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Thermochemical investigations on chloro-elpasolites of lanthanum[1]

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Abstract

Elpasolites A_2BLaCl_6 with alkali metal chlorides (LiCl excepted) have been prepared from the melts. They are $Cs_2RbLaCl_6$ (dimorphous), Cs_2KLaCl_6 (trimorphous), $Cs_2NaLaCl_6$ and Rb_2KLaCl_6 which is stable only at $T \geqslant 748\,K$. According to X-ray diffraction measurements of crystal powders all compounds have modifications with the cubic elpasolite structure, space group $Fm3m$. The room-temperature modification of Cs_2KLaCl_6 is slightly distorted to a tetragonal structure (subgroup $P4/mnc$), while low-temperature $Cs_2RbLaCl_6$ is more strongly distorted to a monoclinic modification (Cs_3BiCl_6 type; subgroup $C2/c$). The transition enthalpies are 0.92 kJ mol^{-1} and 5.79 kJ mol^{-1}, respectively. The enthalpies for the formation from the binary components ACl, BCl and $LaCl_3$ reveal that $Cs_2NaLaCl_6$ is the compound formed with the greatest gain in lattice enthalpy. This correlates with the fact, that its "tolerance factor", derived by Babel from the perovskites, is next to 1.0.

INTRODUCTION

Our investigations of systems $ACl/LnCl_3$ (A is Na–Cs, Ln is La–Gd) during the last few years have revealed that dimorphic compounds A_3LnCl_6 exist in all systems in which A is Cs, Rb and most systems in which A is K; the high-temperature modifications (≥400°C) crystallize with a cubic elpasolite-like structure and the low temperature phases with the distorted arrangements of the monoclinic Cs_3BiCl_6 and K_3MoCl_3 type structure [1]. It could be shown by solution calorimetry and e.m.f. versus T measurements, that all these compounds with isolated $LnCl_6^{3-}$ octahedra are stable at temperatures higher than 0 K: they are formed with a loss of (lattice) enthalpy from the compounds adjacent in the phase diagrams (mostly ACl and A_2LnCl_5) and also from the binary parent compounds ACl and $LnCl_3$. (We have previously demonstrated this feature for Cs compounds [2].)

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[1] Dedicated to Hans Georg Wiedemann.

In heating-experiments the compounds are formed according to the equation

$$ACl + A_2LnCl_5 = A_3LnCl_6,$$

when in the Gibbs–Helmholtz relation $\Delta G = \Delta H - T\Delta S$ the endothermic reaction enthalpy

$$\Delta H = \Delta H(A_3LnCl_6) - [\Delta H(ACl) + \Delta H(A_2LaCl_5)]$$

is compensated by a sufficiently high $T\Delta S$ term, so that $\Delta G \leqslant 0$.

Genuine halogeno elpasolites of lanthanides are compounds A_2BLnCl_6 where A and B are alkali metals, with $r(A^+) > r(B^+)$. Their structure is related to the perovskite structure: if we write for $AMCl_3$ the doubled formula $A_2M_2Cl_6$ and replace the two M^{2+} ions by B^+ and M^{3+} we have constructed an elpasolite. In the ideal elpasolite structure with space group *Fm*3*m* a closest packed arrangement of $[ACl_3]$ layers exists, in which all octahedral holes, formed only by Cl^- ions, are occupied by B^+ and M^{3+} ions. So the larger A^+ ions have a coordination number (CN) of 12 and the smaller B^+ and M^{3+} ions have CN 6. This arrangement should be more favourable than that for the "pseudo-elpasolites" $(A_2A)LnCl_6$ with A the same as B. The question is, whether this geometric factor is sufficient to generate compounds which are stable also at 0 K, or in other words, which exist by a gain in lattice enthalpy and not by a high reaction entropy.

A synopsis of halogeno-elpasolites of lanthanides and rare earth elements was given by Meyer [3], who has himself prepared and determined the structures of $Cs_2LiLaCl_6$ and $CsRbNaLaCl_6$. Two other chlorolanthanides are now known $Cs_2NaLaCl_6$ [4] and Cs_2KLaCl_6 [5].

EXPERIMENTAL

Preparation of compounds

Anhydrous $LaCl_3$ was prepared from $LaCl_3 \cdot xH_2O$, treated in a vacuum oven at 60°C by heating in an HCl stream for one day, raising the temperature slowly from 100°C to 700°C and subsequently cooling in an argon stream. The hydrate was obtained from a solution of La_2O_3 (p.A., Fa. Merck) in hydrochloric acid; the alkaline chlorides (Merck, p.A.) were dried in an HCl stream at 500°C. The quaternary chlorides were obtained by melting adequate mixtures in vacuum-sealed quartz ampoules using a gas flame. The melt was homogenized by shaking and solidified by rapid cooling. It is not possible to prepare La-elpasolites from aqueous solutions.

Differential thermal analysis

The laboratory-built DTA device has already been described [6]. The samples (about 0.5 g) were prepared in the same way as described for the quaternary chlorides. The solids thus obtained were sufficiently homogeneous for the measurement of heating curves and for annealing experiments. Thermal effects could be detected down to 0.2 J for the generally used heating rate of 2 K min^{-1}.

X-Ray diffraction

Powder patterns at room temperature were taken with a Philips PW 1050/25 goniometer equipped with a proportional counter and a vacuum attachment. During exposure (Cu Kα radiation) the samples were under helium atmosphere. An Enraf–Nonius-553 Simon–Guinier camera was used for photographs at continuously varying temperatures. The samples were encapsulated in quartz tubes of 0.3 mm diameter. For the determination of cell dimensions, some Al_2O_3 was added to the samples as an internal standard; the calculations were carried through with the least-squares computer program of Warczewski and De Wolff [7] for the various temperatures. All other calculations were done with the LAZY PULVERIX program [8].

Solution calorimetry

The apparatus used was a laboratory-built isoperibolic calorimeter [9] with a volume of 1.3 l. Samples of 3–6 g thus yielded virtually ideal solutions (dissolution ratio 1:3500 mol). Each ΔH was measured at least three times; the alkaline chlorides were dissolved in a solution of $LaCl_3$ of adequate concentration.

Differential scanning calorimetry

The transition enthalpies were measured with the DSC 7 Perkin Elmer apparatus (12–20 mg substance in sealed aluminium crucibles). The temperature range was ($T_{trans.}$ ± 25) K, the heating/cooling rate 10 K min^{-1}. The proportionality factor $K = \Delta H_{lit.}/\Delta H_{exp.}$ was determined with $\Delta H_{lit.}$/kJ mol^{-1} for In = 3.283 ± 0.013; Sn = 7.138 ± 0.028; Pb = 4.78 ± 0.01; Zn =

TABLE 1

Temperatures of phase transition

$Cs_2NaLaCl_6$					phase I	$\xrightarrow[(757°C)]{930\text{ K}}$	melt
Cs_2KLaCl_6	phase III	$\xrightarrow[(-97°C)]{176\text{ K}}$	phase II	$\xrightarrow[(81°C)]{354\text{ K}}$	phase I	$\xrightarrow[(703°C)]{976\text{ K}}$	melt
$Cs_2RbLaCl_6$			phase II	$\xrightarrow[(336°C)]{609\text{ K}}$	phase I	$\xrightarrow[(750°C)]{1023\text{ K}}$	melt
Rb_2KLaCl_6			mixed crystals	$\xrightarrow[(475°C)]{748\text{ K}}$	phase I	$\xrightarrow[(655°C)]{928\text{ K}}$	melt

7.026 ± 0.040. The temperature dependence of K yielded a regression line $K(\vartheta) = 5.349 \times 10^{-5}\vartheta + 1.0679$.

RESULTS OF DIFFERENTIAL THERMAL ANALYSIS (DTA) AND X-RAY DIFFRACTION (XRD)

DTA measurements, controlled by XRD investigations with crystal powders, revealed that with Cs, Rb, K and Na, four quaternary chlorides of the elpasolite group exist: $Cs_2NaLaCl_6$, Cs_2KLaCl_6, $Cs_2RbLaCl_6$ and Rb_2KLaCl_6.

The compounds $Cs_2RbLaCl_6$ and Cs_2KLaCl_6 are polymorphic. In Table 1 the temperatures of the phase transitions determined from DTA heating curves are compiled. Rb_2KLaCl_6 is stable at temperatures higher than 748 K. Below this temperature mixed crystals between $Rb_{2-x}K_xLaCl_5$ and $Rb_xK_{1-x}Cl$ exist with $x = 0.66$ at the special composition of the decomposition product. When heating a sample quenched from the melt, in addition to the formation reaction at 748 K the melt peak of Rb_2LaCl_5 at 892 K [10] is to be seen. It disappears after annealing the sample for some hours at about 900 K (Fig. 1). Elpasolites in which A is Rb, K and B is Na could not be detected.

All phases I (these are the Cs_2Na and Rb_2K compounds and the high-temperature phases of the Cs_2K and Cs_2Rb elpasolites) crystallize in the space group $Fm3m$ (Table 2); they are members of the cubic face-centred aristotype of the elpasolite family (in the literature a values of 1099.23 pm are given for $Cs_2NaLaCl_6$ [4] and 1137.9 pm for Cs_2KLaCl_6 [5]). Cs_2KLaCl_6 transforms below 81°C to a tetrahedrally distorted modification. (It is important to use samples quenched from the melt and then annealed, because the compound melts incongruently.) Intensity calculations (Fig. 2) revealed that the most probable space group is $P4/mnc$; we had already found this structure for the mean-temperature modification of $K_2NaCrCl_6$ [11]. The distortion is the same as for the mean-temperature phase II of K_2SnCl_6 [12]: HK_2SnCl_6 crystallizes with the K_2PtCl_6 structure ($Fm3m$); in

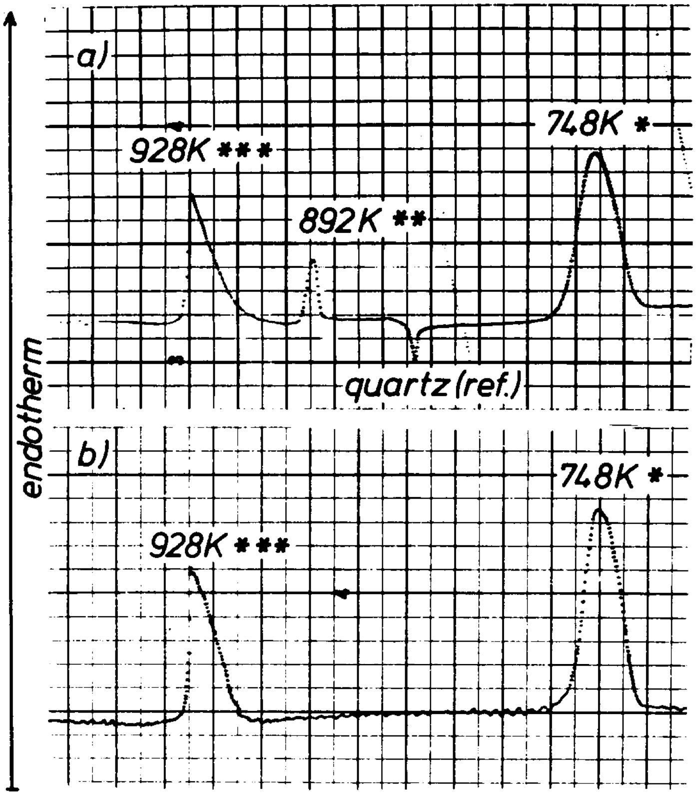

Fig. 1. DTA traces for Rb_2KLaCl_6 (heating curves): (a) quenched sample; (b) annealed sample. *, Transition phase II → phase i; **, melting point of Rb_2LaCl_5; ***, melting point of Rb_2KLaCl_6.

TABLE 2

Crystal structures

Compound	Temp. of exposure/K	Space group	a/pm	b/pm	c/pm	β/deg	V/cm^3 mol^{-1}
(a) Phases I with the cubic elpasolite structure							
$Cs_2NaLaCl_6$	298	$Fm3m$	1099.5(2)				200.1
Cs_2KLaCl_6	400	$Fm3m$	1139.7(5)				222.9
$Cs_2RbLaCl_6$	670	$Fm3m$	1155.9(5)				232.5
Rb_2KLaCl_6	770	$Fm3m$	1122.6(5)				213.0
Cs_3LaCl_6 [10]	720	$Fm3m$	1179.4(2)				247.0
Rb_3LaCl_6 [10]	820	$Fm3m$	1153.2(1)				230.9
(b) Phases II with distorted arrangements							
Cs_2KLaCl_6	298	$P4/mnc$	802.4(7)		1139.4(9)		220.9
$Cs_2RbLaCl_6$	298	$C2/c$	2693.8(7)	791.8(3)	1371.4(3)	99.76(3)	217.0
Cs_3LaCl_6 [1]	298	$C2/c$	2728.6(5)	829.06(2)	1330.46(2)	99.64(2)	223.4
Rb_3LaCl_6 [1]	298	$C2/c$	2617.1(9)	821.9(3)	1283.2(4)	96.49(3)	206.5

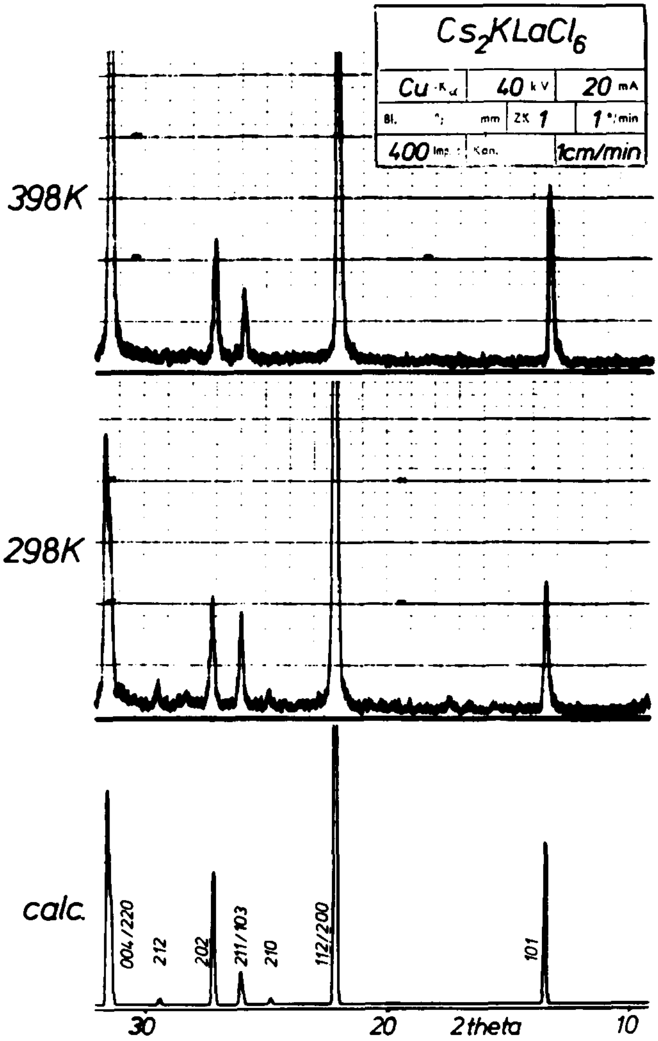

Fig. 2. XRD powder patterns of Cs_2KLaCl_6 at 398 K (phase I) and 298 K (phase II).

phase II (sub-group *P*4/*mnc*) the $[MCl_6]$ octahedra show an alternating rotation in layers perpendicular to the *c* axis. The space group *P*4/*nbm* which Meyer and Dietzel [13] had found for $Rb_2NaTmCl_6$ and also for $CsRbNaLaCl_6$ could be excluded, because in this arrangement (which involves additionally a small removal of the A ions from their ideal sites) the two small reflexes of Cs_2KLaCl_6 at $2\vartheta = 24.8°$ and 29.4° must have the intensity zero.

The room temperature modification of $Cs_2RbLaCl_6$ crystallizes with the Cs_3BiCl_6 structure [14] as do Cs_3LaCl_6 and metastable Rb_3LaCl_6 which can be obtained by quenching the cubic high-temperature modification [1]; their lattice constants are included in Table 2.

THERMODYNAMIC PROPERTIES

Solution enthalpies of all compounds stable at ambient temperature (these are all compounds containing Cs) were measured. With the solution enthalpies of $LaCl_3$ (-134.6 ± 0.6 kJ mol^{-1}) and of the alkali metal chlorides CsCl (18.1 ± 0.2 kJ mol^{-1}), RbCl (17.7 ± 0.1 kJ mol^{-1}), KCl (18.1 ± 0.1 kJ mol^{-1}) and NaCl (4.5 ± 0.1 kJ mol^{-1}), all taken from ref. 10, enthalpies $\Delta_r H^{\ominus}_{298}$ for the reactions

$$2ACl + BCl + LaCl_3 = A_2BLaCl_6$$

were calculated. They are compiled together with enthalpies $\Delta_{r'} H^{\ominus}_{298}$ for

$$A_2LaCl_5 + BCl = A_2BLaCl_6$$

in Table 3. The solution enthalpy of Cs_2LaCl_5 is -65.1 kJ mol^{-1} [10]. For $Cs_2NaLaCl_6$ only one measurement of solution enthalpy has been reported; Morss [15] found a value of -83.1 kJ mol^{-1} which is somewhat higher than our result of -79.8 kJ mol^{-1}.

In the last column of Table 3 transition enthalpies at the transition temperatures, found by DSC measurements, are given. For the formation of Rb_2KLaCl_6 at 748 K an endothermic enthalpy of 49 ± 1 kJ mol^{-1} was found.

DISCUSSION OF THE RESULTS

Babel et al. [16] have shown that in analogy to perovskites AMX_3 for elpasolites a tolerance factor t' can be defined, which becomes 1.0 when all ions are in direct contact with the adjacent ions. One has to take the mean $(r(B) + r(M))/2$ instead of $r(M)$ for perovskites. For the chloro-elpasolites

TABLE 3

Thermodynamic properties (in kJ mol^{-1}) of lanthanum-chloro-elpasolites

Compound	$\Delta_l H^{\ominus}_{298}$ [a]	$\Delta_r H^{\ominus}_{298}$ [b]	$\Delta_{r'} H^{\ominus}_{298}$ [c]	$\Delta_{tr} H^{\ominus}_{Tu}$ [d]
$Cs_2NaLaCl_6$	−79.8(5)	−14.1	+10.9	
Cs_2KLaCl_6 II	−75.2(2)	−5.2	+28.1	0.92(2)
$Cs_2RbLaCl_6$ II	−71.5(1.3)	−9.2	+24.1	5.79(3)
Cs_3LaCl_6	−65.5(8)	−14.8	+18.5	7.84(6)
Rb_3LaCl_6	–	+19.0 [e]	+50.4 [e]	

[a] Solution enthalpy.

[b] Reaction enthalpy for the formation from $ACl + BCl + LaCl_3$.

[c] Reaction enthalpy for the formation from A_2LaCl_5 and BCl.

[d] Transition enthalpy at T_{tr}.

[e] Values from e.m.f. measurements [10].

TABLE 4

Tolerance factors and increase of the molar volumes

Compound	t'	Structure at $T = 298$ K	$\Delta V_m/\mathrm{cm^3\,mol^{-1}}$
$Cs_2NaLaCl_6$	0.92	Cubic	+4.7
Cs_2KLaCl_6	0.87	Tetragonal	+15.2
$Cs_2RbLaCl_6$	0.85	Monoclinic	+6.3
Rb_2KLaCl_6	0.83	–	(+27.5)
"$Cs_2CsLaCl_6$"	0.82	Monoclinic	+2.6
"$Rb_2RbLaCl_6$"	0.81	–	(+16.0)

of lanthanum this factor is

$$t' = \frac{\sqrt{2}\,(r(\mathrm{A}^+) + r(\mathrm{Cl}^-))}{r(\mathrm{B}^+) + r(\mathrm{La}^{3+}) + 2r(\mathrm{Cl}^-)}$$

Using Shannon radii [17] for the CN 6 for La^{3+} (1.06 Å) and the B^+ ions, and those for the CN 12 for A^+ ions, one obtains the values given in Table 4 ($r(\mathrm{Cl}^-) = 1.81$ Å).

With decreasing values of t' we find an enlarged distortion of the ideal elpasolite structure. With $t' = 0.85$ the monoclinic Cs_3BiCl_6 type results, in which the MCl_6 octahedra show a rotation around all three space axes, so that CN becomes 11 for A^+ and 8 for B^+. The transition to the cubic high-temperature modification needs 5.8 kJ mol^{-1} while the enthalpy for the transition of the slightly tetragonally distorted Cs_2KLaCl_6 is only 0.9 kJ mol^{-1}.

The compounds Rb_2KLaCl_6 and Rb_3LaCl_6 are stable only at temperatures higher than about 450°C. They crystallize with the cubic structure as do the other high-temperature modifications. This can be explained by the fact that the A^+ ions in the large dodecahedral sites get a higher thermal motion than the smaller B^+ ions in octahedral surroundings. Thus, the "effective" t' is enlarged in direction to 1.0.

It is an interesting question as to whether t' can become equal to or greater than 1.0, so that hexagonal elpasolites result. According to Meyer and Gaebell [18] this is the case if $r(\mathrm{M}^{3+}) \leqslant r(\mathrm{Lu}^{3+})$ and $\mathrm{B} = \mathrm{Li}^+$ (e.g. $Cs_2LiLuCl_6$, Cs_2LiVCl_6). However, $Cs_2LiLaCl_6$ with $t' = 0.96$ has the cubic structure.

The formation enthalpies $\Delta_r H^{\ominus}_{298}$ for the formation from ($2\mathrm{ACl} + \mathrm{BCl} + \mathrm{LaCl_3}$) are negative for all compounds which are stable at 298 K, Cs_3LaCl_6 included, though they all are formed with an increase in molar volume (Table 4)

$$\Delta V_m = V_m(\mathrm{exp.}) - \sum V_m(\mathrm{comp.})$$

where V_m(exp.) is taken from the X-ray measurements (Table 3) and $\sum V_m$(comp.) is the sum of the molar volumes of $LaCl_3$ (63.6 $cm^3 mol^{-1}$ [19]) and the alkali metal chlorides; for CsCl the cubic face-centred structure with 52.4 $cm^3 mol^{-1}$ was taken.

Related to the formation from A_2LaCl_5 and BCl, all reaction enthalpies are positive. These $\Delta_{r'}H^{\ominus}_{298}$ values are identical with the difference in lattice enthalpies of the elpasolite and (A_2LaCl_5 + BCl). If the compounds are "thermodynamically stable" their $\Delta_{r'}G^{\ominus}$ values must be negative due to a gain in entropy. As pointed out before, the energy term $|T\Delta_r S^{\ominus}|$ must be greater than $\Delta_{r'}H^{\ominus}$. For Rb_3LaCl_6 this is the case at 717 K. For Cs_3LaCl_6 we have recently found [1] that this temperature is 462 K (198°C), so that the compound is only metastable at room temperature. Because the $\Delta_{r'}H^{\ominus}_{298}$ values for the "real elpasolites" are of the same magnitude this conclusion should also hold for them. All chloro-elpasolites of lanthanum are phases which are unstable at least at 0 K against the decomposition to A_2LaCl_5 and BCl! A significant difference from the pseudo-elpasolites A_3LaCl_6 does not exist.

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