

# The Crystal Structures of the Hydrated Alkalimetal-/Rare Earth(III) Chlorides $ALnCl_4 \cdot 4H_2O$ ( $A = NH_4, K, Rb, Cs$ ; $Ln = La-Sm$ ) and $CsLaCl_4 \cdot 3H_2O$

Gert Reuter, Heinrich Fink, and Gerlinde Frenzen

*Inorganic Chemistry, University Gh. Kassel, Heinrich-Plett-Strasse 40, 34109 Kassel, Germany*

Received February 12, 1996; in revised form April 29, 1996; accepted June 3, 1996

The crystal structures of the compounds  $RbLaCl_4 \cdot 4H_2O$  and  $CsNdCl_4 \cdot 4H_2O$  have been determined by single crystal X-ray analysis. These compounds precipitate from aqueous solution upon evaporation at 50°C.  $RbLaCl_4 \cdot 4H_2O$  ( $a = 1140.1$  pm,  $b = 701.8$  pm,  $c = 668.8$  pm) and  $CsNdCl_4 \cdot 4H_2O$  ( $a = 1127.1$  pm,  $b = 711.5$  pm,  $c = 678.7$  pm) crystallize in the orthorhombic space group  $P 2_1 2_1 2$  with  $Z = 2$ . The unit cell parameters of the isotopic compounds  $KLnCl_4 \cdot 4H_2O$  ( $Ln = Ce-Nd$ ),  $NH_4LnCl_4 \cdot 4H_2O$  ( $Ln = La-Pr$ ),  $RbLnCl_4 \cdot 4H_2O$  ( $Ln = Ce-Sm$ ), and  $CsLnCl_4 \cdot 4H_2O$  ( $Ln = Ce, Pr$ ) were determined from powder patterns. The structure is composed of layers of edge-bridged polyhedra around both cations. The anionic part of the structure around the rare earth ions consists of the monomeric units  $[LnCl_4(H_2O)_4]^-$ . The coordination number of both the alkali- and the rare earth-ions is 8, independent of the changes in their ionic radii. Instead of the expected tetrahydrate " $CsLaCl_4 \cdot 4H_2O$ " a trihydrate  $CsLaCl_4 \cdot 3H_2O$  was precipitated under the same conditions. This compound crystallizes with the  $CsUCl_4 \cdot 3H_2O$ -type structure with the coordination number 9 for La. © 1996 Academic Press, Inc.

## INTRODUCTION

The ternary systems  $ACl/LnCl_3/H_2O$  ( $A = Na, NH_4, K, Rb, Cs$  and  $Ln = La, Nd, Gd$ ) have been investigated at various temperatures by the group around *Shevchuk* (1–8). They described eutectic systems with  $A = Na, NH_4$ , and  $K$ . In the case of  $A = Rb$  and  $Cs$  they found hydrated ternary compounds of different compositions with decreasing water content at increasing temperature. Characterizations of the compounds were performed by chemical analysis and partly by X-ray powder patterns. However, they never reported any crystal structure of the compounds they prepared.

One reason for our interest in the structures of hydrated alkalimetal-/rare earth chlorides is based on the change of the coordination number (hereafter CN) of the rare earth ions and the parameters influencing these changes. The influence of organic cations on the anionic structure of

complex water containing lanthanide chlorides was discussed by Mackenstedt and Umland (9, and literature cited there). In this content the change of the CN from 9 in the heptahydrates to 8 in the hexahydrates (10) of the rare earth chlorides should be mentioned. Furthermore, the CN decreases from 9 (in the case of La (11)) to 8 (in the case of Ce–Tb (12)) in the trihydrates of these chlorides.

We recently reported the structures of  $Rb_3LnCl_6 \cdot 2H_2O$  ( $Ln = La-Nd$ ) (13) and  $Cs_3LnCl_6 \cdot 3H_2O$  ( $Ln = La-Nd$ ) (14) and found the CN to increase from 8 in the Rb-compounds to 9 in the Cs-compounds. The thermal dehydration of these compounds takes place in one step. This is in contrast to the findings of Fink *et al.* for the compounds  $RbLaCl_4 \cdot 4H_2O$  and  $CsLaCl_4 \cdot 3H_2O$  (15): they reported semihydrates for both compounds annealed at  $\sim 100^\circ C$ , which seem to be isotopic from their powder patterns. In this paper we are reporting the crystal structures of both compounds.

## EXPERIMENTAL

### *X-Ray Analysis*

Single-crystal data were collected with an CAD 4 diffractometer (Enraf Nonius) at ambient temperature ( $MoK\alpha$  radiation, graphite monochromator). Data reduction was performed using the program XCAD4 (16). The structures were solved by SHELXS 86 (direct methods) (17) and refined by SHELXL 93 (full matrix least squares) (18). The graphics were drawn using SCHAKAL 92 (19) and ZORTEP (20). Powder patterns were taken with a Phillips PW 1050/25 goniometer equipped with a proportional counter and a vacuum attachment. During exposure ( $CuK\alpha$  radiation) the samples were under an He atmosphere. The digital data were collected and analyzed with PROFIL (21). The calculations were performed with the program LAZY PULVERIX (22). The cell parameters were determined from powder patterns (internal standard:

$\alpha$ -Al<sub>2</sub>O<sub>3</sub>, trigonal,  $R\bar{3}c$ ,  $a = 475.917$  pm,  $c = 1298.997$  pm with the least-squares method of Warczewski and de Wolff (23).

### IR-Spectroscopy

The IR-data were collected with a FT-IR FTS-40A (BIO RAD) in the range of 500–4000 cm<sup>-1</sup>. The compounds were measured as powder samples in Nujol.

### Materials

All compounds were prepared by evaporation of a stoichiometric solution of Ln<sub>2</sub>O<sub>3</sub> (99.99%, Johnson Matthey GmbH, Karlsruhe) and AlCl (p.A., Merck, Darmstadt) in hydrochloric acid at 50°C. Recrystallization was performed from distilled water. Single crystals were selected and washed with dried diethylether. They were sealed in Lindemann capillaries.

All compounds except those with  $A = K$  were checked for purity using X-ray powder pattern analysis. These compounds precipitate with the contamination of KCl and LnCl<sub>3</sub> · 7H<sub>2</sub>O due to the low solubility of KCl.

## RESULTS OF THE STRUCTURAL INVESTIGATIONS

### $ALnCl_4 \cdot 4H_2O$ ( $A = NH_4, K, Rb, Cs$ and $Ln = La-Sm$ )

The compounds NH<sub>4</sub>LnCl<sub>4</sub> · 4H<sub>2</sub>O ( $Ln = La-Pr$ ), KLnCl<sub>4</sub> · 4H<sub>2</sub>O ( $Ln = Ce-Nd$ ), RbLnCl<sub>4</sub> · 4H<sub>2</sub>O ( $Ln = La-Sm$ ) and CsLnCl<sub>4</sub> · 4H<sub>2</sub>O ( $Ln = Ce-Nd$ ) are isotypic.

**TABLE 1**  
Experimental Data and Structure Refinement Parameters for RbLaCl<sub>4</sub> · 4H<sub>2</sub>O and CsNdCl<sub>4</sub> · 4H<sub>2</sub>O

Formula:	RbLaCl <sub>4</sub> · 4H <sub>2</sub> O	CsNdCl <sub>4</sub> · 4H <sub>2</sub> O
Crystal system	Orthorhombic	Orthorhombic
Space group	$P 2_1 2_1 2$ (No. 18)	$P 2_1 2_1 2$ (No. 18)
Lattice parameters (pm)	$a = 1140.1(1)$	$a = 1127.1(2)$
determined at 298 K with	$b = 701.8(1)$	$b = 711.5(1)$
20 reflections	$c = 668.8(2)$	$c = 678.7(2)$
Number of F.U.	2	2
Calculated density (g/cm <sup>3</sup> )	2.667	2.947
Scan-width ( $\omega$ -scan)	$\omega$ -scan: $2.6^\circ + 0.35(\tan \theta)^\circ$	$\omega/2\theta$ -scan: $2.6^\circ + 0.35(\tan \theta)^\circ$
Collected reflections within	$1103$ ( $3 < \theta < 25$ )	$673$ ( $3 < \theta < 26$ )
	$-13 \leq h \leq 13$	$0 \leq h \leq 13$
	$-8 \leq k \leq 0$	$-8 \leq k \leq 0$
	$0 \leq l \leq 7$	$-8 \leq l \leq 0$
Independent reflections with $F_o > 0$	946	652
Absorption coefficient (mm <sup>-1</sup> )	9.47	9.01
Absorption correction	DIFABS (31)	DIFABS (31)
Number of refined parameters	47	47
Flack parameter	-0.05(3)	-0.06(6)
Reliability factors <sup>a</sup>	$R = 0.021$ for $F_o > 2\sigma$ $wR2 = 0.055$ for all data Goof = 0.97	$R = 0.029$ for $F_o > 2\sigma$ $wR2 = 0.078$ for all data Goof = 1.07

<sup>a</sup> Definitions of reliability factors:  $R = \sum |F_o| - |F_c| / \sum |F_o|$ ,  $wR2 = [\sum (F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$ .

**TABLE 2**  
Atomic Coordinates and Equivalent Temperature Parameters (10<sup>-1</sup> pm<sup>2</sup>) in RbLaCl<sub>4</sub> · 4H<sub>2</sub>O and CsNdCl<sub>4</sub> · 4H<sub>2</sub>O

RbLaCl <sub>4</sub> · 4H <sub>2</sub> O				
Atom	$x/a$	$y/b$	$z/c$	$U_{eq}^a$
Rb	0	0.5	0.5362(1)	43(1)
La	0	0	0.0261(1)	18(1)
Cl1	0.6295(1)	0.8328(2)	0.8637(2)	28(1)
Cl2	0.8459(1)	0.8654(2)	0.3373(2)	30(1)
O1	0.8903(3)	0.7090(6)	0.8803(6)	27(1)
O2	0.1180(3)	0.8952(6)	0.7213(5)	28(1)
CsNdCl <sub>4</sub> · 4H <sub>2</sub> O				
Atom	$x/a$	$y/b$	$z/c$	$U_{eq}^a$
Cs	0	0.5	0.4553(1)	37(1)
Nd	0	0	0.9688(1)	16(1)
Cl1	0.3757(2)	0.1691(3)	0.1231(4)	25(1)
Cl2	0.1560(2)	0.1182(4)	0.6651(4)	28(1)
O1	0.1121(6)	0.2734(9)	0.1006(10)	22(1)
O2	0.8810(6)	0.0942(10)	0.2649(11)	28(2)

*Note.* Further information on the structure determination is available at: Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, 76344 Eggenstein-Leopoldshafen 2, with specification of the identification numbers RbLaCl<sub>4</sub> · 4H<sub>2</sub>O: CSD 400637 and CsNdCl<sub>4</sub> · 4H<sub>2</sub>O: CSD 400636, the authors, and the citation of the journal.

$$^a U_{eq} = 1/3[U_{11} + U_{22} + U_{33}] \quad (32).$$

To our knowledge no structure of this type is known so far.<sup>1</sup> Information on single-crystal data collection and analysis of the structure for RbLaCl<sub>4</sub> · 4H<sub>2</sub>O and CsNdCl<sub>4</sub> · 4H<sub>2</sub>O are compiled in Table 1. Atomic positions together with their equivalent thermal parameters are given in Table 2. In Table 3 main internuclear distances and angles are collected.

The absolute configurations of the measured crystals in the acentric space group are inverted with respect to each other, which is manifested in the atomic positions given in Table 2. The attempt to refine the atomic positions of CsNdCl<sub>4</sub> · 4H<sub>2</sub>O with those of RbLaCl<sub>4</sub> · 4H<sub>2</sub>O yielded a Flack parameter (24) of 0.94. We assume that both compounds crystallize as a racemate and just by chance we picked crystals of opposite configurations. The unit cell parameters of the isotypic compounds are given in Table 4. The molar volumes decrease with an increased atomic number of the lanthanides and increase with an increased atomic number of the alkalimetal. As expected, those of the compounds NH<sub>4</sub>LnCl<sub>4</sub> · 4H<sub>2</sub>O are nearly identical with those of the corresponding Rb compounds.

The coordination spheres of the rare earth ions and of

<sup>1</sup> After submission of the manuscript this structure type was published for (NH<sub>4</sub>)UCl<sub>4</sub> · 4H<sub>2</sub>O in (34).

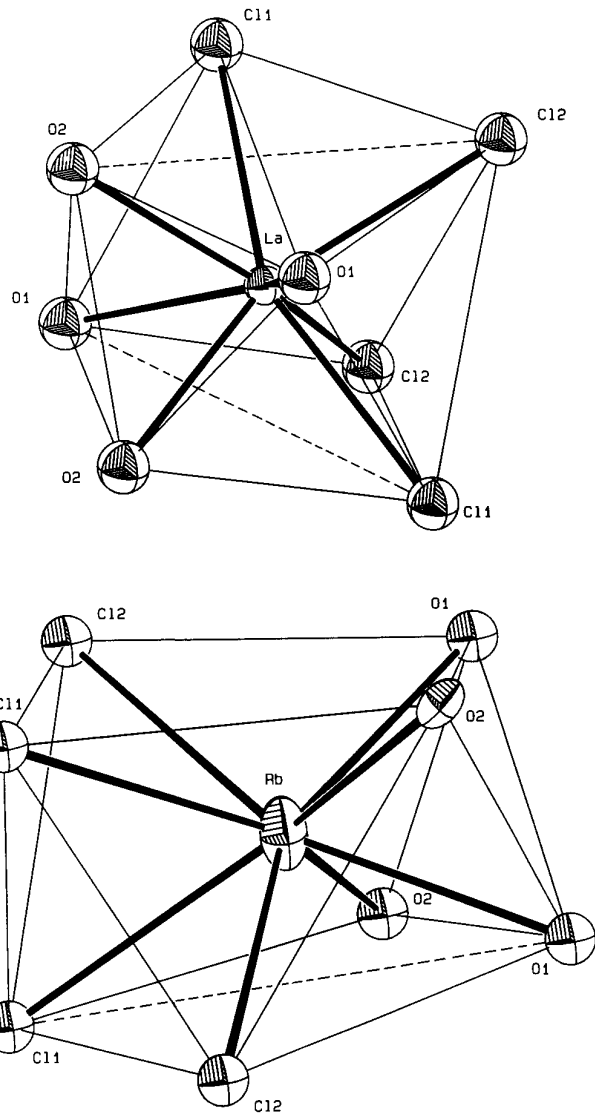
**TABLE 3**  
**Interatomic Distances (pm) and Bridging Angles (°) with**  
**ESDs in RbLaCl<sub>4</sub> · 4H<sub>2</sub>O and CsNdCl<sub>4</sub> · 4H<sub>2</sub>O**

RbLaCl <sub>4</sub> · 4H <sub>2</sub> O					
La-polyhedron			Rb-polyhedron		
La-Cl1( <i>e, j</i> )	286.0(1)		Rb-Cl1( <i>d, e</i> )	327.3(2)	
La-Cl2( <i>b, k</i> )	288.3(1)		Rb-Cl2( <i>b, c</i> )	338.1(2)	
La-O1( <i>h, i</i> )	258.6(4)		Rb-O1( <i>b, c</i> )	300.2(4)	
La-O2( <i>f, g</i> )	255.0(4)		Rb-O2( <i>, a</i> )	332.2(4)	
	La-Cl1-Rb	105.69(4)			
	La-Cl2-Rb	102.47(4)			
	La-O1-Rb	118.3(1)			
	La-O2-Rb	109.0(1)			
Symmetry transformations used to generate equivalent atoms:					
<i>a</i> = - <i>x</i> , - <i>y</i> + 1, <i>z</i>	<i>f</i> = - <i>x</i> , - <i>y</i> + 1, <i>z</i> - 1		<i>k</i> = <i>x</i> - 1, <i>y</i> - 1, <i>z</i>		
<i>e</i> = - <i>x</i> + 1/2, <i>y</i> - 1/2, <i>z</i> + 1	<i>j</i> = <i>x</i> - 1/2, - <i>y</i> + 1/2, - <i>z</i> + 1		<i>d</i> = <i>x</i> - 1/2, - <i>y</i> + 3/2, <i>z</i> + 1		
<i>i</i> = - <i>x</i> + 1, - <i>y</i> + 1, <i>z</i> - 1	<i>c</i> = <i>x</i> - 1, <i>y</i> , <i>z</i>		<i>h</i> = <i>x</i> - 1, <i>y</i> - 1, <i>z</i> - 1		
<i>b</i> = - <i>x</i> + 1, - <i>y</i> + 1, <i>z</i>	<i>g</i> = <i>x</i> , <i>y</i> - 1, <i>z</i> - 1				
CsNdCl <sub>4</sub> · 4H <sub>2</sub> O					
Nd-polyhedron			Cs-polyhedron		
Nd-Cl1( <i>, a</i> )	281.0(2)		Cs-Cl1( <i>f, g</i> )	340.6(3)	
Nd-Cl2( <i>d, e</i> )	283.7(3)		Cs-Cl2( <i>h, i</i> )	353.5(3)	
Nd-O1( <i>b, c</i> )	248.6(6)		Cs-O1( <i>c, j</i> )	316.1(7)	
Nd-O2( <i>, a</i> )	250.7(7)		Cs-O2( <i>, k</i> )	343.6(7)	
	Nd-Cl1-Cs	106.1(1)			
	Nd-Cl2-Cs	102.3(1)			
	Nd-O1-Cs	118.0(2)			
	Nd-O2-Cs	108.5(2)			
Symmetry transformations used to generate equivalent atoms:					
<i>a</i> = - <i>x</i> , - <i>y</i> + 1, <i>z</i>	<i>f</i> = <i>x</i> , <i>y</i> , <i>z</i> + 1		<i>k</i> = - <i>x</i> , - <i>y</i> , <i>z</i>		
<i>e</i> = - <i>x</i> + 1, - <i>y</i> + 1, <i>z</i>	<i>j</i> = - <i>x</i> + 1/2, <i>y</i> - 1/2, - <i>z</i> + 1		<i>d</i> = <i>x</i> - 1, <i>y</i> , <i>z</i>		
<i>i</i> = <i>x</i> - 1, <i>y</i> , <i>z</i> + 1	<i>c</i> = <i>x</i> - 1/2, - <i>y</i> + 1/2, - <i>z</i> + 1		<i>h</i> = - <i>x</i> + 1, - <i>y</i> , <i>z</i> + 1		
<i>b</i> = - <i>x</i> + 1/2, <i>y</i> + 1/2, - <i>z</i> + 1	<i>g</i> = - <i>x</i> , - <i>y</i> , <i>z</i> + 1				

the alkali metal ions consist of two Cl1, two Cl2, two O1, and two O2 with the CN 8. They can be described as complex monomeric anions [LnCl<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>-</sup> and [ACl<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>3-</sup>. Interestingly, contrary to what one expects from Born repulsion, both chloride ions are found

**TABLE 4**  
**Unit Cell Parameters for ALnCl<sub>4</sub> · 4H<sub>2</sub>O Obtained from**  
**Powder Patterns**

	<i>a</i> [pm]	<i>b</i> [pm]	<i>c</i> [pm]	<i>V</i> <sub>mol</sub> [cm <sup>3</sup> · mol <sup>-1</sup> ]	<i>V</i> <sub>molH<sub>2</sub>O</sub> [cm <sup>3</sup> · mol <sup>-1</sup> ]
NH <sub>4</sub> LaCl <sub>4</sub> · 4H <sub>2</sub> O	1141.6(5)	702.1(3)	664.4(5)	160.3(2)	15.3
NH <sub>4</sub> CeCl <sub>4</sub> · 4H <sub>2</sub> O	1138.6(5)	700.5(3)	662.7(5)	159.2(2)	15.4
NH <sub>4</sub> PrCl <sub>4</sub> · 4H <sub>2</sub> O	1133.3(5)	697.0(3)	660.0(5)	156.9(2)	15.1
KCeCl <sub>4</sub> · 4H <sub>2</sub> O	1145.2(8)	689.1(3)	655.8(6)	155.8(2)	14.0
KPrCl <sub>4</sub> · 4H <sub>2</sub> O	1142.6(5)	686.6(2)	653.4(3)	154.3(1)	13.8
KNdCl <sub>4</sub> · 4H <sub>2</sub> O	1139.8(9)	685.2(4)	650.9(7)	152.9(2)	13.7
RbLaCl <sub>4</sub> · 4H <sub>2</sub> O	1142.4(9)	702.7(4)	669.9(5)	161.4(2)	13.7
RbCeCl <sub>4</sub> · 4H <sub>2</sub> O	1136.5(8)	701.2(7)	667.8(5)	159.1(2)	13.4
RbPrCl <sub>4</sub> · 4H <sub>2</sub> O	1134.1(8)	698.2(6)	666.3(4)	158.9(2)	13.6
RbNdCl <sub>4</sub> · 4H <sub>2</sub> O	1132.7(8)	697.4(6)	663.8(4)	157.3(2)	13.5
RbSmCl <sub>4</sub> · 4H <sub>2</sub> O	1125.3(7)	693.3(5)	659.5(4)	154.9(2)	13.2
CsCeCl <sub>4</sub> · 4H <sub>2</sub> O	1127.9(9)	715.6(5)	684.3(6)	165.7(3)	15.3
CsPrCl <sub>4</sub> · 4H <sub>2</sub> O	1129.6(9)	714.2(4)	681.6(4)	165.0(2)	15.3
CsNdCl <sub>4</sub> · 4H <sub>2</sub> O	1130.8(8)	712.7(4)	680.4(3)	164.6(2)	15.5



**FIG. 1.** Coordination spheres of the cations in RbLaCl<sub>4</sub> · 4H<sub>2</sub>O.

in one hemisphere of the coordination polyhedron and both water molecules are found in the other hemisphere. The coordination polyhedra of both cations are shown in Fig. 1 for RbLaCl<sub>4</sub> · 4H<sub>2</sub>O.

Attempts to relate the coordination polyhedra in RbLaCl<sub>4</sub> · 4H<sub>2</sub>O either to an archimedean antiprism or a triangular dodecahedron were performed with the “best planes” method given by Lippard and Russ (25); the polyhedron around La is best described as a dodecahedron-like distorted antiprism and that around Rb as a dodecahedron distorted toward a doubly capped trigonal prism. These descriptions are suggested in Fig. 1.

Since the alkalimetal ions are nearly centering four lanthanide ions in a coplanar way and vice versa, the polyhedra are sharing common edges to four polyhedra of the

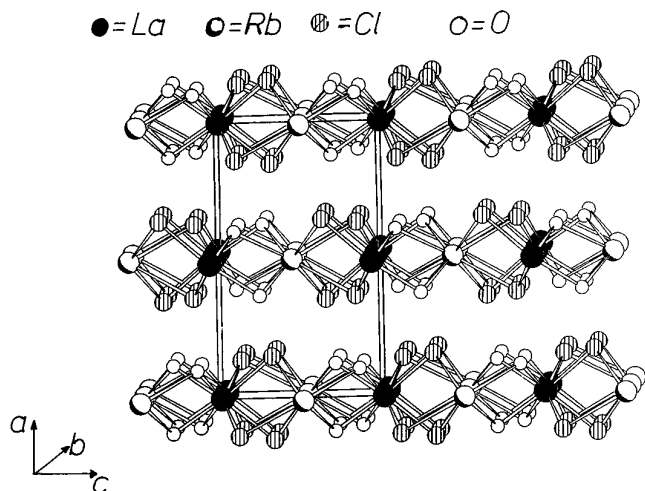


FIG. 2. The layers of edge-connected polyhedra in the [010]-direction in  $\text{RbLaCl}_4 \cdot 4\text{H}_2\text{O}$ .

other cation. These common edges are Cl1–Cl2 (two times) and O1–O2 (two times) with  $d$  (Cl1–Cl2) 355.6(4) pm and (O1–O2) 309.5(9) pm in  $\text{RbLaCl}_4 \cdot 4\text{H}_2\text{O}$  (352.2(6) pm and 284.4(9) pm in  $\text{CsNdCl}_4 \cdot 4\text{H}_2\text{O}$ ).

Thus layers of the edge-connected polyhedra in (011) planes are stacked along the [100] direction. These layers are shifted about  $b/2$  in the [010] direction with respect to each other. Furthermore, the chloride ions and water molecules occupy opposite halves of the coordination polyhedra in the two following layers. The very short distances  $d$  (O–Cl) between O and Cl of different layers ( $\text{RbLaCl}_4 \cdot 4\text{H}_2\text{O}$ ,  $d$  (O1–Cl1) 310.0(8) pm and  $d$  (O2–Cl2) 309.7(8) pm;  $\text{CsNdCl}_4 \cdot 4\text{H}_2\text{O}$ ,  $d$  (O1–Cl1) 306.6(9) pm and  $d$  (O2–Cl2) 313.7(9) pm) are an indication of the existence of hydrogen bonds between the layers. A part of the stacked layers in  $\text{RbLaCl}_4 \cdot 4\text{H}_2\text{O}$  is shown in Fig. 2.

### $\text{CsLaCl}_4 \cdot 3\text{H}_2\text{O}$

$\text{CsLaCl}_4 \cdot 3\text{H}_2\text{O}$  crystallizes isotypically with respect to  $\text{CsUCl}_4 \cdot 3\text{H}_2\text{O}$  (26). Details of the single-crystal data collection and analysis are compiled in Table 5. Atomic positions, the equivalent thermal parameters, and the main internuclear distances and angles are given in Table 6.

The coordination sphere of the lanthanum consists of four Cl1 and two Cl2 chloride ions forming a slightly distorted trigonal prism triply capped by water molecules (Fig 3a). Thus, the CN is 9. The polyhedra are connected by Cl1–Cl1 edges with a Cl1–Cl1 distance of 346.5 pm. This could be described as well as an asymmetric double bridge with a bridging angle La–Cl1–La of 109.4°. The asymmetry is a result of the two different internuclear distances La–Cl1. The nearly *trans*-standing polyhedra form zigzag chains  $[\text{LaCl}_2\text{Cl}_{4/2}\text{O}_3]_{\infty}^-$  in the [010] direction. Sections of these chains are shown in Fig. 3b.

TABLE 5  
Experimental Data and Structure Refinement Parameters for  $\text{CsLaCl}_4 \cdot 3\text{H}_2\text{O}$

Crystal system	Monoclinic
Space group	$P2_1/m$ (No. 11)
Lattice parameters (pm) determined at 298 K with 20 reflections	$a = 711.9(1)$ $b = 868.2(1)$ $c = 808.6(1)$ $\beta = 99.4(1)$
Number of F.U.	2
Calculated density ( $\text{g}/\text{cm}^3$ )	3.157
Scan-width ( $\omega$ -scan)	$\omega$ -scan: $1.2^\circ + 0.9(\tan \theta)^\circ$
Collected reflections within	1214 ( $3 < \theta < 26$ ) $-8 \leq h \leq 6$ $0 \leq k \leq 10$ $-9 \leq l \leq 10$
Independent reflections with $F_o > 0$	1053
Absorption coefficient ( $\text{mm}^{-1}$ )	9.02
Absorption correction	DIFABS (31)
Number of refined parameters	49
Reliability factors <sup>a</sup>	$R = 0.020$ for $F_o > 2\sigma$ $wR2 = 0.053$ for all data GooF = 1.22

<sup>a</sup> Definitions of reliability factors:  $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$ ,  $wR2 = \frac{\sum w(F_o^2 - F_c^2)^2}{\sum [(wF_o^2)^2]}^{1/2}$ .

TABLE 6  
Atomic Coordinates and Equivalent Temperature Parameters ( $\text{pm}^2$ ), Interatomic Distances (pm), and Bridging Angles (°) with ESDs in  $\text{CsLaCl}_4 \cdot 3\text{H}_2\text{O}$

Atom	$x/a$	$y/b$	$z/c$	$U_{eq}^a$
La	0.9161(1)	0.25	0.8684(1)	13(1)
Cs	0.5487(1)	0.25	0.2835(1)	27(1)
Cl1	0.2282(1)	0.0315(1)	0.9587(1)	20(1)
Cl2	0.7818(2)	0.0246(1)	0.6103(1)	24(1)
O1	0.9893(7)	0.25	0.1908(5)	24(1)
O2	0.1419(7)	0.25	0.6458(5)	25(1)
O3	0.5572(6)	0.25	0.8532(7)	29(1)
La–O3	253.8(4)	La–O1( <i>a</i> )	256.9(4)	
La–O2( <i>b</i> )	259.7(4)	La–Cl2(, <i>c</i> )	290.3(1)	
La–Cl1( <i>b</i> , <i>d</i> )	292.2(1)	La–Cl1( <i>e</i> , <i>f</i> )	307.3(1)	
La( <i>k</i> )–Cl1–La( <i>f</i> )	109.43(3)			
Cs–O1	334.1(5)	Cs–Cl2(, <i>c</i> )	348.0(1)	
Cs–O3( <i>g</i> )	348.2(5)	Cs–Cl2( <i>h</i> , <i>i</i> )	355.1(1)	
Cs–Cl1( <i>h</i> , <i>i</i> )	365.0(1)	Cs–Cl1( <i>g</i> , <i>j</i> )	370.5(1)	
Cs–O1( <i>k</i> )	393.1(5)			

Symmetry transformations used to generate equivalent atoms:

$$\begin{aligned}
 a = x, y, z + 1 & & b = x + 1, y, z & & c = x, -y + 1/2, z & & d = x + 1, -y + 1/2, z \\
 e = -x + 1, y + 1/2, -z + 2 & & f = -x + 1, -y, -z + 2 & & g = x, y, z - 1 & & h = -x + 1, y + 1/2, -z + 1 \\
 i = -x + 1, -y, -z + 1 & & j = x, -y + 1/2, z - 1 & & k = x - 1, y, z
 \end{aligned}$$

Note. Further information on the structure determination is available at: Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, 76344 Eggenstein-Leopoldshafen 2, with specification of the identification number CSD 400635, the authors, and the citation of the journal.

$$^a U_{eq} = 1/3[U_{22} + 1/\sin^2\beta(U_{11} + U_{33} + 2U_{13} \cos \beta)] \quad (32).$$

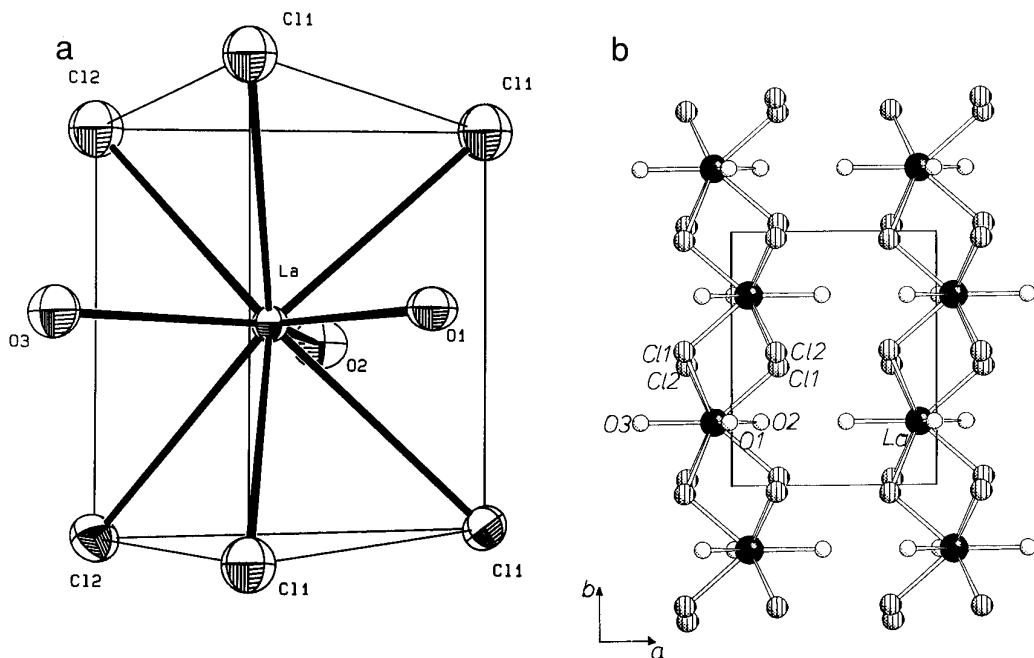


FIG. 3. Coordination sphere of  $\text{La}^{3+}$  (a) and a segment of the edge-connected chains  $[\text{La}(\text{H}_2\text{O})_3\text{Cl}(2)\text{Cl}(1)_{4/2}]_n^-$  in  $\text{CsLaCl}_4 \cdot 4\text{H}_2\text{O}$  (without  $\text{Cs}^+$ ), (b).

The cesium ion is coordinated by four Cl1, four Cl2, one O1, and one O3. Its CN is 10. The polyhedra share two common Cl1–Cl1 and two common Cl2–Cl2 edges with four other polyhedra. This leads to layers of connected polyhedra of cesium in (011) planes as shown in Fig. 4. A more detailed description of this structure type is given by Krämer *et al.* (26).

## DISCUSSION

Chains of edge-connected polyhedra as in  $\text{CsLaCl}_4 \cdot 3\text{H}_2\text{O}$  are not unusual in complex water containing lanthanide(III)-chlorides. Anionic chains of triply capped trigonal prisms with CN 9 for lanthanum are present in  $\text{Cs}_3\text{LaCl}_6 \cdot 3\text{H}_2\text{O}$  (14) and  $(\text{CH}_3\text{NH}_3)_3\text{LaCl}_6 \cdot$

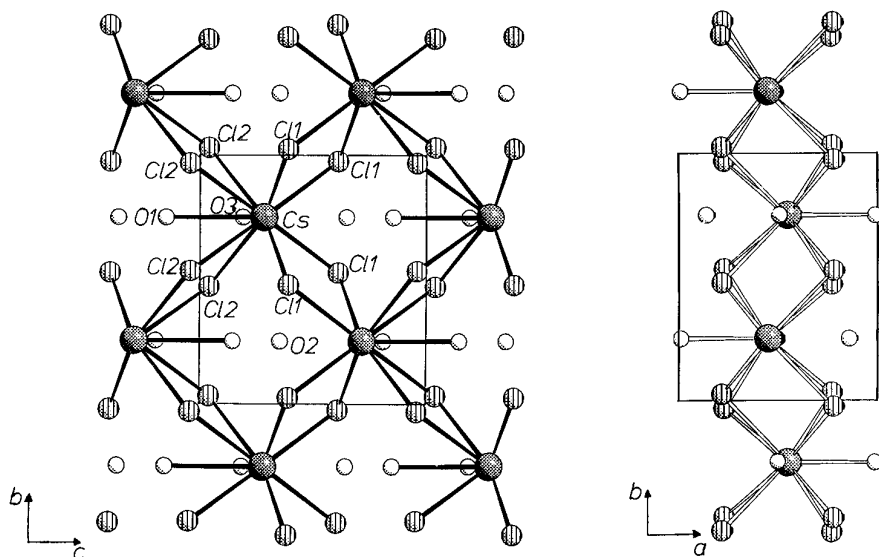


FIG. 4. The polyhedra layers around  $\text{Cs}^+$  in the [110] and [011] direction in  $\text{CsLaCl}_4 \cdot 4\text{H}_2\text{O}$  (without  $\text{La}^{3+}$ ).

3H<sub>2</sub>O (27). Because of the very similar structure motifs of CsLaCl<sub>4</sub> · 3H<sub>2</sub>O and Cs<sub>3</sub>LaCl<sub>6</sub> · 3H<sub>2</sub>O it is possible to prepare Cs<sub>3</sub>LaCl<sub>6</sub> · 3H<sub>2</sub>O by grinding CsLaCl<sub>4</sub> · 3H<sub>2</sub>O and 2 CsCl in a ball mill for 12 hours. In compounds of the earlier lanthanoids the CN 8 was observed in accordance to their decreasing ionic radii. Examples for this are (CH<sub>3</sub>NH<sub>3</sub>)<sub>8</sub>[NdCl<sub>6</sub>][NdCl<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>Cl<sub>3</sub> (28) and (CH<sub>3</sub>NH<sub>3</sub>)<sub>3</sub>PrCl<sub>6</sub> · 2H<sub>2</sub>O (29).

In the compounds *ALnCl*<sub>4</sub> · 4H<sub>2</sub>O complex monomeric anions [*LnCl*<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>-</sup> with the CN 8 of the rare earth ion are found for the first time. Cationic monomeric units exist in the compounds *LnCl*<sub>3</sub> · 6H<sub>2</sub>O (*Ln* = Ce–Lu) (10, 12) and *ALnCl*<sub>4</sub> · 8H<sub>2</sub>O (*A* = arsonium, phosphonium) (30).

In contrast to other complex water containing rare earth chlorides the structure motif consists of layers of connected polyhedra around both cations. As mentioned above, very short Cl–O distances between O and Cl of different layers indicate the presence of hydrogen bonds between the layers. This view is supported by a comparison of the IR-spectra of the compounds CsLaCl<sub>4</sub> · 3H<sub>2</sub>O and RbLaCl<sub>4</sub> · 4H<sub>2</sub>O. Whereas in CsLaCl<sub>4</sub> · 3H<sub>2</sub>O the asymmetric and symmetric OH-stretching mode are well resolved (3440 cm<sup>-1</sup> and 3331 cm<sup>-1</sup>), in RbLaCl<sub>4</sub> · 4H<sub>2</sub>O the first shoulder at 3393 cm<sup>-1</sup> is shifted significantly to smaller wavenumbers. In this broad mode asymmetric and symmetric OH-stretching modes are not resolved.

The molar volume of one crystal water was calculated from

$$V_{\text{mol}}(\text{H}_2\text{O}) = [V_{\text{mol}}(\text{ALnCl}_4 \cdot 4\text{H}_2\text{O}) - V_{\text{mol}}(\text{LnCl}_3) - V_{\text{mol}}(\text{ACl})]/4.$$

The results are given in Table 4. (The analogous calculated molar volume of one crystal water in CsLaCl<sub>4</sub> · 3H<sub>2</sub>O is 14.0 cm<sup>3</sup> · mol<sup>-1</sup>). They are in good agreement with the values 14.75 and 15 cm<sup>3</sup> · mol<sup>-1</sup> evaluated from homologous series of binary compounds with increasing water content by Leclaire and Monier (31) and Reuter *et al.* (12). The smaller values for the compounds with *A* = K and Rb are a result of the larger molar volumes of the NaCl-type versus CsCl-structures. In this context the increasing cell parameter *a* of the Cs-compounds from Ce–Nd should be mentioned.

The *d* values of the X-ray diffractograms of the “penta-hydrates” *ALnCl*<sub>4</sub> · 5H<sub>2</sub>O (*A* = Rb and Cs) given in (6) could be completely indexed on the basis of the tetrahydrate structures. Furthermore, the existence of the incongruently soluble compounds *ALnCl*<sub>4</sub> · 4H<sub>2</sub>O (*A* = NH<sub>4</sub> and K) shows that the corresponding systems are not eutectic, in contrast to what is suggested in (5).

## ACKNOWLEDGEMENT

The Support of Prof. Dr. H. J. Seifert is acknowledged. We dedicate this paper to him on the occasion of his last “first fine day.”

## REFERENCES

1. L. L. Kost, Y. V. Shirai, and V. G. Shevchuk, *Russ. J. Inorg. Chem.* **25**, 579 (1980).
2. Y. V. Shirai and V. G. Shevchuk, *Russ. J. Inorg. Chem.* **26**, 1046 (1981).
3. N. M. Lazorenko and V. G. Shevchuk, *Russ. J. Inorg. Chem.* **28**, 1517 (1983).
4. N. M. Lazorenko and V. G. Shevchuk, *Russ. J. Inorg. Chem.* **28**, 1521 (1983).
5. Y. V. Shirai, *Russ. J. Inorg. Chem.* **31**, 598 (1986).
6. D. A. Storozhenko, N. M. Lazorenko, and V. I. Omelyan, *Russ. J. Inorg. Chem.* **32**, 1234 (1987).
7. N. V. Bunyakina, D. A. Storozhenko, N. B. Senenko, and V. G. Shevchuk, *Russ. J. Inorg. Chem.* **36**, 756 (1991).
8. N. V. Bunyakina, D. A. Storozhenko, and V. G. Shevchuk, *Russ. J. Inorg. Chem.* **37**, 1103 (1992).
9. D. Mackenstedt and W. Urland, *J. Alloys Comp.* **207/208**, 189 (1994).
10. C. J. Kepert, B. W. Skelton, and A. H. White, *Aust. J. Chem.* **47**, 385 (1994).
11. G. Reuter and G. Frenzen, *Acta Crystallogr.* **C50**, 844 (1994).
12. G. Reuter, H. Fink, and H. J. Seifert, *Z. Anorg. Allg. Chem.* **620**, 665 (1994).
13. G. Reuter, M. Roffe, and G. Fenzen, *Z. Anorg. Allg. Chem.* **621**, 630 (1995).
14. G. Reuter and G. Frenzen, *J. Solid State Chem.* **116**, 329 (1995).
15. H. Fink, H. Imgrund, H.-J. Seifert, and G. Thiel, *Thermochim. Acta* **160**, 57 (1990).
16. K. Harms, “XCAD 4, Program for LP-Correction of Diffraction Data.” University of Marburg, 1993.
17. G. M. Sheldrick, *Acta Crystallogr.* **A46**, 467 (1990).
18. G. M. Sheldrick, “SHELXL 93, Program for the Refinement of Crystal Structures.” University of Göttingen, 1993.
19. E. Keller, “SCHAKAL 92, Program for Graphic Presentation of Crystal Structures.” University of Freiburg, 1993.
20. L. Zsolnai, “ZORTEP.” University of Heidelberg, Germany, 1994.
21. H. Fink, “PROFIL, Program for Data Collection and Analysis of X-Ray Powder Patterns.” University of Kassel, 1983.
22. K. Yvon, W. Jeitschko, and E. Parthé, *J. Appl. Crystallogr.* **10**, 73 (1977).
23. J. Warczewski and P. M. de Wolff, *J. Appl. Crystallogr.* **7**, 585 (1974).
24. H. D. Flack, *Acta Crystallogr.* **A39**, 876 (1983).
25. S. J. Lippard and B. J. Russ, *Inorg. Chem.* **7**, 1686 (1968).
26. K. Krämer, G. Meyer, M. Karbowski, and J. Drozdynski, *J. Less-Common Met.* **175**, 347 (1991).
27. P. Runge and W. Urland, “Thesis Runge.” University of Hannover, 1990.
28. P. Runge, M. Schulze, and W. Urland, *Z. Allg. Anorg. Chem.* **592**, 115 (1991).
29. P. Runge, M. Schulze, and W. Urland, *Z. Naturforsch.* **45B**, 603 (1990).
30. W. Urland and U. Schwanz-Schüller, *Ang. Chem. Suppl.*, 1399 (1983).
31. P. A. Leclaire and J. C. Monier, *Acta Crystallogr.* **B38**, 724 (1982).
32. N. Walker and D. Stuart, *Acta Crystallogr.* **A39**, 158 (1983).
33. R. X. Fischer and E. Tillmanns, *Acta Crystallogr.* **C44**, 775 (1988).
34. M. Karbowski, J. Drozdynski, and J. Janczak, *Polyhedron* **15**, 241 (1996).