# COMPLEX FORMATION VS. DISPROPORTIONATION: LANTHANIDE(II) CHLORIDES, $MCl_2$ (M $\equiv$ Nd, Sm, Eu, Dy, Tm, Yb), UNDER THE INFLUENCE OF ALKALI CHLORIDES\*

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#### Summary

The products of the action of alkali metals ( $A \equiv Li$ , Na) on lanthanide-(III) chlorides, MCl<sub>3</sub> ( $M \equiv Nd$ , Sm, Eu, Dy, Tm, Yb), principally ACl + MCl<sub>2</sub> or LiCl + LiM<sub>2</sub>Cl<sub>5</sub>, were reacted with CsCl in sealed tantalum containers. Complex formation (CsMCl<sub>3</sub>) and disproportionation (to Cs<sub>2</sub>AMCl<sub>6</sub> + M) are the competing reaction types. The presence of alkali chloride (LiCl, NaCl) has no effect on complex formation for  $M \equiv Eu$ , Yb, and only minimal effect for  $M \equiv Sm$ . For  $M \equiv Tm$  disproportionation is the principal and for  $M \equiv Dy$ , Nd the exclusive process. These observations may be explained with the aid of calculated or assessed enthalpies of reaction  $\Delta H_R^\circ$ , for the two reaction types.

### 1. Introduction

The existence of lanthanide(II) chlorides,  $MCl_2$ , is well established for the elements  $M \equiv Nd$ , Sm, Eu, Dy, Tm, Yb [1, 2]. Several routes are known for their synthesis of which the two most important are synproportionation, eqn. (1), and "metallothermic" reduction with alkali metals (A, commonly lithium or sodium [3]), eqn. (2):

$$2MCl_3 + M = 3MCl_2 \tag{1}$$

 $MCl_3 + A = MCl_2 + ACl$ 

With the exception of  $M \equiv Nd$ , Dy, ternary perovskite-type chlorides may be obtained [4], for example via:

(2)

<sup>\*</sup>Dedicated to Professor Harald Schäfer on the occasion of his 75th birthday.

$$MCl_2 + CsCl = CsMCl_3$$
(3)

(4)

or

 $MCl_3 + Cs = CsMCl_3$ 

In many cases, metallothermic reductions with alkali metals were found to be convenient routes for crystal growth especially when, as in eqn. (2), alkali chlorides are formed *in situ*. These chlorides are then believed to serve as solvents for flux growth of single crystals. Additionally, reaction temperatures are usually considerably lower when following routes (2) or (4) as opposed to route (1) [5].

Therefore, it was hoped that the reaction products of (2),  $MCl_2 + ACl$ , could serve as starting materials for the synthesis of chlorides like  $CsMCl_3$ , even for  $M \equiv Nd$ , Dy. In other words: does the additional alkali chloride in all cases just act as a solvent or does it influence the "stability" of the divalent state?

To answer this question, the products of reactions  $A + MCl_3$  ( $A \equiv Li$ , Na; M as above), usually  $ACl + MCl_2$  following eqn. (2), have been reacted with CsCl at moderate temperatures to find out whether in all or some cases reactions like

$$(ACl + MCl_2) + CsCl = CsMCl_3 + ACl$$
(5)

would take place.

# 2. Experimental details

The lanthanide(III) chlorides, MCl<sub>3</sub> ( $M \equiv Nd$ , Sm, Eu, Dy, Tm, Yb), were prepared from the rare earths, M<sub>2</sub>O<sub>3</sub> (Johnson Matthey; purity, 99.99%), following the "wet" variant of the ammonium chloride route [6, 7]. Lithium, sodium and cesium chloride (E. Merck) were used without further purification. Cesium was obtained from CsCl by reduction with calcium metal [8] and distilled twice. All subsequent handling took place under strictly dry and anaerobic conditions utilizing, for example, an argon dry box (M. Braun, München). Reactions were carried out in helium-arc welded tantalum ampoules that were sealed under vacuum in silica jackets and heated to 500 -800 °C for one week. A typical reaction mixture was 5.8 mg lithium and 207.6 mg NdCl<sub>3</sub> (following eqn. (2)), and subsequently 106.9 mg of the reaction product (LiCl + NdCl<sub>2</sub>) plus 69.9 mg CsCl for the attempted synthesis of "CsNdCl<sub>3</sub>" (following eqn. (5)). Different reaction conditions (temperature, time) were tried but were found to have no influence on the product(s).

The reaction products were characterized by X-ray powder patterns; Guinier-Simon technique [10, 11], camera FR 553, Enraf-Nonius, Cu K $\alpha_1$  radiation.

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## 3. Results

The action of lithium and sodium on lanthanide(III) chlorides,  $MCl_3$ , has been investigated previously [3]. The products are summarized for convenience in Table 1 together with the products of the cesium reduction of the same trichlorides.

Whereas most of the results of the reactions are self-explanatory and were discussed in detail [3], the action of sodium on NdCl<sub>3</sub> yields the unusual mixed-valence NaNd<sub>2</sub>Cl<sub>6</sub>  $\equiv$  (Na<sup>+</sup>)(Nd<sup>2+,3+</sup>)<sub>2</sub>(Cl<sup>-</sup>)<sub>6</sub> [12]. Regardless of the products, CsCl was mixed with (MCl<sub>2</sub> + ACl) (A  $\equiv$  Li, Na) in equimolar amounts for the subsequent reactions.

Two types of products were then obtained from the subsequent reactions,  $CsMCl_3$  and  $Cs_2AMCl_6 + M$ . Hence, either *complex formation* took place via eqn. (5) or

$$1/2(\text{LiM}_2\text{Cl}_5 + \text{LiCl}) + \text{CsCl} = \text{CsMCl}_3 + \text{LiCl}$$
(6)

or the presence of the additional alkali chloride forced the divalent lanthanide into *disproportionation*, *e.g.* 

$$(MCl_2 + ACl) + 4/3CsCl = 2/3Cs_2AMCl_6 + 1/3M + 1/3ACl$$
(7)

Table 2 lists the results. Therefore, in the cases of  $M \equiv Eu$ , Yb, the reactions went exclusively via eqns. (5) or (6), and for  $M \equiv Nd$ , Dy no evidence was found for reaction to proceed via eqns. (5) or (6). Instead, disproportionation of the divalent lanthanide resulting in the formation of elpasolites,  $Cs_2AMCl_6$ , and metal, M, via eqn. (7) took place. Samarium and thulium occupy intermediate positions. In the presence of NaCl,  $CsSmCl_3$  (complexation) and  $Cs_2NaTmCl_6$  (disproportionation) are obtained as the most stable products (see below). Reaction with LiCl appears to be more complicated. In both cases ( $M \equiv Sm$ , Tm), mixtures of  $Cs_2LiMCl_6$  and  $CsMCl_3$  are obtained in different proportions. For  $M \equiv Sm$ ,  $CsSmCl_3$  is the main product, and for  $M \equiv Tm$ ,  $CsTmCl_3$  is the minor product.

The lattice constants as given in Table 2 for perovskites,  $CsMCl_3$  (indexed in the cubic or tetragonal systems), and elpasolites,  $Cs_2LiMCl_6$  and  $Cs_2NaMCl_6$  (all f.c.c.), are very close to those reported in the literature [13].

TABLE 1

Results of the action of lithium, sodium and cesium on several lanthanide (III) chlorides,  $\mathrm{MCl}_3$ 

MCl <sub>3</sub>	$A \equiv Li$	Na	Cs	
NdCla	LiCl + NdCl <sub>2</sub>	NaCl + NaNd <sub>2</sub> Cl <sub>6</sub>	$CsCl/NdCl_3^a + Nd$	
SmCla	$LiCl + SmCl_2$	$NaCl + SmCl_2$	CsSmCla	
EuCl <sub>3</sub>	$LiCl + EuCl_2$	NaCl + EuCl <sub>2</sub>	CsEuCl	
DvCl <sub>3</sub>	$LiCl + LiDv_{2}Cl_{5}$	$NaCl + DvCl_2$	$C_{s}Cl/D_{v}Cl_{3}^{a} + Dv$	
TmCl <sub>2</sub>	LiCl + LiTm <sub>2</sub> Cl <sub>5</sub>	$NaCl + TmCl_2$	CsTmCl <sub>3</sub>	
YbCl	$LiCl + LiYb_2Cl_5$	$NaCl + YbCl_2$	CsYbCl <sub>3</sub>	

<sup>a</sup>These may yield one or more ternary chlorides according to the phase diagrams.

#### TABLE 2

Results of the reactions of CsCl with the products of metallothermic reductions as listed in Table 1 together with lattice constants, a and c (pm), of the cubic or tetragonal perovskites, CsMCl<sub>3</sub>, and the f.c.c. elpasolites, Cs<sub>2</sub>AMCl<sub>6</sub> (A  $\equiv$  Li, Na)

М	Products according to eqns. (5) - (7)			
	+LiCl	+NaCl		
Eu	$CsEuCl_3$ a = 558.45(3), c = 562.17(6)	CsEuCl <sub>3</sub>		
Yb	$CsYbCl_3$ a = 543.43(2)	CsYbCl <sub>3</sub>		
Sm	CsSmCl <sub>3</sub> <sup>a</sup> a = 560.31(4), c = 564.08(6) Cs <sub>2</sub> LiSmCl <sub>6</sub> <sup>b</sup> a = 1057.66(4)	$\mathrm{CsSmCl}_3$		
Tm	$Cs_{2}LiTmCl_{6}^{a} + Tm$ $a = 1044.08(4)$ $CsTmCl_{3}^{b}$ $a = 545.77(2)$	$\begin{array}{l} \mathrm{Cs_2NaTmCl_6} + \mathrm{Tm} \\ a = 1068.60(4) \end{array}$		
Dy	$Cs_2LiDyCl_6 + Dy$ a = 1049.40(4)	$Cs_2NaDyCl_6 + Dy$ a = 1074.63(5)		
Nd	$Cs_{2}LiNdCl_{6} + Nd$ a = 1061.96(5)	$Cs_2NaNdCl_6 + Nd$ a = 1088.82(5)		

<sup>a</sup>Main product.

<sup>b</sup>By-product (about 30%).

## 4. Discussion

Apparently, the presence of alkali chloride (LiCl, NaCl) either as a binary component or incorporated in a ternary chloride (LiM<sub>2</sub>Cl<sub>5</sub> or NaNd<sub>2</sub>Cl<sub>6</sub>) in the reaction mixture has no influence on complex formation via eqns. (5) or (6) in the cases of  $M \equiv Eu$ , Yb and only little in the case of  $M \equiv Sm$ . With  $M \equiv Tm$ , Cs<sub>2</sub>ATmCl<sub>6</sub> plus thulium metal is the main product, especially with  $A \equiv Na$  where no CsTmCl<sub>3</sub> could be observed. No indication was found for the formation of a complex chloride CsMCl<sub>3</sub> in the cases of  $M \equiv Dy$ , Nd, neither following eqn. (4), nor attempting reactions (5) or (6). We therefore conclude that neither CsDyCl<sub>3</sub> nor CsNdCl<sub>3</sub> exist.

These observations may be explained semiquantitatively making use of thermodynamic data for the chlorides involved which are found in refs. 14 - 16. From these sources, the enthalpies of the reactions (5) and (7) with  $A \equiv \text{Na}$ ,  $\Delta H_{R}^{\circ}(5)$  and  $\Delta H_{R}^{\circ}(7)$ , have been calculated or assessed for ambient temperature and are compared in Table 3. As these reactions were run at fairly low temperatures (about 500 °C), it is assumed that entropy contributions are small or, at least, not significantly different for reactions (5) and (7). Thus,  $\Delta H_{R}^{\circ}$  may be assumed rather safely to be the driving force for these reactions.

#### TABLE 3

М	$\Delta H_{\mathbf{F}}^{\circ}$			$\Delta H^{\circ}_{\mathbf{R}}$	
	$MCl_2$	CsMCl <sub>3</sub>	$Cs_2NaMCl_6$	eqn. (5)	eqn. (7)
Nd	-707	(-1124)	-2384	(+25)	-19
Sm	-803	-1232	-2380	$+13 \pm 7^{a}$	+79
Eu	-824	-1265	-2294	+1.7 ± 8.1	+158
Dy	-693	(-1165)	-2385	(-30)	-34
Tm	-709	-1196	-2392	$-45 \pm 13$	-23
Yb	-800	-1287	-2361	$-45 \pm 12$	+89

Complex formation (eqn. (5)) vs. disproportionation (eqn. (7)), enthalpies of reaction,  $\Delta H_{\mathbf{R}}^{\circ}$ , and pertinent enthalpies of formation,  $\Delta H_{\mathbf{F}}^{\circ}$  (kJ mol<sup>-1</sup>)

<sup>a</sup>Error limits are usually omitted; for  $\Delta H_{\mathbf{R}}^{\circ}(5)$  these were taken from refs. 15 and 16.

Some of the results of these calculations are rather surprising and need some further explanation.  $CsEuCl_3$  and  $CsSmCl_3$  are of only marginal stability relative to the binary components, *e.g.* 

$$CsCl + SmCl_2 = CsSmCl_3 \qquad \Delta H_B^\circ = +13 \pm 7 \text{ kJ mol}^{-1}$$
(8)

This is in sharp contrast to  $CsTmCl_3$  and  $CsYbCl_3$  that both have  $\Delta H_R^{\circ} \approx -45$  kJ mol<sup>-1</sup> for a reaction analogous to eqn. (8). This can, however, be understood in terms of a "thermodynamic" destabilization of the former two whose divalent cations (Eu<sup>2+</sup>, Sm<sup>2+</sup>) are too big to fit well into the octahedral holes of the perovskite lattice. Structurally, distorted perovskite structures are in fact observed for CsSmCl<sub>3</sub> and CsEuCl<sub>3</sub>.

Although of marginal stability,  $CsSmCl_3$  and  $CsEuCl_3$  do exist. In the presence of NaCl, reaction (5) (preservation of the divalent state through complex formation) is much more favorable than reaction (7) (disproportionation) because relatively high positive enthalpies of reaction are calculated for the latter. This is also the case for  $CsYbCl_3$  ( $\Delta H^{\circ}_{R}(5) = -45$  kJ mol<sup>-1</sup>) vs.  $Cs_2NaYbCl_6/Yb$  ( $\Delta H^{\circ}_{R}(7) = +89$  kJ mol<sup>-1</sup>). Not so for the example of thulium where  $\Delta H^{\circ}_{R}(5) = -23$  kJ mol<sup>-1</sup> is already negative and of the same order of magnitude as  $\Delta H^{\circ}_{R}(7) = -45$  kJ mol<sup>-1</sup>. Taking relatively large error limits into consideration, one cannot foresee whether complex formation does occur. The experiment shows that for  $A \equiv Na$  disproportionation is complete while for  $A \equiv Li$  some CsTmCl<sub>3</sub> (approximately 30%) is also observed. Unfortunately,  $\Delta H^{\circ}_{F}(Cs_2LiMCl_6)$  is not known but this observation would suggest a more exothermic  $\Delta H^{\circ}_{F}(Cs_2NaMCl_6)$  which would then explain that in the case of  $A \equiv Na$  disproportionation is more favored than complex formation.

For neodymium and dysprosium, disproportionation is clearly exothermic. Enthalpies of reaction,  $\Delta H^{\circ}_{R}(5)$ , for "CsNdCl<sub>3</sub>" and "CsDyCl<sub>3</sub>" are only rough estimates as the enthalpies of formation,  $\Delta H^{\circ}_{F}$ , cannot be measured. Although many different synthetic routes have been attempted, neither compound has ever been obtained. Still, judging from  $\Delta H^{\circ}_{R}(5)$  alone, "Cs-DyCl<sub>3</sub>" could well exist. But even in the case that no additional alkali chloride (e.g. NaCl) is present, reduction to dysprosium metal competes with dysprosium(II), as the following reactions explain:

$$Cs + DyCl_3 = CsDyCl_3 \qquad \Delta H_R^\circ = -176 \text{ kJ mol}^{-1}$$
(9)

$$Cs + DyCl_3 = 1/3Cs_3DyCl_6 + 1/6Dy + 1/2DyCl_2$$

$$\Delta H_{\rm R}^{\circ} = -158 \, \rm kJ \, mol^{-1}$$
 (10)

In conclusion, the addition of excess alkali chloride in the systems under consideration "destabilizes" the divalent state of the lanthanides because of the competition with the disproportionation reaction. This then leads to the more stable elpasolites,  $Cs_2AMCl_6$ , that all have, for  $A \equiv Na$ , enthalpies of formation,  $\Delta H_F^{\circ}$ , around  $-2385 \text{ kJ mol}^{-1}$  except for  $Cs_2Na$ -EuCl<sub>6</sub> ( $\Delta H_F^{\circ} = -2294 \text{ kJ mol}^{-1}$ ) and  $Cs_2NaYbCl_6$  ( $\Delta H_F^{\circ} = -2361 \text{ kJ mol}^{-1}$ ) [14] illustrating the relative increase of the stability of the divalent vs. the trivalent state.

Again, these experimental observations make it clear that the stability of the divalent state of the lanthanides in bulk chlorides, that is with electronic configurations of  $(Xe)4f^n 5d^06s^0$  with n = 7, 14, 6, 13, 10, 4 for  $M \equiv Eu$ , Yb, Sm, Tm, Dy, Nd decreases in that order. This is in accord with the measured or assessed standard electrode potentials,  $E^\circ$ , for the reduction reaction [17],

$$M^{3+} + e^- = M^{2+}$$
(11)

in aqueous solution, for which  $E^{\circ}(M^{3+}/M^{2+})$  is -0.35, -1.1, -1.5, -2.1, -2.6, -2.8 respectively [14]. This is not surprising if one bears in mind that the comparison of

$$\Delta G_{\mathbf{R}}^{\circ} = \Delta H_{\mathbf{R}}^{\circ} - T \Delta S_{\mathbf{R}}^{\circ} \tag{12}$$

and

$$\Delta G^{\circ} = -F \cdot E^{\circ} (M^{3+}/M^{2+}) \tag{13}$$

indicates that  $\Delta H_{\rm R}^{\circ}$  and  $E^{\circ}({\rm M}^{3+}/{\rm M}^{2+})$  are indeed proportional provided that  $\Delta S_{\rm R}^{\circ}$  is negligible or equal for the reactions under consideration. The trends of the stability of the divalent state may therefore be equally circumscribed by both  $\Delta H_{\rm R}^{\circ}$  and  $E^{\circ}$ , although these represent completely different chemistry, *i.e.* solid state and aqueous solution reactions.

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## References

- 1 Gmelin Handbook of Inorganic Chemistry, Sc, Y, La-Lu, Rare Earth Elements, Part C 4a, Springer, Berlin, 8th edn., 1982.
- 2 G. Meyer, Chem. Rev., 88 (1988).
- 3 G. Meyer and Th. Schleid, J. Less-Common Met., 116 (1986) 187.
- 4 G. Meyer, Naturwissenschaften, 65 (1978) 258.
- 5 G. Meyer and Th. Schleid, Inorg. Chem., 26 (1987) 217.
- 6 G. Meyer and P. Ax, Mater. Res. Bull., 14 (1982) 1447.
- 7 G. Meyer, Inorg. Synth., 26 (1988).
- 8 L. Hackspill, Bull. Soc. Chim. France, 9 (1911) 464.
- 9 J. D. Corbett, Inorg. Synth., 22 (1983) 15.
- 10 A. Simon, J. Appl. Crystallogr., 3 (1970) 11.
- 11 J. Soose and G. Meyer, SOS: Programme zur Auswertung von Guinier-Aufnahmen, Giessen, 1980.
- 12 Th. Schleid and G. Meyer, Inorg. Chim. Acta, 140 (1987) 113.
- 13 G. Meyer, Prog. Solid State Chem., 14 (1982) 141, and references cited therein.
- 14 L. R. Morss, Chem. Rev., 76 (1976) 827.
- 15 D. G. Nocera, L. R. Morss and J. A. Fahey, J. Inorg. Nucl. Chem., 42 (1980) 55.
- 16 L. R. Morss, Th. Schleid and G. Meyer, Inorg. Chim. Acta, 140 (1987) 109.
- 17 G. Meyer, J. Less-Common Met., 93 (1983) 371.