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Enthalpies of Formation of Ternary Lanthanide(II) Chlorides: $CsSmCl_3$, $CsTmCl_3$ and $CsYbCl_3$*

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In 1978 Meyer [1] reported the synthesis and crystal structure of a series of ternary lanthanide chlorides $CsLnCl_3$ (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, $CsEuCl_3$, and calculated the enthalpy of the reaction

$$LnCl_2(s) + CsCl(s) = CsLnCl_3(s) \qquad (1)$$

to be +1.7±8.1 kJ mol^{-1}. They concluded that the stabilization of this perovskite lattice for Eu^{2+} was negligible because Eu^{2+} 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 $CsLnCl_3$ (Ln = Nd, Dy) or $ALnCl_3$ 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

$CsSmCl_3$ and $CsTmCl_3$ were synthesized by metallothermic (Cs) reduction of trichlorides in arc-welded tantalum crucibles. $CsYbCl_3$ was synthesized similarly by metallothermic reduction (Yb) of $Cs_3Yb_2Cl_9$. 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 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^{2+} symbolizes a cation that is oxidized in aqueous solution):

$$Ln^{2+} + H^+ = Ln^{3+} + \tfrac{1}{2}H_2(g) \qquad (2)$$

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

$$Ln^{2+} + \tfrac{1}{4}O_2(aq) + H^+ = Ln^{3+} + \tfrac{1}{2}H_2O \qquad (3)$$

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 $Ln(OH)_3$ precipitation begin. Analytical data are shown in Table I.

TABLE I. Analyses of $CsLnCl_3$ (mass percent)

Compound	Ln(II)		Cl^-	
	Found	Calc.	Found	Calc.
$CsSmCl_3$	38.49	38.60		27.30
$CsTmCl_3$	44.10	41.39	25.22	26.06
$CsYbCl_3$	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 $CsYbCl_3$, 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 $CsYbCl_3$ 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

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

Mass (mg)	q^a (J)	$\Delta H°$ (kJ mol^{-1})
$CsSmCl_3$ in 140 cm^3 of 2.0 mol dm^{-3} 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)
$CsTmCl_3$ in 880 cm^3 of 4.0 mol dm^{-3} HCl(aq)		
57.81	34.63	−244.5
26.34	16.41	−254.3
	Mean	−249 ± 20 (est. confidence)
$CsYbCl_3$ in 140 cm^3 of 4.0 mol dm^{-3} 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)
$CsYbCl_3$ in 140 cm^3 of 0.001 mol dm^{-3} HCl(aq)		
81.69	29.11	−146.9
28.31	9.92	−144.5
	Mean	−145.7 ± 10.8 (est. confidence)

[a] Corrected for evaporation of water into N_2 in ampoule and into H_2 evolved.

that $CsYbCl_3$ 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, $\Delta_f H°(CsYbCl_3,s) = -1285 \pm 10$ kJ mol^{-1}.

From these enthalpies of formation, and from the enthalpies of formation of CsCl (−442.3 ± 0.2 kJ mol^{-1}) [6], $SmCl_2$ (−802.5 ± 3.3 kJ mol^{-1}) [7], $TmCl_2$ (−709.1 ± 4.2 kJ mol^{-1}) [8] and $YbCl_2$ (−800 ± 7 kJ mol^{-1}) [9]*, we calculate the enthalpies of reaction (1) to be +14 ± 7, −43 ± 20 and −43 ± 12 kJ mol^{-1} for $CsSmCl_3$, $CsTmCl_3$ and $CsYbCl_3$, respectively.

Table 3 of the paper by Nocera *et al.* [2] attempted to correlate the crystallographic properties of MCl_2 and $CsMCl_3$ 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 $CsNdCl_3$ and $CsDyCl_3$. 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 $\Delta G°$ must be considered. Some of these competing reactions were presented by Meyer [3]. From Table IV we estimate $\Delta H(1)$ to be +25 kJ mol^{-1} for Nd and we use $\Delta_f H°(NdCl_2,s) = -706.9$ kJ mol^{-1} [8] to calculate $\Delta_f H°(CsNdCl_3,c)$ to be −1124 kJ mol^{-1}; we estimate $\Delta H(1)$ to be −30 kJ mol^{-1} for Dy and we use $\Delta_f H°(DyCl_2,s) = -693$ kJ mol^{-1} [7] to calculate $\Delta_f H°(CsDyCl_3,s)$ to be −1165 kJ mol^{-1}.

For the interesting reaction

$$Cs(s) + NdCl_3(s) = CsNdCl_3(s) \qquad (4)$$

we use $\Delta_f H°(NdCl_3,s) = -1041$ kJ mol^{-1} [8] and calculate $\Delta H°(4) = -83$ kJ mol^{-1}. Even more favorable, however, is the simple reduction

$$Cs(s) + NdCl_3 = CsCl(s) + NdCl_2(s) \qquad (5)$$

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

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*Error limits were estimated from the original literature.

TABLE III. Thermochemical Cycle for $\Delta_f H°(CsLnCl_3, s)$ at 298.15 K

Ln	Soln. (mol dm^{-3})	ΔH_1 (kJ mol^{-1})	ΔH_2 (kJ mol^{-1})	ΔH_3 (kJ mol^{-1})	ΔH_4 (kJ mol^{-1})	ΔH_5 (kJ mol^{-1})	$\Delta_f H°(CsLnCl_3, s)$ (kJ mol^{-1})
Sm	2.0	−212.3 ± 5.9	−690.1 ± 1.3^a	−325.2 ± 0.04^a	−442.3 ± 0.2^c	+15 ± 1^d	−1230 ± 6
Tm	4.0	−249 ± 20	−698.0 ± 1.3^a	−316.8 ± 0.04^b	−442.3 ± 0.2^c	+13.70 ± 0.24^e	−1194 ± 20
Yb	4.0	−134.5 ± 8.5	−617.7 ± 2.8^a	−316.8 ± 0.04^b	−442.3 ± 0.2^c	+13.70 ± 0.24^e	−1283 ± 9
Yb	0.001	−146 ± 11	−674.5 ± 3.0^a	−334.2 ± 0.04^b	−442.3 ± 0.2^c	+17.92 ± 0.42^e	−1287 ± 12

$CsLnCl_3(s) + HCl(soln) = LnCl_3(soln) + CsCl(soln) + \frac{1}{2}H_2(g)$	ΔH_1
$Ln(s) + 3HCl(soln) = LnCl_3(soln) + \frac{3}{2}H_2(g)$	ΔH_2
$H_2(g) + Cl_2(g) = 2HCl(soln)$	ΔH_3
$Cs(s) + \frac{1}{2}Cl_2(g) = CsCl(s)$	ΔH_4
$CsCl(s) = CsCl(soln)$	ΔH_5

[a] Ref. 14. [b] Ref. 15. [c] Ref. 6. [d] Estimated. [e] Ref. 16. [f] $\Delta_f H°(CsLnCl_3,s) = -\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$.

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 $CsMCl_3$	t[a]	ΔH (kJ mol^{-1})
Ni	0.69	$CdCl_2$ (layer)	6	hexag. (2*L*)[b]	6	1.044	−38
Cu	0.73	layer (square planar)	4	hexag. (2*L*)	6	1.027	−36
Zn	0.74	tetrahedral	4	unknown		1.023	
Co	0.745	$CdCl_2$ (layer)	6	hexag. (2*L*)	6	1.021	−40
Fe	0.78	$CdCl_2$ (layer)	6	hexag. (2*L*)	6	1.007	−39
Mn	0.83	$CdCl_2$ (layer)	6	hexag. (9*L*)	6	0.988	−41
Cd	0.95	$CdCl_2$ (layer)	6	hexag. (6*L*)	6	0.945	
Ca	1.00	distorted SnO_2	6	perovskite	6	0.928	−36
Yb	1.02	SrI_2	7	perovskite	6	0.922	−43
Tm	1.03	SrI_2	7	perovskite	6	0.919	−43
Dy	1.07	$SrBr_2$	7, 8	unknown		0.906	
Eu	1.17	$PbCl_2$	7 (or 9)	dist. perovskite	6	0.876	+ 2
Sr	1.18	fluorite	8	dist. perovskite	6	0.872	
Pb	1.19	$PbCl_2$	7 (or 9)	dist. perovskite	6	0.869	
Sm	1.19	$PbCl_2$	7 (or 9)	dist. perovskite	6	0.869	+15
Nd	1.21	$PbCl_2$	7 (or 9)	unknown		0.864	
Ba	1.35	$PbCl_2$	7 (or 9)	unknown		0.826	

[a] Goldschmidt tolerance factor. [b] Ref. 17.

For the parallel Dy system, we have

$$Cs(s) + DyCl_3(s) = CsDyCl_3(s) \qquad (6)$$

We use $\Delta_f H^\circ(DyCl_3, \text{monoclinic}) = -989.1$ kJ mol^{-1} [7] and we calculate $\Delta H^\circ(6) = -176$ 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

$$Cs(s) + DyCl_3(s, \text{monoclinic})$$

$$= \tfrac{1}{3}Cs_3DyCl_6(s) + \tfrac{1}{2}DyCl_2(s) + \tfrac{1}{6}Dy(s) \qquad (7)$$

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

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