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THERMOCHEMICAL AND STRUCTURAL STUDIES OF COMPLEX ACTINIDE CHLORIDES $Cs_2NaAnCl_6$ (An = U–Cf); IONIZATION POTENTIALS AND HYDRATION ENTHALPIES OF An^{3+} IONS *

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ABSTRACT

Preparations of the complex chlorides $Cs_2NaAnCl_6$ (An = U, Np, Am, Cf), growth of a single crystal of Cs_2NaUCl_6, and lattice parameters of these face-centered cubic compounds are reported. The enthalpies of solution of these compounds in suitable media have been measured and their enthalpies of formation have been obtained. The enthalpy changes upon formation of these quaternary chlorides from the corresponding binary chlorides ($\Delta_{cplx}H^{o}_{m}$) are calculated and interpolated to calculate enthalpies of formation of $Cs_2NaCmCl_6$ and $Cs_2NaBkCl_6$. These results are combined with auxiliary structural, spectroscopic and thermodynamic data and with calculated lattice energies, to derive the third ionization potentials of the actinides U–Cf and the hydration enthalpies of their tripositive ions.

INTRODUCTION

The measurement of essential properties of the transuranium elements and the predictive understanding of how these properties change with atomic number have been a challenge to chemists and physicists since the discovery of these elements. Incentives for this understanding have been the choice of experimental conditions to discover new elements, the characterization of their physicochemical properties, the design of safe and efficient nuclear reactor fuels, the methodology of nuclear materials processing, and

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* Dedicated to Professor E.F. Westrum, Jr., on the occasion of his 70th birthday and in honour of his contribution to calorimetry and thermal analysis.

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the mastering of nuclear waste technology. This paper [1] represents an extension of an earlier model that was useful in correlating the energetic properties and in calculating the ionization potentials of the tripositive lanthanide ions [2,3].

Since most of the actinide elements have tripositive ions (for more than half of the actinides the tripositive state is the most stable), it is useful to construct a thermodynamic model that permits the properties of the +3 ions to be understood and interpreted systematically by means of a few fundamental measured properties. Such a model was developed by Nugent et al. [4] and refined by David et al. [5]. It correlated the tripositive aquo-ions with their gaseous atoms by generating a smoothly-changing energetic function $P(\mathrm{M})$ that incorporated experimentally-derived values of sublimation energies, promotion energies of the gaseous atoms to $f^n ds^2$ configurations, and enthalpies of formation of the ions $\mathrm{An}^{3+}(\mathrm{aq})$. There have also been independent efforts to calculate other properties of these ions, namely their ionization energies [6–10] and their hydration enthalpies [11]. More recently, models have been developed that interrelate the di-, tri- and tetrapositive oxidation states of most of the actinides [12–15].

In this work we have synthesized several members of the isostructural elpasolites [16] $\mathrm{Cs_2NaAnCl_6}$ and determined their molar enthalpies of formation by solution microcalorimetry. Following the general cycle described by Morss [2], we have taken advantage of these high symmetry elpasolites [17–20] to combine our new measurements with older and recent thermodynamic and structural data to refine the ionization-potential sums and hydration enthalpies of these elements.

EXPERIMENTAL

Synthesis of $\mathrm{Cs_2NaAnCl_6}$

The actinides chosen for this study were uranium, because it is the lightest An^{3+} available to us and because U^{3+} has a large ionic radius; neptunium and americium, because they complete a series of four adjacent actinides U–Np–Pu–Am (the Pu compound was studied earlier [2]); and californium, because it is the heaviest actinide available in sufficient quantity for calorimetric measurements.

Four methods have been described [2,16,21,22] for the preparation of these elpasolites:

(1) evaporation of a hydrochloric acid solution containing a stoichiometric ratio of the required ions, sometimes followed by hydrochlorination with HCl(g) at 773 K;

(2) supersaturation of a chilled solution, which contains a stoichiometric ratio of the required ions, with HCl(g) in order to precipitate the required elpasolite;

(3) fusion in a sealed tube of the stoichiometric amounts of the requisite anhydrous chlorides;

(4) slow cooling of a hot, dilute aqueous HCl solution of the requisite cations.

The first three methods are in order of increasing difficulty of synthesis but are also in the order of increasing purity of product. (The fourth method was successful only with $Cs_2NaBiCl_6$ [16,17].)

Because of the relative instability of the UCl_6^{3-} complex, the ease of oxidation of U^{3+} in aqueous solution, and the large ionic radius of U^{3+} (which made it probable that Cs_2NaUCl_6 could not be synthesized from aqueous solution), Cs_2NaUCl_6 was prepared by method 3 above. UCl_3 was prepared by hydriding the metal with H_2 at 473 K, converting it to UCl_3 with HCl(g) at 473 K, and subliming it under high vacuum at 1173 K. Stoichiometric amounts of UCl_3, 2CsCl and NaCl (Merck, >99.5% purity) were heated at 1073–1173 K in a sealed quartz tube to obtain Cs_2NaUCl_6. A single crystal was grown by gradient solidification from a melt [2,16,19].

A first attempt at preparation of $Cs_2NaNpCl_6$ by method 2 was unsuccessful: a 6 mol dm^{-3} HCl solution containing equimolar amounts of Cs_2NpCl_6 and NaCl was reduced electrolytically to Np^{3+} under an H_2 blanket and saturated with HCl(g) while being cooled to ca. 233 K; the small amount of grey precipitate that formed was identified as Cs_2NpCl_6. Therefore $Cs_2NaNpCl_6$ was synthesized from the binary chlorides (method 3) using $NpCl_3$ prepared according to the following reactions [23,24]

$$NpO_2(cr) + 2CCl_4(g) \xrightarrow[\text{Ar}]{823\text{ K}} NpCl_4(cr) + 2COCl_2(g) \tag{1}$$

$$2NpCl_4(cr) + Zn(cr) \xrightarrow[\text{vac}]{823\text{ K}} 2NpCl_3(cr) + ZnCl_2(l) \tag{2}$$

with subsequent sublimation of $NpCl_3$ under high vacuum at 1173 K.

$Cs_2NaAmCl_6$ was synthesized from ^{241}Am (half-life 432.7 years) by method 1, since earlier reported syntheses by method 2 gave a low yield [25]. The dry product was further dried and hydrochlorinated by heating in HCl(g) at 1123 K. While this research was in progress, Soderholm et al. [26] prepared a relatively pure sample of $Cs_2NaAmCl_6$ by method 2, although the yield was again rather low.

$Cs_2NaCfCl_6$ was prepared from a 3 mg stock solution of $^{249}Cf^{3+}$ that had been separated by cation exchange from its parent $^{249}Bk^{3+}$ and other common cations [27]. Method 2 was used and, as expected from the small ionic radius of Cf^{3+} and the likely stability of $CfCl_6^{3-}$, nearly quantitative yield was readily achieved. The sample was dried in HCl(g) at ca. 673 K.

X-ray diffraction

Powder patterns were obtained with 57.3 mm diameter Debye–Scherrer cameras with Straumanis film mounting using Ni-filtered Cu radiation.

Films were read by two or more persons. Lattice parameters were calculated from each reading using the least-squares program of Williams [28] and the results were then averaged. Single-crystal X-ray diffraction studies have been completed with the crystal of Cs_2NaUCl_6 grown in this research; the results are cited below [19].

Chemical analysis

Because of the purity of the starting binary chlorides used for Cs_2NaUCl_6, and because of prior successes in syntheses of elpasolites by method 1, only $Cs_2NaAmCl_6$ and $Cs_2NaCfCl_6$ were analyzed. Samples were weighed on a Cahn ultramicrobalance in a dry box, dissolved in dilute nitric acid, and diluted to a known volume. A volumetric aliquot was taken for alpha assay of ^{249}Cf in a 2π proportional counter (which has been calibrated against a standard of the U.S. National Bureau of Standards), using a half-life of 351 years [29], samples were also analyzed volumetrically for Cl^- with potentiometric end-point determination. Analysis: Calculated for Cl in $Cs_2NaAmCl_6$, 28.57%, found 28.4%; calculated for Cf in $Cs_2NaCfCl_6$, 33.18%, found 32.8%; calculated for Cl, 28.34%; found 28.0%.

Calorimetry

All of the thermochemical measurements were obtained in isoperibol microcalorimeters at 298.15 K. The U, Np and Am salts were dissolved in the Liège microcalorimeter [30] and the Cf salt was dissolved in the Argonne microcalorimeter [31]. All samples were handled in inert-atmosphere gloved boxes, weighed on Cahn ultramicrobalances, and sealed into Pyrex microampoules.

Because U^{3+} is unstable in aqueous solution, but is only slowly oxidized to U^{4+} in oxygen-free acid, a solution medium of 1 mol dm^{-3} HCl–0.1 mol dm^{-3} $FeCl_3$ was chosen to oxidize it rapidly and quantitatively to UO_2^{2+}. This reaction was verified to be quantitative by absorption spectrophotometry of the final solution between 300 and 1500 nm. To complete the thermochemical cycle, calorimetric measurements were carried out on UCl_3 in the same medium.

Although Np^{3+} is stable in oxygen-free acid, it was not convenient to load and to maintain the calorimeter solution under these conditions. Therefore, a medium of 1.0 mol dm^{-3} $HClO_4$–0.5 mol dm^{-3} $Fe(ClO_4)_3$ was chosen to oxidize Np^{3+} to NpO_2^+ rapidly and quantitatively [32]. Quantitative dissolution and oxidation to NpO_2^+ were verified by absorption spectrophotometry of the resulting solution between 700 and 1500 nm. It was verified that the final solution was not saturated in $CsClO_4$, despite its low solubility; $Cs_2NaNpCl_6$ dissolves quantitatively without residue or precipitate. As with the uranium cycle, it was necessary to carry out calorimetric measurements on $NpCl_3$ in this medium also.

$Cs_2NaAmCl_6$ and $Cs_2NaCfCl_6$ were dissolved in 1 mol dm^{-3} HCl since Am^{3+} and Cf^{3+} are stable and since auxiliary thermochemical data are available [33] in this medium.

RESULTS

All X-ray powder diffraction films were indexed in the face-centered cubic lattice, and are consistent with the space group *Fm*3*m* found at room temperature for many elpasolites [16–21]. The lattice parameters obtained from X-ray powder diffraction measurements are shown in Table 1, along with literature lattice parameters where available. The cubic lattice parameters are plotted as a function of ionic radius [34] in Fig. 1. We note that a sample of $Cs_2NaAmCl_6$ prepared with ^{243}Am (half-life 7370 years [29]) displayed a significantly larger lattice parameter; we have no satisfactory explanation for this situation.

The calorimetric enthalpies of solution are reported in Tables 2–5; they have been corrected for heats of ampoule breakage and for evaporation of

TABLE 1

Lattice constants for Cs_2NaMCl_6 and terms for calculation of Madelung constants and lattice energies

M	IR	a_{obs}	$d(M^{3+}-Cl^-)$	z	A	$-U_{BL}$	$-U_{BH}$	ΔU
Y	0.900	10.7315	2.616	0.2438 [20]	53.935	6248	6686	438
La	1.032	10.9923	2.749	0.2501	52.990	6007	6388	381
Ce	1.01	10.9458	2.725	0.2490	53.152	6051	6453	402
Pr	0.99	10.9118	2.701	0.2481	53.285	6085	6499	414
Nd	0.983	10.8894	2.696	0.2476 [20]	53.359	6106	6532	426
Dy	0.912	10.7426	2.621	0.2440 [20]	53.904	6253	6691	438
Yb	0.868	10.6697	2.582	0.2422	54.183	6328	6824	496
U	1.025	10.9371	2.723	0.2490 [19]	53.152	6070	6475	405
Np	1.01	10.9065	2.707	0.2482	53.270	6100	6515	415
Pu	1.00	10.8890	2.698	0.2478	53.330	6117	6538	421
Am	0.98 [a]	10.8546	2.681	0.2470	53.449	6150	6582	432
Cm	0.97	10.831 [b]	2.669 [b]	0.2464	53.539	6174	6614	440
Bk	0.96	10.8051	2.656	0.2458	53.630	6199	6649	450
Cf	0.95	10.7879	2.647	0.2453	53.706	6218	6674	456

[a] Shannon [34] gives 0.975 Å but 0.98 Å seems more reasonable by comparison with other IR sets, e.g., J.H. Burns, J.R. Peterson, and R.D. Baybarz, J. Inorg. Nucl. Chem., 35 (1973) 1171.

[b] Estimated by interpolation.

References: IR, ref. 34; a_{obs}, ref. 16, this work; $d(M^{3+}-Cl^-)$, see text; z, see text; A, refs. 39, 40; U_{BL}, eqn. (24); U_{BH}, eqn. (25) or text; $\Delta U = U_{BL} - U_{BH}(Ln)$, see text (An).

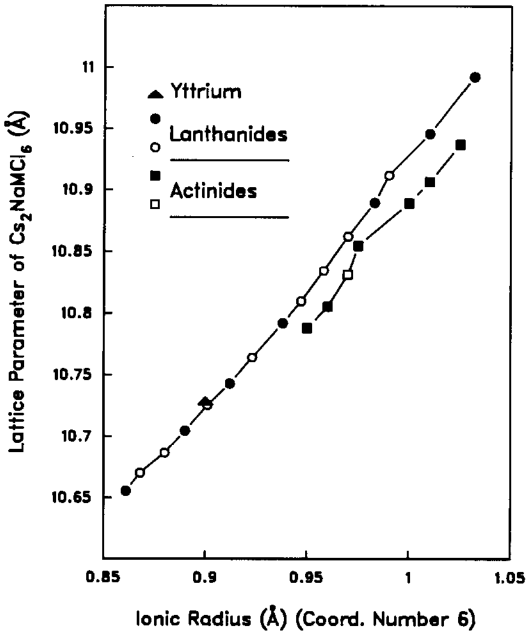

Fig. 1. Cubic lattice parameters of Cs_2NaMCl_6 as a function of ionic radius [34]. Filled symbols, experimental; open symbols, estimated.

TABLE 2

Enthalpies of solution of UCl_3 and Cs_2NaUCl_6 in HCl (1 mol dm^{-3})–$FeCl_3$ (0.1 mol dm^{-3}) at 298.15 K

Compound	Sample mass (mg)	Enthalpy (J) [a]	ΔH_{soln} (kJ mol^{-1})
UCl_3	9.680	−6.232	−221.7
	10.532	−6.832	−223.4
	9.558	−6.184	−222.8
	9.136	−5.914	−222.9
	11.083	−7.184	−223.2
	9.274	−5.965	−221.5
		Mean	−222.6 ± 0.8
Cs_2NaUCl_6	12.958	−3.059	−174.3
	14.142	−3.320	−173.6
	11.200	−2.616	−172.7
	11.342	−2.676	−174.5
	9.316	−2.186	−173.5
		Mean	−173.7 ± 0.8

[a] Corrected for enthalpy of ampoule breakage and of evaporation of solvent into gas in ampoule.

TABLE 3

Enthalpies of solution of $NpCl_3$ and $Cs_2NaNpCl_6$ in $HClO_4$ (1 mol dm^{-3})–$Fe(ClO_4)_3$(0.5 mol dm^{-3}) at 298.15 K

Compound	Sample mass (mg)	Enthalpy (J) [a]	ΔH_{soln} (kJ mol^{-1})
$NpCl_3$	8.764	−1.2872	−50.43
	13.078	−1.9130	−50.22
	13.160	−1.9414	−50.65
	9.668	−1.4117	−50.13
	10.432	−1.5282	−50.30
	8.394	−1.2321	−50.40
		Mean	-50.35 ± 0.18
$Cs_2NaNpCl_6$	10.958	+0.1810	+12.20
	9.432	+0.1527	+11.96
	11.356	+0.1865	+12.13
	11.029	+0.1773	+11.87
	9.325	+0.1515	+12.00
	9.872	+0.1595	+11.95
		Mean	$+12.02 \pm 0.12$

[a] Corrected for enthalpy of ampoule breakage and of evaporation of solvent into gas in ampoule.

TABLE 4

Enthalpy of solution of $Cs_2NaAmCl_6$ in HCl (1 mol dm^{-3}) at 298.15 K

Sample mass (mg)	Enthalpy (J) [a]	ΔH_{soln} (kJ mol^{-1})
12.296	−0.8547	−51.75
11.742	−0.8263	−51.60
11.824	−0.8004	−50.49
16.248	−1.1319	−51.99
15.756	−1.1099	−52.29
	Mean	-51.62 ± 0.85

[a] Corrected for enthalpy of ampoule breakage and of evaporation of solvent into gas in ampoule.

TABLE 5

Enthalpy of solution of $Cs_2NaCfCl_6$ in HCl (1 mol dm^{-3}) at 298.15 K

Sample mass (mg)	Enthalpy (J) [a]	ΔH_{soln} (kJ mol^{-1})
2.545	−0.1199	−35.37
1.947	−0.0922	−35.55
2.522	−0.1187	−35.34
	Mean	-35.59 ± 0.62

Corrected for enthalpy of ampoule breakage and of evaporation of solvent into gas in ampoule.

TABLE 6

Enthalpies of solution (in water at infinite dilution and in 1 mol dm^{-3} HCl or HClO$_4$) and standard enthalpies of formation of MCl$_n$ at 298.15 K

MCl$_n$(cr)	$\Delta_{soln}H^\circ_m$(MCl$_n$) (kJ mol^{-1})	$\Delta_{soln}H$(MCl$_n$)in 1 mol dm^{-3} HCl or HClO$_4$ (kJ mol^{-1})	$\Delta_fH^\circ_m$(MCl$_n$, cr) (kJ mol^{-1})
NaCl	3.878 ± 0.155 [35]	4.46 ± 0.4 [a]	−411.258 ± 0.109 [35]
CsCl	17.568 ± 0.255 [35]	16.69 ± 0.4 [a]	−442.688 ± 0.201 [35]
UCl$_3$	−124.2 ± 4.2 [b]	−116 ± 4 [c]	−866.1 ± 3.8 [33]
NpCl$_3$	−130.1 ± 2.5 [b]	−121.6 ± 2.5 [c]	−898.3 ± 3.3 [33]
PuCl$_3$	−133.4 ± 0.8 [b]	−126.8 ± 0.4 [c]	−959.8 ± 1.7 [33]
AmCl$_3$	−139.58 ± 1.05 [b]	−131.6 ± 1.05 [c]	−977.8 ± 1.3 [33]
CmCl$_3$	−141.8 ± 2.1 [b,d]	−133.3 ± 2.1 [c]	−974.4 ± 5.1 [33]
BkCl$_3$	−145.1 ± 2.9 [d]	−136.2 ± 3.3 [54]	−957.1 ± 5.3 [54]
CfCl$_3$	−148.5 ± 3.8 [d]	−139.5 ± 4 [55]	−929.7 ± 5.7 [55]

[a] Calculated from critical examination of literature data, e.g. P.A.G. O'Hare, W.A. Shinn, F.C. Mrzek and A.E. Martin, J. Chem. Thermodyn., 4 (1972) 401; J. Fuger and D. Brown, J. Chem. Soc. A, (1971) 841; R.C. Gearhart, Jr., J.D. Beck and R.H. Wood, Inorg. Chem., 14 (1975) 2413.

[b] Calculated as $\Delta_fH^\circ_m(\mathrm{An}^{3+}, \mathrm{aq}) + 3\Delta_fH^\circ_m(\mathrm{Cl}^-, \mathrm{aq}) - \Delta_fH^\circ_m(\mathrm{AnCl}_3, \mathrm{cr})$ using refs. 33, 42 and 49.

[c] Calculated as $\Delta_fH^\circ_m(\mathrm{An}^{3+}, 1\ \mathrm{mol\ dm}^{-3}\ \mathrm{HCl}) + 3\Delta_fH^\circ_m(\mathrm{Cl}^-, 1\ \mathrm{mol\ dm}^{-3}\ \mathrm{HCl})$ using refs. 35 and 49.

[d] Estimated by extrapolation using $\Delta_{soln}H^\circ_m(\mathrm{AnCl}_n)$ data from ref. 33, p. 155.

solvent into the dry gas within the ampoule upon breakage. To derive molar enthalpies of formation from these data, several molar enthalpies of solution and formation were extracted from the literature and are compiled in Table

TABLE 7

Thermochemical cycle for calculation of $\Delta_fH^\circ_m$(Cs$_2$NaUCl$_6$, cr, 298 K); all entries kJ mol^{-1}; "soln" = 1.00 mol dm^{-3} HCl − 0.5 mol dm^{-3} FeCl$_3$

Cs$_2$NaUCl$_6$(cr) + 2H$_2$O(soln) + 3FeCl$_3$(soln) = 2CsCl(soln) + NaCl(soln) + UO$_2$Cl$_2$(soln) + 3FeCl$_2$(soln) + 4HCl(soln)	$\Delta H_3 =$	−173.7 ± 0.8
UCl$_3$(cr) + 2H$_2$O(soln) + 3FeCl$_3$(soln) = UO$_2$Cl$_2$(soln) + 3FeCl$_2$(soln) + 4HCl(soln)	$\Delta H_4 =$	−222.6 ± 0.8
U(cr) + 3/2 Cl$_2$(g) = UCl$_3$(cr)	$\Delta H_5 =$	−866.1 ± 3.8
Cs(cr) + 1/2 Cl$_2$(g) = CsCl(cr)	$\Delta H_6 =$	−442.69 ± 0.20
CsCl(cr) = CsCl(soln)	$\Delta H_7 =$	+16.69 ± 0.4
Na(cr) + 1/2 Cl$_2$(g) = NaCl(cr)	$\Delta H_8 =$	−411.26 ± 0.11
NaCl(cr) = NaCl(soln)	$\Delta H_9 =$	+4.46 ± 0.4
2Cs(cr) + Na(cr) + U(cr) + 3Cl$_2$(g) = Cs$_2$NaUCl$_6$(cr)	$\Delta_fH^\circ_m$ [a] =	−2173.8 ± 4.1

[a] $\Delta_fH^\circ_m = -\Delta H_3 + \Delta H_4 + \Delta H_5 + 2\Delta H_6 + 2\Delta H_7 + \Delta H_8 + \Delta H_9$.

TABLE 8

Thermochemical cycle for calculation of $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{Cs_2NaNpCl_6}$, cr, 298 K); all entries kJ $\mathrm{mol^{-1}}$; "soln" = 1.00 mol $\mathrm{dm^{-3}}$ $\mathrm{HClO_4}$–0.5 mol $\mathrm{dm^{-3}}$ $\mathrm{Fe(ClO_4)_3}$

$\mathrm{Cs_2NaNpCl_6(cr) + 2H_2O(soln) + 2Fe(ClO_4)_3(soln)}$ $\mathrm{= 2CsCl(soln) + NaCl(soln)}$ $\mathrm{+ NpO_2Cl(soln) + 2Fe(ClO_4)_2(soln)}$ $\mathrm{+ 2HClO_4(soln) + 2HCl(soln)}$	$\Delta H_{10} =$	$+12.02 \pm 0.12$
$\mathrm{NpCl_3(cr) + 2H_2O(soln) + 2Fe(ClO_4)_3(soln)}$ $\mathrm{= NpO_2Cl(soln) + 2Fe(ClO_4)_2(soln)}$ $\mathrm{+ 2HClO_4(soln) + 2HCl(soln)}$	$\Delta H_{11} =$	-50.35 ± 0.18
$\mathrm{Np(cr) + 3/2\ Cl_2(g) = NpCl_3(cr)}$	$\Delta H_{12} =$	-898.3 ± 3.3
$\mathrm{2Cs(cr) + Na(cr) + Np(cr) + 3Cl_2(g) = Cs_2NaNpCl_6(cr)}$	$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}{}^{\mathrm{a}} =$	-2219.5 ± 3.5

[a] $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}} = -\Delta H_{10} + \Delta H_{11} + \Delta H_{12} + 2\Delta H_6 + 2\Delta H_7 + \Delta H_8 + \Delta H_9$.

6 [33,35,36] for use in Tables 7–9. The enthalpies of formation of complex chlorides have been calculated from thermochemical cycles as shown in Tables 7–9 (eqns. (3)–(18)) respectively and are summarized in Table 10. Some steps in Tables 8 and 9 represent enthalpies listed in Table 7 and are not duplicated in the latter tables.

Standard-state enthalpies of solution, $\Delta_{\mathrm{soln}}H^{\circ}_{\mathrm{m}}(\mathrm{Cs_2NaAnCl_6})$, have been calculated from enthalpies of formation

$$\mathrm{Cs_2NaAnCl_6(cr) = 2Cs^+(aq) + Na^+(aq) + An^{3+}(aq) + 6Cl^-(aq)} \qquad (19)$$

and are listed in Table 10. In most cases $\Delta_{\mathrm{soln}}H^{\circ}_{\mathrm{m}}(\mathrm{Cs_2NaAnCl_6})$ could have been measured directly, but in the case of $\mathrm{Cs_2NaUCl_6}$ spontaneous oxidation of $\mathrm{U^{3+}(aq)}$ would have made direct measurement impossible.

TABLE 9

Thermochemical cycle for calculation of $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{Cs_2NaAmCl_6}$, cr, 298 K) and $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{Cs_2NaCfCl_6}$, cr, 298 K); all entries kJ $\mathrm{mol^{-1}}$; "soln" = 1.00 mol $\mathrm{dm^{-3}}$ HCl

$\mathrm{Cs_2NaAmCl_6(cr) = 2CsCl(soln) + NaCl(soln) + AmCl_3(soln)}$	$\Delta H_{13} =$	-51.62 ± 0.85
$\mathrm{Am(cr) + 3/2\ Cl_2(g) = AmCl_3(cr)}$	$\Delta H_{14} =$	-977.8 ± 1.3
$\mathrm{AmCl_3(cr) = AmCl_3(soln)}$	$\Delta H_{15} =$	-131.6 ± 1.05
$\mathrm{2Cs(cr) + Na(cr) + Am(cr) + 3Cl_2(g) = Cs_2NaAmCl_6(cr)}$	$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}{}^{\mathrm{a}} =$	-2316.6 ± 1.7
$\mathrm{Cs_2NaCfCl_6(cr) = 2CsCl(soln) + NaCl(soln) + CfCl_3(soln)}$	$\Delta H_{16} =$	-35.59 ± 0.62
$\mathrm{Cf(cr) + 3/2\ Cl_2(g) = CfCl_3(cr)}$	$\Delta H_{17} =$	-929.7 ± 5.7
$\mathrm{CfCl_3(cr) = CfCl_3(soln)}$	$\Delta H_{18} =$	-139.5 ± 4
$\mathrm{2Cs(cr) + Na(cr) + Cf(cr) + 3Cl_2(g) = Cs_2NaCfCl_6(cr)}$	$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}{}^{\mathrm{b}} =$	-2292.4 ± 5.8

[a] $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{Cs_2NaAmCl_6}, \mathrm{cr}) = -\Delta H_{13} + \Delta H_{14} + \Delta H_{15} + 2\Delta H_6 + 2\Delta H_7 + \Delta H_8 + \Delta H_9$.
[b] $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{Cs_2NaCfCl_6}, \mathrm{cr}) = -\Delta H_{16} + \Delta H_{17} + \Delta H_{18} + 2\Delta H_6 + 2\Delta H_7 + \Delta H_8 + \Delta H_9$.

TABLE 10

Standard enthalpies of formation, of solution, and of complexation of Cs_2NaMCl_6; standard enthalpies of formation of M(g) and M^{3+}(aq); all entries kJ mol^{-1}

An	$\Delta_f H^\circ_m(Cs_2NaMCl_6, cr)$	$\Delta_{soln} H^\circ_m(Cs_2NaMCl_6)$	$\Delta_{cplx} H^\circ_m(Cs_2NaMCl_6)$	$\Delta_f H^\circ_m(M, g)$	$\Delta_f H^\circ_m(M^{3+}, aq)$
Y	−2396 [a]	−78.2 [b]	−107.1 [c]	421.3 [a]	−736.5 ± 2.6 [52]
La	−2385 [a]	−83.3 [b]	−15.1 [c]	431.0 [a]	−709.4 ± 1.6 [a]
Ce	−2386 [a]	−73.6 [b]	−31.0 [c]	420.1 [a]	−700.4 ± 2.1 [a]
Pr	−2393 [a]	−72.0 [b]	−38.1 [b]	356.9 [a]	−706.2 ± 1.6 [a]
Nd	−2384 [a]	−71.1 [b]	−46.4 [c]	326.9 [a]	−696.6 ± 1.7 [a]
Dy	−2385 [a]	−69.9 [b]	−98.3 [c]	290.4 [a]	−695.6 ± 2.8 [a]
Yb	−2357 [d]	−73.4 [b]	−104.2 [c]	155.6 [a]	−670.5 ± 2.7 [53]
U	−2173.8 ± 4.1 [e]	−74.1 ± 5.9 [e]	−11.1 ± 1.4 [e]	536 [f]	−489.1 ± 3.8 [g]
	−2189.3 ± 3.9 [h]	−58.7 ± 5.5 [h]	−26.55 ± 1.04 [h]		
Np	−2219.5 ± 3.5 [e]	−66.5 ± 4.3 [e]	−24.5 ± 0.9 [e]	465 [f]	−527.2 ± 2.1 [g]
Pu	−2294.9 ± 2.5 [i]	−56.1 ± 1.7 [b]	−38.5 ± 1.7 [i]	342 [f]	−592.0 ± 2.1 [g]
Am	−2316.6 ± 1.7 [e]	−59.0 ± 1.7 [e]	−42.2 ± 1.6 [e]	284 [f]	−616.7 ± 1.3 [g]
Cm	(−2325 ± 7) [j]	(−49 ± 6) [j]	(−54 ± 5) [j]	387 [f]	−615.0 ± 5.0 [g]
Bk	(−2315 ± 7) [j]	(−45 ± 6) [j]	(−61 ± 5) [j]	310 [f]	−601 ± 5 [54]
Cf	−2292.4 ± 5.8 [e]	−43.4 ± 5.8 [e]	−66.1 ± 4.1 [e]	196 [f]	−577 ± 5 [55]

[a] Ref. 3.

[b] Ref. 2.

[c] Eqn. (21) and ref. 2.

[d] Recalculated from ref. 2 using new $\Delta_f H^\circ_m(Yb^{3+}, aq)$ from ref. 53.

[e] This research.

[f] Ref. 14.

[g] Ref. 49.

[h] N.A. Aurov and D.E. Chirkst, Radiokhimiya, 25 (1983) 468.

[i] Ref. 33.

[j] Estimates from interpolation of $\Delta_{cplx} H^\circ_m$; $\Delta_{soln} H^\circ_m$ from eqn. (21) and $\Delta_f H^\circ_m$ from eqn. (20).

Enthalpies of complexation can be calculated directly from the following reaction

$$2\mathrm{CsCl(cr)} + \mathrm{NaCl(cr)} + \mathrm{AnCl_3(cr)} = \mathrm{Cs_2NaAnCl_6(cr)} \qquad \Delta H = \Delta_{\mathrm{cplx}}H^{\circ}_{\mathrm{m}} \tag{20}$$

as the difference between the enthalpy of formation of the complex salt and the enthalpies of formation of the binary salts. However, a more direct approach, which avoids some thermochemical steps (such as the enthalpy of solution of the metals) and their attendant errors is to calculate enthalpies of complexation from the enthalpies of solution of the chlorides in the same medium. We choose the latter approach, making the reasonable assumption that the enthalpies of solution of CsCl and NaCl in 1 mol $\mathrm{dm^{-3}}$ HCl(aq) are not modified significantly by the presence of 0.1 mol $\mathrm{dm^{-3}}$ $\mathrm{FeCl_3}$ or by 0.5 mol $\mathrm{dm^{-3}}$ $\mathrm{Fe(ClO_4)_3}$.

The enthalpies of complexation are calculated as follows

$$\begin{aligned}\Delta_{\mathrm{cplx}}H^{\circ}_{\mathrm{m}}(\mathrm{Cs_2NaAnCl_6}) &= 2\Delta_{\mathrm{soln}}H_{\mathrm{m}}(\mathrm{CsCl}) + \Delta_{\mathrm{soln}}H_{\mathrm{m}}(\mathrm{NaCl})\\ &\quad + \Delta_{\mathrm{soln}}H_{\mathrm{m}}(\mathrm{AnCl_3}) - \Delta_{\mathrm{soln}}H_{\mathrm{m}}(\mathrm{Cs_2NaAnCl_6})\end{aligned} \tag{21}$$

Thus

$$\begin{aligned}\Delta_{\mathrm{cplx}}H^{\circ}_{\mathrm{m}}(\mathrm{Cs_2NaUCl_6}) &= 2(16.69 \pm 0.4) + (4.46 \pm 0.4) + (-222.6 \pm 0.8)\\ &\quad -(-173.7 \pm 0.8) = -(11.1 \pm 1.4)\ \mathrm{kJ\ mol^{-1}};\\ \Delta_{\mathrm{cplx}}H^{\circ}_{\mathrm{m}}(\mathrm{Cs_2NaNpCl_6}) &= 2(16.69 \pm 0.4) + (4.46 \pm 0.4) + (-50.35 \pm 0.18)\\ &\quad -(+12.02 \pm 0.12) = -(24.5 \pm 0.9)\ \mathrm{kJ\ mol^{-1}};\\ \Delta_{\mathrm{cplx}}H^{\circ}_{\mathrm{m}}(\mathrm{Cs_2NaAmCl_6}) &= 2(16.69 \pm 0.4) + (4.46 \pm 0.4) + (-131.6 \pm 1.05)\\ &\quad -(-51.62 \pm 0.85) = -(42.2 \pm 1.6)\ \mathrm{kJ\ mol^{-1}};\\ \Delta_{\mathrm{cplx}}H^{\circ}_{\mathrm{m}}(\mathrm{Cs_2NaCfCl_6}) &= 2(16.69 \pm 0.4) + (4.46 \pm 0.4) + (-139.5 \pm 4)\\ &\quad -(-35.59 \pm 0.62) = -(66.1 \pm 4.1)\ \mathrm{kJ\ mol^{-1}}.\end{aligned}$$

These values are listed in Table 10 and displayed in Fig. 2. For reference, as well as for subsequent calculations, similar entries for rare earth elpasolites are included in Table 10 and Fig. 2.

CALCULATIONS

Enthalpies of complexation were estimated for $\mathrm{Cs_2NaCmCl_6}$ and $\mathrm{Cs_2NaBkCl_6}$ by interpolation as a function of lattice parameter (Table 10). From these estimates, eqns. (21) and (19) were used to calculate enthalpies of solution and of formation respectively.

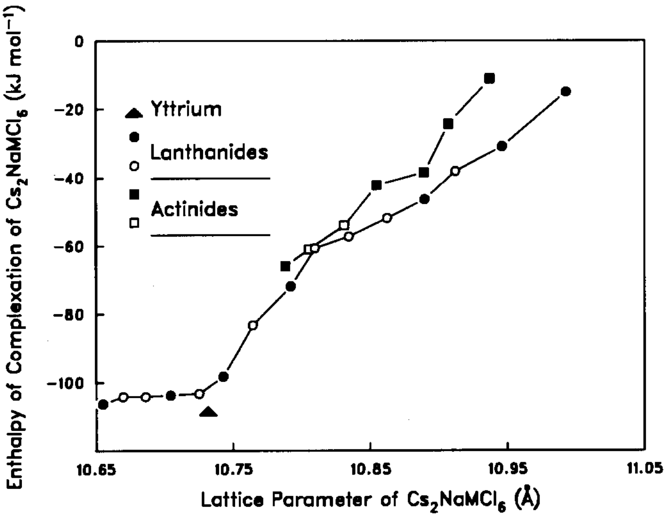

Fig. 2. Enthalpies of complexation of elpasolites Cs_2NaMCl_6. Filled symbols, experimental; open symbols, estimated.

We follow the general approach of Morss [2,3,25] in using a Born–Haber cycle with calculated lattice energies to obtain ionization-potential sums $I_1 + I_2 + I_3 = \Sigma I$ for the process

$$\text{An(g)} = \text{An}^{3+}\text{(aq)} \tag{22}$$

and then, using these ΣI values, to obtain hydration enthalpies $\Delta_{\text{hyd}}H^{\circ}_{\text{m}}$ for the process

$$\text{An}^{3+}\text{(g)} = \text{An}^{3+}\text{(aq)} \tag{23}$$

The first step in this procedure is to calculate lattice energies for the elpasolites. We use the Born–Landé equation 24 (U_{BL}: Born–Landé lattice energy)

$$U_{\text{BL}}(\text{kJ mol}^{-1}) = \frac{-1389.35\,A}{a}\left(1 - \frac{1}{n}\right) \tag{24}$$

as did Morss [2,25] with Madelung constant A, lattice parameter a_0 in Ångstrom units, and effective repulsive coefficients $n = [(2 \times 12) + 7 + 10 + (6 \times 9)]/10 = 9.5$ for Cs_2NaYCl_6, $[(2 \times 12) + 7 + 12 + (6 \times 9)]/10 = 9.7$ for $Cs_2NaLnCl_6$, and $[(2 \times 12) + 7 + 14 + (6 \times 9)]/10 = 9.9$ for $Cs_2NaAnCl_6$, where the coefficients 12, 7, 10, 12, 14, and 9 are the Pauling values for Cs^+, Na^+, Y^{3+}, Ln^{3+}, An^{3+} and Cl^-, respectively [37]. We have utilized the single-crystal structure determination [19] of Cs_2NaUCl_6, which yielded the chlorine positional parameter $z = 0.2490(7)$, nearly the "ideal cryolite" value [38] of 0.2500. The Madelung constant A for the cryolite structure with $z = 0.2490$ is 53.152 and the Coulombic part of the lattice energy (using $a_0 = 10.9371$ Å) is -6751.9 kJ mol^{-1} [39].

Unfortunately, no crystal-structure refinements have been performed on other actinide elpasolites. Therefore it was necessary to estimate the chloride

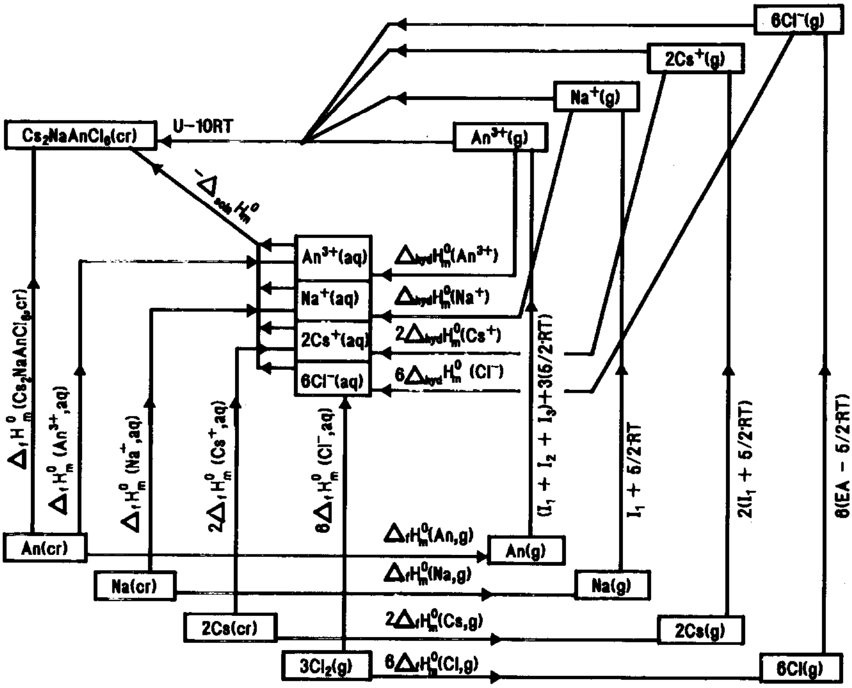

Fig. 3. Terms in Born–Haber cycle for calculation of ionization-potential sums and enthalpies of hydration.

TABLE 11

Ionization potentials (eV) and hydration enthalpies (kJ mol^{-1}) of Y, La, Ce, Pr, Nd, Dy, Yb, U, Np, Pu, Am, Cm, Bk and Cf

M	ΣI [a]	I_1		I_2		I_3		$-\Delta_{\mathrm{hyd}}H^{\circ}_{\mathrm{m}}(\mathrm{M}^{3+})$		
		[14,36,45]	[46]	[15]	This work	[14]	[15]	eqn. (26)	[11]	[12,50,51] [b]
Y	38.89									
La	35.81								3293	
Ce	36.59								3302	
Pr	37.65								3336	
Nd	38.39								3371	
Dy	40.41								3584	
Yb	43.47								3724	
U	37.81	6.194	11.9	11.53	19.7	19.7	20.0	3356	3332	3307
Np	38.49	6.266	11.7	11.39	20.5	20.7	20.7	3388	3361	3345
Pu	39.22	6.062	11.7	11.44	21.5	21.6	21.8	3401	3401	3382
Am	40.05	5.993	12.0	11.64	22.1	22.1	22.4	3448	3443	3417
Cm	39.23	6.021	12.4	12.09	20.8	21.0	21.2	3470	3472	3443
Bk	40.50	6.229	12.3	12.02	22.0	22.3	22.3	3501	3503	3479
Cf	42.17	6.298	12.5	12.20	23.4	23.5	23.6	3524	3533	3504

[a] Y–Yb, refs. 6,56; U–Cf, this work, eqn. (25).

[b] Corrected, see text.

positional parameter z, which is the only one not fixed by symmetry, of transuranic elpasolites from ionic-radius considerations and from the change in z found from the single-crystal refinements done on $Cs_2Na(Y,Nd,Dy)Cl_6$ [20]. This estimation was accomplished by considering the parameter z to vary linearly with a_0. The change $dz/da_0 = 0.0245$ was found for $Cs_2Na(Nd–Dy)Cl_6$ and was used to estimate z values for other lanthanide and actinide elpasolites. (Other estimation methods resulted in z differing by no more than 0.2%.) As a result, the distance $d(M^{3+}–Cl^{-}) = z \times a_0$. The corresponding value of the Madelung constant A was obtained by interpolation of the values shown in Table 43 of the article by Hoppe [40], with conversion from values based upon shortest cation–anion distance to values based upon unit cell length.

The calculation of lattice energies U_{BL} was carried out using the Born–Landé equation (eqn. (24)); the 1986 values of fundamental constants have been used [41]. Thus for Cs_2NaUCl_6, $U_{BL} = -6069.9$ kJ mol^{-1}. This and additional U_{BL} for actinide elpasolites are listed in Table 1.

Since the Born–Landé equation neglects covalent, dipolar, and other interactions, it was necessary to calculate lattice energies empirically wherever possible from a Born–Haber cycle. As shown in Fig. 3, this calculation is possible for elements with accurately assessed ionization potential sums. The critical assessments published by Martin et al. [6] report accurate ionization potentials for some of the lanthanides, from which we calculate $I_1 + I_2 + I_3 = \Sigma I$ for La, Ce, Pr, and Yb (Table 11). For these elements Table 1 shows the empirical lattice energies U_{BH}(BH: Born–Haber) obtained from the equation

$$\begin{aligned}\Delta_f H^\circ_m(Cs_2NaMCl_6, cr) &= 2\ \Delta_f H^\circ_m(Cs,g) + \Delta_f H^\circ_m(Na,g) + \Delta_f H^\circ_m(M,g)\\ &\quad + 6\Delta_f H^\circ_m(Cl,g) + 2\ I_1(Cs) + I_1(Na)\\ &\quad + (I_1 + I_2 + I_3)(M) + 6EA(Cl) + U_{BH} - 10RT\\ &= 2(76.5 \pm 1.0) + (107.5 \pm 0.7) + \Delta_f H^\circ_m(M,g)\\ &\quad + 6 \times (121.301 \pm 0.008) + 2(375.702 \pm 0.001)\\ &\quad + (495.842 \pm 0.001) + (I_1 + I_2 + I_3)(M)\\ &\quad + 6(-348.99) + U_{BH} - 24.79\\ &= \Delta_f H^\circ_m(M,g) + (I_1 + I_2 + I_3)(M) + U_{BH}\\ &\quad + (116.8 \pm 2.1)\ \text{kJ mol}^{-1} \qquad (25)\end{aligned}$$

where terminology follows Morss [2]. Numerical entries for $\Delta_f H^\circ_m(M,g)$ and $\Delta_f H^\circ_m(Cl,g)$ are taken from the latest CODATA evaluation [42] and $I_1(Cs)$ and $I_1(Na)$ from Wagman et al. [36]. The electron affinity of Cl, EA(Cl), was taken from a more recent review [43]. Table 1 also shows the differences ΔU obtained by subtraction of U_{BH} from U_{BL} for $Cs_2Na(Y,La,Ln)Cl_6$. The difference function ΔU was estimated for actinide compounds from a linear fit of $Cs_2Na(La,Ln)Cl_6$ to lattice parameters. The ΔU values for Cs_2NaYCl_6 and $Cs_2NaDyCl_6$ were not used for this fit because the assessed ionization potentials Y(II) and Dy(III) have uncertainties of 0.12 and 0.3 eV respectively [56]. These estimated actinide ΔU values (Table 1) were used to correct the actinide lattice energies U_{BL} to values U_{BH} appropriate for Born–Haber cycle calculations. The corrected U_{BH} for actinide elpasolites were used to calculate ionization-potential sums for the corresponding elements by means of eqn. 25; these ionization-potential sums, ΣI, are listed in Table 11.

The first ionization potentials of the actinides have been derived by Sugar [44] from interpolations of the series properties of the $5f^N7s^2$ and $5f^N7s8s$ configurations; slightly revised values have been derived for U and Np [45] (Table 11). Second ionization potentials (Table 11) were calculated independently by Sugar [46] and by Bratsch and Lagowski [15]. From our ΣI and Sugar's I_1 and I_2 we have calculated I_3 as shown in Table 11. They compare well with those calculated by Morss [14] and by Bratsch and Lagowski [15] except that our values for I_3 are significantly smaller than those of Bratsch and Lagowski (ca. 0.3 eV), which were derived from thermochemical cycles for which no details were given. This discrepancy arises because the I_2 values of Bratsch and Lagowski (derived from Ahrens' [47] relationship between I_1 and I_2 for s electrons) are ca. 0.3 eV smaller than those of Sugar.

We note that there are a few ionization potentials for the rare earths that have large error limits. Among these are Y(II) (12.15 ± 0.12 eV) [56] and Dy(III) (22.8 ± 0.3 eV) [6]. The ΔU values that we calculate for these elements deviate significantly from the straight line of lanthanum and the other rare earths; it may be appropriate for spectroscopists to re-examine the assignments of the Y(II) and Dy(III) series limits.

Enthalpies of hydration can readily be calculated from the cycle of Fig. 4

$$\begin{aligned}
\Delta_{\text{hyd}}H^{\circ}_{\text{m}}(\text{M}^{3+}) &= \Delta_{\text{f}}H^{\circ}_{\text{m}}(\text{An}^{3+},\text{aq}) - \Delta_{\text{f}}H^{\circ}_{\text{m}}(\text{An},\text{g}) \\
&\quad - (I_1 + I_2 + I_3)(\text{An}) + 3\Delta_{\text{f}}H^{\circ}_{\text{m}}(\text{H}^{+},\text{g}) \\
&\quad + 3\Delta_{\text{hyd}}H^{\circ}_{\text{m}}(\text{H}^{+}) - 15/2\ RT \\
&= \Delta_{\text{f}}H^{\circ}_{\text{m}}(\text{An}^{3+},\text{aq}) - \Delta_{\text{f}}H^{\circ}_{\text{m}}(\text{An},\text{g}) \\
&\quad - (I_1 + I_2 + I_3)(\text{An}) + 3(1536.2) \\
&\quad + 3(-1090.8 \pm 10.5) - 18.59 \\
&= \Delta_{\text{f}}H^{\circ}_{\text{m}}(\text{An}^{3+},\text{aq}) - \Delta_{\text{f}}H^{\circ}_{\text{m}}(\text{An},\text{g}) \\
&\quad - (I_1 + I_2 + I_3)(\text{An}) + 1317.6\ \text{kJ mol}^{-1} \qquad (26)
\end{aligned}$$

To establish these enthalpies of hydration on an absolute scale the corresponding absolute $\Delta_{\text{hyd}}H^{\circ}_{\text{m}}(\text{H}^{+}) = -(1091 \pm 10)$ kJ mol^{-1} of Halliwell and Nyburg [48] was used. Enthalpies of formation of the aquo ions, $\Delta_{\text{f}}H^{\circ}_{\text{m}}(\text{An}^{3+},\text{aq})$ were taken from Fuger and Oetting [49] and are reproduced

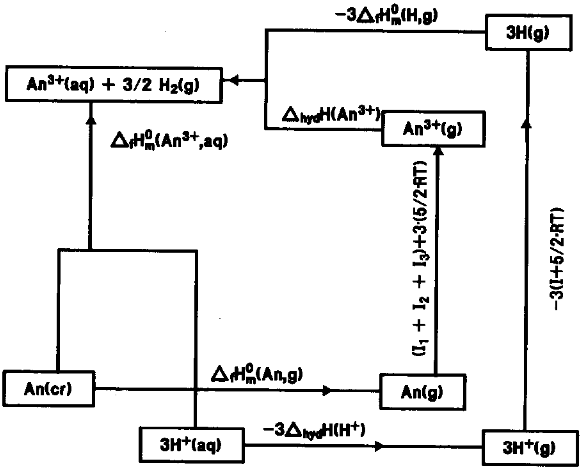

Fig. 4. Thermodynamic cycle used for calculation of absolute enthalpies of hydration of actinide ions.

in Table 10. The resultant $\Delta_{\text{hyd}}H^{\circ}_{\text{m}}$ for the actinides are listed in Table 11.

Hydration enthalpies were calculated some time ago by Goldman and Morss [11] and more recently by David [12,50] and David et al. [51], both methods using semi-empirical models. For comparison these values are included in Table 11. Our values would be ca. 50 kJ mol^{-1} smaller (more positive) than those tabulated by David [50], who used $\Delta_{\text{hyd}}H^{\circ}_{\text{m}}(\text{H}^{+}) = -1114$. For ease of comparison, we have recalculated David's hydration enthalpies on the basis of $\Delta_{\text{hyd}}H^{\circ}_{\text{m}}(\text{H}^{+}) = -1091$ kJ mol^{-1} [48] and these recalculated hydration enthalpies are shown in Table 11; the agreement is remarkably good.

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