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DETERMINATION OF STANDARD MOLAR ENTHALPIES OF FORMATION FOR RARE EARTH ISOTHIOCYANATE HYDRATES *

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ABSTRACT

The integral heats of solution of $RE(NCS)_3 \cdot nH_2O$ ($n = 7$ for RE ≡ La, Ce, Pr, Nd; $n = 6$ for RE ≡ Sm, Eu, Gd, Dy, Ho, Yb, Y) in aqueous KCl solution and those of KSCN in aqueous $RECl_3$ solution (RE, the rare earth elements mentioned above) have been measured calorimetrically at 298.15 K. By means of a thermochemical cycle suggested in this paper, the standard molar enthalpies of formation for the above eleven rare earth isothiocyanate hydrates were obtained and their lattice energies were calculated. Furthermore, corresponding data for four other compounds ($RE(NCS)_3 \cdot 6H_2O$ where RE ≡ Tb, Er, Tm, Lu) were estimated.

INTRODUCTION

Great interest has been aroused in the study of the coordination chemistry of the rare earth isothiocyanate hydrates because they can combine with various kinds of ligands to form coordinate compounds.

Spedding et al. [1–3] have done much work on the thermochemistry of rare earth chlorides. However, rare earth isothiocyanates as pseudohalides have scarcely been investigated by thermochemical methods. Thus, there are few thermochemical data available in the literatures concerning these isothiocyanates. The standard molar enthalpies of formation of rare earth isothiocyanate hydrates have not yet been reported.

In this paper, we suggest the following thermochemical cycle for deriving the standard molar enthalpies of formation of rare earth isothiocyanate hydrates:

$$KCl(c) + xH_2O(l) \xrightarrow{\Delta H_1} KCl \cdot xH_2O(aq) \tag{1}$$

$$RECl_3(c) + (3x+n)H_2O(l) \xrightarrow{\Delta H_2} RECl_3 \cdot (3x+n)H_2O(aq) \tag{2}$$

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$$\mathrm{RE(NCS)_3 \cdot \mathit{n}H_2O(c) + 3(KCl \cdot \mathit{x}H_2O)(aq)} \xrightarrow{\Delta H_3} \mathrm{RE(NCS)_3 \cdot 3KCl \cdot (3\mathit{x} + \mathit{n})H_2O(aq)} \qquad (3)$$

$$\mathrm{KSCN(c) + \tfrac{1}{3}[RECl_3 \cdot (3\mathit{x} + \mathit{n})H_2O](aq)} \xrightarrow{\Delta H_4} \mathrm{KSCN \cdot \tfrac{1}{3}RECl_3 \cdot \tfrac{1}{3}(3\mathit{x} + \mathit{n})H_2O(aq)} \qquad (4)$$

where $x = 200$ for RE ≡ La, Pr, Nd, Sm, Eu, Gd, Dy, Yb and $x = 500$ for RE ≡ Ce, Ho, Y.

Combining the above equations as follows gives eqn. (5):

eqn. (2) + 3 × eqn. (4) − 3 × eqn. (1) − eqn. (3) → eqn. (5)

$$\mathrm{RECl_3(c) + 3KSCN(c) + \mathit{n}H_2O(l)} \xrightarrow{\Delta H_5} \mathrm{RE(NCS)_3 \cdot \mathit{n}H_2O(c) + 3KCl(c)} \qquad (5)$$

$$\Delta H_5 = \Delta H_2 + 3\,\Delta H_4 - 3\,\Delta H_1 - \Delta H_3$$

In this study, we use Spedding's empirical equation for the relative apparent molar enthalpies of $RECl_3$ in aqueous solution [1–2], the best values of $\Delta H^\circ_{f\,RECl_3(c)}$ and $\Delta H^\circ_{f\,RE^{3+}(aq)}$ given by Morss [4] and the value of $\Delta H^\circ_{f\,Cl^-(aq)}$ recommended in ref. 5 to calculate ΔH_2. ΔH_1 could be selected from ref. 6. ΔH_3 and ΔH_4 have been measured calorimetrically by the present researchers.

EXPERIMENTAL

RE_2O_3 (99.9–99.99%), sulphuric acid (reagent grade), $Ba(OH)_2 \cdot 8H_2O$ (analytical grade) and NH_4SCN (reagent grade) were used to prepare $RE(NCS)_3 \cdot nH_2O$ by the following double decompositon reaction:

$$\mathrm{3Ba(NCS)_2 + RE_2(SO_4)_3 \rightarrow 3BaSO_4 + 2RE(NCS)_3}$$

After recrystallization, the $RE(NCS)_3 \cdot nH_2O$ crystals were put into a desiccator containing 50–55% H_2SO_4 until the weight of crystals became constant.

Both chemical analyses and molecular structure determinations by means of a Nicolet P3/F four-circle single-crystal X-ray diffractometer proved that the compositions of $RE(NCS)_3 \cdot nH_2O$ are as follows: $n = 7$ for RE ≡ La, Ce, Pr, Nd; $n = 6$ for RE ≡ Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y) [7]. The results of emission spectroscopic analysis show that the purity of $RE(NCS)_3 \cdot nH_2O$ is greater than 99.9%.

A modified RD-I heat conducting automatic calorimeter (144 pairs of thermocouples) was used for the calorimetric measurements. Heat changes up to 2 J could be exactly measured.

Two calorimetric components with the same structure are arranged symmetrically in an aluminium block kept at constant temperature and connected in opposition to form a twin system. Therefore, attention should be paid to the symmetry and equivalence of the "working element" and the "reference element" in all respects when carrying out the calorimetric measurements.

The heat effects due to the breaking of the glass ampoules are negligible compared with the measured heat.

The reliability of the calorimetric system was monitored in the present experiments by measuring the heat of reaction of Tris (about 0.1 g) and HCl (0.0998 N, 20 ml) at 298.15 K. The measured value is -29.75 ± 0.22 kJ mol^{-1}, which is consistent with the literature value of -29.771 kJ mol^{-1} [8]. The integral heat of solution of 1 mol KSCN in 500 mol water was also measured at 298.15 K as 24.45 ± 0.14 kJ mol^{-1}, in good agreement with the literature value of 24.44 kJ mol^{-1} [6].

According to the thermochemical cycle mentioned above, we measured the integral enthalpies of solution of $\mathrm{RE(NCS)_3 \cdot }n\mathrm{H_2O}$ in aqueous KCl solution ($\mathrm{KCl:H_2O} = 1:200$ mol/mol for RE ≡ La, Pr, Nd, Sm, Eu, Gd, Dy, Y; $\mathrm{KCl:H_2O} = 1:500$ for RE ≡ Ce, Ho, Y) and those of KSCN in aqueous $\mathrm{RECl_3}$ solution ($\mathrm{RECl_3:H_2O} = 1:607$ for RE ≡ La, Pr, Nd; $\mathrm{RECl_3:H_2O} = 1:606$ for RE ≡ Sm, Eu, Gd, Dy, Yb; $\mathrm{RECl_3:H_2O} = 1:1507$ for RE ≡ Ce; $\mathrm{RECl_3:H_2O} = 1:1506$ for RE ≡ Ho, Y).

The calorimetric system was calibrated electrically before and after the measurement of each set of integral enthalpies of solution and the mean value was taken for the calorimeter's heat constant K.

The uncertainty of the experimental results is expressed as twice the standard deviation of the mean.

RESULTS AND DISCUSSION

Integral enthalpies of solution of $\mathrm{RE(NCS)_3 \cdot }n\mathrm{H_2O}$ in aqueous KCl solutions, ΔH_3, integral enthalpies of solution of KSCN in aqueous $\mathrm{RECl_3}$ solutions, ΔH_4, and the total heat of reaction ΔH_5 are summarized in Table 1.

The calculation of standard molar enthalpies of formation of $\mathrm{RE(NCS)_3 \cdot }n\mathrm{H_2O}$ is shown below:

$$\Delta H^{\circ}_{\mathrm{f\,RE(NCS)_3 \cdot }n\mathrm{H_2O(c)}} = \Delta H_5 + \Delta H^{\circ}_{\mathrm{f\,RECl_3(c)}} + 3\Delta H^{\circ}_{\mathrm{f\,KSCN(c)}}$$
$$+ n\,\Delta H^{\circ}_{\mathrm{f\,H_2O(l)}} - 3\,\Delta H^{\circ}_{\mathrm{f\,KCl(c)}}$$

$\Delta H^{\circ}_{\mathrm{f\,H_2O(l)}} = -285.83$ kJ mol^{-1} (see ref. 9)

$\Delta H^{\circ}_{\mathrm{f\,KSCN(c)}} = -200.16$ kJ mol^{-1} (see ref. 6)

$\Delta H^{\circ}_{\mathrm{f\,KCl(c)}} = -436.75$ kJ mol^{-1} (see ref. 6)

TABLE 1

Heats of the thermochemical cycle at 298.15 ± 0.1 K

RE	$\Delta H^{\circ}_{f\,RE^{3+}(aq)}$ [a] (kJ mol^{-1})	$\Delta H^{\circ}_{f\,RECl_3(c)}$ [a] (kJ mol^{-1})	$\phi_{L\,RECl_3}$ [b] (kJ mol^{-1})	ΔH_2 [c] (kJ mol^{-1})	ΔH_4 (kJ mol^{-1})	ΔH_1 [e] (kJ mol^{-1})	ΔH_3 (kJ mol^{-1})	ΔH_5 (kJ mol^{-1})
La	−709.4	−1073.2	4.57	−132.87	24.31 ± 0.09	17.556	14.89 ± 0.12	−127.50
Ce	−700.4	−1058.0	3.68	−139.96	24.48 ± 0.15	17.560	14.78 ± 0.19	−133.98
Pr	−706.2	−1059.0	4.73	−143.71	24.40 ± 0.09	17.556	15.06 ± 0.12	−138.24
Nd	−696.6	−1041.8	4.69	−151.35	24.30 ± 0.12	17.556	15.27 ± 0.16	−146.39
Sm	−691.1	−1026.0	4.77	−161.57	24.34 ± 0.08	17.556	13.36 ± 0.15	−154.58
Eu	−605.6	−936.5	4.90	−165.44	24.34 ± 0.09	17.556	14.31 ± 0.12	−159.40
Gd	−687.0	−1007.6	4.95	−175.69	24.40 ± 0.09	17.556	14.34 ± 0.11	−169.50
Tb	−698.0	−1007.0	4.99	−187.25	24.38 [d]	17.556	14.00 [d]	−180.78 [d]
Dy	−695.9	−990.1	5.03	−202.01	24.36 ± 0.09	17.556	13.68 ± 0.11	−195.28
Ho	−707.0	−995.0	3.71	−209.53	24.41 ± 0.12	17.560	12.76 ± 0.16	−201.74
Er	−705.0	−995.0	4.91	−206.33	24.42 [d]	17.556	13.10 [d]	−198.84 [d]
Tm	−705.2	−991.0	4.92	−210.52	24.45 [d]	17.556	12.81 [d]	−202.65 [d]
Yb	−674.5	−960.0	4.86	−210.88	24.48 ± 0.11	17.556	12.52 ± 0.12	−202.63
Lu	−702.6	−985.7	4.91	−213.23	24.51 [d]	17.556	12.23 [d]	−204.60 [d]
Y	−715.0	−996.0	4.76	−215.48	24.56 ± 0.10	17.560	10.54 ± 0.16	−205.02

[a] From ref. 4.

[b] Example of the calculation of ϕ_L ($\phi_{L\,RECl_3}$ is the relative apparent molar enthalpy of $RECl_3$ in aqueous solution) [1,2]:

$$\phi^{0.09145m}_{L\,LaCl_3} = 6990.00m^{0.5} - 18851.9306m + 56881.9234m^{1.5} - 66921.7907m^{1.75} + 25185.78432m^{2} - 700.23677m^{2.75}$$

$$= 4.568 \text{ kJ mol}^{-1} \left(m \text{ denotes a molality of 1 mol kg}^{-1}\right).$$

[c] $\Delta H_2 = \Delta H^{\circ}_S + \phi_L = \Delta H^{\circ}_{f\,RE^{3+}(aq)} + 3\,\Delta H^{\circ}_{f\,Cl^-(aq)} - \Delta H^{\circ}_{f\,RECl_3(c)} + \phi_L$
$\Delta H^{\circ}_{f\,Cl^-(aq)} = -167.08$ kJ mol^{-1} (see ref. 5).

[d] Estimated value.

[e] From ref. 6.

TABLE 2

Standard molar enthalpies of formation ΔH_f° (298.15 K) of $RE(NCS)_3 \cdot nH_2O$

RE	ΔH_5 (kJ mol^{-1})	$\Delta H^\circ_{f\,RECl_3(c)}$ (kJ mol^{-1})	$\Delta H^\circ_{f\,RE(NCS)_3 \cdot nH_2O(c)}$ (kJ mol^{-1})
La	−127.50	−1073.2	−2491.7
Ce	−133.98	−1058.0	−2483.0
Pr	−138.24	−1059.0	−2488.3
Nd	−146.39	−1041.8	−2479.2
Sm	−154.58	−1026.0	−2185.8
Eu	−159.40	−936.5	−2101.1
Gd	−169.50	−1007.6	−2182.3
Tb	−180.78 [a]	−1007.0	−2193.0 [a]
Dy	−195.28	−990.1	−2190.6
Ho	−201.74	−995.0	−2202.0
Er	−198.84 [a]	−995.0	−2199.0 [a]
Tm	−202.65 [a]	−991.0	−2198.9 [a]
Yb	−202.63	−960.0	−2167.8
Lu	−204.60 [a]	−985.7	−2195.5 [a]
Y	−205.02	−996.0	−2206.0

[a] Estimated value.

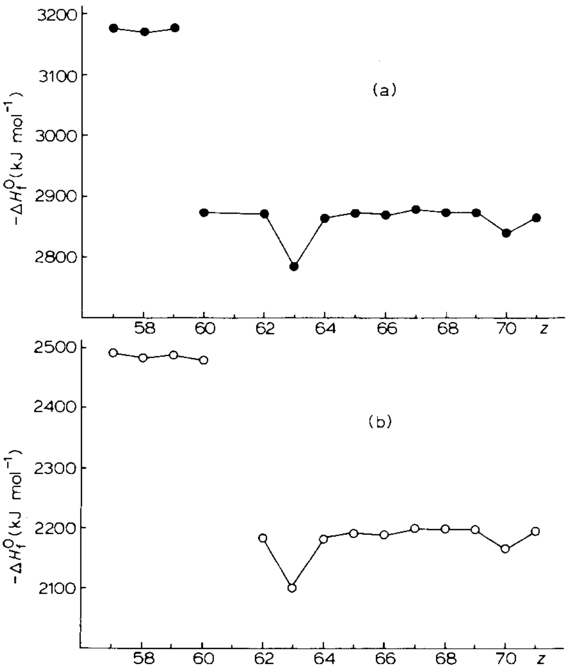

Fig. 1. A plot of $-\Delta H^\circ_{f\,LnCl_3 \cdot nH_2O}$ and $-\Delta H^\circ_{f\,Ln(NCS)_3 \cdot nH_2O}$ against the atomic numbers of the lanthanoids: (a) $LnCl_3 \cdot nH_2O$; (b) $Ln(NCS)_3 \cdot nH_2O$.

The best values of $\Delta H^\circ_{\mathrm{f\,RECl_3(c)}}$ were taken from the literature [4]. The results of the calculations are given in Table 2.

In Fig. 1, $-\Delta H^\circ_{\mathrm{f\,RE(NCS)_3 \cdot \mathit{n}H_2O}}$ and $-\Delta H^\circ_{\mathrm{f\,RECl_3 \cdot \mathit{n}H_2O}}$ are plotted against the atomic numbers of the elements in the lanthanide series. It is seen from Fig. 1 that $-\Delta H^\circ_{\mathrm{f\,RE(NCS)_3 \cdot \mathit{n}H_2O}}$ is smaller than $-\Delta H^\circ_{\mathrm{f\,RECl_3 \cdot \mathit{n}H_2O}}$ by about 670–690 kJ mol^{-1} and a "double peak" is observed at the position of europium and ytterbium on the two curves. The similarity of the two curves in Fig. 1 was interpreted as due to the pseudohalogen nature of NCS$^-$.

We also calculated the lattice energies of $\mathrm{RE(NCS)_3 \cdot \mathit{n}H_2O}$ as follows:

$$\mathrm{RE^{3+}(g) + 3SCN^-(g) + \mathit{n}H_2O(g) \xrightarrow{\Delta H^\circ_L} RE(NCS)_3 \cdot \mathit{n}H_2O(c)}$$

$$\Delta H^\circ_{\mathrm{L}} = \Delta H^\circ_{\mathrm{f\,RE(NCS)_3 \cdot \mathit{n}H_2O(c)}} - \Delta H^\circ_{\mathrm{f\,RE^{3+}(g)}} - 3\,\Delta H^\circ_{\mathrm{f\,SCN^-(g)}} - n\,\Delta H^\circ_{\mathrm{f\,H_2O(g)}}$$

$$\Delta H^\circ_{\mathrm{L}} = \Delta U^\circ_{\mathrm{L}} + \Delta nRT$$

$$\Delta U^\circ_{\mathrm{L}} = \Delta H^\circ_{\mathrm{f\,RE(NCS)_3 \cdot \mathit{n}H_2O(c)}} - \Delta H^\circ_{\mathrm{f\,RE^{3+}(g)}} - 3\,\Delta H^\circ_{\mathrm{f\,SCN^-(g)}}$$

$$- n\,\Delta H^\circ_{\mathrm{f\,H_2O(g)}} - \Delta nRT$$

$\Delta H^\circ_{\mathrm{f\,H_2O(g)}} = -241.82$ kJ mol^{-1} (see ref. 9)

TABLE 3

Lattice energies ΔU_{L} (298.15 K) of $\mathrm{RE(NCS)_3 \cdot \mathit{n}H_2O}$

RE	$\Delta H^\circ_{\mathrm{f\,RE(g)}}$ [a] (kJ mol^{-1})	$I_1 + I_2 + I_3$ [a] (0 K) (kJ mol^{-1})	$I_1 + I_2 + I_3$ (298.15 K) (kJ mol^{-1})	$\Delta H^\circ_{\mathrm{f\,RE^{3+}(g)}}$ [b] (kJ mol^{-1})	$\Delta H^\circ_{\mathrm{f\,RE(NCS)_3 \cdot \mathit{n}H_2O}}$ (kJ mol^{-1})	$\Delta U^\circ_{\mathrm{L\,RE(NCS)_3 \cdot \mathit{n}H_2O}}$ (kJ mol^{-1})
La	431.0	3456	3474.6	3905.6	−2491.7	−4432
Ce	420.1	3523	3541.6	3958.7	−2483.0	−4477
Pr	356.9	3628	3646.6	4003.5	−2488.3	−4527
Nd	326.9	3697	3715.6	4042.5	−2479.2	−4557
Sm	206.7	3869	3887.6	4094.3	−2185.8	−4559
Eu	177.4	4036	4054.6	4232.0	−2101.1	−4612
Gd	397.5	3750	3768.6	4166.1	−2182.3	−4628
Tb	388.7	3790	3808.6	4197.3	−2193.0 [c]	−4669 [c]
Dy	290.4	3898	3916.6	4207.0	−2190.6	−4677
Ho	300.6	3923	3941.6	4242.2	−2202.0	−4723
Er	316.4	3934	3952.6	4269.0	−2199.0 [c]	−4747 [c]
Tm	232.2	4044	4062.6	4294.8	−2198.9 [c]	−4773 [c]
Yb	155.6	4194	4212.6	4368.2	−2167.8	−4815
Lu	427.6	3910	3928.6	4356.2	−2195.5 [c]	−4831 [c]
Y	421.3	3776	3794.6	4215.9	−2206.0	−4701

[a] See ref. 3.

[b] $\Delta H^\circ_{\mathrm{f\,RE^{3+}(g)}} = \Delta H^\circ_{\mathrm{f\,RE(g)}} + \Sigma_1^3 I_{\mathrm{RE}}$.

[c] Estimated value.

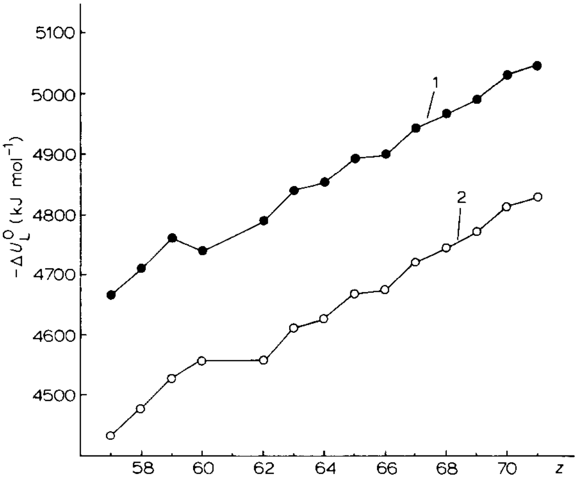

Fig. 2. A plot of $-\Delta U^o_{L\,LnCl_3 \cdot nH_2O}$ and $-\Delta U^o_{L\,Ln(NCS)_3 \cdot nH_2O}$ against the atomic numbers of the lanthanoids: curve 1, $LnCl_3 \cdot nH_2O$; curve 2, $Ln(NCS)_3 \cdot nH_2O$.

The method given in the literature [10] was used to calculate $\Delta H^o_{f\,SCN^-(g)}$:

$$\begin{aligned}\Delta H^o_{f\,SCN^-(g)} &= \Delta H^o_{f\,SCN^-(aq)} - \Delta H^o_{h\,SCN^-(g)}(\mathrm{ab}) - \Delta H^o_{f\,H^+(aq)}(\mathrm{ab}) \\ &= 76.44 - (-248.53) - 406.68 \\ &= -81.71\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

$\Delta H^o_{f\,SCN^-(aq)} = 76.44$ kJ mol^{-1} (see ref. 9)

$\Delta H^o_{h\,SCN^-(g)}(\mathrm{ab}) = -248.53$ kJ mol^{-1} (see ref. 11)

$\Delta H^o_{f\,H^+(aq)}(\mathrm{ab}) = 406.68$ kJ mol^{-1} (see ref. 10)

The results of the calculations are shown in Table 3.

A plot of $-\Delta U^o_{L\,RE(NCS)_3 \cdot nH_2O}$ and $-\Delta U^o_{L\,RECl_3 \cdot nH_2O}$, using values calculated by the present researchers from literature data [4,9,10], against the atomic numbers of the elements in the lanthanide series is shown in Fig. 2.

One can see that $-\Delta U^o_{L\,RE(NCS)_3 \cdot nH_2O}$ is smaller than $-\Delta U^o_{L\,RECl_3 \cdot nH_2O}$ by about 220–240 kJ mol^{-1}, since the thermochemical radius of SCN^- (195 pm) is larger than that of Cl^- (181 pm) and lattice energies are inversely proportional to the thermochemical radii of anions.

The magnitude of the lattice energy of $Y(NCS)_3 \cdot 6H_2O$ falls between those of $Dy(NCS)_3 \cdot 6H_2O$ and $Ho(NCS)_3 \cdot 6H_2O$. It has been proved once again that yttrium belongs to the group of heavy rare earth elements.

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