

## Orthorhombic low-temperature modifications of compounds $\text{Cs}_3\text{LnCl}_6$ (Ln = Nd–Yb)-preparation and thermodynamic stability

Gert Reuter, Jörg Sebastian, Mark Roffe, Hans-Joachim Seifert\*

*Department of Inorganic Chemistry, University Gh Kassel, Heinrich-Plett Strasse 40, D-34109 Kassel, Germany*

Received 13 September 1996; received in revised form 23 September 1996; accepted 26 January 1997

### Abstract

The compounds  $\text{Cs}_3\text{LnCl}_6$  (Ln=Nd–Yb) can be obtained from aqueous solutions with an orthorhombic structure /S.G. Pbcm/, whereas from solutions in anhydrous acetic acid a modification with the monoclinic  $\text{Cs}_3\text{BiCl}_6$  structure /S.G. C 2/c/ is formed. By solution calorimetry, the orthorhombic phase could be proved to be the low temperature modification. Molar volumes determined from X-ray powder patterns increase from Pbcm to C 2/c. The transition from the orthorhombic into the monoclinic phase is irreversible for kinetical reasons. © 1997 Elsevier Science B.V.

**Keywords:** Cesium hexachloro lanthanoates (III); Distorted elpasolite structures; Solution calorimetry

### 1. Introduction

In 1993 we published results of investigations on the relationship between crystal structures and thermodynamic properties of compounds  $\text{A}_3\text{LnCl}_6$  with A = Rb, Cs and Ln = La to Gd [1]. All these compounds have high temperature modifications above 400°C with the cubic elpasolite structure /S.G.:  $\text{Fm}\bar{3}\text{m}$ /. At ambient temperature their structure is that of  $\text{Cs}_3\text{BiCl}_6$  /S.G.: C 2/c / [2]. For  $\text{Cs}_3\text{LaCl}_6$  the atomic positions could be determined from powder patterns with the Rietveld method. Later we found the same structural relations for  $\text{Cs}_3\text{TbCl}_6$  [3] and  $\text{Cs}_3\text{DyCl}_6$  [4].

Mattfeld and Meyer [5] completed these findings for  $\text{Cs}_3\text{ErCl}_6$ ,  $\text{Cs}_3\text{YCl}_6$  and the Rb-compounds with Ln = Tb–Lu. For  $\text{Rb}_3\text{YCl}_6$  they could

perform a complete single crystal structure determination.

Reuter and Frenzen [6] prepared hydrated compounds  $\text{Cs}_3\text{LnCl}_6 \cdot 3\text{H}_2\text{O}$  with Ln = La–Nd from hydrochloric acid; they can be dehydrated at 100°C. With neodyme the anhydrous compound could be obtained directly from hot solutions as single crystals. Thus, for  $\text{Cs}_3\text{NdCl}_6$  a complete structure determination was performed. It crystallizes in the orthorhombic space group Pbcm.

In this work these investigations are expanded to the other lanthanoides (Pm and Lu excepted), because it was not known whether the new elpasolite variant is either a metastable dehydration product or a thermodynamically stable low temperature modification, which cannot be prepared from the melt for kinetical reasons. The thermodynamic relations between the phases were investigated by solution calorimetry.

\*Corresponding author. Fax: 00490561-8044010

## 2. Experimental

### 2.1. Materials

The compounds  $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$  were prepared by dissolving the oxides (99.99%, Fa. Johnson-Matthey, Karlsruhe, Germany) in hydrochloric acid, evaporating the solutions and drying the chloride hydrates at  $60^\circ\text{C}$ . Cesium acetate (reinst, Merck, Darmstadt, Germany) was dried at  $200^\circ\text{C}$  in vacuum. Acetic acid (99–100%, Fa. Merck) was treated for 24 h with  $\text{P}_4\text{O}_{10}$ , then refluxed for 4 h and distilled. Acetyl chloride and thionyl chloride (Fa. Merck, zur Synthese) were purified by distillation.

### 2.2. X-ray analysis

Powder patterns from ambient temperature to  $130^\circ\text{C}$  were taken with a Phillips PW 1050/25 goniometer equipped with a proportional counter and a vacuum attachment. During exposure ( $\text{Cu-K}_\alpha$  radiation) the samples were under He atmosphere. The digital data were collected and analyzed with PROFIL [7]. The calculations were performed with the program LAZY PULVERIX [8]. The graphic was drawn by SCHAKAL 92 [9]. Cell parameters were determined from powder patterns (internal standard:  $\alpha\text{-Al}_2\text{O}_3$ ,  $a=475.9$  pm;  $b=1299.0$  pm) with the least squares method of Warczewski and de Wolff [10].

### 2.3. Thermochemical methods

The thermal behavior of the compounds was investigated by means of the differential scanning calorimeter DSC 7 (Perkin Elmer) (heating rates:  $10$  to  $1$   $\text{K min}^{-1}$ , purge gas flow:  $\text{N}_2$   $10$   $\text{ml min}^{-1}$ ) in the temperature range from  $40$  to  $500^\circ\text{C}$ . The heats of solution were measured using an isoperibolic under water calorimeter firstly described in 1978 [11].

The reaction vessel is made of silver. The substances are in thin-walled glass ampoules which are cracked under water at the beginning of the measurement. The solution heat generates a temperature change  $\Delta T$  against the surroundings. A thermostat with a temperature constance of  $2 \cdot 10^{-4}^\circ\text{C}$  is used.  $\Delta T$  is measured with a thermopile and corrected for the inevitable heat-loss according to the Dickinson-compensation. This corrected temperature change

$\Delta T^*$  is calibrated by Joule's heat  $Q_E$ , giving a temperature change  $\Delta T_E$ . The heat of solution  $Q_L$  is finally calculated from the relation

$$\frac{Q_L}{\Delta T^*} = \frac{Q_E}{\Delta T_E}$$

The volume of the vessel is 1.3 l. Thus, samples of 3–4 g yielded virtually ideal solutions (dissolution ratio 1 : 15 000 mol). At least two samples of each substance were measured. For the solution enthalpy of KCl we found  $17.67 \pm 0.08$   $\text{kJ mol}^{-1}$ , compared with  $17.54 \pm 0.05$   $\text{kJ mol}^{-1}$  from literature [12].

## 3. Results

### 3.1. Preparation of ternary lanthanoide chlorides from acetic acid (HAc)

Solutions of lanthanoide chloride hydrates in HAc were dehydrated by boiling with acetyl chloride. After adding dried cesium acetate the ternary chlorides were precipitated with gaseous HCl. The composition of the precipitated compounds does not depend on the molar ratios  $\text{A}^+/\text{Ln}^{3+}$ ; it is only determined by the thermal stability of the compounds. Beginning with praseodyme the 3 : 1 compounds  $\text{Cs}_3\text{LnCl}_6$  are stable at ambient temperature and therefore are precipitated, because they are less soluble than the as well stable compounds  $\text{Cs}_2\text{LnCl}_5$ . As found from e.m.f.-measurements  $\text{Cs}_3\text{LaCl}_6$  and  $\text{Cs}_3\text{CeCl}_6$  [1] are stable only at elevated temperatures; in this case the 2 : 1 compounds are precipitated from the solutions.

A typical procedure is given for  $\text{Cs}_3\text{GdCl}_6$ : 0.005 mol (1.86 g)  $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$  were heated together with 20 ml acetic acid in a three-necked flask fitted with a reflux condenser and hot-plate magnetic stirrer until all particles were dissolved. Then 8 ml acetyl chloride were added. This solution was heated to approximately  $80^\circ\text{C}$ . 0.015 mol cesium acetate (2.88 g) were dissolved in acetic acid and added to the first solution.  $\text{Cs}_3\text{GdCl}_6$  was precipitated by saturating the solution with gaseous HCl. The precipitate was filtered, washed twice with acetic acid and absolute ether.

The precipitated Cs compounds possess the  $\text{Cs}_3\text{BiCl}_6$ -structure, only with neodyme at room temperature the orthorhombic modification is formed,

Table 1

Lattice parameters for Cs<sub>3</sub>LnCl<sub>6</sub> (Ln = Nd to Yb) obtained from powder patterns, their molar volumes and  $\Delta V_m$  ( $V_m$  mon. -  $V_m$  orth.)

	S.G.	a/pm	b/pm	c/pm	$\beta/^\circ$	$V_m/\text{cm}^3\text{mol}^{-1}$	$\Delta V_m/\text{cm}^3\text{mol}^{-1}$
Cs <sub>3</sub> NdCl <sub>6</sub>	Pbcm	824.7(3)	1324.2(3)	2668.6(8)		219.3	
	C2/c	2719.3(7)	824.8(2)	1327.9(2)	99.96(2)	220.8	1.5
Cs <sub>3</sub> SmCl <sub>6</sub>	Pbcm	822.4(3)	1317.5(3)	2660.9(5)		217.0	
	C2/c	2705.4(7)	820.2(2)	1321.9(4)	99.94(2)	217.5	0.5
Cs <sub>3</sub> EuCl <sub>6</sub>	Pbcm	820.4(3)	1315.3(3)	2658.0(8)		215.9	
	C2/c	2706.5(8)	819.2(2)	1320.3(4)	99.93(2)	217.1	1.2
Cs <sub>3</sub> GdCl <sub>6</sub>	Pbcm	818.5(2)	1314.2(3)	2655.7(5)		215.0	
	C2/c	2702.2(7)	818.9(2)	1318.1(3)	100.01(2)	216.2	1.2
Cs <sub>3</sub> TbCl <sub>6</sub>	Pbcm	816.0(3)	1311.4(3)	2652.2(7)		213.6	
	C2/c	2699.0(8)	818.0(3)	1317.1(4)	99.97(2)	215.8	2.2
Cs <sub>3</sub> DyCl <sub>6</sub>	Pbcm	815.5(3)	1308.2(4)	2648.1(8)		212.7	
	C2/c	2694.6(8)	815.4(3)	1313.7(4)	100.15(2)	213.9	1.2
Cs <sub>3</sub> HoCl <sub>6</sub>	Pbcm	815.8(3)	1306.6(5)	2645.7(7)		212.3	
	C2/c	2692.7(8)	813.1(2)	1313.9(5)	100.23(3)	213.1	0.8
Cs <sub>3</sub> ErCl <sub>6</sub>	Pbcm	814.6(3)	1307.4(6)	2644.2(7)		211.9	
	C2/c	2690.7(8)	813.2(2)	1307.7(4)	99.96(2)	212.2	0.3
Cs <sub>3</sub> TmCl <sub>6</sub>	Pbcm	811.5(2)	1304.3(3)	2636.6(7)		210.1	
	C2/c	2685.1(8)	811.5(2)	1308.9(6)	100.14(3)	211.3	1.2
Cs <sub>3</sub> YbCl <sub>6</sub>	Pbcm	808.9(3)	1307.7(3)	2636.6(7)		209.9	
	C2/c	2683.8(9)	817.4(4)	1303.5(4)	100.22(3)	211.8	1.9

from hot solution the Cs<sub>3</sub>BiCl<sub>6</sub> modification is also obtained.

### 3.2. Double chlorides from aqueous solutions

In this case the composition depends on the ratio  $A^+/\text{Ln}^{3+}$  and often on temperature. In molar ratios  $A^+:\text{Ln}^{3+}$  3 : 1 and 4 : 1, with Ln = La–Nd hydrates are precipitated with HCl or by evaporating below 60 °C. In all other cases Cs<sub>3</sub>LnCl<sub>6</sub> (Ln = Nd–Yb) in the orthorhombic modification is obtained. As recently found [13] Cs<sub>4</sub>LnCl<sub>7</sub> with Ln = Ho–Yb is formed when the molar ratio is 4 : 1.

In the molar ratio, 2 : 1, compounds of the composition Cs<sub>2</sub>LnCl<sub>5</sub>·6H<sub>2</sub>O exist below 50 °C with Ln = Nd–Ho, beginning with erbium monohydrates Cs<sub>2</sub>LnCl<sub>5</sub>·H<sub>2</sub>O (erythrosiderite type- S.G. Pnma [14]) crystallize above 90 °C.

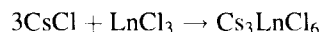
### 3.3. Crystal structure determinations

X-ray powder patterns of all new phases crystallizing in the S.G. Pbcm were indexed in analogy to the structure of Cs<sub>3</sub>NdCl<sub>6</sub>, which was known from our previous single crystal work [6]. The unit cell parameters and the molar volumes were calculated from

patterns with Al<sub>2</sub>O<sub>3</sub> as inner standard. The results are compiled in Table 1, together with values for the C 2/c - modifications. The lattice parameters were either derived from our older paper [1] or calculated in this work. In some cases (Tb [3], Dy [4] and Er [5]) older findings had to be slightly corrected. In both modifications slightly distorted octahedra exist, which are mutually orientated in different ways.

### 3.4. Thermodynamic properties of the compounds

For the determination of the solution enthalpies of both modifications 3–4 g of Cs<sub>3</sub>LnCl<sub>6</sub> for each measurement were used. From two results with deviations in general less than 1.0 KJ mol<sup>-1</sup> the mean values were formed. For Cs<sub>3</sub>LnCl<sub>6</sub> in S.G. C2/c with Ln = Nd to Tb values from older papers were used. The formation enthalpies  $\Delta_f H^0$  for the reactions



can be calculated with the equation

$$\Delta_f H^0(\text{Cs}_3\text{LnCl}_6) = \{ \Delta_{\text{sol}} H^0(\text{LnCl}_3) + 3\Delta_{\text{sol}} H^0(\text{CsCl}) \} - \Delta_{\text{sol}} H^0(\text{Cs}_3\text{LnCl}_6).$$

The transformation enthalpies Pbcm → C2/c are:

Table 2  
Solution enthalpies in  $\text{kJ mol}^{-1}$  for  $\text{Cs}_3\text{LnCl}_6$  in S.G. Pbcm and C2/c

Compound	$\Delta_{\text{sol}}H^0$ (Pbcm)		$\Delta_{\text{sol}}H^0$ (C2/c)		Difference
	Meas. values	Mean values	Meas. values	Mean values	
$\text{Cs}_3\text{NdCl}_6$	–50.12 –50.37	–50.3(2)	x	–56.3 <sup>a</sup>	6.0
$\text{Cs}_3\text{SmCl}_6$	–50.80 –50.17	–50.5(3)	x	–54.1 <sup>a</sup>	3.6
$\text{Cs}_3\text{EuCl}_6$	–52.59 –53.16	–52.9(3)	x	–57.3 <sup>a</sup>	4.4
$\text{Cs}_3\text{GdCl}_6$	–54.21 –55.65	–54.9(7)	x	–59.3 <sup>a</sup>	4.4
$\text{Cs}_3\text{TbCl}_6$	–56.14 –55.98	–56.1(1)	x	–61.0 <sup>a</sup>	4.9
$\text{Cs}_3\text{DyCl}_6$	–56.10 –57.17	–57.6(5)	–60.40 –60.46	–60.4(1)	2.8
$\text{Cs}_3\text{HoCl}_6$	–60.38 –59.92	–60.1(3)	–62.98 –63.16	–63.1(1)	3.0
$\text{Cs}_3\text{ErCl}_6$	–60.91 –61.13	–61.0(2)	–63.09 –64.08	–63.6(5)	2.6
$\text{Cs}_3\text{TmCl}_6$	–62.22 –63.15	–62.7(5)	–63.75 –63.90	–63.8(1)	1.1
$\text{Cs}_3\text{YbCl}_6$	–63.28 –63.87	–63.6(3)	–64.55 –64.71	–64.6(1)	1.0

( ) = range of error for values, measured for this paper

<sup>a</sup> = values from own older papers

$$\begin{aligned}\Delta_{\text{tr}}H^0 &= \Delta_{\text{f}}H^0(2/c) - \Delta_{\text{f}}H^0(\text{Pbcm}) \\ &= -\Delta_{\text{sol}}H^0(\text{C2/c}) + \Delta_{\text{sol}}H^0(\text{Pbcm})\end{aligned}$$

The latter values are compiled together with the measured solution enthalpies and their mean values in Table 2. Obviously all solution enthalpies of the Pbcm-modifications are less exothermic than those of the C2/c modifications; the difference between both decrease with decreasing size of lanthanoid ions. For  $\text{Cs}_3\text{YbCl}_6$  the difference is  $1.0 \text{ kJ mol}^{-1}$  and therefore at the border of significance. Nevertheless, for all hypothetical transitions  $\text{Pbcm} \rightarrow \text{C2/c}$  the transition enthalpy is endothermic.

With this knowledge we tried to measure this phase transition directly by DSC with heating rates down to  $1 \text{ K min}^{-1}$ . However, no transition of the orthorhombic into the monoclinic modification occurred; but at about  $400^\circ\text{C}$  the transition into the cubic high temperature modification was observed. After cooling to ambient temperature, the X-ray pattern of the monoclinic modification as now metastable phase was found.

Due to these findings annealing experiments with both modifications were performed for about 6 weeks in the range from  $200$  to  $350^\circ\text{C}$ . It was not possible to transfer the monoclinic modification to that with the Pbcm structure. Otherwise at  $250^\circ\text{C}$  a partial transition from Pbcm to C2/c occurs; at  $300^\circ\text{C}$  it is completed in about 10 h.

#### 4. Discussion

Both modifications can be described as derivatives of the elpasolite-structure  $\text{A}_2\text{BMX}_6$ :  $\text{AX}_3$  layers with octahedral holes, partially filled with B and M are stacked with the motif of cubic close-packing along the space-diagonal of the cubic unit cell. In the compounds  $\text{A}_3\text{MCl}_6$  A- and B-ions are identical. In the  $\text{Cs}_3\text{NdCl}_6$ -type the stacking axis is the orthorhombic c-axis, in  $\text{Cs}_3\text{BiCl}_6$  it is standing perpendicular to the rectangular bc-plane, the monoclinic a-axis forms an angle of about  $10^\circ$  with this axis. To characterize the different mutal

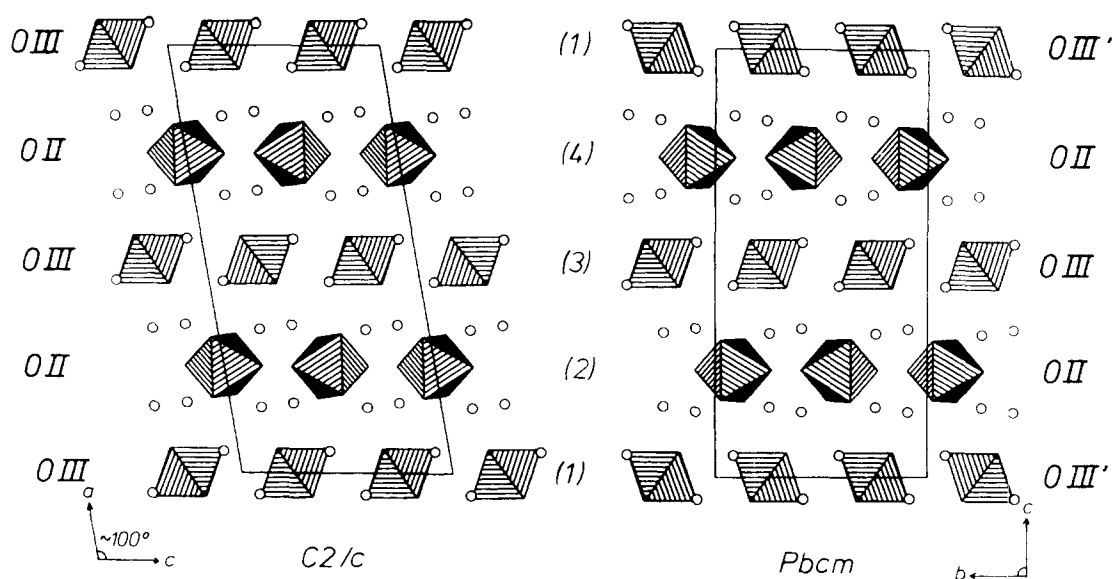


Fig. 1. Projections of layer sequences to the bc-planes.

orientations of the octahedra in the two modifications. A description given by Benachenhou et al. [2] is used:  $MX_6$  octahedra are considered as entities either orientated in the packing direction with their threefold (O III) or with their twofold symmetry axis (O II). As Fig. 1 shows each layer consists of only one type of octahedra; layers of O III and O II alternate. It should be pointed out, that in the cubic elpasolite structure /S.G.  $Fm\bar{3}m$  / only O III layers exist.

Neglecting the monoclinic inclination of the  $a$ -axis in  $C2/c$ , for both modifications the layers (2), (3) and (4) are identical. However, in  $Pbcm$  the octahedra in (1) are rotated  $180^\circ/6=30^\circ$  around the stacking axis; they are denoted as O III. (An easier description, used by Mattfeld and Meyer [5] cannot describe this differences, as discussed by Frenzen and Reuter [6])

The thermodynamic measurements have revealed, that the  $Pbcm$ -modification is the more stable one at ambient temperature. The transformation to the  $Cs_3BiCl_6$  structure is an endothermic process, which is strongly kinetical hindered. It occurs only after a long time of annealing. Using the heating rate of DTA-about  $1\text{ Kmin}^{-1}$  after a certain degree of overheating a direct transition to the stable high temperature mod-

ification, crystallizing in the space group  $Fm\bar{3}m$ , takes place at about  $400^\circ\text{C}$ .

Our actual knowledge about compounds  $A_3MCl_6$  ( $A=\text{Cs,Rb,K}$ ) is as follows:

1. All compounds are forming cubic high temperature modifications with the elpasolite structure.
2. All Cs and Rb compounds of the lanthanoids crystallize with the  $Cs_3BiCl_6$ , the potassium compounds with the  $K_3MoCl_6$  structure.
3. For compounds  $Cs_3LnCl_6$  from Nd to Yb (Lu?) at temperatures below  $90^\circ\text{C}$  the orthorhombic modification in  $Pbcm$  is stable.
4. Compounds  $Cs_3MCl_6$  with  $M=\text{Mo}$  [15]; Fe and V crystallize with the  $Cs_3CrCl_6$  structure ( $Pnmm$ ) [16], while  $Cs_3TiCl_6$  belongs to the  $Cs_3BiCl_6$  type. The Rb and K compounds of these transition elements have the  $K_3MoCl_6$  structure.

### Acknowledgements

Support from the Deutsche Forschungsgemeinschaft (DFG) and the Fonds der Chemischen Industrie is gratefully acknowledged.

**References**

- [1] H.J. Seifert, H. Fink and B. Baumgartner, *J. Solid State Chem.*, 106 (1993) 19.
- [2] F. Benachenhou, G. Mairesse, G. Nowogrocki and D. Thomas, *J. Solid State Chem.*, 65 (1986) 13.
- [3] S. Mitra, J. Uebach and H.J. Seifert, *J. Solid State Chem.*, 115 (1995) 484.
- [4] H.J. Seifert and R. Krämer, *Z. allg. anorg. Chem.*, 620 (1994) 1543.
- [5] H. Mattfeld and G. Meyer, *Z. allg. anorg. Chem.*, 618 (1992) 13.
- [6] G. Reuter and G. Frenzen, *J. Solid State Chem.*, 116 (1995) 329.
- [7] H. Fink, PROFIL, Program for data collection and analysis of X-ray powder patterns, Univ. Kassel (1983).
- [8] K. Yvon, W. Jeitschko and E. Parthe, *J. Appl. Crystallogr.*, 10 (1977) 73.
- [9] E. Keller, SCHAKAL 92, Program for graphic presentation of crystal structures, Univ. Freiburg (1993).
- [10] J. Warczewski and P.M. De Wolff, *J. Appl. Crystallogr.*, 7 (1974) 585.
- [11] H.J. Seifert and G. Thiel, *Thermochim. Acta*, 22 (1978) 363.
- [12] S. Sunner and I. Wadsö, *Acta Chem. Scand.*, 13 (1969) 97.
- [13] G. Reuter, J. Sebastian and G. Frenzen, *Acta Crystallogr.*, C52 (1996) 1859.
- [14] A. Bellanca, *Period. Mineral.*, 17 (1948) 59.
- [15] F. Beier and H.J. Seifert, *J. Therm. Anal.* (1997) in press.
- [16] M. Prien and H.J. Seifert, *J. Thermal Anal.*, 45 (1995) 349.