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Solution enthalpies of hydrates $LnCl_3{\cdot}xH_2O$ (Ln=Ce–Lu)[1]

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Abstract

Trichlorides of the lanthanide elements Ln=Ce–Lu form: (a) isotypic hexahydrates $LnCl_3{\cdot}6H_2O$ with a coordination number (CN) 8 for the Ln^{3+} ions. (b) Two isotypic groups of trihydrates $LnCl_3{\cdot}3H_2O$, in the first group Ln=Ce-Dy the CN is 8; the structure of the second group Ln=Er–Lu is unknown. With Ho no trihydrate exists; a dihydrate is formed. (c) Two isotypic groups of monohydrates $LnCl_3{\cdot}H_2O$ with unknown structure – Ln=Ce–Dy and Ln=Ho–Lu. For all compounds and for anhydrous chlorides $LnCl_3$ solution enthalpies were measured with an isoperibolic calorimeter. The $\Delta_{sol}H^0$ values do not depend only on the difference (lattice enthalpies/hydration enthalpies), but also on the state in solution. According to Spedding the *CN* of the Ln^{3+} ions against water changes from 9 to 8 between Nd and Sm, causing minima in the series of solution enthalpies. Dihydrates $LnCl_3{\cdot}2H_2O$ are found for Ln=Ce, Pr, Nd, Sm and presumably for Eu and Gd. They are not yet well characterised. © 1998 Elsevier Science B.V.

Keywords: Hydrates of lanthanide chlorides; Preparation; Crystal structures; Solution enthalpies

1. Introduction

For two decades we have been investigating the formation of ternary chlorides in pseudobinary systems alkali metal chlorides/$LnCl_3$, where Ln are the elements from Ce to Lu. Starting compounds for the preparation of anhydrous rare earth chlorides are their hexahydrates. For Ln=Nd–Lu they crystallize at ambient temperature from solutions of oxides in hydrochloric acid. The earlier elements La–Pr form hepta-hydrates; however, these are already dehydrated at temperature lower than 50°C to the hexahydrates.

The compounds $LnCl_3{\cdot}6H_2O$ are isotypic: they crystallize in the monoclinic space group P2/n, in which monomeric units $[LnCl_2(H_2O)_6]^+$ are held together by the third Cl^- ions.

With few exceptions the hexahydrates can be dehydrated to trihydrates. Monohydrates, in some cases dihydrates also, were found by thermogravimetry. A comprehensive TG investigation for all elements Ln was performed in 1965 by Haeseler and Matthes [1]. They used air and 1:1 air/HCl mixtures as the gas atmosphere. However, instead of the use of a mixture with HCl, they could not suppress the formation of oxidchlorides by hydrolysis, mainly with smaller ions. These are stronger Pearson acids and are therefore more liable to reactions with water like $LnCl_3+H_2O=LnOCl+2HCl$. As a consequence the mass loss in TG at temperatures higher than ca. 80°C was interpreted repeatedly as the formation of compounds like, for example, $DyCl_3{\cdot}2.5H_2O$.

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[1] Dedicated to Professor Antonius Kettrup on the occasion of his 60th birthday.

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To avoid such misinterpretations we used another strategy when investigating the dehydration of the hydrates of cerium (III) chloride [2]: $CeCl_3{\cdot}xH_2O$ was heated in a drying cabinet and greater than 90°C in an HCl stream to temperatures increasing all 10 h at 5°C. The samples – about 10 g in ceramic boats – were weighed at each step to control the loss of water. If the weight loss was as high as calculated for the formation of an expected lower hydrate, the composition of the sample was controlled by X-ray diffraction (XRD). Thus, we could find out if either a new phase was formed or if we had a mixture of the two phases. This decision was possible by comparing the pattern with that of analogous hydrates of other lanthanide chlorides. Thus, we could prepare the existing hydrates in amounts sufficient for measuring solution enthalpies. These measurements are described in this paper; the $\Delta_{sol}H^0$ values are discussed depending on the ionic radii of the Ln^{3+} ions.

2. Experimental

2.1. Preparation of hexahydrates $LnCl_3{\cdot}6H_2O$

Lanthanide oxides (99.9%, Fa. Heraeus, Hanau) were dissolved in concentrated hydrochloric acid and evaporated to saturation at ca. 50°C. Under cooling with ice the chloride–hexahydrates were precipitated with gaseous HCl, sucked off with a glass sinter crucible, washed with ether and dried at ca. 50°C. They were identified by comparing their X-ray patterns with calculated intensities in s.g. $P2/n$, using the site parameters of $PrCl_3{\cdot}6H_2O$ [3]. The correct water content was controlled by thermogravimetry (Thermobalance TG 750, Stanton Redcroft), using dehydration to the trihydrate. (Chemical analysis for Ln and Cl was not applied because the results are not sufficiently sensitive.)

2.2. X-ray powder patterns

Powder patterns were taken at ambient temperature with a Philips PW 1050/25 goniometer equipped with a proportional counter and a vacuum attachment. During exposure (Cu K_α radiation) the samples were kept under a helium atmosphere.

2.3. Solution calorimetry

The heats of solution were measured using an isoperibolic underwater calorimeter first described in 1978 [4]. The solvent H_2O was slightly acidified with HCl (10^{-2} mol l^{-1}). In a silver vessel of 1.3 l volume samples of 2–4 g in thin-walled glass ampoules are cracked under water at the start of the measurement. Thus, with a dissolution rate 1:15 000 virtually ideal solutions are formed. The change of temperature ΔT against the surroundings – a thermostat at ca. 25°C with a temperature constancy of 2×10^{-4}°C – generated by the solution enthalpy is measured with a thermopile. The inevitable heat loss is compensated according to Dickinson: The corrected temperature change ΔT^* is obtained by setting $F_1=F_2$ in Fig. 1. The calibration was done by Joule's heat giving a temperature change ΔT_E. The heat of solution Q_L is finally calculated from the equation

$$\frac{Q_L}{\Delta T^*} = \frac{Q_E}{\Delta T_E}$$

For the solution enthalpy of KCl we found 17.67±0.05 kJ mol^{-1} from the literature [5].

3. Results

In Table 1 the measured solution enthalpies are compiled. Each value is the mean of two measurements with the deviation for the last digit in brackets.

Below these values the preparation temperatures at which the weight loss of ca. 10 g hydrate has become greater than ca. 0.05 g in 10 h are given. Then, the sample was kept at this temperature till the weight loss reached the calculated value. Experience had proved that at temperatures higher than ca. 70°C the formation of oxide chlorides by hydrolysis became effective. As a consequence only the dehydration of hexahydrates up to $NdCl_3{\cdot}6H_2O$ could be performed in air, using a drying cabinet.

One example for this method: From 10.00 g $HoCl_3{\cdot}6H_2O$, 8.56 g $HoCl_2{\cdot}2H_2O$ will be formed. The temperature of a perceptible degree of dehydration was 70°C. This procedure had to be performed in an HCl atmosphere. After 30 h the formation of the dihydrate was complete; this was controlled by an XRD record.

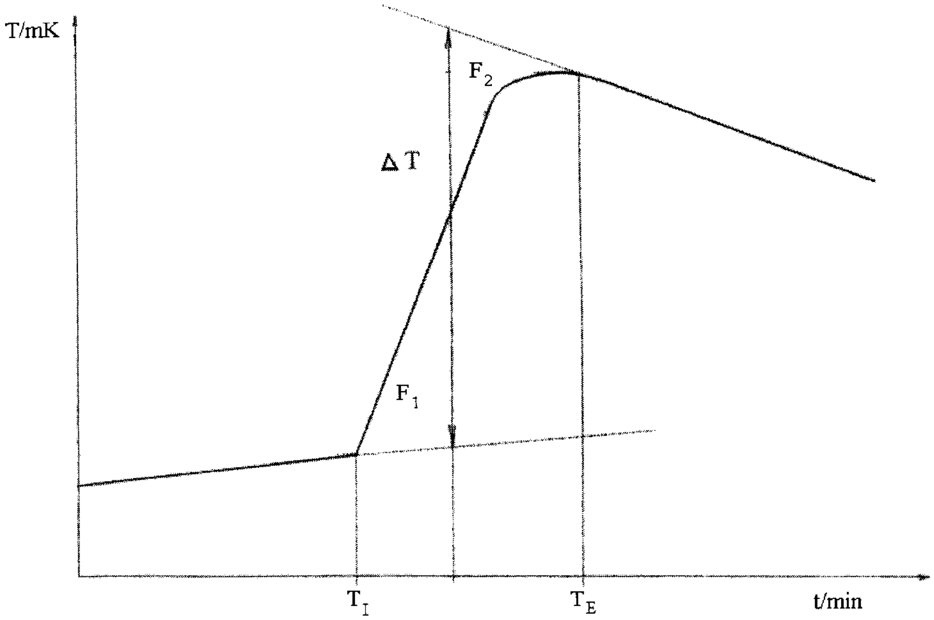

Fig. 1. Temperature–time diagram for an exothermic dissolution reaction in an isoperibolic calorimeter.

The preparation of monohydrates in HCl could be made without difficulty because their range of existence is ca. 50°C. For instance, $HoCl_3 \cdot 2H_2O$ is dehydrated to $HoCl_3 \cdot H_2O$ at 100–120°C. The formation of anhydrous $HoCl_3$ begins above 180°C. However, it is necessary to increase the temperature slowly to prevent partial hydrolysis. Thus, the dehydration of 10 g $HoCl_3 \cdot 6H_2O$ to $HoCl_3$ takes altogether 2 weeks.

The proof that for $HoCl_3$, no trihydrate exists, is given in Fig. 2. An X-ray pattern of a preparation with the composition ($HoCl_3$+$3H_2O$) reveals a superposition of the peaks from $HoCl_3 \cdot 2H_2O$ and $HoCl_2 \cdot 2H_2O$. The dihydrate itself has another peaks-motif than the trihydrates of $TbCl_3 \cdot 3H_2O$ and $ErCl_3 \cdot 3H_2O$, respectively.

In the same way it could be proved that for dysprosium the lower hydrates $DyCl_3 \cdot 3H_2O$ and $DyCl_3 \cdot 1H_2O$ exist, but no hydrate with 2.5 H_2O [1].

$DyCl_3 \cdot 3H_2O$ belongs to an isotypic group of trihydrates ranging from $CeCl_3 \cdot 3H_2O$ to $TbCl_3 \cdot 3H_2O$. It crystallizes in Pnma with Z=4. The structure consists of $[LnCl_{4/2}Cl(H_2O)_3]$ chains where two Ce^{3+} ions are connected via two chloride ions.

Lattice parameters: a=12.22 Å; b=8.56 Å; c=6.68 Å. *hkl* values and intensities for the reflexes up to 20° are given in Table 2; site parameters for the intensity calculation are taken from $CeCl_3 \cdot 3H_2O$ [2].

A special problem was the further dehydration of the trihydrates $LnCl_3 \cdot 3H_2O$ with Ln=Ce–Gd. According to the TG measurements dihydrates should exist. We could confirm this for the elements Ln=Ce, Pr, Nd and Sm; for Eu and Gd we obtained no unequivocal results. The prepared dihydrates are very hygroscopic, give only poor X-ray patterns and reveal a high tendency to lose water under the formation of monohydrates. Thus, the temperature range for their preparation is only ca. 5°C.

From the literature only solution enthalpies of anhydrous chlorides and their hexadrates are known, compiled in [6,7]. It must be pointed out that our values for the hexahydrates are 1.0–1.5 kJ mol^{-1} less negative than those from the literature.

For completeness the solution enthalpies for the existing heptahydrates $LnCl_3 \cdot 7H_2O$ (Ln=Ce, Pr) at ambient temperature were also measured. These compounds were prepared by precipitation with HCl gas from saturated solutions at 0°C, washing with ether and drying in a N_2 stream at 25°C.

Measured values in kJ mol^{-1}: $CeCl_3 \cdot 7H_2O$: −25.3(2) ([8]: −28.9) $PrCl_3 \cdot 7H_2O$: −26.1(1) ([8]: −29.5)

Table 1
Solution enthalpies $\Delta_{sol}H^0$ in kJ mol^{-1} and preparation temperatures

	$LnCl_3\cdot 6H_2O$	$LnCl_3\cdot 3H_2O$	$LnCl_2\cdot 2H_2O$	$LnCl_3\cdot H_2O$	$LnCl_3$
Ce	− 39.4(1)	− 89.3(5)	− 108.6(6)	− 118.1(8)	− 138.9(8)
	−/50°	−85°/75°	100°/85°	−140°/120°	
Pr	−38.1(1)	−85.4(1)		−112.6(2)	−145.8(5)
	55°/70°	90°/75°	108°/90°	155°/>120°	
Nd	−36.5(1)	−91.9(8)	−112.2(3)	−116.1(4)	−149.5(4)
	−/75°	−/85°	−/100°	−/150°	
Sm	−33.2(2)	−93.5(4)		−137.0(2)	−164.7(2)
	55°/75°	95°/95°	115°/110°	130°/>150°	
Eu	−34.1(2)	−97.9(4)		−144.3(1)	−171.5(3)
	−/85°	−/120°		−/>150°	
Gd	−36.5(1)	−−100.7(8)		−149.5(3)	−180.3(5)
	55°/85°	75°/120°	110°/−	150°/160°	
Tb	−37.5(2)	−107.5(4)		−155.9(3)	−188.8(4)
	60°/90°	−/>130°	125°/−	∼200°/180°	
Dy	−39.4(5)	−107.6(2)		−157.6(2)	−197.1(3)
	∼65°/90°	120°/>120°		230°/190°	
Ho	−41.2(2)	Not ex.	−135.1(9)	−166.1(9)	−209.4(9)
	85°/95°	−	135°/>120°	210°/>190°	
Er	−42.8(2)	−112.7(1)		−167.3(1)	−211.9(1)
	80°/95°	(115°)/>120°	130°/−	210°/>190°	
Tm	−43.9(4)	−115.1(3)	−	−170.1(6)	−212.2(7)
	−/95°	−/>120°		−/>190°	
Yb	−45.9(2)	−119.5(3)	−	−175.4(4)	−212.9(8)
	−/100°	−/>120°		−/>190°	
Lu	−47.2(5)	−111.3(7)	−	−172.7(3)	(−211.6 (6)
	−/100°	−/>120		−/>190	

TG values [1] cursive.

4. Discussion

4.1. The existence of chloride–hydrates

The main issue is how to prepare chloride–hydrates with the exact amount of hydrate water. Neither the method of dehydration by heating at ambient pressure or in vacuum nor TG measurements are equilibrium methods, because the H_2O pressure at an applicated temperature is disturbed by spreading to an unlimited volume either by a gas stream or by an applied vacuum. Thus, one has to control the dehydration process by continued weighing. It is appropriate to choose the preparation temperature as low as possible. Thus, this temperature will be in general lower than that found by 'rapid' method thermogravimetry. However, it must be pointed out, that equilibrium processes are also possible: TG measurement in labyrinth crucibles work quasiisobar and preparative methods working with a gas stream of controlled H_2O pressure are also possible, but are rather unwieldy.

As described for the dehydration of $HoCl_3\cdot 6H_2O$, the existence or non-existence of a lower hydrate was insured by X-ray patterns. This can be done exactly when the structures of all involved phases are known, so that peak intensities can be calculated. According to our findings monohydrates exist for all lanthanide elements. The compounds $LnCl_3\cdot H_2O$ with Ln=Ce–Tb are isotypic; a second group of isotypic monohydrates ranges from $DyCl_3\cdot 6H_2O$ to $LuCl_3\cdot 6H_2O$. For trihydrates again two groups exist. The structures for the compounds $LnCl\cdot 3H_2O$ with Ln=CE–Tb were recently determined in our group [2]. The structure of the isotypic group Ln=Ho–Lu is not yet known. Trihydrates with Ho and also Y do not exist; here dihydrates are formed. The issue of the existence of other dihydrates has already been discussed in Section 3.

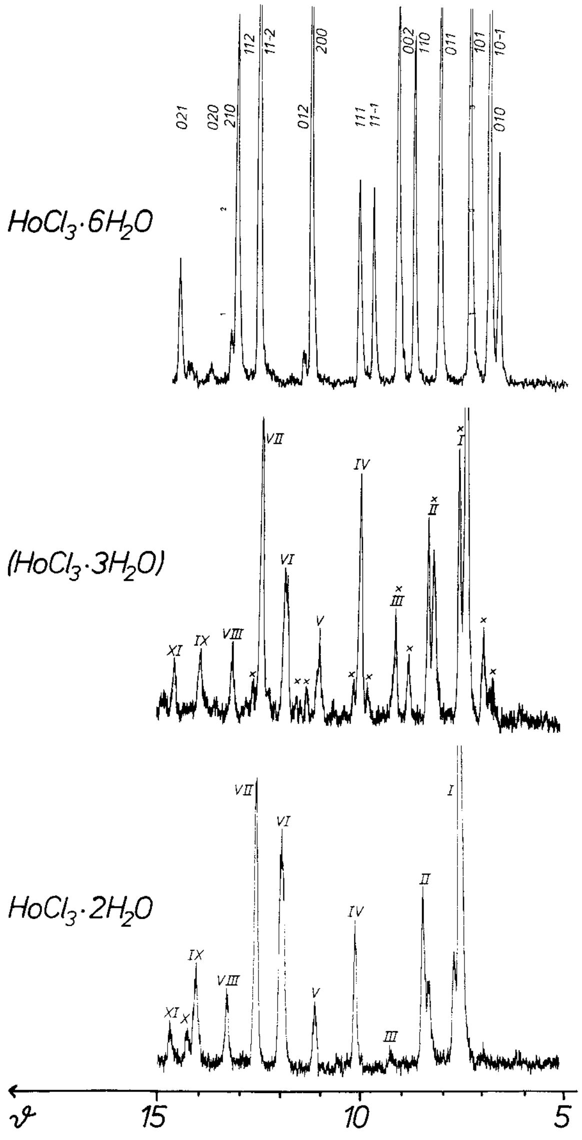

Fig. 2. Measured X-ray peaks for $HoCl_3{\cdot}6H_2O$, $HoCl_3{\cdot}2H_2O$ and a sample with the composition ($HoCl_3+3H_2O$).

In the literature other hydrates are also described, like $NdCl_3{\cdot}5H_2O$ and $NdCl_3{\cdot}4H_2O$ [9]. As discussed in an earlier paper [2], we could not confirm their existence.

Table 2
X-ray powder pattern for $DyCl_3{\cdot}3H_2O$

ϑ/grad	hkl	$I_{exp.}$	$I_{cal.}$
7.25	200	64	84
7.56	101	100	100
8.36	011	29	34
8.39	210	17	14
10.28	020	23	23
11.10	211	22	29
12.62	220	20	18
12.78	121	33	32
13.82	311	24	18
14.26	221	17	14
14.77	112	23	28
15.54	410	21	18
	031		7
16.92	411	41	7
	022		14
17.36	122	15	5
18.00	420	23	11
18.14	312	28	21
18.50	231	32	24
19.25	421	20	13

Cu K_α, ϑ=0-20°; s.g. Pnma.

4.2. Dependence of $\Delta_{sol}H^0$ on ionic radii

As the thermodynamic circle for the solution of anhydrous chlorides shows, solution enthalpies can be expressed as $\Delta_{sol}H^0=-\Delta_{lat.}H^0+\Delta_{hyd.}H^0$, where $\Delta_{lat.}H^0$=lattice enthalpy, $\Delta_{hyd.}H^0$=hydration enthalpy

$$\begin{tikzcd}
LnCl_3 \arrow[rr, "\Delta_{sol}H^0"] \arrow[dr, "-\Delta_{lat.}H^0"'] & & Ln(H_2O)_x^{3+} + 3Cl(H_2O)_y^- \\
& (Ln^{3+} + 3Cl^-)_g \arrow[ur, "\Delta_{hyd}H^0"'] &
\end{tikzcd}$$

Both energies vary with $1/r(Ln^{3+})$. Thus, with decreasing radii in the series $Ce^{3+}\Rightarrow Lu^{3+}$ a greater affordance of vaporising the crystal lattice (endothermic $\Delta_{lat.}H^0$) will be more or less compensated by a gain in $\Delta_{hyd}H^0$.

Hydration enthalpies are the sum of the hydration of the Ln^{3+} ions and Cl^- ions, whereby the second will be constant for all compounds. According to Spedding et al. [10] the coordination number of the Ln^{3+} ions against H_2O in aqueous solution is 9 for La^{3+}–Nd^{3+} and 8 for Gd^{3+}–Er^{3+}. Between these groups a 'displacement equilibrium' exists for Pm^{3+}, Sm^{3+} and Eu^{3+}. They derive their findings from partial molar volume data, calculated from specific gravimetry measurements of $LnCl_3$ solutions. On the other hand,

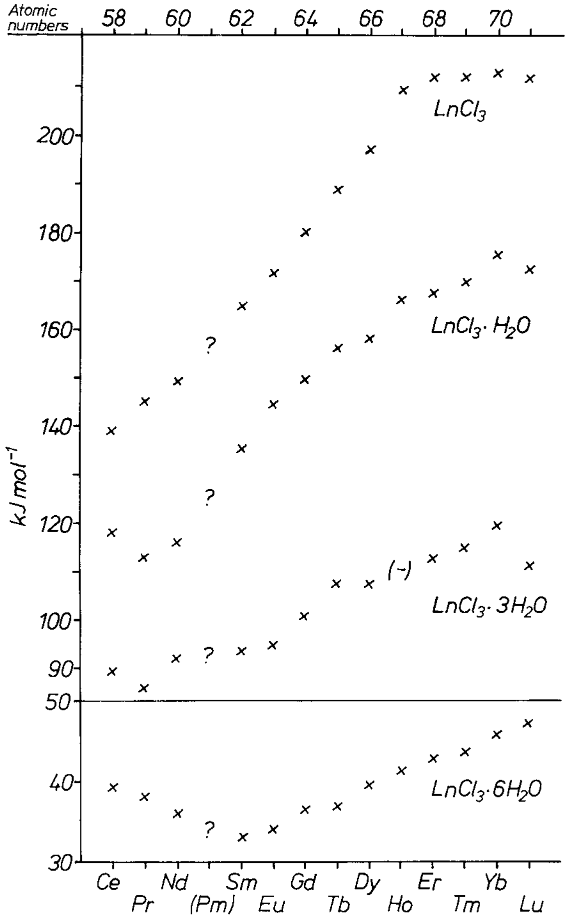

Fig. 3. Solution enthalpies in dependence on the atomic number.

all hexahydrates $LnCl_3{\cdot}6H_2O$ [11] have the same crystal structure with a coordination $[Ln(H_2O)_6Cl_2]^+$; their mole volumina, which are in a first approximation a measure for lattice enthalpy, decrease continuously from Ce^{3+} to Lu^{3+} (Fig. 3). That is, the energy to overwhelm these lattice forces becomes larger, and if this effect would be the only one the solution enthalpies should become more positive, and less exothermic.

However, the plot for all hydrates in Fig. 3 shows that from Sm^{3+} to Lu^{3+} the solution enthalpies become continuously more exothermic – they are determined by the increasing gain in energy by increasing hydration enthalpies. From Ce^{3+} to Nd^{3+} the coordination number decreases from 9 to 8 which causes a decrease in produced hydration enthalpy. This, however, must be the 'displacement equilibrium' as predicted by Spedding, over the whole range of Ce^{3+} to Sm^{3+}, otherwise a distinct falling-off would exist. This is in correspondence with the results of Helm et al. [12] obtained by the neutron scattering first-order difference technique with isotypic substitution. Kinks in the lines for the three- and monohydrates, might depend on change in crystal structure between Dy and Er for $LnCl_3{\cdot}3H_2O$ and between Dy and Ho for $LnCl_3{\cdot}H_2O$.

This 'displacement effect' is less distinct for anhydrous chlorides. As already pointed out by Burgess and Kijowski [7], "the general trend of increasing negative enthalpies of solution going from $LaCl_3$ to $LuCl_3$ indicates that hydration enthalpies, which for the 3+ -cations increase in this direction as ionic radii decrease, dominate increasingly over lattice enthalpies." The fact, that from $HoCl_3$ to $LuCl_3$, solution enthalpies are almost constant means, that the term $(-\Delta_{\text{lat.}}H^0 + \Delta_{\text{hyd.}}H^0)$ has become constant: lattice enthalpy and $\Delta_{\text{hyd.}}H^0$ (Ln^{3+}) change in the same degree.

4.3. Quantitative estimations

Gunsilius et al. [13] have calculated with single crystal dates at ambient temperature the stable modification of $TbCl_3$ (UCl_3-type) and the Madelung part of lattice energy as 4520 kJ mol^{-1}. With a Born coefficient n=10 – mean of 3 Cl^- (n=9) and one Ln^{3+} (n=12) – the factor $(1-1/n)$ (see textbooks of solid state chemistry) is 0.9 and the lattice energy $E_L=E_{Mad}-E_{Rep}=4067$ kJ mol^{-1}. The van der Waals energy will be somewhat greater than that of $BaCl_2$ (110 kJ mol^{-1}) [14]), so that the lattice energy is more than 4200 kJ mol^{-1}. Thus anion polarisation is not considered.

This value must be compared with the experimental value in the equation $\Delta_{\text{sol}}H^0=\Delta_{\text{lat}}H^0-\Delta_{\text{hyd}}H^0(Tb^{3+})-3\Delta_{\text{hyd}}H^0(Cl^-)$. Hydration enthalpies are taken from Morss [15] who has derived them using solution enthalpies of the cubic elpasolites $Cs_2NaLnCl_6$: for $Tb^{3+}=-3604$ kJ mol^{-1}; for $Cl^- = -363.2$ kJ mol^{-1}. With $\Delta_{\text{sol}}H^0(TbCl_3)=-188.8$ kJ mol^{-1} one obtains $\Delta_{\text{lat}}H^0(TbCl_3)$ kJ mol^{-1} $=+189-3604-1090=-4505$.

The difference of 300 kJ mol^{-1} must be related to the polarisation effect. Thus the solution enthalpy is the difference of two big numbers, 4505 kJ mol^{-1} and $\Delta_{hyd}H^0_{ges}$ = 4694 kJ mol^{-1} – not a favourable situation for calculating solution enthalpies from these quantities.

An estimation can be made for the lattice enthalpies of $TbCl_3 \cdot 3H_2O$ and $TbCl_3 \cdot 6H_2O$. Taking into account that the CN for Tb^{2+} in solution is 8, the energy for forming one Tb^{3+}–H_2O bond is −450 kJ mol^{-1}.

Trihydrate: $[TbCl_{4/2}Cl(H_2O)_3]+5H_2O \Rightarrow [Tb(H_2O)_8]^{3+}$; $(\Delta_{hyd}H^0)_{eff} = -2250$ kJ mol^{-1}

$\Delta_{lat}H^0$ ($TbCl_3 \cdot 3H_2O$) kJ mol^{-1} = + 108−2250−1090 = −3232

Hexahydrate: $[TbCl_2Cl(H_2O)_6]^+ + 2H_2O \Rightarrow [Tb(H_2O)_8]^{3+}$; $(\Delta_{hyd}H^0)_{eff} = -900$ kJ mol^{-1}

$\Delta_{lat}H^0$($TbCl_3 \cdot 6H_2O$) kJ mol^{-1} = +38− 900−1090 = −1952.

To make such calculations for the second group of trihydrates and monohydrates, their crystal structures have to be determined.

Acknowledgements

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References

[1] G. Haeseler, F. Mattes, J. Less-Common Met. 9 (1965) 133.
[2] G. Reuter, H. Fink, H.J. Seifert, Z. Anorg. Allg. Chem. 620 (1994) 665.
[3] J. Chen, O. Xu, L. Li, J. Wu, G. Xui, Acta Crystallogr. C47 (1991) 1074.
[4] G. Thiel, H.J. Seifert, Thermochim. Acta 14 (1982) 363.
[5] S. Sunner, I. Wadsö, Acta Chem. Scand. 13 (1969) 97.
[6] H. Bommer, E. Hohmann, Z. Anorg. Allg. Chem. 248 (1941) 373.
[7] J. Burgess, J. Kijowski, Advanc. Inorg. Chem. Radiochem. 24 (1981) 57.
[8] R.J. Hinchey, J.W. Cobble, Inorg. Chem. 9 (1970) 917.
[9] G.J. Kipouros, R.A. Sharma, J. Less-Common Met. 160 (1990) 85.
[10] F.H. Spedding, M.J. Pikal, B.O. Ayers, J. Phys. Chem. 70 (1966) 2440.
[11] E.J. Gaeber, G.H. Conrad, S.F. Duliere, Acta Crystallogr. 21 (1966) 1012.
[12] L. Helm, D.H. Powell, A.E. Merbach, Swiss Neutron News 5 (1994) 16.
[13] H. Gunsilius, H. Borrmann, A. Simon, W. Urland, Z. Naturforsch. B43 (1988) 1023.
[14] T.E. Brackett, E.B. Brackett, J. Phys. Chem. 69 (1965) 3611.
[15] L.R. Morss, J. Phys. Chem. 75 (1971) 392.