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Thermochemistry of Some Chlorocomplex Compounds of the Rare Earths; Third Ionization Potentials and Hydration Enthalpies of the Trivalent Ions[1]

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Abstract

Heats of solution of the complex chlorides Cs_2NaMCl_6 (M = Y, La, Ce, Nd, Gd, Dy, Er, Lu, Pu) were measured in a new microcalorimeter. Heats of formation of these compounds have been derived and are compared with heats of formation of the uncomplexed chlorides. Using auxiliary thermodynamic data, the third ionization potentials of the lanthanide elements and the hydration enthalpies of the trivalent rare-earth ions have been calculated. The variation in the third ionization potentials of the lanthanides may be attributed to the change (upon ionization) of exchange energy of unpaired electrons. However, the variation in enthalpies of hydration and complexing cannot be interpreted in terms of ligand-field stabilization.

Introduction

The gradually changing chemical properties of the rare-earth elements and their compounds may sometimes be interpreted simply in terms of changing nuclear charge and electronic configuration. However, structural changes, hydration effects, nonstoichiometry, or electronic interactions may perturb the relationship being studied as one proceeds along the lanthanide or actinide series. It is necessary to resort to thermochemical cycles to circumvent (3,4,5,6) such effects.[3-6]

Recently-prepared and characterized complex compounds Cs_2NaMCl_6, where M may be almost any trivalent cation, appeared suitable for (7,8) straightforward comparisons of thermochemical properties.[7,8] The desirable characteristics of these compounds are the following:

(1) They are preparable for yttrium, all the lanthanides, and all actinides attempted (Pu, Am, Cm, Bk). The compounds are easily prepared in high purity and are less sensitive to atmospheric moisture than are the respective trichlorides.

(2) They are all rapidly water-soluble, making aqueous solution calorimetry feasible.

(3) Extensive thermochemical data are available on the corresponding binary chlorides from which the complex chlorides are formed, and on their aqueous solutions.

(4) As contrasted with binary compounds such as the trichlorides

or sesquioxides, the complex chlorides are all isostructural, and of high symmetry-- enabling simple calculation and interpretation of lattice energies.

The initial goals of this investigation were to determine the heats of formation of the compounds Cs_2NaMCl_6 and to evaluate the stability gained by the complexed salts,

$$2\ CsCl + NaCl + MCl_3 = Cs_2NaMCl_6. \qquad (1)$$

Because of the precise and accurate heats of solution, and the regularity with which the heat changed with atomic number of M, it was possible to use the thermochemical and crystallographic information obtained for these compounds to estimate third ionization potentials for the lanthanide elements and to calculate heats of hydration of the trivalent rare-earth ions.

Experimental Section

The compds Cs_2NaMCl_6 were prepared as single crystals from the corresponding anhyd binary chlorides (CsCl, NaCl, and
(9) sublimed MCl_3) by gradient solidification from a melt.[8,9] The source of anhyd $PuCl_3$ for $Cs_2NaPuCl_6$ was a single crystal, sublimed
(10) and grown by J. Fuger.[10])

A piece of clear single crystal was broken out from the center of each cylindrical crystal of Cs_2NaMCl_6. This selected sample was crushed in a mortar to fragments ca. 0.5 mm in size; replicate samples were loaded into calorimeter bulbs. All sample-handling

procedures were carried out in a dry box, even though all samples except those of Cs_2NaYCl_6 showed no evidence of deliquescence in laboratory air.

Weighings were carried out on an Ainsworth FM microbalance (not in the dry box) by enclosing each calorimeter bulb in a micro weighing bottle, with the ground-glass joint sealed with petroleum jelly. To prevent a buoyancy error when capping the weighing bottles, a small hole was drilled through the ground glass of each cap and bottle, so that pressure could be equilibrated after closing the bottle by rotating the cap. (Precision of weighings was established as ±0.02 mg by weighing and reweighing empty bulbs.)

A 30-ml gold-plated copper microcalorimeter was used for heats of solution. The microcalorimeter had an energy equivalent of 34.5 cal/$^{\circ}$C, thermal leakage modulus of 0.001 min^{-1}, sensitivity 0.0002 cal, and precision 0.06% (standard deviation of a typical electrical energy heat calibration). A detailed description of the calorimeter
(11) has been published.[11]

Heats of solution were measured at $(25 \pm 0.1)^{\circ}$ in 0.001 N HCl. (This pH avoids hydrolysis of any of the trivalent rare-earth ions.) All chlorocomplex compounds dissolved within 2 min and gave clear solutions, except for one slightly-clouded crystal of $Cs_2NaLuCl_6$ which required about an hour to complete evolution of heat. (This run was rejected.)

The calorimeter's energy equivalent was determined twice before

and twice after each run by precise inputs of electrical energy which approximated the chemical heat evolution in quantity and duration. The heats of solution of Mg metal in 1 N HCl and of "tris" in 0.1 N HCl served as checks on the accuracy of the microcalorimeter (Table I). All results are reported in defined calories (1 cal = 4.184 abs J).

Table I. Heats of Solution of Standard Substances

Substance	Wt., mg.	Cal.	ΔH(soln), kcal/mol Found	Lit.
Mg metal	0.5938	2.7184	111.30	111.285[a]
"Tris"	39.41	2.3106	7.102	7.109[b]
"Tris"	29.905	1.7567	7.116	

a. C. H. Shomate and E. Huffman, J. Amer. Chem. Soc., 65, 1625 (1943).

b. J. O. Hill, G. Öjelund, and I. Wadsö, J. Chem. Thermodynamics, 1, 111 (1969).

Corrections were applied for water evaporated into the dry nitrogen of each bulb (and in the case of metal dissolution, for hydrogen evolved); for heat of bulb breakage (measured five times, mean -0.0002 ± 0.0002 cal); and for reducing observed data to infinite dilution. The last correction was made to the heats of soln of Cs_2NaMCl_6 by assuming only two significant heat effects to

be corrected: the nonideality of M(III) salt solutions (considered equivalent to the heat of dilution of the corresponding MCl_3 soln to infinite dilution) and the complexing of M(III) with chloride ion (which proceeds significantly only as far as the monochloro-complex ion). At molalities achieved in these experiments (final molality of Cs_2NaMCl_6 typically 0.004 m, the former correction amounts to -70 cal/mol and the latter to about -400 cal/mol (that is, both dilution effects are exothermic). Heats of dilution have been measured accurately for YCl_3 and for all lanthanide trichloride
(12-15) solutions;[12-15] the comparable correction for $PuCl_3$ was estimated from that of the lanthanide with comparable ionic radius, $NdCl_3$. The equilibrium constant and enthalpy of complexing of M(III) with chloride have only been estimated for a few rare-earth ions; the
(16) calorimetric estimate of Montgomery[16] for the formation of $CeCl^{2+}$ ($K = 1$, $\Delta H = 5.4$ kcal/mol) has been used for all the rare earths.

Results

Table II reports the results of the basic experimental data obtained in this research. The averaged heats of solution for the lanthanide chlorocomplex compounds, corrected to infinite dilution, are plotted in Figure 1. It may be seen that these heats of solution change slowly and regularly, so that it is safe to interpolate heats of solution for other lanthanide chlorocomplex compounds (most of which have been prepared and found to be isostructural).[8]

Table II. Heats of Solution of Cs_2NaMCl_6

Compound	Wt., mg.	Calories evolved	$-\Delta H$, kcal/mol Uncorr.	Corr.
Cs_2NaYCl_6	69.44	2.1605	18.37	18.84
Cs_2NaYCl_6	50.30	1.5503	18.20	18.59
$Cs_2NaLaCl_6$	77.89	2.3565	19.38	19.85
$Cs_2NaLaCl_6$	101.25	3.0545	19.32	19.87
$Cs_2NaCeCl_6$	72.87	1.9552	17.22	17.65
$Cs_2NaCeCl_6$	81.71	2.1886	17.19	17.65
$Cs_2NaNdCl_6$	63.18	1.6213	16.57	16.99
$Cs_2NaNdCl_6$	59.28	1.5282	16.65	17.05
$Cs_2NaGdCl_6$	81.90	2.0237	16.28	16.78
$Cs_2NaGdCl_6$	78.68	1.9427	16.27	16.76
$Cs_2NaDyCl_6$	82.25	2.0108	16.23	16.70
$Cs_2NaDyCl_6$	89.47	2.1899	16.25	16.75
$Cs_2NaErCl_6$	67.89	1.7021	16.77	17.19
$Cs_2NaErCl_6$	96.91	2.4167	16.68	17.19
$Cs_2NaLuCl_6$	33.37	0.8370	16.97	17.26
$Cs_2NaLuCl_6$	36.69	0.9078	16.74	17.04[a]
$Cs_2NaLuCl_6$	65.83	1.6593	17.05	17.48
$Cs_2NaPuCl_6$	93.50	1.6443	13.02	13.50
$Cs_2NaPuCl_6$	93.57	1.6331	12.92	13.40

[a] Rejected because dissolution was slow and incomplete.

Taking the heat of solution of CsCl as 4250 ± 100 cal/mol, and
(17) that of NaCl as 928 ± 5 cal/mol,[17] heats of complexing ($\Delta \underline{H}$ for eq 1) may be calculated as follows:

$$\Delta \underline{H}_1 = \Delta \underline{H}^{o}(\text{soln, } MCl_3) + 2\,\Delta \underline{H}^{o}(\text{soln, CsCl}) + \Delta \underline{H}^{o}(\text{soln, NaCl}) - \Delta \underline{H}^{o}(\text{soln, } Cs_2NaMCl_6)$$

The necessary enthalpies of solution of MCl_3, and calculated values of $\Delta \underline{H}_1$, are collected in Table III. In order to calculate $\Delta \underline{H}_1$, all heats of solution have been corrected to infinite dilution.

Heats of formation of compounds Cs_2NaMCl_6 have been calculated, and the values listed in Table III, from the following relationship:

$$\Delta \underline{H}^{o}_f(Cs_2NaMCl_6) = 2\Delta \underline{H}^{o}_f(\text{CsCl,c}) + \Delta \underline{H}^{o}_f(\text{NaCl,c}) + \Delta \underline{H}^{o}_f(MCl_3\text{,c}) + \Delta \underline{H}_1$$

For this calculation, necessary values of heats of formation of MCl_3 are tabulated in Table III; the corresponding values for
(18) CsCl(c) and NaCl(c) are -98.2 and -106.9 kcal/mol.[18]

Enthalpies ($\Delta \underline{H}_2$) corresponding to the hydration of Cs_2NaMCl_6

$$Cs_2NaMCl_6(c) + \underline{n}\ H_2O(\ell) = 2\ CsCl(c) + NaCl(c) + MCl_3 \cdot \underline{n}H_2O(c) \qquad (2)$$

are listed in Table III. Although they may be calculated directly from the heats of formation of the compounds in eq 2, an equivalent (and more precise) calculation from the heats of solution at infinite

Table III. Thermochemical Properties of MCl_3 and Cs_2NaMCl_6 at 25°C (all entries kcal/mol)[a]

M	ΔH^o_f (MCl_3,c)[b]	ΔH^o (soln,MCl_3,c)	ΔH^o(soln, Cs_2NaMCl_6,c)	ΔH_1[c]	ΔH^o_f (Cs_2NaMCl_6,c)	ΔH_2[c,d]
Y	-239.0	-53.7	-18.7 ± 0.2	-25.6	-576.6 ± 1.1	---
La	-255.9	-32.9	-19.9 ± 0.1	-3.6	-571.5 ± 0.9	-22.6
Ce	-251.5	-34.4	-17.6 ± 0.1	-7.4	-570.9 ± 1.2	-20.1
Pr	-252.0	-35.7	(-17.2)	(-9.1)	(-573.1 ± 1.1)	(-16.9)
Nd	-248.7	37.5	-17.0 ± 0.1	-11.1	-571.8 ± 1.0	-17.3
Pm	---	(-38.7)	(-16.9)	(-12.4)	---	---
Sm	-244.1	-39.9	(-16.8)	(-13.7)	(-569.8 ± 1.0)	(-17.6)
Eu	-219.5	-40.7	(-16.8)	(-14.5)	(-546.0 ± 2.2	(-17.5)
Gd	-239.6	-43.4	-16.8 ± 0.1	-17.2	-568.8 ± 1.0	-17.1
Tb	-238.4	-46.0	(-16.7)	(-19.9)	(-570.3 ± 1.8)	(-16.6)
Dy	(-236.6)	(-50.0)	-16.7 ± 0.1	(-23.9)	(-572.5 ± 3.3)	-16.2
Ho	-237.8	-51.0	(-16.9)	(-24.7)	(-574.5 ± 2.7)	(-15.9)
Er	-238.0	-51.4	-17.2 ± 0.1	-24.8	-574.8 ± 2.0	-15.9

(continued on page 0)

Table III. (Continued)

M	ΔH^o_f (MCl_3,c)[b]	ΔH^o $(soln,MCl_3,c)$	$\Delta H^o(soln)$, $Cs_2NaMCl_6,c)$	ΔH_1[c]	ΔH^o_f (Cs_2NaMCl_6,c)	ΔH_2[c,d]
Tm	-236.3	-51.6	(-17.3)	(-24.9)	(-573.2 ± 1.1	(-15.6)
Yb	-229.4	-51.6	(-17.3)	(-24.9)	(-566.3 ± 1.2)	(-15.2)
Lu	-234.5	-52.2	-17.4 ± 0.3	-25.4	-571.9 ± 1.4	-15.0
Pu	-227.0	-31.8	-13.4 ± 0.1	-9.0	-548.0 ± 1.1	-14.6

[a]Estimated values in parentheses.

[b]As quoted in ref 11 ("best values" evaluated by author from experimental literature data).

[c]See text (eqs 1 and 2) for definition.

[d]For $(La,Ce)Cl_3 \cdot 7H_2O$; others hexahydrates.

dilution has been utilized:

$$\Delta \underline{H}_2 = \Delta \underline{H}^o(\text{soln, } Cs_2NaMCl_6\text{, c}) - 2\Delta \underline{H}^o(\text{soln, CsCl, c}) - \Delta \underline{H}^o(\text{soln, NaCl, c}) - \Delta \underline{H}^o(\text{soln, } MCl_3 \cdot \underline{n}H_2O\text{, c})$$

The heats of solution of the hydrated chlorides necessary for this calculation are those quoted by ref 11 from experimental literature data (mostly from Spedding and co-workers).[14,15]

Calculations

Lattice energies were calculated by taking advantage of the precisely determined and regularly changing unit cell dimensions of these complex chlorides, as well as the high symmetry (face-centered cubic, "ideal cryolite" structure) indicated by X-ray powder patterns.[8] These lattice energies were necessary for Born-Haber cycle determinations of ionization potentials and hydration enthalpies. Although compressibilities and precise atomic parameters for chloride positions are required for direct calculation of <u>absolute</u> lattice energies, values which are accurate <u>relative</u> to one another may be determined from a simple Born-Landé equation and then corrected to absolute energies by completing a Born-Haber cycle for elements whose ionization potentials are known.

First, the lattice energy of $Cs_2NaLaCl_6$ was calculated from the

(19) Born-Landé equation:[19]

$$U_o = \frac{\alpha^2 e^2 NA}{ra} \left(1 - \frac{1}{n}\right)$$

$$= -332.06 \frac{A}{a} \left(1 - \frac{1}{n}\right) \text{ kcal/mol}$$

$\underline{A}$ = Madelung constant, relative to unit cell length

$\underline{a}$ = unit cell length (Å)

$\underline{n}$ = power of $(1/\underline{r})$ in repulsive potential

For the "ideal cryolite" structure of $M_2M'M''X_6$ with X atomic parameters (0, 0, 0.25), $\underline{A}$ has been calculated to be 53.005.[19] Powder-pattern intensities for $Cs_2NaLaCl_6$[8] yield Cl^- parameters (0, 0, 0.247 ± 0.01), consistent with the above parameters for X. Following Pauling's rules for estimation of compressibilities,[20] $\underline{n}$ = 9.7, whereupon (20)

$$\underline{U}_o = \frac{-332.06\ (53.005)}{10.992}\left(1 - \frac{1}{9.7}\right)$$

$$= -1436.1 \text{ kcal/mol.}$$

Table IV presents the values for a conventional Born-Haber cycle for Cs_2NaMCl_6 at 25° C:

$$\Delta\underline{H}^o_f(Cs_2NaMCl_6, c) = 2\ \underline{S}(Cs) + \underline{S}(Na) + \underline{S}(M) + 3\ \underline{D}(Cl_2) + 2\ \underline{I}(Cs) + \underline{I}(Na) + (\underline{I}_1 + \underline{I}_2 + \underline{I}_3)(M) + 6\ \underline{E}(Cl) + \underline{U}_o(Cs_2NaMCl_6) - 10\ \underline{RT} \quad (4)$$

$\underline{S}$ = heat of sublimation

$\underline{D}$ = enthalpy of dissociation

$\underline{I}_i$ = ionization potential of $M^{(i-1)+}$ to M^{i+}

$\underline{E}$ = -(electron affinity)

Since the first three ionization potentials for La have been experimentally determined to high accuracy, the Born-Haber cycle

Table IV. Born-Haber Enthalpy Cycle (and Madelung Constant, A) for Cs_2NaMCl_6 at 25°C

(all entries kcal/mol)

M	ΔH^{o}_{f} [a]	S(M) [b]	ΣI(M) [c]	Misc. [d]	U_o [e]	A [f]	U_o(calc)
Y	-576.6	101.5	900.0	16.6	-1594.7	54.546	-1509.6
La	-571.5	103.0	826.0	16.6	-1517.1	53.005	-1436.1
Ce	-570.9	101.0	843.1	16.6	-1531.6	53.284	-1449.8
Pr	-573.1	85.0	867.5	16.6	-1542.2	53.488	-1459.9
Nd	-571.8	78.3	882.6	16.6	-1549.3	53.622	-1466.6
Pm	--	--	--	16.6	-1558.0	53.787	-1474.8
Sm	-569.8	49.4	931.1	16.6	-1566.9	53.954	-1483.2
Eu	-546.0	42.4	969.7	16.6	-1574.7	54.102	-1490.6
Gd	-568.8	95.0	900.0	16.6	-1580.4	54.208	-1496.0
Tb	-570.3	92.9	908.9	16.6	-1588.7	54.363	-1503.9
Dy	-572.5	69.4	937.7	16.6	-1596.2	54.503	-1511.0
Ho	-574.5	71.9	940.3	16.6	-1603.3	54.633	-1517.7
Er	-574.8	75.8	941.5	16.6	-1608.7	54.733	-1522.8
Tm	-573.2	55.5	969.4	16.6	-1614.7	54.843	-1528.5
Yb	-566.3	36.4	1000.7	16.6	-1620.0	54.939	-1533.5
Lu	-571.9	102.2	934.3	16.6	-1625.0	55.029	-1538.2
Pu	-548.0	84.1	904.3	16.6	-1553.0	53.625	-1470.1

[a] Transposed from Table III.

(continued on page 14)

Table IV (continued)

[b] R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys," John Wiley, New York, 1963, plus supplements issued through July 1969.

[c] Calculated to close cycle (except entry for La as quoted by ref 5).

[d] 2 $\underline{S}(Cs)$ + $\underline{S}(Na)$ + 3$\underline{D}(Cl_2)$ + 2 $\underline{I}(Cs)$ + $\underline{I}(Na)$ + 6 $\underline{E}(Cl)$ - 10 RT = 2(18.67) + 25.85 + 3(58.16) + 2(89.7) + 118.4 + 6(-85.5) - 5.92 = 16.55. References: $\underline{D}$, D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties; Tables for the First Thirty-Four Elements in the Standard Order of Arrangement," National Bureau of Standards Technical Note 270-3, U. S. Government Printing Office, Washington, D. C., 1968; $\underline{I}$, $\underline{E}$, D. Cubicciotti, J. Chem. Phys., 31, 1646 (1959); 33, 1579 (1960); 34, 2189 (1961).

[e] $\underline{U}_o = \underline{U}_o(calc) \cdot 1.0564$ (see text).

[f] Calculated in ref 11.

(eq 4) for $Cs_2NaLaCl_6$ may be used to estimate the lattice energy of $Cs_2NaLaCl_6$, -1517.1 kcal/mol. This empirical lattice energy encompasses any errors which appear systematically in Born-Haber cycles for all these compounds, as well as non-Coulombic contributions
(21) to the lattice energies.[21] All lattice energies for other compounds calculated by eq 3 (last column in Table IV) have been corrected by 1517.1/1436.1 = 1.0564.

For the calculation of other lattice energies in Table IV, lattice parameters, a, for eq 3 were taken from published values.[8] The change in Madelung constant has been estimated for various chloride z-parameters[11] and the calculated values of A for each compound Cs_2NaMCl_6 are tabulated for information in Table IV.

The results of these thermochemical cycles yield the sum of the first three ionization potentials, $\Sigma I(M)$, for most of the rare-earth elements. In Table V these values have been converted into electron volts. Using values selected from the literature by Johnson[6] for the first and second ionization potentials, the third ionization potentials, I_3, of these rare earths have been calculated.

Appropriate Born-Haber cycles may also serve to calculate hydration properties of ions. The heat of hydration (not to be confused with the process of eq 2 which unfortunately bears the same name) of the ions corresponding to Cs_2NaMCl_6 may be derived from either of the following relationships:

Table V. Ionization Potentials and Hydration Enthalpies

M	ΣI[a]	I_1[b]	I_2[b]	I_3[a]	I_3[c]	I_3[d]	$\Delta H(hyd, M^{3+})$[a]
Y	39.03	6.38	12.23	20.42	(20.5)[e]	--	-869.3
La	35.82[e]	5.58	11.06	19.18[e]	--	(19.18)	-792.9
Ce	36.56	5.60	10.85	20.11	20.0	(20.08)	-805.1
Pr	37.62	5.41	10.55	21.66	21.6	(21.57)	-815.3
Nd	38.27	5.49	10.72	22.06	22.2	22.07	-822.2
Pm	--	5.55	10.90	--	--	--	-830.8
Sm	40.38	5.62	11.07	23.68	23.7	23.68	-839.6
Eu	42.05	5.67	11.25	25.13	24.9	24.92	-847.4
Gd	39.03	6.16	12.15	20.72	20.6	20.83	-853.1
Tb	39.41	5.90	11.52	21.99	21.9	21.70	-861.3
Dy	40.66	5.88	11.67	23.11	22.9	22.94	-868.8
Ho	40.77	5.95	11.80	23.02	23.1	(22.81)	-876.1
Er	40.83	6.03	11.93	22.87	22.6	22.44	-881.8
Tm	42.04	6.10	12.05	23.89	23.8	23.56	-887.9
Yb	43.39	6.25	12.18	24.96	25.3	(25.04)	-893.2
Lu	40.51	5.32	13.9	21.29	21.2	--	-898.3
Pu	39.21	--	--	--	--	--	-822.3

[a] This research.

[b] As quoted by Table I of ref 6; values for Y and Lu as quoted by ref 5.

[c] Calculated by ref 5.

[d] Calculated by ref 6; parenthetical values are from other sources as quoted by ref 6.

[e] As quoted by ref 5.

$$2\,\Delta\underline{H}(\text{hyd, } Cs^+) + \Delta\underline{H}(\text{hyd, } Na^+) + \Delta\underline{H}(\text{hyd, } M^{3+}) + 6\Delta\underline{H}(\text{hyd, } Cl^-) = \Delta\underline{H}^o_f(Cs_2NaMCl_6\text{, aq}) - 2\,\underline{S}(Cs) - \underline{S}(Na) - \underline{S}(M) - 3\,\underline{D}(Cl_2) - 2\,\underline{I}(Cs) - \underline{I}(Na) - (\underline{I}_1 + \underline{I}_2 + \underline{I}_3)(M) - 6\,\underline{E}(Cl) \tag{5}$$

$$= \underline{U}_o(Cs_2NaMCl_6) - 10\,\underline{RT} + \Delta\underline{H}^o(\text{soln}, Cs_2NaMCl_6) \tag{6}$$

These two equations must yield identical results, since eq 5 reduces to eq 6 by substitution of eq 4 and by use of the definition

$$\Delta\underline{H}^o_f(Cs_2NaMCl_6\text{, aq}) = \Delta\underline{H}^o_f(Cs_2NaMCl_6\text{, c}) + \Delta\underline{H}^o(\text{soln, } Cs_2NaMCl_6).$$

In order to consider the heats of hydration for the rare-earth ions independently of the other ions in Cs_2NaMCl_6, it is necessary to separate the heats of hydration of the alkali halides into "cation" and "anion" contributions. The most useful approach is to separate the individual ionic contributions so that "absolute" values will be generated for each ion. Halliwell and Nyburg have reduced this problem to the determination of the enthalpy of hydration of the
(22) proton.[22] They recommend a "best value" of $\Delta\underline{H}(\text{hyd, } H^+\text{, abs}) = -260.7 \pm 2.5$ kcal/mol. Consistent with this reference value, and with experimental enthalpies as tabulated by Halliwell and Nyburg, "absolute" hydration enthalpies have been calculated for Cs^+, Na^+, and Cl^- as -66.1, -97.0 and -86.8 kcal/mol respectively.[18] Using these values and eq 6, "absolute" hydration enthalpies have been

calculated for the rare-earth ions and are tabulated in Table V.

Discussion

Both the ionization potentials and the hydration enthalpies of Table V may be compared with other recently-published values. For convenience, two such sets of ionization potentials are listed in Table V. Some published values of $\Delta \underline{H}(\text{hyd}, M^{3+})$ based at least in part on experimental values are as follows: La, -806, varying
(23-25) smoothly to Lu, -878;[23] La, -780;[24] Pu, -821.[25] Figure 2 displays the lanthanide ionization potentials and hydration energies as calculated in this research, as a function of atomic number, or, more significantly, as a function of the number of *f* electrons in the trivalent ions. The dashed lines are second-order polynomials fitted to the data points through La, Gd, and Lu.

Ionization potentials. It should be noted that all three sets of ionization potentials (those calculated in this research, by Faktor and Hanks,[5] and by Johnson[6]) use Born-Haber cycles with nearly identical values for I_1 and I_2. The use of such common data facilitates comparison of the three sets of I_3 values (in fact, the author chose ionization potentials quoted by Johnson[6] wherever possible, not only because of their detailed documentation, but also for consistency). However, the neglect of conflicting ionization potentials from alternative sources misleadingly implies that these I_3 values are as accurate as they are in mutual agreement. For
(26) example, the value of I_2(La) tabulated by Moore[26] is 11.43 ± 0.07 eV,

differing from the value quoted by Johnson[6] in Table V by 0.37 eV. It is suggested, therefore, that tabulated I_3 values are not accurate to better than ±0.4 eV, although relative errors may be less than ±0.2 eV.

The ionization potentials generated from chlorocomplex compounds have some attributes which suggest their preferential use. The lattice energies used in their calculation are generated from the Born-Landé equation, based upon a single set of structurally-similar, highly symmetric, predominantly ionic compounds. In addition, only a single empirical correction factor of 1.0564 is required for these lattice energies, and it is generated from the relatively trustworthy ionization potentials of lanthanum. In contrast, the ionization potentials of Faktor and Hanks[5] and of Johnson[6] are empirically based on three or more sets of ionization potentials (experimental values by different techniques differing by more than 1 eV in some cases) and both are based at least partially on thermochemical and structural data on cubic sesquioxides (requiring the collection and generation of thermochemical and structural data from numerous sources of varying accuracy).

The deviation of I_3's from the dashed curve in Figure 2 may be interpreted as the effect of exchange energy on an $f^{n+1} \rightarrow f^n$ ionization.
(27) This interpretation, drawn from its equivalent for d electrons,[27] has been discussed in more detail by Johnson.[6] The exchange energy is proportional to the number of pairs of parallel spins, $n(n-1)/2$.

Upon ionization of $f^{n+1} \rightarrow f^n$, an exchange energy of

$$(n+1)n/2 - n(n-1)/2 = n$$

is lost; this loss is reflected in the increasing deviation of I_3 from the dashed line as $n \rightarrow 6$. The transition $Gd^{2+} \rightarrow Gd^{3+}$ ($f^8 \rightarrow f^7$) however involves no exchange energy, since the lost electron had spin anti-parallel to all the others; because no exchange energy is lost on this ionization, $\underline{I}_3$ is low, like that of $La^{2+} \rightarrow La^{3+}$. Subsequent $\underline{I}_3$ values show the effect of increasing loss of exchange energy, until the final ionization, $Lu^{2+} \rightarrow Lu^{3+}$, which also involves no loss of *f* electron exchange energy.

Heats of hydration. Error limits for $\Delta \underline{H}$(hyd) of Table V can be accurately estimated. The absolute accuracy of $\Delta \underline{H}$(hyd, La^{3+}) is estimated as ±11 kcal/mol by propagating estimated standard deviations of all terms in eq 5. The relative accuracy of each ΔH(hyd) with respect to the others, estimated by lumping all constant terms or by use of eq 6, is ± 2 kcal/mol.

The thermodynamics of hydration and similar complexing processes are unrelated to ionization potentials, of course, since these processes encompass no oxidation steps. The energetics of these transformations are functions of ionic size, ligand polarizability and electronegativity, coordination number, and ligand field. It is desirable to study these functional relationships independently of each other.

There is little agreement with respect to the "coordination

number[1] of rare-earth ions in aqueous solution. The complicated variation of many thermodynamic complexation processes as a function of lanthanide atomic number has been used to invoke a relatively sudden change in hydration number of the lanthanide ions near the
(28) midpoint of the series.[3,23,28] However, there is fundamental thermodynamic evidence (the aqueous ionic entropies) which shows no
(29) such distinct change in coordination number.[29] The enthalpies of hydration, as calculated in this research and plotted in Figure 2, should reflect any such coordination change. The bicuspid shape of the hydration-enthalpy-vs.-atomic-number plot is much like that of the lattice-energy/atomic-number relationship (for which there is no coordination change, the bicuspid shape being caused by the similar variation in lattice parameter of Cs_2NaMCl_6 with atomic number).[8] Thus, hydration enthalpies of the lanthanide ions do not show a discrete change in hydration number. (This conclusion is supported by Figure 1, since the heat of solution is the difference between hydration enthalpy and lattice enthalpy. Heats of solution of other isomorphic lanthanide compounds vary in a similarly smooth fashion.[3,23])

Effect of ligand field. It is tempting to ascribe the more exothermic thermodynamic properties of lanthanide ions with non-spherical f-electron subshells to a small ligand-field stabilization. Such a stabilization is suggested by the double-humped plots of lattice energy (not shown) and hydration enthalpy (Figure 2)--plots

similar to the well-known stabilizations observed for the d-transition metal ions. With respect to the smooth curve through La^{3+}, Gd^{3+}, and Lu^{3+}, both the lattice energy and the hydration enthalpy of Cs_2NaMCl_6 become most exothermic at about Pr^{3+} (f^2) by about 4 kcal/mol and at Dy^{3+} (f^9) by about 1.4 kcal/mol. These variations are traceable to the similar variation in lattice parameter mentioned above;[8] any ion with non-spherical electron distribution favors certain spatial orientations of electron orbitals and ligands which minimize mutual repulsions and which permit the ligands to be drawn closer than they would if the same electrons were spherically distributed. A smaller ionic radius is observed for such ions, from which the thermodynamic "stabilizations" follow. It is inappropriate to consider the magnitude of such an effect as
(30) a measure of ligand-field stabilization.[30]

A second approach is to compare thermodynamic cycles for ions of similar size but of different electronic configurations. The ions Y^{3+} (f^0) and Ho^{3+} ($4f^{10}$) have very similar ionic radii (0.900 and 0.901Å), as do the ions Ce^{3+} ($4f^1$) and Pu^{3+} ($5f^5$) (1.01 and
(31) 1.01 Å).[31] For both pairs of ions, the heat of hydration is more exothermic for the ion with more f electrons. Although one might surmise that this is due to the participation of f electrons in bonding, and to the greater participation of 5f than of 4f electrons, the data are neither extensive enough nor accurate enough to permit such a conclusion. In particular, the heats of hydration depend for

their calculation on lattice energies, which are sensitive functions of ionic radii and of n, the repulsive constant; the former is dependent upon coordination number and upon various crystallographic estimations (such as constancy of anion radius)[31] and the latter has only been estimated for Cs_2NaMCl_6.[20]

A final approach, by which the effect of varying hydration number may be circumvented, is to compare the heat of transformation from a series of isostructural lanthanide salts to solvated species in which the inner coordination sphere is saturated by polydentate ligands. The enthalpies of formation from the aquated ions have been measured for the 1:n complexes of the diglycolate and dipicolinate ions (n = 1, 2, 3) and for the 1:1 complex of the
(32) diethylenetriaminepenta-acetate ion (DTPA).[4,32] The former ligands are each tridentate, and since it is probable that the 1:3 complexes
(33) of both ligands are 9-coordinate,[33] it is likely that these 1:3 complexes have no water molecules in the inner coordination sphere. Likewise, it is possible that the DTPA ion, which is potentially octadentate, saturates the inner coordination sphere.[4] Therefore, if the heats of solution of a series of isostructural rare-earth salts are added to the heats of complexing with these ligands, the intermediate state (the aqueous ions, with varying states of hydration) can be eliminated.

Staveley et al. measured the heats of solution of the hydrated ethylsulfates and bromates of most of the lanthanide elements.[3]

When their heats of solution were added to the heats of complexing with the ligands described above, the more negative enthalpies for lanthanides other than La, Gd, and Lu were attributed to ligand-field stabilizations of a few hundred calories.[3,4]

The heats of solution of the chlorocomplex compounds Cs_2NaMCl_6 ought to be more suitable than the corresponding heats measured by Staveley et al., because the structures of Cs_2NaMCl_6 are clearly identical, they can be prepared in high purity, and the heats of solution were more reproducible and free from the corrections necessary for included mother liquor. By adding the heats of solution (Table III) to the $\Delta\mathcal{H}_3^{\circ}$ values defined by Grenthe,[32] and to the ΔH_c values defined by Carson et al.,[4] heats of transformation for the reactions

$$Cs_2NaMCl_6(c) + 3(diglyc^{2-})(aq) = 2\ Cs^+(aq) + Na^+(aq) + 6\ Cl^-(aq) + M(diglyc)_3^{3-}(aq) \quad (7)$$

$$Cs_2NaMCl_6(c) + 3(dipic^{2-})(aq) = 2\ Cs^+(aq) + Na^+(aq) + 6\ Cl^-(aq) + M(dipic)_3^{3-}(aq) \quad (8)$$

and

$$Cs_2NaMCl_6(c) + DTPA^{5-}(aq) = 2\ Cs^+(aq) + Na^+(aq) + 6\ Cl^-(aq) + M(DTPA)^{2-}(aq) \quad (9)$$

can be calculated. Each of these composite reactions meets the conditions set by Staveley et al. for observation of ligand-field stabilization. Plots of ΔH_7, ΔH_8, and ΔH_9 vs. lanthanide atomic

number (Figure 3) may be compared with the corresponding graphs of Staveley *et al.* (Figures 1 and 2, ref 3) and with Carson *et al.* (Figure 2, ref 4). Not only is there no bicuspid depression to any of the graphs, but there is no trend simple enough to draw a smooth curve within estimated error limits.

The possibility remains that the nonlinear contraction of lanthanide ionic radii is responsible for the apparent ligand-field stabilizations observed by Staveley *et al.*[3] and by Carson *et al.*[4] In any event, since the splitting of ground-state *f* electron configurations by ligand fields does not necessarily produce thermochemical stabilization,[30] and since ionic-radius contractions can produce enthalpy effects much greater than expected ligand-field stabilizations, it is perhaps inappropriate to consider that thermochemical variations which have been observed in lanthanide complexes are caused by true ligand-field effects.

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Figure Captions

Figure 1. Averaged heats of solution, Cs_2NaMCl_6 (corrected to infinite dilution).

Figure 2. Lanthanide ionization potentials and hydration enthalpies.

Figure 3. Heats of complexing of $Cs_2NaLnCl_6$ with diglycolate, DTPA, and dipicolinate.

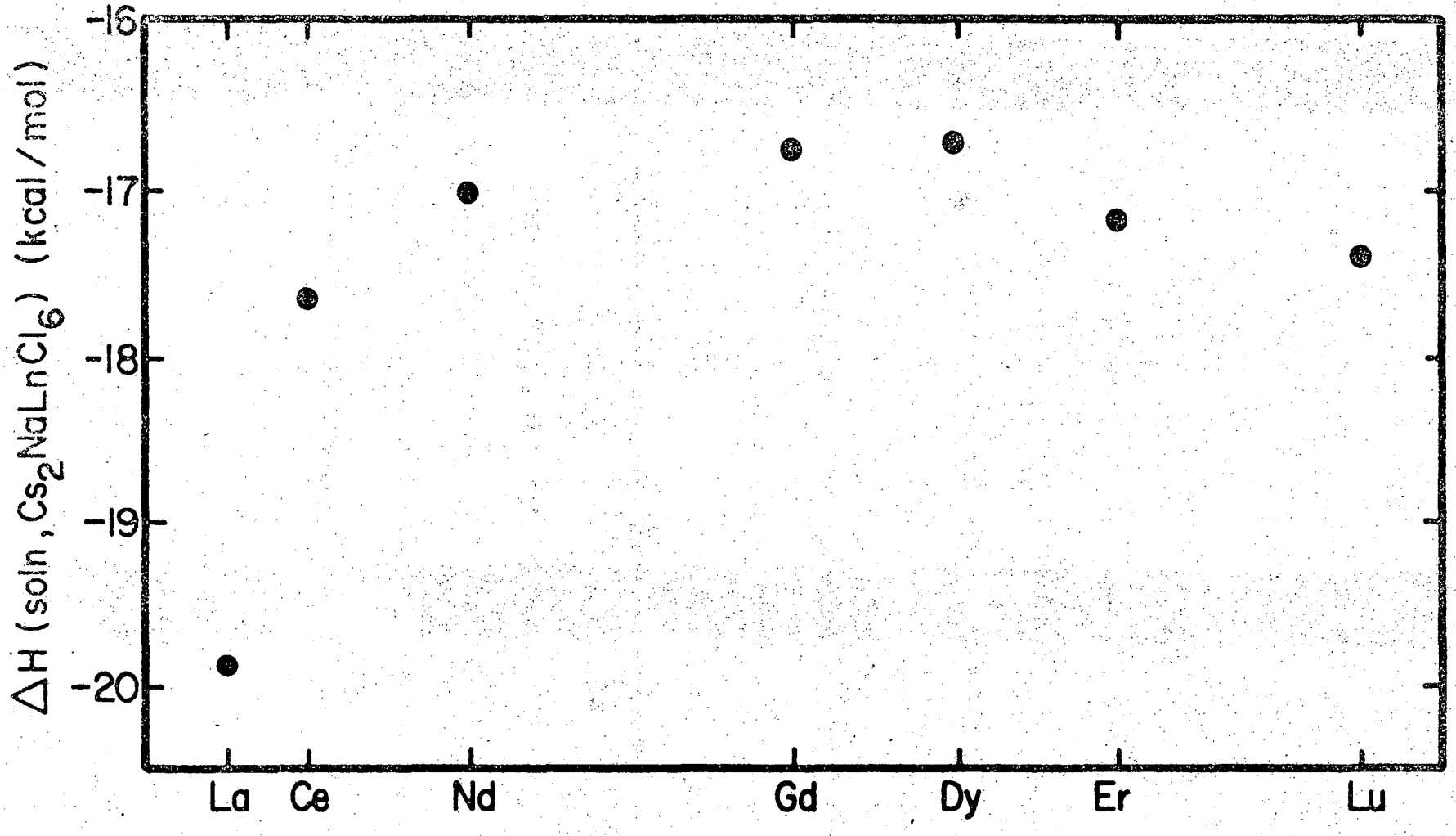

Fig. 1

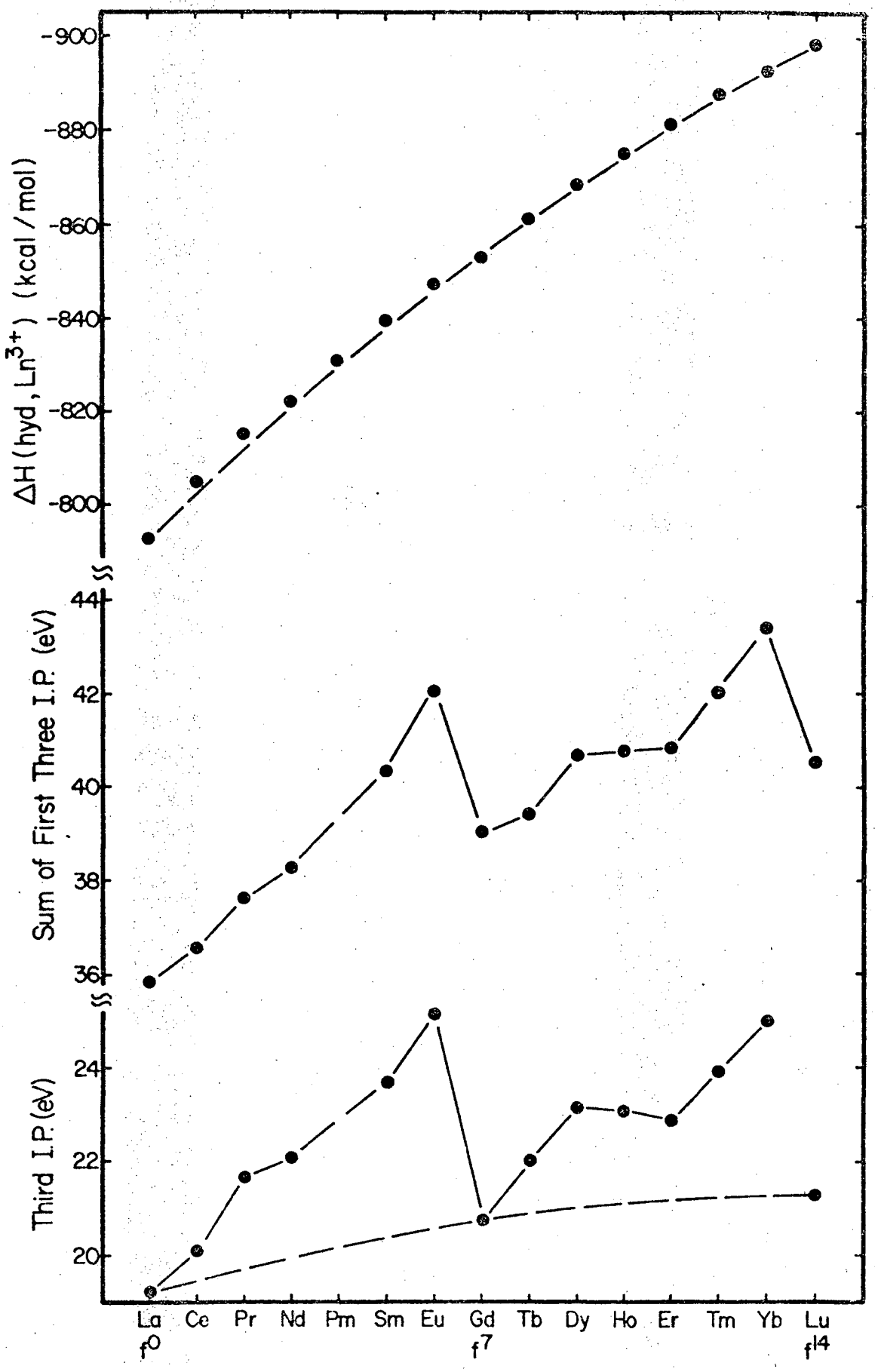
-900
-880
-860
-840
-820
-800
ΔH (hyd, Ln3+) (kcal / mol)
44
42
40
38
36
Sum of First Three I.P. (eV)
24
22
20
Third I.P. (eV)
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
f0
f7
f14

Fig. 2

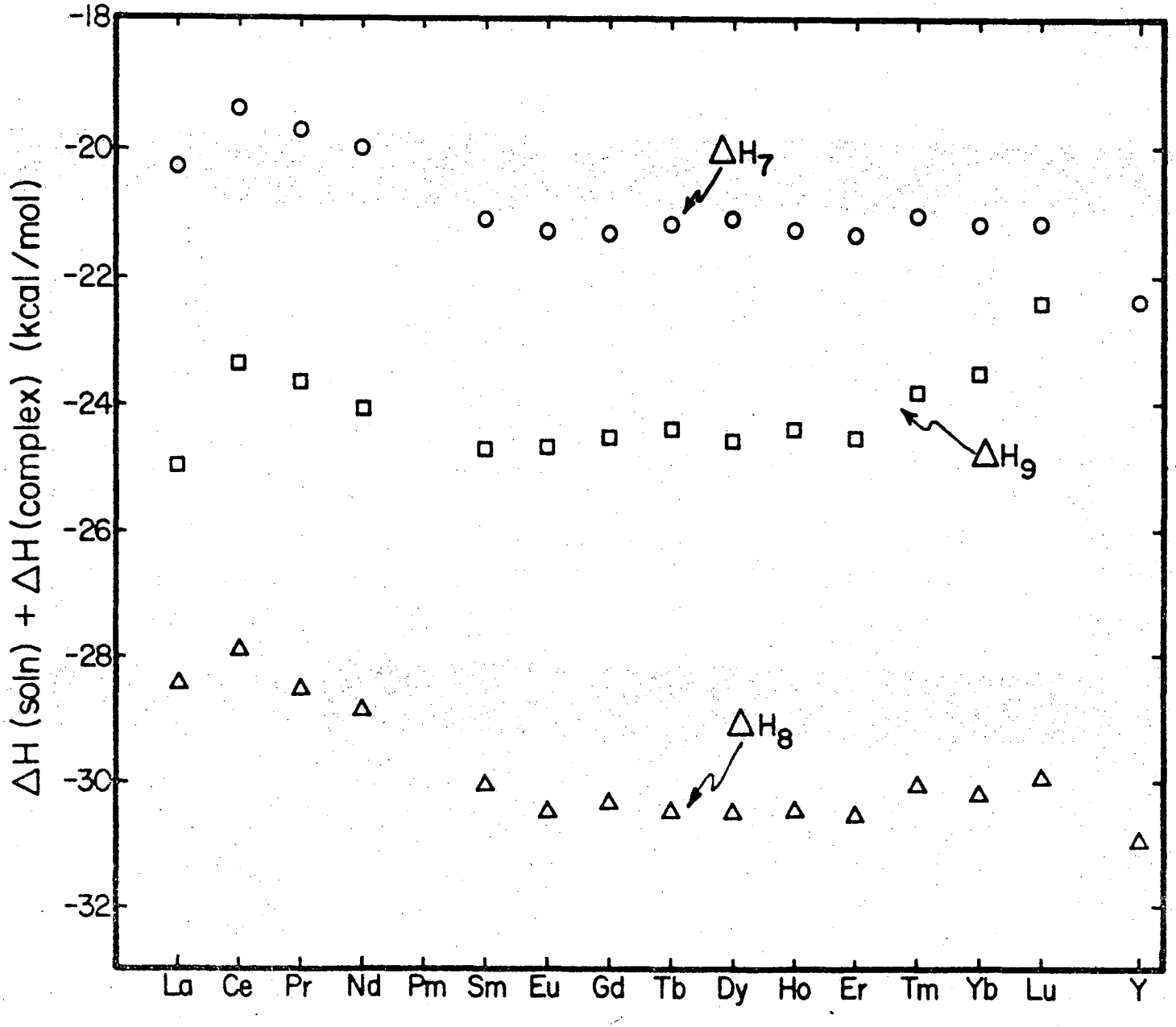
ΔH (soln) + ΔH (complex) (kcal/mol)
-18
-20
-22
-24
-26
-28
-30
-32
ΔH7
ΔH9
ΔH8
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Y

Fig. 3

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