

### Enthalpies of Formation of Ternary Lanthanide(II) Chlorides: CsSmCl<sub>3</sub>, CsTmCl<sub>3</sub> and CsYbCl<sub>3</sub>\*

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In 1978 Meyer [1] reported the synthesis and crystal structure of a series of ternary lanthanide chlorides CsLnCl<sub>3</sub> (Ln = Sm, Eu, Tm, Yb). The first two of these compounds are distorted perovskites and the last two have the 'ideal perovskite' structure. Shortly thereafter, Nocera *et al.* [2] reported the enthalpy of formation of one of these compounds, CsEuCl<sub>3</sub>, and calculated the enthalpy of the reaction



to be +1.7±8.1 kJ mol<sup>-1</sup>. They concluded that the stabilization of this perovskite lattice for Eu<sup>2+</sup> was negligible because Eu<sup>2+</sup> is too large an ion for stable octahedral chloride coordination.

At that time other divalent ternary lanthanide chlorides could not be synthesized. Numerous efforts have failed to produce CsLnCl<sub>3</sub> (Ln = Nd, Dy) or ALnCl<sub>3</sub> for any cases where A is a light alkali metal (Li, Na) [3]. Some reasons for the existence or non-existence of some of these halides have been given [3, 4]. To provide a more quantitative basis for understanding the energetics of reaction (1) the present study was undertaken.

### Experimental

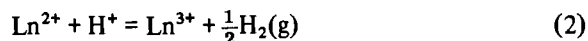
CsSmCl<sub>3</sub> and CsTmCl<sub>3</sub> were synthesized by metallothermic (Cs) reduction of trichlorides in arc-welded tantalum crucibles. CsYbCl<sub>3</sub> was synthesized similarly by metallothermic reduction (Yb) of Cs<sub>3</sub>Yb<sub>2</sub>Cl<sub>9</sub>. Reagents as well as products were handled only in an inert-gas dry box. Characterization of each compound was made by its X-ray powder pattern, by observation of complete dissolution in dilute HCl(aq) (thereby confirming the absence of appreciable oxychloride), and by chemical analysis

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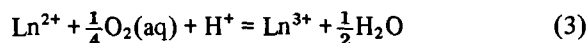
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for chloride (by potentiometric titration) and for Ln(II) as described in the following paragraph.

A reduced halide that is free of oxyhalide reacts with dilute acid as follows (Ln<sup>2+</sup> symbolizes a cation that is oxidized in aqueous solution):



If oxygen is present in the solution, the same amount of acid is still consumed:



Therefore, a reduced halide can be analysed for reducing power by adding a weighed sample to a known excess of dilute acid, waiting for complete dissolution, and titrating the excess acid with dilute base. The end-point of the titration, best observed with a pH meter, occurs in the pH 5–6 region; the pH ceases to rise as Ln(III) hydrolysis and Ln(OH)<sub>3</sub> precipitation begin. Analytical data are shown in Table I.

TABLE I. Analyses of CsLnCl<sub>3</sub> (mass percent)

Compound	Ln(II)		Cl <sup>-</sup>	
	Found	Calc.	Found	Calc.
CsSmCl <sub>3</sub>	38.49	38.60		27.30
CsTmCl <sub>3</sub>	44.10	41.39	25.22	26.06
CsYbCl <sub>3</sub>	41.64	41.97	24.28	25.80

Calorimetry was carried out in multiple-batch isoperibol solution calorimeters, either the one described by Nocera *et al.* [2] or a semimicro model [5]. In each case, the acid was degassed so that the reaction corresponded to eqn. (2) and not to eqn. (3). The HCl concentrations were chosen to correspond to other steps in each thermochemical cycle. Enthalpies of solution are shown in Table II. For CsYbCl<sub>3</sub>, it is crucial that the solution be degassed to avoid reaction (3) since reaction (2) is rather slow. Therefore, a check of the acid solution reaction was performed by carrying out the calorimetry of CsYbCl<sub>3</sub> in extremely dilute HCl(aq), as shown in the lowest entries of Table II. The rapid enthalpy of solution of the compound was followed by a slow (8–22 min) oxidation step that was interpreted as reaction (2).

### Results and Conclusions

Enthalpies of formation are derived as the sums of the enthalpies that comprise the thermochemical cycles shown in Table III. The two entries for Yb are particularly interesting in that they test the hypothesis

TABLE II. Enthalpies of Solution ( $\text{kJ mol}^{-1}$ ) at 298.15 K

Mass (mg)	$q^a$ (J)	$\Delta H^\circ$ ( $\text{kJ mol}^{-1}$ )
CsSmCl <sub>3</sub> in 140 cm <sup>3</sup> of 2.0 mol dm <sup>-3</sup> HCl(aq)		
29.30	16.04	-213.3
37.25	20.47	-214.1
32.40	17.43	-209.6
Mean -212.3 ± 5.9 (95% confidence)		
CsTmCl <sub>3</sub> in 880 cm <sup>3</sup> of 4.0 mol dm <sup>-3</sup> HCl(aq)		
57.81	34.63	-244.5
26.34	16.41	-254.3
Mean -249 ± 20 (est. confidence)		
CsYbCl <sub>3</sub> in 140 cm <sup>3</sup> of 4.0 mol dm <sup>-3</sup> HCl(aq)		
54.54	18.29	-138.3
44.22	14.33	-133.6
22.73	7.26	-131.6
Mean -134.5 ± 8.5 (95% confidence)		
CsYbCl <sub>3</sub> in 140 cm <sup>3</sup> of 0.001 mol dm <sup>-3</sup> HCl(aq)		
81.69	29.11	-146.9
28.31	9.92	-144.5
Mean -145.7 ± 10.8 (est. confidence)		

<sup>a</sup>Corrected for evaporation of water into N<sub>2</sub> in ampoule and into H<sub>2</sub> evolved.

that CsYbCl<sub>3</sub> is oxidized according to reaction (2) rather than reaction (3). The agreement between the results confirms this hypothesis to a satisfactory degree; thus we accept the average of the two sets of experiments,  $\Delta_f H^\circ(\text{CsYbCl}_3, \text{s}) = -1285 \pm 10 \text{ kJ mol}^{-1}$ .

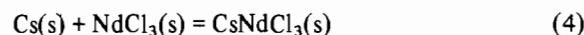
From these enthalpies of formation, and from the enthalpies of formation of CsCl ( $-442.3 \pm 0.2 \text{ kJ mol}^{-1}$ ) [6], SmCl<sub>2</sub> ( $-802.5 \pm 3.3 \text{ kJ mol}^{-1}$ ) [7],

TmCl<sub>2</sub> ( $-709.1 \pm 4.2 \text{ kJ mol}^{-1}$ ) [8] and YbCl<sub>2</sub> ( $-800 \pm 7 \text{ kJ mol}^{-1}$ ) [9]\*, we calculate the enthalpies of reaction (1) to be  $+14 \pm 7$ ,  $-43 \pm 20$  and  $-43 \pm 12 \text{ kJ mol}^{-1}$  for CsSmCl<sub>3</sub>, CsTmCl<sub>3</sub> and CsYbCl<sub>3</sub>, respectively.

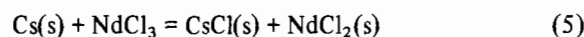
Table 3 of the paper by Nocera *et al.* [2] attempted to correlate the crystallographic properties of MCl<sub>2</sub> and CsMCl<sub>3</sub> compounds. We can utilize the results of this research to expand their table as Table IV. In this Table we have included the hypothetical perovskite chlorides CsNdCl<sub>3</sub> and CsDyCl<sub>3</sub>. Clearly the energetics of reaction (1) correlate well with structural factors as symbolized by the Goldschmidt tolerance factor  $t$  [2].

In discussing the reasons why a particular compound is or is not stable, one must remember that stability is a relative concept; *i.e.*, that all possible reactions and their  $\Delta G^\circ$  must be considered. Some of these competing reactions were presented by Meyer [3]. From Table IV we estimate  $\Delta H(1)$  to be  $+25 \text{ kJ mol}^{-1}$  for Nd and we use  $\Delta_f H^\circ(\text{NdCl}_2, \text{s}) = -706.9 \text{ kJ mol}^{-1}$  [8] to calculate  $\Delta_f H^\circ(\text{CsNdCl}_3, \text{c})$  to be  $-1124 \text{ kJ mol}^{-1}$ ; we estimate  $\Delta H(1)$  to be  $-30 \text{ kJ mol}^{-1}$  for Dy and we use  $\Delta_f H^\circ(\text{DyCl}_2, \text{s}) = -693 \text{ kJ mol}^{-1}$  [7] to calculate  $\Delta_f H^\circ(\text{CsDyCl}_3, \text{s})$  to be  $-1165 \text{ kJ mol}^{-1}$ .

For the interesting reaction



we use  $\Delta_f H^\circ(\text{NdCl}_3, \text{s}) = -1041 \text{ kJ mol}^{-1}$  [8] and calculate  $\Delta H^\circ(4) = -83 \text{ kJ mol}^{-1}$ . Even more favorable, however, is the simple reduction



for which  $\Delta H^\circ(5) = -108 \text{ kJ mol}^{-1}$ .

\*Error limits were estimated from the original literature.

TABLE III. Thermochemical Cycle for  $\Delta_f H^\circ(\text{CsLnCl}_3, \text{s})$  at 298.15 K

Ln	Soln. (mol dm <sup>-3</sup> )	$\Delta H_1$ ( $\text{kJ mol}^{-1}$ )	$\Delta H_2$ ( $\text{kJ mol}^{-1}$ )	$\Delta H_3$ ( $\text{kJ mol}^{-1}$ )	$\Delta H_4$ ( $\text{kJ mol}^{-1}$ )	$\Delta H_5$ ( $\text{kJ mol}^{-1}$ )	$\Delta_f H^\circ(\text{CsLnCl}_3, \text{s})$ ( $\text{kJ mol}^{-1}$ )
Sm	2.0	$-212.3 \pm 5.9$	$-690.1 \pm 1.3^a$	$-325.2 \pm 0.04^a$	$-442.3 \pm 0.2^c$	$+15 \pm 1^d$	$-1230 \pm 6$
Tm	4.0	$-249 \pm 20$	$-698.0 \pm 1.3^a$	$-316.8 \pm 0.04^b$	$-442.3 \pm 0.2^c$	$+13.70 \pm 0.24^e$	$-1194 \pm 20$
Yb	4.0	$-134.5 \pm 8.5$	$-617.7 \pm 2.8^a$	$-316.8 \pm 0.04^b$	$-442.3 \pm 0.2^c$	$+13.70 \pm 0.24^e$	$-1283 \pm 9$
Yb	0.001	$-146 \pm 11$	$-674.5 \pm 3.0^a$	$-334.2 \pm 0.04^b$	$-442.3 \pm 0.2^c$	$+17.92 \pm 0.42^e$	$-1287 \pm 12$
CsLnCl <sub>3</sub> (s) + HCl(soln) = LnCl <sub>3</sub> (soln) + CsCl(soln) + $\frac{1}{2}$ H <sub>2</sub> (g)					$\Delta H_1$		
Ln(s) + 3HCl(soln) = LnCl <sub>3</sub> (soln) + $\frac{3}{2}$ H <sub>2</sub> (g)					$\Delta H_2$		
H <sub>2</sub> (g) + Cl <sub>2</sub> (g) = 2HCl(soln)					$\Delta H_3$		
Cs(s) + $\frac{1}{2}$ Cl <sub>2</sub> (g) = CsCl(s)					$\Delta H_4$		
CsCl(s) = CsCl(soln)					$\Delta H_5$		

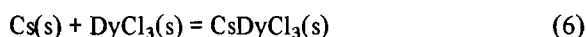
<sup>a</sup>Ref. 14. <sup>b</sup>Ref. 15. <sup>c</sup>Ref. 6. <sup>d</sup>Estimated. <sup>e</sup>Ref. 16. <sup>f</sup> $\Delta_f H^\circ(\text{CsLnCl}_3, \text{s}) = -\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$ .

TABLE IV. Crystallographic and Thermochemical Comparisons of  $MCl_2$  and  $MCl_3$ 

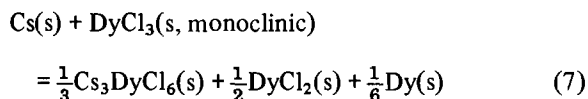
M	$M^{2+}$ (IR) (Å)	Crystal structure of $MCl_2$	$M^{2+}$ (CN) in $MCl_2$	Crystal structure of $CsMCl_3$	$M^{2+}$ (CN) in $CsMCl_3$	$r^a$	$\Delta H$ (kJ mol $^{-1}$ )
Ni	0.69	CdCl <sub>2</sub> (layer)	6	hexag. (2L) <sup>b</sup>	6	1.044	-38
Cu	0.73	layer (square planar)	4	hexag. (2L)	6	1.027	-36
Zn	0.74	tetrahedral	4	unknown		1.023	
Co	0.745	CdCl <sub>2</sub> (layer)	6	hexag. (2L)	6	1.021	-40
Fe	0.78	CdCl <sub>2</sub> (layer)	6	hexag. (2L)	6	1.007	-39
Mn	0.83	CdCl <sub>2</sub> (layer)	6	hexag. (9L)	6	0.988	-41
Cd	0.95	CdCl <sub>2</sub> (layer)	6	hexag. (6L)	6	0.945	
Ca	1.00	distorted SnO <sub>2</sub>	6	perovskite	6	0.928	-36
Yb	1.02	SrI <sub>2</sub>	7	perovskite	6	0.922	-43
Tm	1.03	SrI <sub>2</sub>	7	perovskite	6	0.919	-43
Dy	1.07	SrBr <sub>2</sub>	7, 8	unknown		0.906	
Eu	1.17	PbCl <sub>2</sub>	7 (or 9)	dist. perovskite	6	0.876	+ 2
Sr	1.18	fluorite	8	dist. perovskite	6	0.872	
Pb	1.19	PbCl <sub>2</sub>	7 (or 9)	dist. perovskite	6	0.869	
Sm	1.19	PbCl <sub>2</sub>	7 (or 9)	dist. perovskite	6	0.869	+15
Nd	1.21	PbCl <sub>2</sub>	7 (or 9)	unknown		0.864	
Ba	1.35	PbCl <sub>2</sub>	7 (or 9)	unknown		0.826	

<sup>a</sup>Goldschmidt tolerance factor. <sup>b</sup>Ref. 17.

For the parallel Dy system, we have



We use  $\Delta_f H^\circ(DyCl_3, \text{monoclinic}) = -989.1 \text{ kJ mol}^{-1}$  [7] and we calculate  $\Delta_f H^\circ(6) = -176 \text{ kJ mol}^{-1}$ . Neglecting entropy effects, which for solid-solid reactions are small, we might expect reaction (6) to proceed. However, a competing reaction is



Taking  $\Delta_f H^\circ(Cs_3DyCl_6, s) = -2401.4 \text{ kJ mol}^{-1}$  [10] and  $\Delta_f H^\circ(DyCl_2, s) = -693 \text{ kJ mol}^{-1}$ , as above, we calculate  $\Delta_f H^\circ(7) = -158 \text{ kJ mol}^{-1}$ .

Several researchers have devoted much effort to the measurement and interpretation of the thermodynamics of complex-salt formation. Systematic energetic trends can be based upon enthalpy effects [10], lattice energies [11], or complex-ion formation [12].

In the case of  $AB-MCl_2$  interactions, Seifert and coworkers [13 and earlier papers] have carried out solid-state EMF measurements and they conclude that in some cases the energetics of symproportionation of nearest neighbors in the phase diagram is most important, and in these cases small but significant effects can compensate for small endothermic enthalpies of reaction to yield favorable free energies of reaction. Unfortunately we do not know of any reports on the  $CsCl-MCl_2$  energetics for large spherical divalent cations such as  $M = Sr$  and  $Ba$  with which to compare our results.

## Acknowledgements

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## References

- 1 G. Meyer, *Naturwissenschaften*, **65**, 258 (1978).
- 2 D. G. Nocera, L. R. Morss and J. A. Fahey, *J. Inorg. Nucl. Chem.*, **42**, 55 (1980).
- 3 G. Meyer, *J. Less-Common Met.*, **93**, 371 (1983).
- 4 G. Meyer, *Prog. Solid State Chem.*, **14**, 141 (1982).
- 5 J. W. Bruno, T. J. Marks and L. R. Morss, *J. Am. Chem. Soc.*, **105**, 6824 (1983).
- 6 G. K. Johnson and K. H. Gayer, *J. Chem. Thermodyn.*, **11**, 41 (1979).
- 7 L. R. Morss and J. A. Fahey, *Proc. 12th Rare Earth Res. Conf.*, Vail, Colo., U.S.A., 1976, p. 443.
- 8 L. R. Morss and M. C. McCue, *Inorg. Chem.*, **14**, 1624 (1975).
- 9 D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney and R. L. Nuttall, 'The NBS Tables of Chemical Thermodynamic Properties', *J. Phys. Chem. Ref. Data*, **11**, Suppl. 2 (1982).
- 10 R. Blachnik and D. Selle, *Z. Anorg. Allg. Chem.*, **454**, 82 (1979).
- 11 J. Fuger, *J. Phys. (Paris)*, **40**, Colloq. C4, 207 (1979).
- 12 H. D. B. Jenkins and K. F. Pratt, *Adv. Inorg. Chem. Radiochem.*, **22**, 1 (1979); *Prog. Solid State Chem.*, **12**, 125 (1979).

- 13 H.-J. Seifert, H. Fink, G. Thiel and J. Uebach, *Z. Anorg. Allg. Chem.*, **520**, 151 (1985).
- 14 L. R. Morss, *Chem. Rev.*, **76**, 827 (1976).
- 15 V. B. Parker, D. D. Wagman and D. Garvin, *U.S. Natl. Bur. Stand. Report, NBSIR 75-968*, 1975.
- 16 V. B. Parker, *U.S. Natl. Bur. Stand. Report, NSRDS-NBS2*, 1965; A. D. Westland and M. T. H. Tarafder, *Can. J. Chem.*, **61**, 1573 (1983).
- 17 T.-I. Li, G. D. Stucky and G. L. McPherson, *Acta Crystallogr., Sect. B*, **29**, 1330 (1973).