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Thermochemical and Structural Investigations on the Systems $NaCl/TbCl_3$ and $NaCl/DyCl_3$†

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The pseudobinary systems $NaCl/TbCl_3$ and $NaCl/DyCl_3$ were investigated by DTA and X-ray diffraction. Three incongruently melting compounds exist in both systems: $NaLn_2Cl_7$ (KDy_2Cl_7 structure), $NaLnCl_4$ ($NaGdCl_4$ structure) and dimorphic Na_3LnCl_6. Additionally, a compound Na_2TbCl_5 (K_2PrCl_5 structure) was found in the system with terbium chloride. The high-temperature compounds H-Na_3LnCl_6 have the cryolite structure, the low-temperature compounds L-Na_3LnCl_6 crystallize in the 'stuffed $LiSbF_6$'-type. The analogous Eu- and Gd-compounds are stable only at higher temperature in the cryolite structure, the '$LiSbF_6$' phases can be obtained metastable by quenching. By solution calorimetry and EMF vs. T measurements in galvanic cells for solid electrolytes the enthalpies ΔH° and free enthalpies ΔG° for the formation of the ternary chlorides from the compounds adjacent in the systems were determined. Most stable are the $NaLnCl_4$ compounds.

In the literature some partial aspects of the two systems $NaCl/TbCl_3$[1] and $NaCl/DyCl_3$[2] are described. These phase diagrams were investigated in 1965–66. Two incongruently melting compounds were found, respectively: Na_3LnCl_6 and $NaTb_2Cl_7/NaDy_3Cl_{10}$. Structural information about the 3:1 compounds, based on single-crystal X-ray diffraction, were given by Meyer.[3] According to his findings Na_3TbCl_6 has a trigonal unit cell like Na_3EuCl_6 and Na_3GdCl_6 at ambient temperature (stuffed $LiSbF_6$-type), while Na_3DyCl_6 is isotypic to Na_3ErCl_6 (monoclinic cryolite structure).

We ourselves investigated the systems $NaCl/EuCl_3$[4] and $NaCl/GdCl_3$[5] and found that both systems contain three compounds: $NaLnCl_4$, Na_2LnCl_5 and Na_3LnCl_6. In the system with $GdCl_3$ a fourth compound, $NaGd_2Cl_7$, exists only in a small temperature range (393–422 °C). Na_3EuCl_6 is stable above 388 °C, but could be quenched to a phase with the stuffed $LiSbF_6$ structure. Na_3GdCl_6 exhibits two modifications: above 265 °C a stable phase with the cryolite structure exists. On cooling it to ambient temperature the trigonal structure is formed; however, it is a metastable phase which decomposes exothermically (!) at ca. 210 °C to a mixture of NaCl and Na_2GdCl_5.

In this paper the results of a reinvestigation of the systems $NaCl/TbCl_3$ and $NaCl/DyCl_3$ are given. Two issues should be elucidated: (1) Do the compounds $NaLnCl_4$ and Na_2LnCl_5 exist additionally to the findings of Korshunov and Drobot?[1,2] (2) What are the structural features of the compounds Na_3LnCl_6, and which correlations to the analogous Eu- and Gd-compounds exist?

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Experimental

$TbCl_3$ and $DyCl_3$ were prepared by dehydrating their hexahydrates (99.9% Fa. Heraeus, Hanau) in an HCl stream. Precautions must be taken into account to avoid the formation of oxychlorides (details are given in papers about the systems $ACl/TbCl_3$[6] and $ACl/DyCl_3$[7] with A = Cs, Rb, K). NaCl was dried by heating to 500 °C.

The samples for DTA were prepared by melting adequate mixtures (ca. 0.5 g) in vacuum-sealed quartz ampoules with a gas flame. The melt was homogenized by shaking and solidified by rapid cooling. The ampoules thus prepared could be used directly or after annealing at selected temperatures. The home-built devices for DTA[8] and solution calorimetry[9] have been described previously.

For the determination of the (Gibbs) enthalpies of formation of each compound from NaCl and the next, $LnCl_3$-richer, neighbour compound in the system, a galvanic cell for solid electrolytes was used. The set-up for the $LnCl_3$-richest compound ($Na_{0.5}LnCl_{3.5}$) was: (graphite + Cl_2)|NaCl|Na^+ conducting diaphragm|$LnCl_3$ (+ $Na_{0.5}LnCl_{3.5}$) | (graphite + Cl_2). The diaphragm was prepared according to a formula developed by Østvold in

Trondheim.[10] It could be used for temperatures higher than ca. 280 °C. A detailed description of the whole cell is given in Ref. 11.

Results

Phase diagrams and crystal structures. Fig. 1 illustrates the results of the DTA measurements. The lattice parameters of the existing compounds are given in Table 1.

As described earlier, both binary lanthanide chlorides reveal a phase transition near 350 °C: $TbCl_3$[6] from the UCl_3 to the $PuBr_3$ structure, $DyCl_3$[7] from the $PuBr_3$ to the $AlCl_3$ structure. The findings of Korshunov and Drobot[1,2] concerning the compounds $NaLn_2Cl_7$ and $NaDy_2Cl_7$ could be confirmed. They crystallize with the monoclinic KDy_2Cl_7 structure,[12] the coordination number (CN) of the Ln^{3+} ions to chloride is 7. The compounds Na_3LnCl_6 have well reversible phase transitions at 153 °C (Na_3TbCl_6) and ca. 120 °C (Na_3DyCl_6). This is demonstrated in Fig. 2: a sample of Na_3TbCl_6 was measured in several cycles at ambient temperature and at ca. 160 °C. H-Na_3LnCl_6 has the monoclinic cryolite structure, L-Na_3LnCl_6 the trigonal 'stuffed $LiSbF_6$'-structure. In both structure types the Ln^{3+} ions have octahedral surroundings (CN 6).

Additional to the older results, incongruently melting compounds $NaLnCl_4$ were found, which are isotypic to $NaGdCl_4$[13] (triclinic space group $P\bar{1}$). The CN of Ln^{3+} is 7.

The compound Na_2TbCl_5 could not be detected by DTA alone, because the formation during cooling is suppressed in the timescale of DTA (2 K min^{-1}) by kinetic hindrance. Evidence for this was provided by EMF measurements (Fig. 3), where the timescale is much greater: the EMF vs. T curves were measured in steps of 7 K; the time for each step was ca. 8 h. After having annealed a 2:1 sample for two weeks at ca. 300 °C, an endothermic effect in the heating curve was found at 345 °C. EMF measurements and annealing experiments in the system $NaCl/DyCl_3$ gave no evidence for the existence of an analogous compound. Na_2TbCl_5 has the orthorhombic K_2PrCl_5/Y_2HfS_5 structure,[14] the CN for Tb^{3+} is 7.

Solution calorimetry. The isoperibolic solution calorimeter had a volume of 1.3 l. Samples of 3–6 g thus yielded virtually ideal solutions (dissolution ratio 1:3500 mol). The $\Delta_{sol}H°_{298}$-values in Table 2 are always the mean of three measurements. The range of error was ± 0.5 kJ mol^{-1}. The enthalpies $\Delta_f H°_{298}$ for the formation from NaCl and $LnCl_3$ were calculated with the equation

$$\Delta_f H° = \{n\Delta_{sol}H°(NaCl) + \Delta_{sol}H°(LnCl_3)\} - \Delta_{sol}H°(A_n LnCl_{3+n})$$

The solution enthalpies for the compounds L-$TbCl_3$ and L-$DyCl_3$ are in good agreement with values from the literature[15] (−186.9 to −192.5 for $TbCl_3$, ca. 198 for $DyCl_3$). The synproportionation enthalpies $\Delta_{syn}H°$ are exothermic only for the compounds $NaLnCl_4$; they are virtually zero for the formation of Na_2TbCl_5 from Na_3TbCl_6 and $NaTbCl_4$ and of Na_3DyCl_6 from NaCl and $NaDyCl_4$.

EMF measurements. EMF values were measured for the formation of each compound from NaCl and the adjacent $LnCl_3$-richer compound in a temperature range ca. 300–

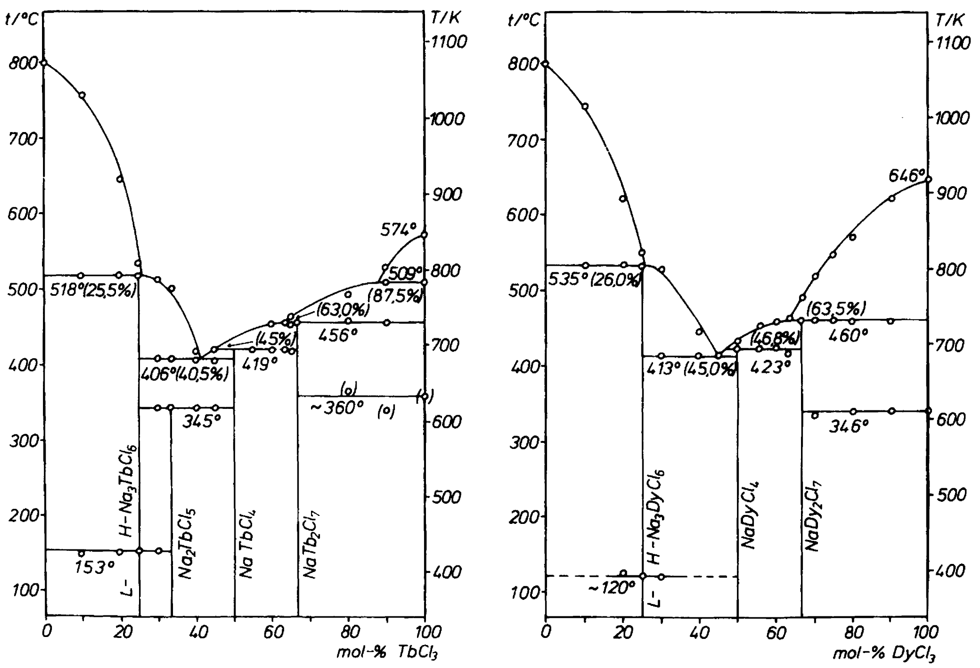

Fig. 1. Phase diagrams of the systems $NaCl/TbCl_3$ and $NaCl/DyCl_3$.

Table 1. Unit-cell parameters of ternary chlorides Na_nLnCl_{3+n} in pm.

$NaLn_2Cl_7$: KDy_2Cl_7-type (monoclinic; $P2_1/c$)						
$NaTb_2Cl_7$:	a=667.2;	b=1277.8;	c=1295.6;	β=90°		
$NaDy_2Cl_7$:	a=671.5;	b=1285.2;	c=1286.8;	β=90°		
$NaLnCl_4$: $NaGdCl_4$-type (triclinic; $P\bar{1}$)						
$NaTbCl_4$:	a=700.6;	b=672.3;	c=662.1;	α=100.2°	β=91.2°	γ=89.0°
$NaDyCl_4$:	a=699.1;	b=666.7;	c=662.7;	α=100.3°	β=91.0°	γ=89.7°
Na_2TbCl_5: K_2PrCl_5/Y_2HfS_5-type (orthorhombic; $Pnma$)						
	a=1201.0;	b=827.4;	c=764.3;			
H-Na_3LnCl_6: cryolite-type (monoclinic; $P2_1/n$)						
Na_3EuCl_6:	a=700.6;	b=731.7;	c=1035.3;	β=90.3°		
Na_3GdCl_6:	a=700.5;	b=735.9;	c=1035.6;	β=90.1°	(Meyer, 1987)	
Na_3TbCl_6:	a=689.1;	b=727.6;	c=1019.3;	β=90.2°	(Meyer, 1987)	
Na_3DyCl_6:	a=687.9;	b=720.8;	c=1017.5;	β=90.2°	(Meyer, 1987)	
L-Na_3LnCl_6: stuffed $LiSbF_6$-type (trigonal; $R\bar{3}$)						
Na_3EuCl_6:	a=701.8;		c=1882.5;		(Meyer, 1984)	
Na_3GdCl_6:	a=700.7;		c=1879.1;		(Meyer, 1984)	
Na_3TbCl_6:	a=698.7;		c=1872.5;			
Na_3DyCl_6:	a=697.4;		c=1868.7;			

400 °C. In this range the dependence of EMF on T was linear. Thus, the equations for the regression lines could be transformed by multiplication with $-nF$ to the Gibbs–Helmholtz equation $\Delta_r G° = \Delta_r H° - T\Delta_r S°$. By means of thermodynamic cycles these functions were transformed to those for the reactions nACl + $LnCl_3$ = A_nLnCl_{3+n}, denoted $\Delta_f G°$, $\Delta_f H°$ and $\Delta_f S°$, and further to the free enthalpies of synproportionation, $\Delta_S G°$, from the two neighbouring compounds. For high-temperature modifications the temperatures of formation (decomposition) were calculated by the condition $\Delta_S G° = 0$.

As an example a description for the evaluation of the measurements concerning the reaction 2NaCl + $NaTbCl_4$ = H-Na_3TbCl_6 is given. According to Fig. 1 it occurs in the temperature range 345–406 °C.

Two cycles gave the regression lines:

$$\text{EMF/mV} = -36.11 + 0.1372\ T/\text{K}$$
$$\text{EMF/mV} = -36.60 + 0.1413\ T/\text{K}$$

The mean regression line is

$$\text{EMF/mV} = -36.36 + 0.1393\ T/\text{K}.$$

By multiplication with $-nF$ ($n = 2$) the Gibbs–Helmholtz equation $\Delta_r G°/\text{kJ mol}^{-1} = 7.0 - 0.0269\ T/\text{K}$ was given [reaction (5) in Fig. 3].

In the following the Gibbs–Helmholtz equations for

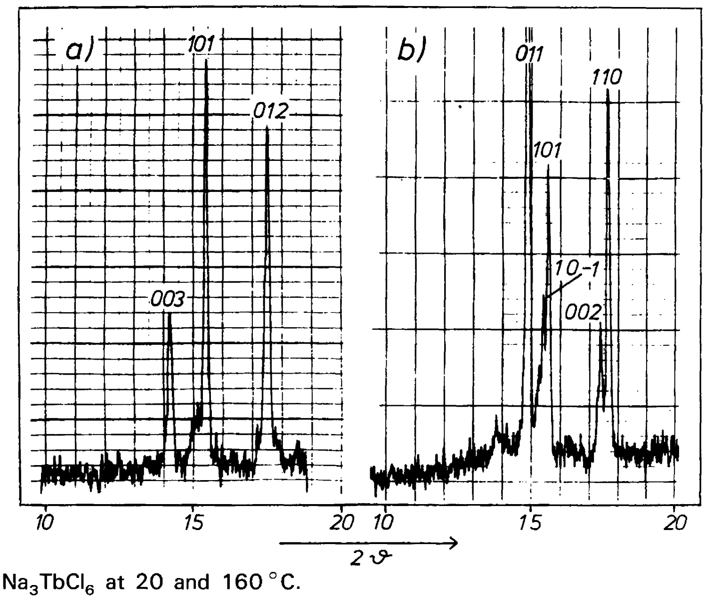

Fig. 2. X-Ray patterns for Na_3TbCl_6 at 20 and 160 °C.

Table 2. Enthalpy values (in kJ mol^{-1}) from solution calorimetry.[a]

		Tb	$\Delta_{syn}H^\circ$	Dy	$\Delta_{syn}H^\circ$
NaCl	$\Delta_{sol}H^\circ$	+4.5		+4.5	
Na_3LnCl_6	$\Delta_{sol}H^\circ$	−179.1	+1.6	−181.7	±0
	$\Delta_f H^\circ$	+3.8		−1.9	
Na_2LnCl_5	$\Delta_{sol}H^\circ$	−182.0	−0.1		
	$\Delta_f H^\circ$	+2.2			
$NaLnCl_4$	$\Delta_{sol}H^\circ$	−185.0	−4.4	−190.7	−4.7
	$\Delta_f H^\circ$	+0.7		−1.9	
0.5 $NaLn_2C_7$	$\Delta_{sol}H^\circ$	−193.1	+6.2	−198.8	+4.9
	$\Delta_f H^\circ$	+6.6		+4.0	
L-$LnCl_3$	$\Delta_{sol}H^\circ$	−188.8		−197.1	

[a] $\Delta_{sol}H^\circ$ = solution enthalpy; $\Delta_f H^\circ$ = formation enthalpy from *n*NaCl and $LnCl_3$; $\Delta_{syn}H^\circ$ = enthalpy of synproportionation from the neighboured compounds.

the reactions in the cell and for the formation from ACl and $LnCl_3$ are listed, together with the temperature ranges of the measurements. The range of error was smaller than ±1 kJ mol^{-1} for the energy values and ±0.8 J K^{-1} mol^{-1} for the entropies.

System NaCl/TbCl₃

$0.5\ NaCl + H\text{-}TbCl_3 = Na_{0.5}TbCl_{3.5}$ (290–400 °C) (1)

$\Delta_r G^\circ/\text{kJ mol}^{-1} = 6.1 - 0.0213\ T/\text{K}$
id. $\Delta_f G^\circ$

$0.5\ NaCl + Na_{0.5}TbCl_{3.5} = NaTbCl_4$ (310–410 °C) (2)

$\Delta_r G^\circ/\text{kJ mol}^{-1} = -4.9$
$\Delta_f G^\circ/\text{kJ mol}^{-1} = 1.2 - 0.0213\ T/\text{K}$

$NaCl + NaTbCl_4 = Na_2TbCl_5$ (290–320 °C) (3)

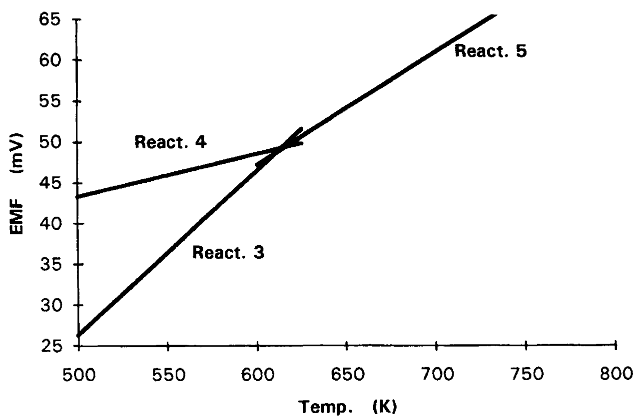

Fig. 3. EMF vs. *T* curves for the reactions (3)–(5) in the system NaCl/$TbCl_3$.

$\Delta_r G^\circ/\text{kJ mol}^{-1} = -1.6 - 0.0051\ T/\text{K}$
$\Delta_f G^\circ/\text{kJ mol}^{-1} = -0.4 - 0.0264\ T/\text{K}$

$NaCl + Na_2TbCl_5 = H\text{-}Na_3TbCl_6$ (290–330 °C) (4)

$\Delta_r G^\circ/\text{kJ mol}^{-1} = 7.2 - 0.0195\ T/\text{K}$
$\Delta_f G^\circ/\text{kJ mol}^{-1} = 6.8 - 0.0459\ T/\text{K}$

$2\ NaCl + NaTbCl_4 = H\text{-}Na_3TbCl_6$ (330–400 °C) (5)

$\Delta_r G^\circ/\text{kJ mol}^{-1} = 7.0 - 0.0269\ T/\text{K}$
$\Delta_f G^\circ/\text{kJ mol}^{-1} = 8.2 - 0.0482\ T/\text{K}$

The $\Delta_f G^\circ$-values from reactions (4) and (5) should be identical; the difference of 1.4 kJ mol^{-1} for $\Delta_f H^\circ$ and 2.3 J K^{-1} mol^{-1} for $\Delta_f S^\circ$ is caused by the uncertainity of the measurements. The temperature of decomposition for Na_2TbCl_5 is given by the conditions $\Delta_r G^\circ$ (3) = $\Delta_r G^\circ$ (5) and $\Delta_r G^\circ$ (4) = $\Delta_r G^\circ$ (5), respectively. The values are 615 and 611 K, which gives a mean of 613 K (340 °C). As expected from kinetic reasons,[16] it is somewhat lower than the value of 345 °C found from DTA heating curves.

System NaCl/DyCl₃

$0.5\ NaCl + H\text{-}DyCl_3 = Na_{0.5}DyCl_{3.5}$ (300–400 °C) (1)

$\Delta_r G^\circ/\text{kJ mol}^{-1} = -6.4 - 0.0025\ T/\text{K}$
id. $\Delta_f G^\circ$

$0.5\ NaCl + Na_{0.5}DyCl_{3.5} = NaDyCl_4$ (300–400 °C) (2)

$\Delta_r G^\circ/\text{kJ mol}^{-1} = -5.2$
$\Delta_f G^\circ/\text{kJ mol}^{-1} = -11.6 - 0.0025\ T/\text{K}$

$2NaCl + NaDyCl_4 = H\text{-}Na_3DyCl_6$ (310–400 °C) (3)

$\Delta_r G°/\text{kJ mol}^{-1} = 3.6 - 0.0257\ T/\text{K}$
$\Delta_f G°/\text{kJ mol}^{-1} = 8.0 - 0.0282\ T/\text{K}$

It must be pointed out that the EMF measurements relate to the modifications that are stable in the applied temperature range. Thus, $\Delta_f H°$-values from EMFs cannot be compared with the values from solution calorimetry found at ambient temperature. For that they had to be converted with the transformation enthalpies L-$LnCl_3$ to H-$LnCl_3$ and L-Na_3LnCl_6 to H-Na_3LnCl_6. These values are known with too poor a quality to justify such a conversion. The same considerations are valid for the calculation of the stability ranges from synproportionation enthalpies not very different from zero.

Discussion

Our hitherto existing results on systems $NaCl/LnCl_3$ have yielded the following general conclusions:

The systems from $LaCl_3$ to $SmCl_3$ are dominated by a more or less entended mixed crystal region between $LnCl_3$ and $Na_3Ln_5Cl_{18}$. The crystal structures of these phases were solved by single crystal measurements on $K_3La_5Cl_{18}$.[17]

Compounds Na_2LnCl_5, crystallizing with the K_2PrCl_5 structure, were found in the systems from Sm to Tb, not in the system $NaCl/DyCl_3$. The compounds with Ln = Sm, Eu, Gd melt incongruently at ca. 430 °C, Na_2TbCl_5 decomposes in the solid state at 340 °C.

The formation enthalpies $\Delta_f H°$ (formation from 2NaCl and $LnCl_3$) are endothermic. Gibbs enthalpies $\Delta_r G°$ for the reactions NaCl + $Na_3Sm_5Cl_{18}$[18] and NaCl + L-$NaEuCl_4$[4] yielded decomposition temperatures of ≥ 150 °C and 69 °C, respectively. For Na_2GdCl_5 no EMF measurements with L-$NaGdCl_4$ could be done. However, from solution calorimetry the enthalpy for the reaction NaCl + L-$NaGdCl_4$ = Na_2GdCl_5 is known. It is 3.0 kJ mol^{-1} less endothermic than for Na_2EuCl_5 (corrected value from Ref. 4 = 5.7 kJ mol^{-1}). Thus the range of stability should stretch to lower temperatures than for Na_2EuCl_5; the same is true for Na_2TbCl_5, with a $\Delta_{syn}H°$-value not significantly different from zero (Table 2).

Beginning with $NaEuCl_4$ these 1:1 compounds are the most stable in the systems. That is, the $\Delta_f H°$-values are identical with $\Delta_{syn}H°$. From EMF measurements on L-$NaEuCl_4$ $\Delta_f G°/\text{kJ mol}^{-1} = 5.1 - 0.0179\ T/\text{K}$ was obtained, which gives 285 K (12 °C) as the lowest temperature of stability. $\Delta_f H°$-values for the other compounds are 5.4 kJ mol^{-1} for $NaGdCl_4$, 0.7 for $NaTbCl_4$ and − 1.9 for $NaDyCl_4$. The last compound must be stable down to 0 K.

In the system $NaCl/GdCl_3$ a compound $NaGd_2Cl_7$ exists only in a small temperature range (393–422 °C). For the incongruently melting compounds $NaTb_2Cl_7$ and $NaDy_2Cl_7$ no decomposition could be detected by DTA. However, the relatively strong endothermic $\Delta_{syn}H°$-values in Table 2 indicate that the compounds can be stable only at temperatures where the loss of enthalpy is compensated by a sufficiently high gain in entropy the ($T\Delta S$-term).

Compounds Na_3TbCl_6 and Na_3DyCl_6 exist at temperatures higher than ca. 100 °C with the cryolite structure. Below this temperature they transform reversibly to the hexagonal stuffed '$LiSbF_6$'-type. Na_3GdCl_6[5] is stable only above 265 °C. It can be quenched to a metastable '$LiSbF_6$' phase, which decomposes exothermally when heated to ca. 210 °C. With this knowledge we had to correct our previous interpretation for the compound Na_3EuCl_6. It is stable above 388 °C. However, it does not crystallize with the hexagonal structure, which must be attached to a metastable phase, formed by quenching. This phase decomposes at ca. 180 °C to NaCl and Na_2EuCl_5. The structure of the stable high-temperature phase was determined by means of high-temperature Guinier photos; the cell parameters are given in Table 1.

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