdot 13H_2O$ crystallizes in the monoclinic phase with two molecules per unit cell.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) $U_{eq} = \frac{1}{3}\sum_i \sum_j u_{ij} a_i^* a_j^* a_i a_j$

Atoms	x	y	z	U_{eq}
Ce	0.6253(2)	0.7310(1)	0.9555(1)	0.0153(3)
Cd(1)	0.2640(2)	0.4471(1)	0.6385(1)	0.0155(4)
Cd(2)	0.7655(2)	0.4482(1)	0.6426(1)	0.0163(4)
Cd(3)	0.4307(2)	0.5467 (1)	0.3722(1)	0.0176(4)
Cd(4)	−0.0652(2)	0.5547(1)	0.3903(1)	0.0173(4)
Cl(1)	0.1856(6)	0.4457(4)	0.4052(5)	0.0166(12)
Cl(2)	0.0107(7)	0.3464(4)	0.6284(5)	0.0171(13)
Cl(3)	0.5023(7)	0.5547(4)	0.6092(5)	0.0148(12)
Cl(4)	0.6763(7)	0.6502(4)	0.3756(5)	0.0202(14)
Cl(5)	0.0060(7)	0.5568(4)	0.6145(5)	0.0158(12)
Cl(6)	0.6996(7)	0.4458(4)	0.4103(5)	0.0170(12)
Cl(7)	0.3229(7)	0.4599(4)	0.8525(5)	0.0187(13)
Cl(8)	0.5119(7)	0.3474(4)	0.6336(5)	0.0223(15)
Cl(9)	0.8333(7)	0.4547(4)	0.8563(5)	0.0203(13)
Cl(10)	0.3982(9)	0.5106(4)	0.1643(5)	0.0260(14)
Cl(11)	0.1832(7)	0.6476(4)	0.3652(5)	0.0196(13)
O(1)	−0.159(2)	0.535(1)	0.191(1)	0.028(4)
O(2)	0.718(2)	0.764(1)	0.165(1)	0.021(4)
O(3)	0.345(2)	0.687(2)	0.812(2)	0.061(7)
O(4)	0.565(3)	0.823(1)	0.787(2)	0.038(5)
O(5)	0.769(3)	0.681(1)	0.796(2)	0.051(6)
O(6)	0.424(2)	0.837(1)	0.998(1)	0.014(3)
O(7)	0.847(2)	0.839(1)	0.987(2)	0.029(4)
O(8)	0.610(2)	0.583(1)	0.944(2)	0.026(4)
O(9)	0.917(2)	0.663(1)	0.048(1)	0.026(4)
O(10)	0.409(2)	0.676 (1)	0.068(2)	0.026(4)
OW(1)	0.175(2)	0.764(1)	0.162(1)	0.028(4)
OW(2)	0.096(2)	0.875(1)	0.858(2)	0.030(5)
OW(3)	0.089(3)	0.605(1)	0.894(2)	0.038(5)

The structure was refined by assuming the non-centrosymmetric space group $P2_1$, undertaking and evaluating the absolute structure. The value of x Flack absolute structure parameter [16] and its standard uncertainty u is $x(u) = 0.17(6)$. From the full text of Flack and Bernardinelli [17], one can understand that the value of $u = 0.06$ indicates that the inversion-distinguishing power is strong and the domains around the value of x should be well defined and clearly distinguishable from one another. The Flack parameter $x(u) = 0.17(6)$ indicates that the crystal is twinned by inversion [18] and it is not possible to determine the absolute structure of such a crystal which is considered as constituted by a mixture of inverted structures. A final refinement taking in account these domains by way of the TWIN/BASF instructions as recommended by Shelxl97 program converged to an R index of 0.064 and a weighted R_w factor of 0.140. Therefore, a test of centric symmetry carried out with PLATON program [19] does not indicate the presence of any inversion center in the unit cell. Final positional and thermal parameters are listed in Tables 2 and 3.

By comparing with the structure of $SrCd_2Cl_6 \cdot 8H_2O$ [12] which was found to be twinned and exhibits a pseudo-monoclinic symmetry involving in the triclinic crystals defined by a two-fold axis [001], one can clearly observe that in the case of $SrCd_2Cl_6 \cdot 8H_2O$ only the Cd, Cl and O atoms show two-by-two correspondence by $c/2$ pseudo-translation and strontium atoms do not obey this law, whereas, in the main compound all atoms follow a $b/2$ translation. The twin element that has a helicoidal binary axis [001] in $SrCd_2Cl_6 \cdot 8H_2O$ becomes a real one [010] in the $CeCd_4Cl_{11} \cdot 13H_2O$ compound.

In this monoclinic structure, the cadmium atoms Cd(1), Cd(2) and Cd(3) are each one bonded to six chlorine atoms while the cadmium atom Cd(4) is surrounded by five chlorine and one oxygen neighbor to form distorted $Cd(1)Cl_6$, $Cd(2)Cl_6$ and $Cd(3)Cl_6$ and $Cd(4)OCl_5$ octahedra (Table 4). The juxtaposition of the two simple chains resulting from the connection of $Cd(1)Cl_6$ and $Cd(2)Cl_6$, $Cd(3)Cl_6$, and $Cd(4)OCl_5$ generates isolated endless double chains running along the a-axis (Figs. 3 and 4) where different octahedra are sharing four edges each with four adjacent octahedra. The averages of Cd–Cl distances are: $\langle$Cd(1)–Cl$\rangle$ = 2.6395 Å and $\langle$Cd(2)–Cl$\rangle$ = 2.6428 Å, $\langle$Cd(3)–Cl$\rangle$ = 2.6335 Å, $\langle$Cd(4)–Cl$\rangle$ = 2.6162 Å and the Cd(4)–O distance is equal to 2.374(17) Å. As a result of this octahedral arrangement the chlorine atoms are of three categories judging from their contribution to the cadmium coordination:

- Cl(7), Cl(9) and Cl(10) belong to one cadmium atom forming the shortest Cd–Cl bonds which range from 2.513(6) to 2.531(6) Å.
- Cl(2), Cl(4), Cl(8) and Cl(11) join one to two cadmium atoms making up Cd–Cl distances ranging from 2.558(6) to 2.613(6) Å.
- Cl(1), Cl(3), Cl(5) and Cl(6) are considered the most internal chlorine atoms in the octahedral double chains. They are linked to three cadmium atoms each making up the longest distances of Cd–Cl which range from 2.630(6) to 2.782(6) Å.

The coordination sphere of the cerium atoms consists of six oxygen ions disposed on the corners of a slightly distorted triangular prism tricapped by three oxygen atoms O(3), O(7) and O(9) which belong to three water molecules (Fig. 5). Thus the coordination number is nine. The two bases of this polyhedron are triangular and built on O(10), O(6), O(8) and O(2), O(4), O(5) atoms with an average $\langle$O–O$\rangle$ distance of 3.04 Å. The average of the distance $\langle$Ce–O$\rangle$ was found to be equal to 2.54 Å. However, we noted seven oxygen and two chlorine atoms surrounding strontium cations in $SrCd_2Cl_6 \cdot 8H_2O$ with an average of the distance $\langle$Sr–O$\rangle$ = 2.62 Å (Table 5).

$CeCd_4Cl_{11} \cdot 13H_2O$ is the first double-salt hydrate with the coordination number nine for cerium atoms which is also present in $CeCl_3 \cdot 7H_2O$ [20].

The structure contains three water molecules, which are not coordinated to cations, one water molecule

Table 3
Anisotropic displacement parameters (in 10^{-3}Å^2). The anisotropic displacement exponent takes the form ($-2\pi^2$ [$h^2a^{*2}u_{11} + \cdots + 2hka^*b^*u_{12}$])

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ce	0.0158(5)	0.0156(7)	0.0155(6)	−0.0008(7)	0.0054(5)	−0.0018(7)
Cd(1)	0.0116(7)	0.0182(10)	0.0177(8)	0.0025(8)	0.0053(7)	0.0001(7)
Cd(2)	0.0131(8)	0.0182(9)	0.0183(8)	0.0029(8)	0.0045(7)	0.0010(8)
Cd(3)	0.0129(8)	0.0197(10)	0.0211(9)	0.0031(8)	0.0057(7)	0.0006(8)
Cd(4)	0.0135(8)	0.0203(11)	0.0189(9)	0.0041(8)	0.0050(7)	0.0009(8)
Cl(1)	0.014(2)	0.019(3)	0.018(3)	−0.002(3)	0.006(2)	−0.003(3)
Cl(2)	0.012(3)	0.018(3)	0.021(3)	0.003(3)	0.003(2)	−0.001(2)
Cl(3)	0.014(2)	0.013(3)	0.018(3)	0.005(3)	0.003(2)	0.002(3)
Cl(4)	0.012(3)	0.013(3)	0.036(3)	0.005(3)	0.006(2)	0.002(2)
Cl(5)	0.019(3)	0.016(3)	0.013(2)	0.007(3)	0.004(2)	0.002(3)
Cl(6)	0.014(2)	0.015(3)	0.021(3)	0.000(3)	0.002(2)	−0.003(3)
Cl(7)	0.018(3)	0.024(3)	0.013(3)	−0.003(3)	0.001(2)	−0.004(3)
Cl(8)	0.011(3)	0.020(4)	0.037(4)	0.010(3)	0.007(3)	0.003(2)
Cl(9)	0.019(3)	0.024(3)	0.019(3)	0.003(3)	0.007(2)	0.003(3)
Cl(10)	0.042(4)	0.018(3)	0.019(3)	−0.006(3)	0.008(3)	−0.007(3)
Cl(11)	0.016(3)	0.013(3)	0.033(3)	0.003(3)	0.012(2)	0.004(2)
O(1)	0.020(8)	0.039(12)	0.026(9)	0.005(9)	0.005(7)	0.005(8)
O(2)	0.013(7)	0.035(11)	0.014(8)	−0.006(7)	0.001(6)	0.011(7)
O(3)	0.026(10)	0.072(18)	0.077(17)	0.041(14)	−0.012(10)	−0.010(11)
O(4)	0.044(11)	0.050(14)	0.022(10)	−0.007(9)	0.012(9)	−0.019(11)
O(5)	0.056(12)	0.071(18)	0.035(11)	0.006(11)	0.032(10)	0.025(12)
O(6)	0.023(8)	0.005(8)	0.017(8)	0.001(7)	0.011(7)	0.005(7)
O(7)	0.043(10)	0.025(11)	0.027(10)	−0.009(9)	0.026(9)	−0.015(9)
O(8)	0.018(8)	0.021(10)	0.040(10)	−0.005(8)	0.012(8)	0.014(8)
O(9)	0.024(8)	0.028(10)	0.021(9)	−0.018(8)	−0.007(7)	0.009(8)
O(10)	0.006(7)	0.029(11)	0.043(11)	0.006(9)	0.006(7)	−0.001(7)
OW(1)	0.051(11)	0.011(9)	0.014(9)	0.001(7)	−0.009(8)	−0.001(9)
OW(2)	0.023(9)	0.040(12)	0.022(10)	0.018(9)	−0.003(8)	0.002(9)
OW(3)	0.038(11)	0.026(12)	0.056(13)	−0.009(10)	0.022(10)	−0.009(9)

Table 4
Polyhedra of cadmium: selected distance (Å)

Polyhedra	Distances (Å)
Cd(1) Cl_6 octahedron	Cd(1)–Cl(7) = 2.520(6)
	Cd(1)–Cl(8) = 2.579(6)
	Cd(1)–Cl(2) = 2.596(6)
	Cd(1)–Cl(3) = 2.685(6)
	Cd(1)–Cl(5) = 2.719(6)
	Cd(1)–Cl(1) = 2.736(6)
Cd(2) Cl_6 octahedron	Cd(2)–Cl(9) = 2.509(6)
	Cd(2)–Cl(8) = 2.602(6)
	Cd(2)–Cl(2)[a] = 2.609(6)
	Cd(2)–Cl(5)[a] = 2.704(6)
	Cd(2)–Cl(3) = 2.706 (6)
	Cd(2)–Cl(6) = 2.724(6)
Cd(3) Cl_6 octahedron	Cd(3)–Cl(10) = 2.530(6)
	Cd(3)–Cl(11) = 2.570(6)
	Cd(3)–Cl(4) = 2.596(6)
	Cd(3)–Cl(1) = 2.657(6)
	Cd(3)–Cl(6) = 2.673 (6)
	Cd(3)–Cl(3) = 2.782(6)
Cd(4) OCl_5 octahedron	Cd(4)–O(1) = 2.371(17)
	Cd(4)–Cl(11) = 2.558(6)
	Cd(4)–Cl(4)[b] = 2.561(6)
	Cd(4)–Cl(5) = 2.629(5)
	Cd(4)–Cl(6)[b] = 2.656 (6)
	Cd(4)–Cl(1) = 2.678(6)

Symmetry code: [a] $x+1, y, z$; [b] $x-1, y, z$.

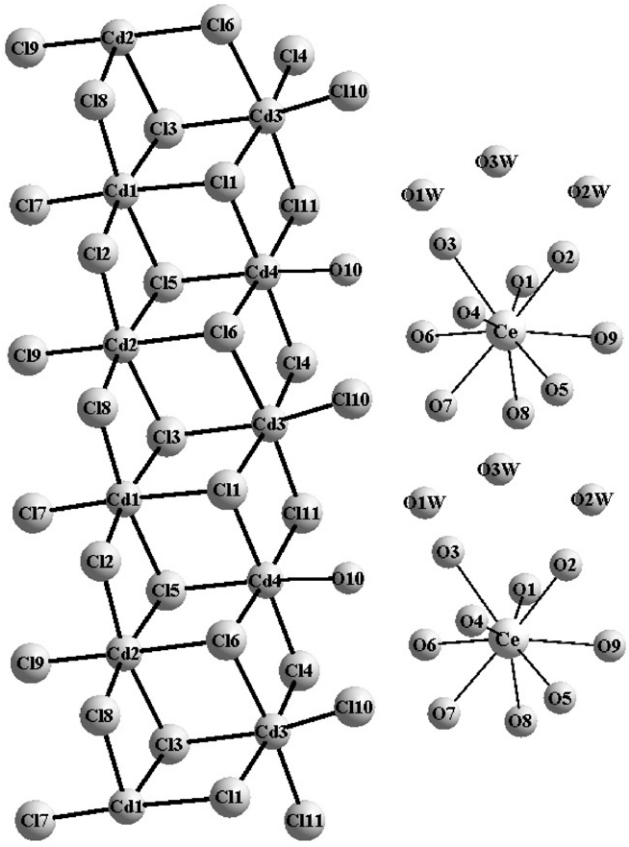

Fig. 3. View of the title compound showing the labeling of the atoms.

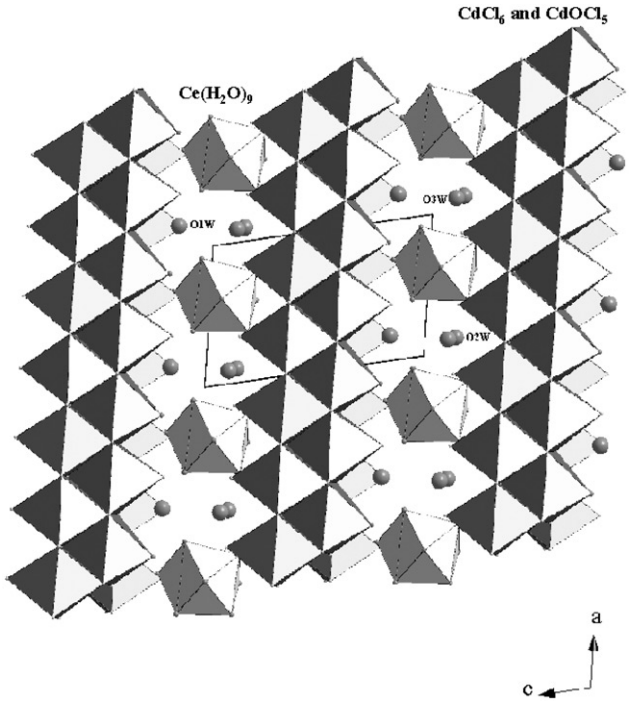

Fig. 4. Polyhedral representation of $CeCd_4Cl_{11} \cdot 13H_2O$ viewed down the *b*-axis.

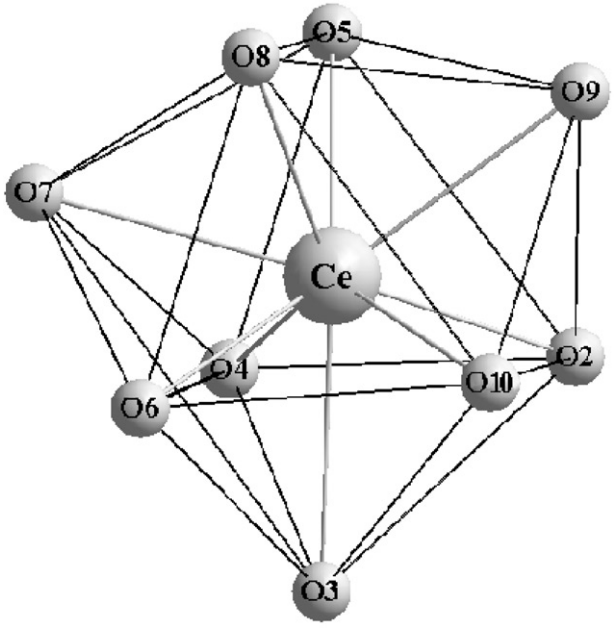

Fig. 5. Polyhedron of cerium: tricapped triangular prism.

linked to a cadmium atom and the remaining water molecules surround cerium atoms. Thus, three categories of water molecules which are differently coordinated to Cd, Ce, Cl and O atoms (Table 6).

As indicated in Table 6, very short distances O–Cl and O–O between oxygen and chlorine atoms of different

Table 5
Polyhedra of cerium: selected distances (Å)

Polyhedra	Distances (Å)
Ce $(H_2O)_9$ polyhedron	Ce–O (7) = 2.511 (18) Ce–O (6) = 2.514 (15) Ce–O (10)[c] = 2.523 (16) Ce–O (2)[c] = 2.527 (15) Ce–O (5) = 2.538 (19) Ce–O (4) = 2.55 (2) Ce–O (8) = 2.570 (18) Ce–O (9)[c] = 2.577 (16) Ce–O (3) = 2.58 (2)

Symmetry code: [c] $x, y, z+1$.

polyhedra are in agreement with the presence of two types of hydrogen bonds in the structure, O–H···O and O–H···Cl. These bonds ensure the connection of endless double chains of cadmium–chlorine octahedra via isolated cerium polyhedra and free water molecules, which are interposed between them. The distances O–Cl and O–O range from 3.103(2) to 3.447(1) and from 2.666(4) to 3.213(2), respectively.

3.2. DSC, DTA and TG measurements

As we can see in Fig. 1, DSC measurements on single-crystal samples of $CeCd_4Cl_{11} \cdot 13H_2O$ in the temperature range 293–573 K offer five endothermic anomalies on heating. The enthalpy change for the first peak at 333 K is $\Delta H_1 = 60\,J\,g^{-1}$. The second, the third and the fourth peaks at 363, 418 and 443 K overlap with $\Delta H_2 = 341\,J\,g^{-1}$ as an enthalpy change for the sum of these peaks. The calculated transition enthalpy for the last peak at 484 K is $\Delta H_3 = 31\,J\,g^{-1}$.

From the DTA curve as represented in Fig. 2, we notice the same five endothermic peaks detected by DSC at $T_1 = 349$, $T_2 = 387$, $T_3 = 434$, $T_4 = 450$ and $T_5 = 490$ K. The temperatures of these peaks correspond to the decomposition of $CeCd_4Cl_{11} \cdot 13H_2O$ with departure of water molecules.

The process of the dehydration occurs through four stages mainly explained by the strength of different bonds in the structure. In fact, between 335 and 401 K, the first weight loss (observed 6.2%, calculated 6.06%) corresponds to the release of four water molecules which may be $H_2Ow(1)$, $H_2Ow(2)$ and $H_2Ow(3)$ not coordinated to cations and $H_2O(4)$ which establishes the weakest hydrogen bonds in the structure (O(4)···Cl ranges from 3.3022(3) to 3.4472(13)). The second weight loss (observed 7.63%, calculated 7.57%) occurring between 401 and 438 may be attributed to the departure of five structural water molecules coordinated to cerium cations $H_2O(2)$, $H_2O(8)$, $H_2O(5)$, $H_2O(6)$ and $H_2O(7)$ and showing short hydrogen contacts (see Table 6). The release of three further water molecules which may be those coordinated to cerium cations $H_2O(3)$, $H_2O(10)$

Table 6
Short distances between the oxygen atoms of the water molecules and Cl, Cd, Ce

Atoms	Distances O...X (Å)	Atoms	Distances O...X (Å)
O(1)	O(1)···Cd(4) = 2.371(17)	O(9)	O(9)···Ce^{e} = 2.577(16)
	O(1)···Cl(10)^{b} = 3.3733(10)		O(9)···OW(1)^{e} = 2.7809(26)
	O(1)···O W(2)^{b} = 2.8945(11)		O(9)···OW(3)^{b} = 2.6663(37)
	O(1)···O(9)^{d} = 2.9314(15)		O(9)···O(1)^{f} = 2.9314(11)
O(2)	O(2)···Ce^{e} = 2.527(15)	O(10)	O(10)···Ce^{e} = 2.523(16)
	O(2)···Cd(1)^{e} = 3.9425(7)		O(10)···OW(1)^{e} = 2.7613(28)
	O(2)···Cl(2)^{e} = 3.2303(4)		O(10)···OW(3) = 3.1280(09)
	O(2)···Cl(7)^{e} = 3.4189(15)		O(10)···Cl(10)^{j} = 3.1027(17)
	O(2)···Cl(4)^{f} = 3.2699(1)	OW(1)	OW(1)···Cd(2)^{a} = 3.9379(7)
O(3)	O(3)···Ce = 2.58(2)		OW(1)···Cl(2)^{a} = 3.4363(17)
	O(3)···OW(3)^{b} = 2.7599(28)		OW(1)···Cl(8)^{a} = 3.3920(12)
O(4)	O(4)···Ce = 2.55(2)		OW(1)···Cl(9)^{a} = 3.3225(17)
	O(4)···Cl(10) = 3.4472(13)		OW(1)···O(7)^{k} = 3.2128(17)
	O(4)···Cl(5)^{g} = 3.3022(3)		OW(1)···O(9)^{k} = 2.7809(26)
O(5)	O(5)···Ce = 2.538(19)		OW(1)···O(10)^{c} = 2.7613(28)
	O(5)···OW(3)^{b} = 2.8298(21)		OW(1)···Cl(11)^{h} = 3.1468(12)
O(6)	O(6)···Ce = 2.514 (15)		OW(2)···O(1)^{a} = 2.8945(15)
	O(6)···OW(2) = 2.8051(23)	OW(2)	OW(2)···O(6) = 2.8051(23)
O(7)	O(7)···Ce = 2.511(18)		OW(2)···O(7)^{a} = 2.7625(28)
	O(7)···Cl(7)^{e} = 3.2812(1)	OW(3)	OW(3)···O(3) = 2.7599(28)
	O(7)···Cl(9)^{e} = 3.4176(15)		OW(3)···O(5)^{a} = 2. 8298(21)
	O(7)···OW(1)^{g} = 3.2128(17)		OW(3)···O(9)^{a} = 2.6663(37)
	O(7)···OW(2)^{b} = 2.7625(28)		OW(3)···O(10) = 3.1280(9)
O(8)	O(8)···Ce = 2.570(18)		OW(3)···Cl(5)^{h} = 3.3796(11)
	O(8)···Cl(7)^{h} = 3.1052(16)		OW(3)···Cl(7) = 3.1866(8)
	O(8)···Cl(9)^{i} = 3.1178(15)		OW(3)···Cl(9) = 3.2413(3)

Symmetry codes: $^{a}1+x, y, z$; $^{b}-1+x, y, z$; $^{c}x, y, 1+z$; $^{d}-x, 1/2+ y, -z$; $^{e}x, y, -1+z$; $^{f}-x, -1/2+y,-z$; $^{g}-1+x, y,-1+z$; $^{h}1-x, -1/2+y, 1-z$; $^{i}-x, -1/2+y, 1-z$; $^{j}1-x, -1/2+y, -z$; $^{k}1+x, y, 1+z$.

and $H_2O(9)$ and making the strongest hydrogen bonds in the structure (Table 6), is detected between 438 and 463 K (observed 4.64%, calculated 4.54%). Finally, between 463 and 509 K the fourth weight loss may match to the loss of the last water molecule $H_2O(1)$ which is well closed to cadmium cation (observed 1.44%, calculated 1.51%).

4. Conclusion

The synthesis and structure determination of the new hydrated double-salt $CeCd_4Cl_{11}\cdot 13H_2O$ is described in a monoclinic system. Samples were characterized through X-ray diffraction and chemical analysis. Differential scanning calorimetry shows that the title compound exhibits five endothermic peaks, which correspond to the loss of all water molecules as an interpretation given from thermogravimetry. In contrast to other complex water containing rare earth chlorides, the structural motif consists of double chains of $CdCl_6$ and $CdOCl_5$ octahedra and isolated tricapped triangular prisms around the cerium cations. As mentioned above, very short Cl–O and O–O distances between water molecules and chlorine atoms of different polyhedra indicate the existence of hydrogen bonds that ensure the cohesion of the structure.

From the comparison with the structure of $SrCd_2Cl_6\cdot 8H_2O$, it follows that the substitution of strontium by cerium(III) cations lead to an increase of the symmetry. In fact, a disappearance of the twin phenomena is observed. The same effect was detected when heating $SrCd_2Cl_6\cdot 8H_2O$ to 323. On the other hand, the environment of cations is conserved.

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