Thermochemical and Structural Investigations on the Systems NaCl/TbCl₃ and NaCl/DyCl₃

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The pseudo-binary systems NaCl/TbCl₃ and NaCl/DyCl₃ were investigated by DTA and X-ray diffraction. Three incongruently melting compounds exist in both systems: Na₃LnCl₆ (KD₂Cl₂ structure), Na₄LnCl₆ (NaGdCl₆ structure) and di-morphic Na₅LnCl₆. Additionally, a compound Na₂TbCl₅ (K₂PrCl₅ structure) was found in the system with terbium chloride. The high-temperature compounds H-Na₃LnCl₆ have the cerystolite structure, the low-temperature compounds L-Na₃LnCl₆ crystallize in the 'stuffed LiSbF₆'-type. The analogous Eu- and Gd-compounds are stable only at higher temperature in the cerystolite structure, the 'LiSbF₆'-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 Na₅LnCl₆ compounds.

In the literature some partial aspects of the two systems NaCl/TbCl₃ and NaCl/DyCl₃ are described. These phase diagrams were investigated in 1965–66. Two incongruently melting compounds were found, respectively: Na₃LnCl₆ and Na₅Tr₂Cl₇/Na₅Dy₂Cl₇. Structural information about the 3:1 compounds, based on single-crystal X-ray diffraction, were given by Meyer. According to his findings Na₃TbCl₆ has a trigonal unit cell like Na₃EuCl₆ and Na₃GdCl₆ at ambient temperature (stuffed LiSbF₆-type), while Na₃DyCl₆ is isotypic to Na₃ErCl₆ (monoclinic cerystolite structure).

We ourselves investigated the systems NaCl/EuCl₃ and NaCl/GdCl₃ and found that both systems contain three compounds: Na₂LnCl₆, Na₃LnCl₆ and Na₅LnCl₆. In the system with GdCl₃ a fourth compound, Na₅GdCl₇, exists only in a small temperature range (393–422 °C). Na₃EuCl₆ is stable above 388 °C, but could be quenched to a phase with the stuffed LiSbF₆ structure. Na₃GdCl₆ exhibits two modifications: above 265 °C a stable phase with the cerystolite 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 Na₃GdCl₅.

In this paper the results of a reinvestigation of the systems NaCl/TbCl₃ and NaCl/DyCl₃ are given. Two issues should be elucidated: (1) Do the compounds Na₅LnCl₆ and Na₅LnCl₆ exist additionally to the findings of Korshunov and Drobot? (2) What are the structural features of the compounds Na₅LnCl₆, and which correlations to the analogous Eu- and Gd-compounds exist?

Experimental

TbCl₃ and DyCl₃ 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 ACI/TbCl₅ and ACI/DyCl₅ 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 and solution calorimetry have been described previously.

For the determination of the (Gibbs) enthalpies of formation of each compound from NaCl and the next, LnCl₃-richer, neighbour compound in the system, a galvanic cell for solid electrolytes was used. The set-up for the LnCl₃-richer compound (Na₃₀.₅LnCl₅) was: (graphite + Cl₂)|NaCl|Na⁺ conducting diaphragm|LnCl₃ (+ Na₃₀.₅LnCl₅) | (graphite + Cl₂). The diaphragm was prepared according to a formula developed by Østvold in

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Trondheim. 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: TbCl₃, from the UCl₃ to the PuBr₃ structure, DyCl₃, from the PuBr₃ to the AlCl₃ structure. The findings of Korshunov and Drobot concerning the compounds NaLn₂Cl₅ and NaLn₅Cl₇ could be confirmed. They crystallize with the monoclinic K₂DyCl₅ structure, the coordination number (CN) of the Ln³⁺ ions to chloride is 7. The compounds Na₃LnCl₆ have well reversible phase transitions at 153 °C (Na₃TbCl₆) and ca. 120 °C (Na₃DyCl₆). This is demonstrated in Fig. 2: a sample of Na₂TbCl₆ was measured in several cycles at ambient temperature and at ca. 160 °C. H-Na₃LnCl₆ has the monoclinic cryolite structure. L-Na₃LnCl₆, the trigonal 'stuffed LiSbF₆'-structure. In both structure types the Ln²⁺ ions have octahedral surroundings (CN 6).

Additional to the older results, incongruently melting compounds Na₃LnCl₄ were found, which are isotypic to Na₃GdCl₄ (triclinic space group P1). The CN of Ln³⁺ is 7.

The compound Na₂TbCl₅ 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/DyCl₃ gave no evidence for the existence of an analogous compound. Na₂TbCl₅ has the orthorhombic K₂PrCl₅/Y₂HfS₃ structure, the CN for Tb³⁺ is 7.

Solution calorimetry. The isoperibolic solution calorimeter had a volume of 1.31 l. Samples of 3–6 g thus yielded virtually ideal solutions (dissolution ratio 1:3500 mol). The Δₛ,mH°,values in Table 2 are always the mean of three measurements. The range of error was ±0.5 kJ mol⁻¹. The enthalpies Δₛ,mH° for the formation from NaCl and LnCl₃ were calculated with the equation

\[ Δₛ,mH° = (nΔₛ,mH°(NaCl) + Δₛ,mH°(LnCl₃)) - Δₛ,mH°(A₅,LnCl₅₋₋₉) \]

The solution enthalpies for the compounds L₅-TbCl₅ and L₅-DyCl₅ are in good agreement with values from the literature (126.9 to 192.5 for TbCl₅, ca. 198 for DyCl₅). The synproportionation enthalpies Δₛ,mH° are exothermic only for the compounds Na₃LnCl₄; they are virtually zero for the formation of Na₂TbCl₅ from Na₃TbCl₆ and NaTbCl₄ and of Na₃DyCl₅ from NaCl and NaDyCl₅.

EMF measurements. EMF values were measured for the formation of each compound from NaCl and the adjacent LnCl₃-rich compound in a temperature range ca. 300–650 °C.

Fig. 1. Phase diagrams of the systems NaCl/TbCl₅ and NaCl/DyCl₃.
Table 1. Unit-cell parameters of ternary chlorides Na₃LnCl₃ₓ in pm.

- NaLnCl₄: KD₂Cl₄-type (monoclinic; P2₁/c)
  - Na₃EuCl₄: \(a = 677.2\); \(b = 1277.8\); \(c = 1295.6\); \(\beta = 90^\circ\)
  - Na₃GdCl₄: \(a = 671.5\); \(b = 1285.2\); \(c = 1286.8\); \(\beta = 90^\circ\)

- NaLnCl₆: NaGdCl₄-type (triclinic; \(\overline{P} \overline{T}\))
  - Na₃TbCl₆: \(a = 700.6\); \(b = 672.3\); \(c = 662.1\); \(\alpha = 100.2^\circ\); \(\beta = 91.2^\circ\); \(\gamma = 89.0^\circ\)
  - Na₃DyCl₆: \(a = 699.1\); \(b = 666.7\); \(c = 662.7\); \(\alpha = 100.3^\circ\); \(\beta = 91.0^\circ\); \(\gamma = 89.7^\circ\)

- Na₂TbCl₆: K₂PrCl₆/Y₂HfS₆-type (orthorhombic; \(Pnma\))
  - \(a = 1201.0\); \(b = 827.4\); \(c = 764.3\)

- H-Na₃LnCl₆: cryolite-type (monoclinic; \(P2₁/n\))
  - Na₃EuCl₆: \(a = 700.6\); \(b = 731.7\); \(c = 1035.3\); \(\beta = 90.3^\circ\)
  - Na₃GdCl₆: \(a = 700.5\); \(b = 735.9\); \(c = 1035.6\); \(\beta = 90.1^\circ\) (Meyer, 1987)
  - Na₃TbCl₆: \(a = 689.1\); \(b = 727.6\); \(c = 1019.3\); \(\beta = 90.2^\circ\) (Meyer, 1987)
  - Na₃DyCl₆: \(a = 687.9\); \(b = 720.8\); \(c = 1017.5\); \(\beta = 90.2^\circ\) (Meyer, 1987)

- L-Na₃LnCl₆: stuffed LiSbF₆-type (trigonal; \(R\bar{3}\))
  - Na₃EuCl₆: \(a = 701.8\); \(b = 1882.5\); \(c = 1879.1\); \(\beta = 90.2^\circ\) (Meyer, 1984)
  - Na₃GdCl₆: \(a = 700.7\); \(b = 1872.5\); \(c = 1868.7\); \(\beta = 90.2^\circ\) (Meyer, 1984)
  - Na₃TbCl₆: \(a = 698.7\); \(b = 1872.5\); \(c = 1868.7\); \(\beta = 90.2^\circ\)

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 \(\Delta G^\circ = \Delta_f H^\circ - T \Delta_f S^\circ\). By means of thermodynamic cycles these functions were transformed to those for the reactions \(n\text{ACl} + \text{LnCl}_3 = A_x\text{LnCl}_{3+x}\), denoted \(\Delta_g G^\circ\, \Delta_f H^\circ\) and \(\Delta_f S^\circ\), and further to the free enthalpies of synproportionation, \(\Delta_x G^\circ\, \Delta_f H^\circ\) from the two neighbouring compounds. For high-temperature modifications the temperatures of formation (decomposition) were calculated by the condition \(\Delta_x G^\circ = 0\).

As an example a description for the evaluation of the measurements concerning the reaction \(2\text{NaCl} + \text{NaTbCl}_4 = \text{H-Na}_3\text{TbCl}_6\) is given. According to Fig. 1 it occurs in the temperature range 345–406 °C.

Two cycles gave the regression equation: \(\text{EMF/mV} = -36.11 + 0.1372 T/K\) \(\text{EMF/mV} = -36.60 + 0.1413 T/K\)

The mean regression line is \(\text{EMF/mV} = -36.36 + 0.1393 T/K\).

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

In the following the Gibbs–Helmholtz equations for

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Fig. 2. X-Ray patterns for Na₃TbCl₆ at 20 and 160 °C.
Table 2. Enthalpy values (in kJ mol\(^{-1}\)) from solution calorimetry.\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>(\Delta_{sol} H^\circ)</th>
<th>(\Delta_{syn} H^\circ)</th>
<th>Dy</th>
<th>(\Delta_{syn} H^\circ)</th>
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<td>+4.5</td>
<td>+4.5</td>
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<td>Na(_2)LnCl(_6)</td>
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<td>(\Delta_{syn} H^\circ)</td>
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<td></td>
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<td>+0</td>
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<tr>
<td>Na(_2)LnCl(_5)</td>
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<td>(\Delta_{syn} H^\circ)</td>
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<tr>
<td>0.5 NaLn(_2)C(_7)</td>
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<td></td>
<td>(\Delta_{syn} H^\circ)</td>
<td>-188.8</td>
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</table>

\(^a\) \(\Delta_{sol} H^\circ\) = solution enthalpy; \(\Delta_{syn} H^\circ\) = 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 AC\(_l\) and LnCl\(_3\) are listed, together with the temperature ranges of the measurements. The range of error was smaller than \(\pm 1\) kJ mol\(^{-1}\) for the energy values and \(\pm 0.8\) J K\(^{-1}\) mol\(^{-1}\) for the entropies.

**System NaCl/TbCl\(_3\)**

0.5 NaCl + H-TbCl\(_3\) = Na\(_{0.5}\)TbCl\(_{3.5}\) \((290–400 \text{°C})\) \((1)\)
\[\Delta G^\circ /kJ \text{ mol}^{-1} = 6.1 - 0.0213 \text{ T/K} \]
\[\Delta r G^\circ /kJ \text{ mol}^{-1} = -4.9\]
\[\Delta r G^\circ /kJ \text{ mol}^{-1} = 1.2 - 0.0213 \text{ T/K}\]

NaCl + NaTbCl\(_4\) = Na\(_2\)TbCl\(_5\) \((290–320 \text{°C})\) \((3)\)

The \(\Delta G^\circ\)-values from reactions (4) and (5) should be identical; the difference of 1.4 kJ mol\(^{-1}\) for \(\Delta r H^\circ\) and 2.3 J K\(^{-1}\) mol\(^{-1}\) for \(\Delta r S^\circ\) is caused by the uncertainty of the measurements. The temperature of decomposition for Na\(_2\)TbCl\(_5\) 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 \((345 \text{°C})\). As expected from kinetic reasons,\(^16\) it is somewhat lower than the value of 345 °C found from DTA heating curves.

**System NaCl/DyCl\(_3\)**

0.5 NaCl + H-DyCl\(_3\) = Na\(_{0.5}\)DyCl\(_{3.5}\) \((300–400 \text{°C})\) \((1)\)
\[\Delta G^\circ /kJ \text{ mol}^{-1} = -6.4 - 0.0025 \text{ T/K} \]
\[\Delta r G^\circ /kJ \text{ mol}^{-1} = -5.2\]
\[\Delta r G^\circ /kJ \text{ mol}^{-1} = -11.6 - 0.0025 \text{ T/K}\]

2NaCl + NaDyCl\(_4\) = H-Na\(_3\)DyCl\(_6\) \((310–400 \text{°C})\) \((3)\)

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Fig. 3. EMF vs. \(T\) curves for the reactions (3)-(5) in the system NaCl/TbCl\(_3\).
\[ \Delta_r G^\circ / \text{kJ mol}^{-1} = 3.6 - 0.0257 \ T/\text{K} \]
\[ \Delta_r G^\circ / \text{kJ mol}^{-1} = 8.0 - 0.0282 \ T/\text{K} \]

It must be pointed out that the EMF measurements relate to the modifications that are stable in the applied temperature range. Thus, \( \Delta_r H^\circ \)-values from EMFs cannot be compared with the values from solution calorimetry found at ambient temperature. For that they had to be corrected with the transformation enthalpies \( \text{L-LnCl}_3 \) to \( \text{H-LnCl}_3 \) and \( \text{L-Na}_3\text{LnCl}_6 \) to \( \text{H-Na}_3\text{LnCl}_6 \). 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 \( \text{NaCl/LnCl}_3 \) have yielded the following general conclusions:

The systems from \( \text{LaCl}_3 \) to \( \text{SmCl}_3 \) are dominated by a more or less extended mixed crystal region between \( \text{LnCl}_3 \) and \( \text{Na}_3\text{LnCl}_6 \). The crystal structures of these phases were solved by single crystal measurements on \( \text{K}_3\text{LaCl}_6 \).\(^{17}\)

Compounds \( \text{Na}_3\text{LnCl}_6 \), crystallizing with the \( \text{K}_3\text{PrCl}_6 \) structure, were found in the systems from \( \text{Sm} \) to \( \text{Tb} \), not in the system \( \text{NaCl/DyCl}_3 \). The compounds with \( \text{Ln} = \text{Sm} \), \( \text{Eu} \), \( \text{Gd} \) melt incongruently at ca. 430°C, \( \text{Na}_2\text{TbCl}_5 \) decomposes in the solid state at 340°C.

The formation enthalpies \( \Delta_f H^\circ \) (from formation of \( 2\text{NaCl} \) and \( \text{LnCl}_3 \)) are endothermic. Gibbs enthalpies \( \Delta_f G^\circ \) for the reactions \( \text{NaCl} + \text{Na}_3\text{Sm}_2\text{Cl}_18 \) and \( \text{NaCl} + \text{L-NaEuCl}_4 \) yielded decomposition temperatures of \( \geq 150^\circ C \) and \( 69^\circ C \), respectively. For \( \text{Na}_2\text{GdCl}_6 \) no EMF measurements with \( \text{L-NaGdCl}_4 \) could be done. However, from solution calorimetry the enthalpy for the reaction \( \text{NaCl} + \text{L-NaGdCl}_4 = \text{Na}_2\text{GdCl}_6 \) is known. It is 3.0 kJ mol\(^{-1} \) less endothermic than for \( \text{Na}_2\text{EuCl}_6 \) (corrected value from Ref. 4 = 5.7 kJ mol\(^{-1} \)). Thus the range of stability should stretch to lower temperatures than for \( \text{Na}_2\text{EuCl}_6 \); the same is true for \( \text{Na}_2\text{TbCl}_6 \), with a \( \Delta_{\text{syny}} H^\circ \) value not significantly different from zero (Table 2).

Beginning with \( \text{NaEuCl}_4 \) these 1:1 compounds are the most stable in the systems. That is, the \( \Delta_r H^\circ \)-values are identical with \( \Delta_{\text{syny}} H^\circ \). From EMF measurements on \( \text{L-NaEuCl}_4 \) \( \Delta_r G^\circ / \text{kJ mol}^{-1} = 5.1 - 0.0179 \ T/\text{K} \) was obtained, which gives 285 K (12°C) as the lowest temperature of stability. \( \Delta_r H^\circ \)-values for the other compounds are 5.4 kJ mol\(^{-1} \) for \( \text{NaGdCl}_6 \), 0.7 for \( \text{NaTbCl}_4 \) and 1.9 for \( \text{NaDyCl}_4 \). The last compound must be stable down to 0 K.

In the system \( \text{NaCl/GdCl}_3 \) a compound \( \text{NaGd}_2\text{Cl}_7 \) exists only in a small temperature range (393–422°C). For the incongruently melting compounds \( \text{NaTb}_2\text{Cl}_7 \) and \( \text{NaDy}_2\text{Cl}_7 \) no decomposition could be detected by DTA.

However, the relatively strong endothermic \( \Delta_{\text{syny}} H^\circ \)-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 (TΔS-term).

Compounds \( \text{Na}_3\text{TbCl}_6 \) and \( \text{Na}_3\text{DyCl}_6 \) exist at temperatures higher than ca. 100°C with the cryolite structure. Below this temperature they transform reversibly to the hexagonal stuffed \( \text{LiSbF}_6 \)-type. \( \text{Na}_2\text{GdCl}_6 \) is stable only above 265°C. It can be quenched to a metastable \( \text{LiSbF}_6 \)-phase, which decomposes exothermically when heated to ca. 210°C. With this knowledge we had to correct our previous interpretation for the compound \( \text{Na}_2\text{EuCl}_6 \). 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 \( \text{NaCl} \) and \( \text{Na}_2\text{EuCl}_3 \). 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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**References**


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