since it involves breaking a copper–nitrogen bond, but k_{3a} is favorable because of the addition of a fourth nitrogen group. Step k_{1a} involves the addition of a nitrogen to the complex making it thermodynamically more stable than I. Therefore I to II is more likely than I to III. Step k_{2b} involves the coordination of a sixth N group on copper which makes it very unstable thermodynamically.[16] Therefore a more likely path is II–IV–VI rather than II–V–VI. Structures VIII and XI can also be disregarded since they involve a six-nitrogen-coordinated complex. The most likely pathway to products therefore seems to be I–II–IV–VI–VII–IX–X–XII–XIII. From the kinetic results we know that the rate-determining step must occur quite early in the reaction path.[20] Application of eq 9 to the microscopic reactions shown in this sequence shows that the predicted rate constant agrees quite closely with the observed value for step IV to VI and that the rate of water loss from IV to VI is the probable rate-determining step.

The possibility exists that the intermediate may be converting from octahedral to trigonal bipyramidal. Such a conversion may occur and still be consistent with our interpretation of the data since, in both cases—the octahedral and bipyramidal structures—the number of bonded nitrogens would be the same as would the rate-determining step. The only difference would be in the number of inner coordinated water molecules.

In continuation of our work the ligand-exchange reaction of Cu(tren) + trien is used as a propagating step in the double ligand-exchange reactions of Cu(tren) + Zn(trien). Such coordination reactions have been used for trace metal analysis.[21] By using an all-polyamine coordination chain, a built-in selectivity for analysis of transition metals in the presence of alkaline earths is afforded.

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[20] Tables of the individual values of k_{obsd} and pertinent experimental parameters will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-2104. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

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CONTRIBUTION FROM THE INSTITUTE OF CHEMISTRY,
THE HEBREW UNIVERSITY, JERUSALEM, ISRAEL

Thermochemistry of Lanthanide Complexes in the Thenoyltrifluoroacetone–Bipyridyl System

BY A. S. KERTES* AND E. F. KASSIERER

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The stepwise equilibrium constants, enthalpy, entropy, and free energy changes for the addition of 2,2′-bipyridyl to some tris(thenoyltrifluoroacetonato)lanthanide(III) chelates have been determined by direct titration calorimetry in chloroform solution at 25°. The metal diketonates accept up to two molecules of the base; the stepwise heats and entropies of addition depend on the ionic radii of the lanthanides (La, Nd, Gd, and Lu). The adducts are stabilized by the large exothermic enthalpy changes.

It has been known for some years that many neutral tris(β-diketonato)lanthanide(III) chelates easily accommodate extra donor groups of a variety of oxygen- or nitrogen-containing bases, yielding stable crystalline solids.[1-8] In all these compounds, with a stoichiometry Ln:diketone:base of 1:3:1, the lanthanides exhibit octacoordinate properties. There is a variety of spectral evidence[4,9-11] that all these Lewis bases complex directly to the central cation. The diketones occupy six coordination sites around the lanthanide atom; thus the base molecule, if bound in addition, will raise the coordination number above six, rather than one or more diketone oxygens being displaced. In instances in which the coordinated donors are water molecules,[5,9,12-16] the tris diketonates may have a hydration number as high as three, the dihydrate being the most stable.

There is enough evidence[17] that such mixed-ligand adducts of lanthanides are of considerable stability in solution of organic solvents of low polarity. There is

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even some evidence that the above stoichiometry as well as the eightfold coordination of the metal is preserved in solution.[7,10,14,17–19]

The stability of these mixed-ligand adducts in organic solvents (as a rule, they are insoluble in water) depends on many factors including the terminal groups of the β-diketone, its acidity and steric hindrance, the basicity of the donor atom(s) in the organic base and its structure, and the size of the metal ion. A comparison of their formation constants reveals that the greater the basicity of the donor atom(s), the greater the stability of the adduct formed, but the greater the stability of the metal diketonate, the weaker the adduct that is formed.[17]

We have reported recently[20] the stability constants of mixed adducts of some lanthanides with several β-diketones among them, thenoyltrifluoroacetone as the acidic component, and the donors phenanthroline or bipyridyl, as the neutral component, as determined by a solvent extraction technique. The immense synergic enhancement,[17] up to 10^6, in the distribution ratio of the lanthanides, compared with that with the β-diketone above, certainly points to the fact that the mixed-ligand adducts formed are of considerable stability. The distribution data, interpreted *via* a set of mass action law equilibria, show that in the nonpolar solvents employed, two adducts, with one and with two nitrogen base molecules, coexist in equilibrium. In view of the multiple coordination tendency of the lanthanides and the possibility of the nitrogen bases to act either as mono- or bidentate ligands, the formation of adducts with two base molecules per metal is not surprising, except perhaps that no corresponding solids were isolated.

We now report the results of a direct calorimetric investigation of the system consisting of tris(thenoyltrifluoroacetonato)lanthanide(III) and bipyridyl in chloroform solution at 25°. We are essentially interested in the energetics involved in electron donor–acceptor reactions and the heat of reaction leading to the formation of the adducts. So far little attention seems to have been paid to the thermochemistry of such reactions, and there are no thermodynamic data for the heats of addition reactions for systems involving acceptors and donors directly relevant to the systems under consideration.

Experimental Section

Materials.—2,2′-Bipyridyl (Fluka CP) and 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (Fischer CP), known as thenoyltrifluoroacetone, were recrystallized twice from benzene solution. Chloroform (Malinckrodt) was of analytical purity. Lanthanide oxides (Lindsay) were of 99.9% purity and were converted to the nitrates by digestion with concentrated nitric acid and evaporation of the excess acid.

The tris(thenoyltrifluoroacetonato)lanthanide(III) dihydrates, $LnA_3\cdot 2H_2O$, were prepared by the method of Charles and Ohlmann.[9] None of the dihydrates so prepared loses water under normal laboratory conditions of drying in a desiccator over P_4O_{10} or $Mg(ClO_4)_2$ at room temperature. No hydrolysis of the chelates has been observed. Melting points for chelates are as follows: $LaA_3\cdot 2H_2O$, 148–150°; $NdA_3\cdot 2H_2O$, 158°; $GdA_3\cdot 2H_2O$, 170° dec; $LuA_3\cdot 2H_2O$, 170° dec.

Anal. Calcd for $LaA_3\cdot 2H_2O$: C, 34.4; H, 1.43; La, 16.6. Found: C, 34.6; H, 1.39; La, 16.5. Calcd for $NdA_3\cdot 2H_2O$: C, 34.4; H, 1.42; Nd, 17.1. Found: C, 34.1; H, 1.38; Nd, 17.2. Calcd for $GdA_3\cdot 2H_2O$: C, 33.6; H, 1.40; Gd, 18.3. Found: C, 33.4; H, 1.40; Gd, 18.6. Calcd for $LuA_3\cdot 2H_2O$: C, 32.9; H, 1.37; Lu, 20.0. Found: C, 32.8; H, 1.38; Lu, 20.3.

Apparatus and Procedure.—The automatic continuous-titration calorimeter with digital output (Model 1000A, Tronac, Inc., Orem, Utah) is a revised commercial version of an apparatus described in the literature.[21] The calorimeter, designed to have a very rapid time response, along with a low heat capacity of the reaction vessel assembly (2.40 cal/deg), high sensitivity of the thermistors (0.0276°/mV), in conjunction with a close temperature control (±0.001°) of the water bath, makes it possible to measure temperature changes to ±0.0005° with a reproducibility of better than 0.2% for a heat effect of 2 cal.

The constant-temperature bath, ~120-l. capacity, is controlled by a Tronac PTC temperature controller to keep the temperature variation of the bath at ±0.003° during a 24-hr period, as measured by a 1° Beckmann thermometer. A dewar flask reaction vessel of 25- or 50-ml capacity, easily interchangeable, is mounted on a vertical mobile plate which also supports the synchronous stirring motor of 400 rpm, glass T-line stirrer, heater, thermistor, and a Teflon delivery tube for the titrant. The whole assembly is immersed into the water bath. The titrant is delivered from a glass buret of about 6-ml capacity by a programmed synchronous motor-driven metal piston in contact with mercury, which then displaces the titrant at a desired rate ranging from 0.0825 to 0.825 ml/min.

The temperature is measured by a Wheatstone bridge arrangement using a Fenwal thermistor GB35P2T1 of 5 kΩ as the temperature-sensing element in the reaction vessel. The other arm of the bridge is a 15-kΩ precision metal-film resistor immersed into the constant-temperature bath. The bridge output, fed into an amplifier, is read on a digital millivoltmeter at ±0.01 mV and printed out at desired intervals. The heater in the reaction vessel supplies the heat at rates ranging between 0.1 and 200 mcal/sec. Multiplying the heater current and heater voltage, which are scaled through appropriate dividers, yields the heater power in mcal/sec.

The total heat capacity of the system, that of the reaction vessel and its content, is determined[22] by introducing an exact and known amount of heat by the aid of a precisely calibrated electrical heater over a measured period of time. By subtracting the known heat capacity of the empty reaction vessel (determined by identical measurements but using water as its content) from the known amount of heat supplied, the heat capacity of the chloroform solutions is deduced. Heat capacity data for all systems studied are given in detail elsewhere.[23]

The experimentally obtained heat effects are corrected[24] for nonchemical energy terms, thermal leakage, heats of dilution, etc. Details of these experiments and calculations[25] and the numerical data are not given here because of their length, but full results are recorded elsewhere.[23]

In determining the heat of reaction, 50 ml of freshly prepared 0.005 *M* chloroform solution of the tris(thenoyltrifluoroacetonato)lanthanide is introduced into the reaction vessel. When thermal equilibrium is obtained, after 4 hr in a typical run, a 0.1 *M* bipyridyl solution in chloroform is delivered from the buret continuously at a rate of 0.407 or 0.825 ml/min. The data points were recorded in 10-sec intervals, and in a typical run 36 digital readings served as input to the computer program. Every run was repeated at least three times, the standard deviation being 1% or less.

Calculations.—The principles of calculating the equilibrium constant of a reaction, and the enthalpy change associated with it, have been described by Izatt, *et al.*[25] For the system under

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TABLE I

THERMODYNAMIC DATA FOR THE REACTION OF TRIS(THENOYLFLUOROACETONATO)LANTHANIDE(III) WITH 2,2′-BIPYRIDYL IN CHLOROFORM SOLUTION AT 298.15°K

$Ln(TTA)_3$	MA_3L				MA_3L_2			
Ln =	Log β_1	$-\Delta H_1$, kcal/mol	$-\Delta S_1$, eu	$-\Delta G_1$, kcal/mol	Log β_2	$-\Delta H_2$, kcal/mol	$-\Delta S_2$, eu	$-\Delta G_2$, kcal/mol
La	3.25 ± 0.08	6.62 ± 0.01	7.46 ± 0.01	4.43 ± 0.11	5.50 ± 0.20	12.47 ± 0.25[e]	16.65 ± 0.10	7.50 ± 0.27
Nd	3.61 ± 0.11[a]	7.90 ± 0.02	9.97 ± 0.05	4.93 ± 0.15	6.87 ± 0.12[c]	18.44 ± 0.06[f]	30.42 ± 0.20	9.37 ± 0.16
Gd	3.71 ± 0.10	9.78 ± 0.05	15.63 ± 0.17	5.12 ± 0.14	7.50 ± 0.08	23.18 ± 0.14[g]	43.42 ± 0.65	10.23 ± 0.11
Lu	4.75 ± 0.20[b]	14.32 ± 0.02	26.40 ± 0.06	6.48 ± 0.27	7.75 ± 0.22[d]	29.14 ± 0.50[h]	62.28 ± 1.69	10.75 ± 0.04

[a] 4.84.[20] [b] 4.62.[20] [c] 5.62.[20] [d] 7.70.[20] [e] 11.10 as calculated by the method of Wadsö.[24] [f] 17.89 as calculated by the method of Wadsö.[24] [g] 22.60 as calculated by the method of Wadsö.[24] [h] 28.50 as calculated by the method of Wadsö.[24]

consideration, the addition of bipyridyl (L) to a chloroform solution of tris(thenoyltrifluoroacetonato)lanthanide(III) chelate (MA_3) will lead[20] to the formation of two mixed-ligand adducts according to the equilibria

$$MA_3 + L \rightleftharpoons MA_3L \qquad (1)$$

$$MA_3 + 2L \rightleftharpoons MA_3L_2 \qquad (2)$$

with β_1 and β_2 as the overall equilibrium constants. The corrected heat effect

$$Q_c = \Delta H_1 \Delta n_1 + \Delta H_2 \Delta n_2 = \sum_{s=1}^{2} \Delta H_s \Delta n_s \qquad (3)$$

represents the total heat evolved by the formation of Δn_1 and Δn_2 mol of adducts, when the corresponding enthalpy changes are ΔH_1 and ΔH_2. The Δn values, as functions of β_1 and β_2, can be derived from the concentrations of each species present at any concentration of L. Thus the corresponding enthalpy changes can be calculated.

We consider, however, the present calorimetric data much more precise than those obtained previously[20] by the distribution technique, and choose to evaluate β and ΔH values independently using an iterative technique of least-square analysis of eq 3. Minimizing the error square sum by a computer program kindly provided by Dr. D. Eatough (Brigham Young University, Provo, Utah)

$$U(\beta_s, \Delta H_s) = \sum_{p=1}^{N} (Q_{c,p} - Q_{t,p})^2 \qquad (4)$$

over all data points p for Q_t, expressed as a function of V_t, the volume of titrant added up to point p

$$Q_t = ([MA_3L]\Delta H_1 + [MA_3L_2]\Delta H_2) V_t \qquad (5)$$

Using the auxiliary mass action law relationships

$$c_{MA_3} = [MA_3] + [MA_3L] + [MA_3L_2] \qquad (6)$$

and

$$c_L = [L] + [MA_3L] + 2[MA_3L_2] = [L]^3\beta_2 + [L]^2(\beta_1 + \beta_2(2c_{MA_3} - c_L)) + [L](1 + \beta_1(c_{MA_3} - c_L)) \qquad (7)$$

and β_1, β_2, ΔH_1, and ΔH_2, eq 5 can be rewritten as

$$Q_t = c_{MA_3} V_t([L]\beta_1\Delta H_1 + [L]^2\beta_2\Delta H_2)(1 + [L]\beta_1 + [L]^2\beta_2)^{-1} \qquad (8)$$

Results

The thermograms, plots of Q_c *vs.* millimoles of bipyridyl, of the continuous titrations are constructed in Figure 1 for the four lanthanide complexes investigated. Qualitatively speaking, the S shape of the plots suggests that two complexes coexist in equilibrium and that the (stepwise) formation of the second complex is the more exothermic. The calculated equilibrium constants and the thermodynamic functions, including the entropy and free energy changes calculated simultaneously, are summarized in Table I, with uncertainties expressed as mean deviations.[25]

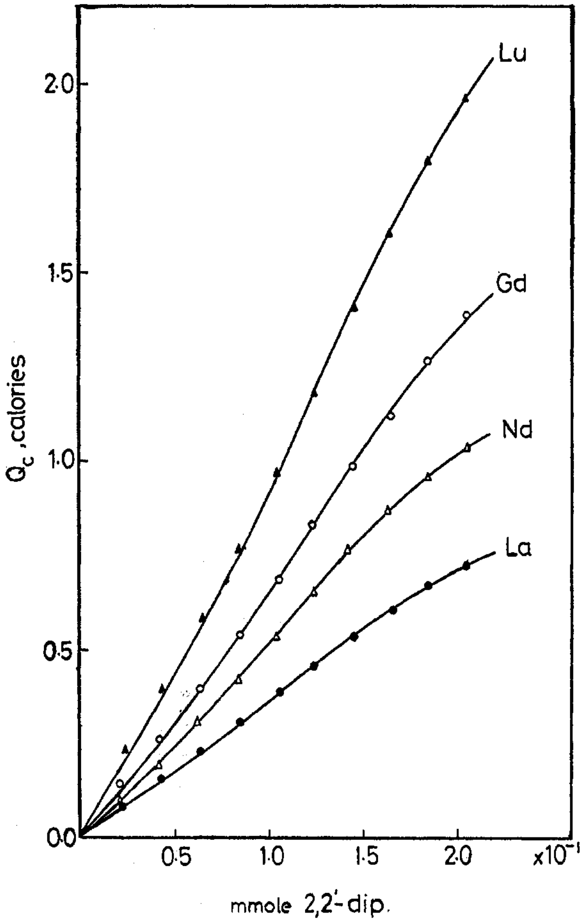

Figure 1.—Corrected heat, Q_c, liberated in the reaction of adduct formation at 25°.

Discussion

We have recently shown that the formation of the lanthanide mixed-ligand complexes under consideration involves the replacement of water molecules from the coordination sphere of the metal ion.[26] Since the bonds between the metal and water are generally quite strong, a considerable amount of energy must be expended in the process of removing the two water molecules from the $MA_3 \cdot 2H_2O$ chelates. The net heat of bipyridyl addition should be thus equated to the heat of the metal–bipyridyl bond minus the heat of the metal–water bond that had to be broken. The large exothermic enthalpy values measured here can thus be explained by a relatively strain-free fitting of the bipyridyl molecules with two potential nitrogen donor atoms. Large exothermic ΔH values are indeed

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characteristic of chelate formation by bidentate nitrogen donor molecules.[27,28] Additionally, the electron-withdrawing effect of the perfluoromethyl group in the thenoyltrifluoroacetone ligand affects the dipole of the complex in such a way as to attract the bipyridyl molecule more strongly.[29] On the other hand, with the exception of neodymium, one cannot expect that with the lanthanides studied here there is an influence of possible ligand-field stabilization on the 4f electrons.[30]

In view of the experimental evidence[5,27] that there is an energy difference in the stepwise removal of the water molecules in tris(β-diketonato)lanthanide(III) hydrates and the plausible assumption that the energy of bonding of bipyridyl to the chelate is different for the first and second base molecule (note that the crystalline mixed-ligand complexes contain invariably only one bidentate base) in forming the adduct in solution, it is not possible from the present ΔH data alone to draw conclusions concerning the replacement process or the structural changes that may be involved.

The observed entropy changes are perhaps more indicative though, again, very little is known with any degree of certainty about the entropy changes in processes discussed here.[27,30] The release of water molecules plays an important role in the entropy change of reaction in spite of the fact that no charged species are involved. Opposing this is a negative contribution originating from the loss of rotational entropy of the donor base molecule as it reacts with the metal chelate. This decrease in entropy is not compensated by the release of water molecules, reflecting strong binding and immobilization of the ligand molecules in the adducts formed. The large differences between ΔS_1 and ΔS_2 values indicate that much of the water release occurs in the formation of the first adduct MA_3L and/or that the second step involves a larger loss of rotational entropy for the bipyridyl molecule. The first effect is probably larger, since the second donor molecule does not have to push aside water molecules (breaking the metal–water bonds) in order to form the MA_3L_2 adduct. The second step will thus yield only a negative entropy for bond formation because of the number of independent particles that has been decreased.

In reality, of course, the situation may be even more complicated by the structural changes that may occur in the stepwise formation of the two adducts. $-\Delta S_1$ values are, *per se*, relatively large as in the first adduct, MA_3L, the bipyridyl molecule acts as a bidentate chelating ligand. Introduction of the second base molecule may cause a reorientation of the first one so as to become a monodentate ligand. This then keeps the coordination number of the lanthanide ion unchanged at 8, although a coordination number of 10 for the lanthanides has been reported.[31,32] The almost linear variation of ΔS_1 and ΔS_2 with the ionic radius for the four lanthanides investigated here suggests that the mechanism is similar, regardless of their atomic number.[30] There is no evidence of an increased steric hindrance as the ionic radius of the lanthanide ions decreases[33] (La, 1.061 Å; Nd, 0.995 Å; Gd, 0.938 Å; Lu, 0.848 Å).

It is apparent that the adducts are stabilized by the large exothermic enthalpy values. The trend with atomic number, evident in ΔH and ΔS terms, largely disappears when the ΔG values are compared. The leveling off of ΔG, essentially a compensation effect, is probably related to the fact that the charge-to-radius ratio plays no significant role in the stability of the adduct. This can be understood in view of the fact that the radius of the MA_3 species is determined mainly by the organic part of the molecule, and the relatively slight differences in the radii of the lanthanide ions are smoothed out in the ΔG values.

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