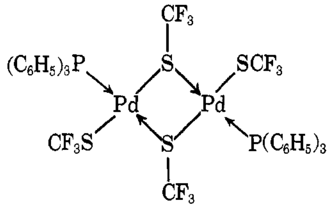
$(SCF_3)_2]_2$ (VI) in 75–80% yields based on the equation

$$4[(C_7H_8SCF_3)Pd]_2(Cl)(SCF_3) + 10(C_6H_5)_3P \longrightarrow 2[(C_6H_5)_3P]_2PdCl_2 + 3[(C_6H_5)_3PPd(SCF_3)_2]_2 + 8C_7H_8$$

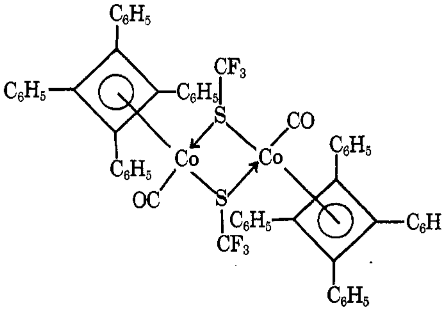
The triphenylphosphine thus breaks the carbon–sulfur bond in each trifluoromethylthionortricyclyl ligand as well as the palladium–carbon bond to this ligand eliminating a C_7H_8 moiety and leaving all of the trifluoromethylthio groups bonded to palladium atoms.



VI

B. Tetraphenylcyclobutadiene Complexes.—The reaction between $[(C_6H_5)_4C_4PdBr_2]_2$ and CF_3SAg proceeds in a normal manner with the replacement of both halogen atoms by CF_3S groups as in the reaction between $C_7H_8PtCl_2$ and CF_3SAg discussed above. Unlike the dimeric cyclobutadienemetal dihalides of the type $[R_4C_4MX_2]_2$ (M = Ni, Pd; R = CH_3, C_6H_5; X = Cl, Br; etc.)[12] the palladium compound $(C_6H_5)_4C_4Pd(SCF_3)_2$ (I) is monomeric as indicated by the molecular weight determination in dichloromethane solution. The ^{19}F nmr chemical shift of the CF_3S group in $(C_6H_5)_4C_4Pd(SCF_3)_2$ (I) lies in the ϕ 26 region characteristic of terminal CF_3S groups (although the above data on $[(C_7H_8SCF_3)Pd]_2(Cl)(SCF_3)$ suggest that this criterion must be applied with caution and is of more value in excluding the presence of terminal CF_3S groups rather than demonstrating the presence of terminal CF_3S groups). The palladium complex $(C_6H_5)_4C_4Pd(SCF_3)_2$ (I) thus appears to be the first example of a cyclobutadiene metal complex with a 16-electron configuration rather than the favored 18-electron configuration.[13]

The cobalt derivatives $R_4C_4Co(CO)_2X$ (R = CH_3, C_6H_5; X = Cl, Br, I) are isoelectronic with the well-known cyclopentadienyliron derivatives $C_5H_5Fe(CO)_2I$ and, like the iron derivatives, are useful intermediates for the preparation of a variety of interesting organometallic derivatives.[7] Reaction of $(C_6H_5)_4C_4Co(CO)_2Cl$ with CF_3SAg results in the loss of carbon monoxide to give a deep red bimetallic derivative $[(C_6H_5)_4C_4Co(CO)SCF_3]_2$ (VII). The ^{19}F nmr chemical shift of the CF_3S group is ϕ 32.3 which is outside the region observed for terminal CF_3S groups. The formation of a bimetallic derivative VII with bridging CF_3S groups in the reaction of CF_3SAg with $(C_6H_5)_4C_4Co(CO)_2Cl$ contrasts with the formation[1] of a monometallic derivative $C_5H_5Fe(CO)_2SCF_3$ in the reaction of CF_3SAg with $C_5H_5Fe(CO)_2I$ but is an obvious consequence of the weaker metal–carbon monoxide bond in the $(C_6H_5)_4C_4Co(CO)_2X$ halides than in the $C_5H_5Fe(CO)_2X$ halides.[6]



VII

Acknowledgment.—We are indebted to the National Institute of General Medical Sciences for partial support of this work under Grant GM-14664-03. We are also indebted to an anonymous reviewer for helpful suggestions.

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The Synthesis and Properties of Diethylenetriamine Chelates of the Tripositive Lanthanide Ions

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The reaction of diethylenetriamine with a lanthanide(III) nitrate salt in anhydrous acetonitrile yields solid compounds of the stoichiometric formulation $[Ln(dien)_3](NO_3)_3$ and $[Ln(dien)_2(NO_3)_2]NO_3$. Infrared data establish coordination by nitrate ion in the bis chelates. Conductivity and enthalpy data show that the $Ln(dien)_2(NO_3)_2^+$ ion is the thermodynamically favored species in acetonitrile. The enthalpy changes observed for a calorimetric titration of lanthanide(III) perchlorate salts in acetonitrile demonstrate the thermodynamic stability of the $Ln(dien)_n^{3+}$ (n = 1–3) species in solution. The variation in enthalpy changes in the lanthanide series are discussed.

Although coordination chemistry of the trivalent lanthanide ions has expanded rapidly in the last 20 years,[1,2] the majority of complexes studied were in aqueous solution and were derived from anionic ligands with oxygen donor atoms. The observation that cationic complexes derived from neutral ligands with nitrogen donor sites could not be isolated from aqueous media prompted the assumption that Ln^{3+}–N interactions were necessarily weaker than Ln^{3+}–O interactions. Recently, however, the use of nonaqueous

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solvent media has provided a means of successful synthesis of lanthanide complexes derived from several N donors such as 1,10-phenanthroline,[3,4] bipyridyl,[5-8] terpyridyl,[9-11] and ethylenediamine.[12] That complexes derived from N donors have coordination numbers of 8 or 9 is perhaps indicative of a stronger Ln^{3+}–N interaction than previously assumed. Calorimetric measurement of the enthalpies of complexation of ethylenediamine with the lanthanide ions in acetonitrile provided the first quantitative evidence for considerable thermodynamic stability of lanthanide complexes based solely upon nitrogen coordination.[13]

We report here the synthesis of the first lanthanide complexes derived from the tridentate N donor diethylenetriamine. These species, isolated as bis and tris chelates of the nitrate salts, provide additional examples of high-coordinate lanthanide complexes utilizing an N donor. These complexes were characterized in the solid state by infrared spectroscopy and in solution by conductivity measurements. Calorimetric measurement of enthalpies of complexation of lanthanide perchlorates in acetonitrile were obtained in order to establish the thermodynamic stability of the metal chelates in solution and to elucidate further the relationship of coordination number to steric requirements of the ligand and metal ion size.

Experimental Section

Materials.—The lanthanide oxides, all of 99.9% purity, were obtained from American Potash and Chemical Corp. The anhydrous lanthanide nitrates, chlorides, and perchlorates were prepared by the general procedures described previously.[12] Reagent grade acetonitrile was dried and purified by distillation from phosphorus(V) oxide. Diethylenetriamine was dried by refluxing over metallic sodium and purified by vacuum distillation (0.1 Torr).

Infrared Measurements.—Infrared spectra in the region 4000–650 cm^{-1} were obtained with a Perkin-Elmer Model 457 grating instrument as Nujol and hexachlorobutadiene mulls supported between sodium chloride plates. Polystyrene film was used to calibrate the instrument.

Enthalpy Measurements.—The calorimeter used was basically of the same design as that used in a previous study.[13] An operational amplifier was utilized to amplify the signal from the thermistor bridge, before it was fed into a Heath Model Eu 20B recorder. The sensitivity of the instrument was such that 2.27 cal of heat added to 125 ml of acetonitrile produced a pen deflection of 100 mm. The calorimeter calibration was checked by measuring the enthalpy of neutralization of aqueous hydrochloric acid solution with aqueous sodium hydroxide solution (lit. value, 13.36 kcal mol^{-1} at infinite dilution; found, 13.39 ± 0.1 kcal mol^{-1} corrected for heat of solution to 0.002 *M*).

The calorimetric measurement of an enthalpy of complexation was effected by the method of increments as described previously.[13] The dewar flask of the calorimeter was contained in a drybag to protect the system from moisture. The solvent was maintained slightly below ambient temperature at 23°, to minimize heat loss, by immersing an 8-mm glass tube containing ice water into the solution. The temperature of the solution was controlled within ±0.2° during each experiment. A 3-mmol quantity of an anhydrous lanthanide salt was dissolved in 125 ml of acetonitrile contained in the calorimeter. Diethylenetriamine was added in 0.139-mmol increments (0.0150 ± 0.0002 ml) using a 0.2-ml Gilmont micrometer syringe. The heats released upon complexation of the increment gave pen deflections of 50–100 mm. Approximately 90 increments of ligand were added in each run, giving 90 independent measurements of heat evolved upon complexation. The heat of solution of diethylenetriamine, found experimentally to be 1.06 ± 0.04 kcal mol^{-1}, was used to correct the measured heats evolved upon complexation. The molar enthalpies of complexation of each increment were calculated by assuming complete reaction of the increment in forming a single complex species.

Conductivity Measurements.—Conductivities were determined with an Industrial Instruments Inc. Model RC 16B2 conductance bridge at 1000 cps in a constant-temperature mineral oil bath maintained at 25 ± 0.01°. The constant-temperature bath was contained in a drybag.

Analyses.—Elemental carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc. Lanthanide analyses were performed in this laboratory by titration with ethylenediaminetetraacetic acid, using xylenol orange as the indicator.

Synthesis of Complex Species.—The complexes were prepared under anhydrous conditions by the direct reaction of diethylenetriamine with a lanthanide salt in acetonitrile. All manipulations were carried out in a drybox. Since the isolation of a stoichiometric product apparently depends upon relative solubilities of the bis and tris chelates, several methods of preparation were used and are described below. Attempted preparations of tris chelates of lanthanides heavier than gadolinium were unsuccessful, resulting in nonstoichiometric mixtures formulated as $Ln(dien)_{2-3}(NO_3)_3$. A complete list of complexes and their analyses are given in Table I.

TABLE I

COMPOUNDS PREPARED AND ANALYTICAL DATA

	Analyses, %					
	C		H		Ln	
Compd[a]	Calcd	Found	Calcd	Found	Calcd	Found
$[La(dien)_3](NO_3)_3$	22.72	22.89	6.20	6.31	21.89	22.03
$[Pr(dien)_3](NO_3)_3$	22.64	22.63	6.18	5.99	22.14	22.45
$[Nd(dien)_3](NO_3)_3$	22.53	22.55	6.14	6.39	22.55	22.18
$[Sm(dien)_3](NO_3)_3$	22.31	22.56	6.09	6.25	23.28	22.93
$[Gd(dien)_3](NO_3)_3$	22.08	22.90	6.02	5.96	24.09	23.90
$[La(dien)_2(NO_3)_2]NO_3$	18.08	18.24	4.93	5.04	26.14	26.16
$[Pr(dien)_2(NO_3)_2]NO_3$	18.02	18.18	4.91	4.75	26.42	26.38
$[Nd(dien)_2(NO_3)_2]NO_3$	17.90	17.77	4.88	4.88	26.88	27.13
$[Sm(dien)_2(NO_3)_2]NO_3$	17.70	17.95	4.83	4.91	27.70	27.96
$[Gd(dien)_2(NO_3)_2]NO_3$	17.48	17.74	4.77	4.45	28.61	28.57
$[Dy(dien)_2(NO_3)_2]NO_3$	17.32	17.49	4.72	4.85	29.29	29.30
$[Er(dien)_2(NO_3)_2]NO_3$	17.17	17.30	4.68	4.74	29.89	30.12
$[Yb(dien)_2(NO_3)_2]NO_3$	16.99	17.17	4.64	4.79	30.60	30.84
$[Y(dien)_2(NO_3)_2]NO_3$	19.95	20.16	5.45	5.57	18.47	18.63

[a] Designation of coordination sphere dictated by conductivity data.

$Ln(dien)_3(NO_3)_3$ (Ln = Pr, Nd, Sm).—Diethylenetriamine (12 mmol) was dissolved in 5 ml of acetonitrile and the resulting solution was added dropwise to a well-stirred acetonitrile solution of a lanthanide nitrate (2 mmol in 15 ml of acetonitrile). Precipitation of the product occurred immediately, but the suspension was refluxed for 24 hr to ensure a stoichiometric product. The solid products obtained from the reaction mixture often contained a ligand to metal ion mole ratio in excess of 3:1. A stoichiometric tris chelate was obtained by heating this product *in vacuo* (56–80°, 0.05 mm). A comparison of the infrared spectrum of the product before and after heating, in the NH stretching region, showed that a band at 3350 cm^{-1}, assigned to lattice diethylenetriamine, disappeared upon heating.

$Ln(dien)_3(NO_3)_3$ (Ln = La, Gd).—An acetonitrile solution of a lanthanide nitrate (2 mmol in 10 ml of acetonitrile) was added dropwise to 10 ml of an acetonitrile solution containing 20 mmol of diethylenetriamine. The precipitated product was collected immediately by filtration without refluxing. The stoichiometric tris chelate was obtained by heating the filtered product, which contained excess ligand, *in vacuo*, as described above. If the suspension is refluxed before filtration, a nonstoichiometric product $Ln(dien)_{2-3}(NO_3)_3$ is obtained. That a mixture of the bis and tris chelate is obtained upon refluxing is attributed to a decreased solubility difference between the two chelates.

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[13] J. H. Forsberg and T. Moeller, *ibid.*, **8**, 889 (1969).

$Ln(dien)_2(NO_3)_3$.—Diethylenetriamine (4 mmol) was dissolved in 5 ml of acetonitrile and the resulting solution was added dropwise to an acetonitrile solution of a lanthanide nitrate (2 mmol in 15 ml of acetonitrile). The resulting suspension was refluxed to ensure a stoichiometric product. An infrared spectrum of the solid compound showed a weak band at 2250 cm^{-1} (ν(CN)), indicating the presence of acetonitrile. The product was heated *in vacuo* (56–80°, 0.05 mm) until a stoichiometric product was obtained.

Results and Discussion

Infrared Studies.—Assignments of the nitrate absorptions, based upon the two possible symmetry types, D_{3h} (free nitrate) and C_{2v} (coordinated nitrate), are given in Table II.[14,15] The identification of ν_2 (C_{2v}) was not possible due to strong absorptions by the ligand in the 1030-cm^{-1} region. The data indicate that the bis chelates contain both coordinated and ionic nitrate groups. Since the infrared spectrum does not distinguish between bidentate and monodentate nitrate coordination (nitrate symmetry being C_{2v} in each case) or the number of coordinated and ionic nitrate groups, the coordination number of the bis chelates may be 7, 8, 9, or 10. Recently, however, the crystal structure of tris(nitrato)bis(dipyridyl)lanthanum(III), $Ln(dipy)_2(NO_3)_3$, was determined, and all three coordinated nitrates were found to be bidentate.[16] The formulation $[Ln(dien)_2(NO_3)_2]NO_3$, containing two bidentate nitrate groups, analogous to that found for tris-ethylenediamine chelates, $[Ln(en)_3(NO_3)_2]NO_3$, appears reasonable, at least for the larger lanthanide ions.

TABLE II

ASSIGNMENT OF INFRARED ABSORPTIONS OF NITRATES

	ν, cm^{-1}	
Assignment	$[Ln(dien)_2(NO_3)_2]NO_3$	$[Ln(dien)_3](NO_3)_3$
$\nu_2(D_{3h})$	830 m	830 m
$\nu_3(D_{3h})$	1370 sh	1360 s
$\nu_1(C_{2v})$	1315 s	. . .
$\nu_3(C_{2v})$	740 w	. . .
$\nu_4(C_{2v})$	1470 s	. . .
$\nu_5(C_{2v})$	720 vw	. . .
$\nu_6(C_{2v})$	820 m	. . .

The spectra of the tris chelates show bands corresponding only to ionic nitrate groups. That addition of a third molecule of diethylenetriamine results in a displacement of coordinated nitrate groups from the coordination sphere is proof that the solid tris complexes contain three coordinated diethylenetriamine molecules and are not bis chelates containing a molecule of diethylenetriamine trapped in the salt lattice. Furthermore, the presence of only three bands in the NH_2 stretching region indicates that all NH_2 groups are coordinated.[17] The tris chelates thus exemplify nine-coordinate lanthanide complexes containing only nitrogen atoms in the coordination sphere.

Conductivity Measurements.—Conductivity data for acetonitrile solutions containing lanthanide salts and diethylenetriamine are given in Table III. All the data for the nitrate solutions containing excess diethylenetriamine are in the range expected for 1:1 electrolytes in acetonitrile[11,18] (1:1, 175 ohm^{-1} cm^2 mol^{-1}; 2:1, 285 ohm^{-1} cm^2 mol^{-1}; 3:1, 400 ohm^{-1} cm^2 mol^{-1}). A plot of molar conductance *vs.* ligand to metal ion mole ratio for a 0.001 *M* $Nd(NO_3)_3$ solution is shown in Figure 1. The curve is characterized by a sharp increase in conductivity between the 1:1 and 2:1 ligand to metal ion mole ratios, indicating the release of a coordinated nitrate ion in this region. The bis chelate existing in solution is formulated as $Ln(dien)_2(NO_3)_2{}^+$, since the conductivities at the 2:1 ligand to metal ion mole ratio are indicative of uni-univalent electrolyte behavior. This formulation is consistent with that postulated for the solid bis chelates.

TABLE III

MOLAR CONDUCTIVITIES OF ACETONITRILE SOLUTIONS CONTAINING LANTHANIDE SALTS AND DIETHYLENETRIAMINE

	Λ_M(ligand:metal), ohm^{-1} cm^2 mol^{-1}		
Lanthanide salt	$\Lambda_M(0:1)^a$	$\Lambda_M(6:1)^a$	$\Lambda^0_M(6:1)^b$
$La(NO_3)_3$	12.4	129	170
$Pr(NO_3)_3$	12.6	135	175
$Nd(NO_3)_3$	17.5	136	160
$Sm(NO_3)_3$	17.5	136	164
$Dy(NO_3)_3$	4.8	137	175
$Er(NO_3)_3$	6.5	157	205
$Yb(NO_3)_3$	5.6	176	210
$Nd(ClO_4)_3{}^b$	465	430	430

[a] Concentration of lanthanide salts is 0.001 *M*. [b] Limiting conductivities at infinite dilution were obtained from extrapolation of the linear portion of a standard conductance plot. The graphs deviate from linearity in the nitrate systems for concentrations less than 1.5 × 10^{-3} *M* due to the presence of the weak electrolyte $Ln(dien)_2(NO_3)_2{}^+$.

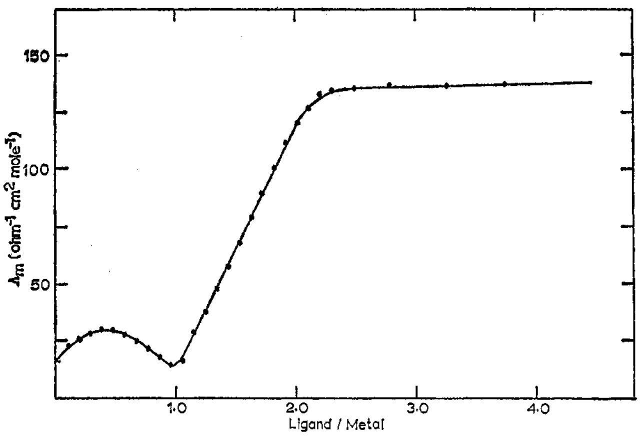

Figure 1.—Conductance titration of $Nd(NO_3)_3$ with diethylenetriamine.

The lack of a further large increase in conductivity beyond the 2:1 ligand to metal ion mole ratio indicates that the third molecule of diethylenetriamine does not compete effectively against the nitrate ligands for the remaining coordination positions of the lanthanide ion. The unfavorable thermodynamic stability of the tris chelate $Ln(dien)_3{}^{3+}$ relative to the bis chelate $Ln(dien)_2(NO_3)_2{}^+$ may be due to the greater steric requirements of diethylenetriamine rather than better donor properties of the nitrate ion. This assumption is based upon the apparent ease with which the first nitrate group is replaced. Significant increases in conductivity of the 0.001 *M* $Er(NO_3)_3$–dien solution and 0.001 *M*

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(14) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, N. Y., 1945, p 178.

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$Yb(NO_3)_3$–dien solution (Table III) are also indicative of increased steric repulsions in the bis chelate with decreasing metal ion size, resulting in ionic dissociation of the $Ln(dien)_2(NO_3)_2^+$ complex. The isolation of pure tris chelates containing no coordinated nitrate groups is apparently due to a greater insolubility of the tris chelates in acetonitrile, since they are not favored thermodynamically.

The molar conductances of a neodymium perchlorate solution and a neodymium perchlorate–diethylenetriamine solution are both in the range expected for uni-trivalent electrolyte behavior. These data clearly demonstrate the weak coordinating ability of perchlorate ion compared to nitrate ion.

Enthalpy Measurements.—The apparent lack of thermodynamic stability of the tris chelates of nitrate salts in acetonitrile raises a question as to the real existence of a $Ln(dien)_3^{3+}$ complex in solution as opposed to their formation solely to satisfy the demands of crystal stability. Calorimetric measurement of the enthalpies of complexation of the lanthanide perchlorates in acetonitrile were determined to provide quantitative evidence for the existence of these complexes in solution. The perchlorate salts were chosen for the thermodynamic studies due to the inability of perchlorate ion to compete with diethylenetriamine as a ligand for the lanthanide ion. A plot of the molar enthalpies of complexation, in terms of the general equation

$$Ln(dien)_{n-1}(CH_3CN)_x^{3+} + dien \rightleftharpoons Ln(dien)_n(CH_3CN)_y^{3+} + (x - y)CH_3CN$$

is given in Figure 2 for gadolinium perchlorate–diethylenetriamine system. The results for the other lanthanide perchlorates are similar. Each curve is characterized by distinct plateaus, indicating formation of the $Ln(dien)_n^{3+}$ (n = 1–3) species in solution. The distinct breaks observed in these enthalpy curves are characteristic of thermodynamically stable complexes, in which the successive stepwise formation constants differ by at least 10^3.[19]

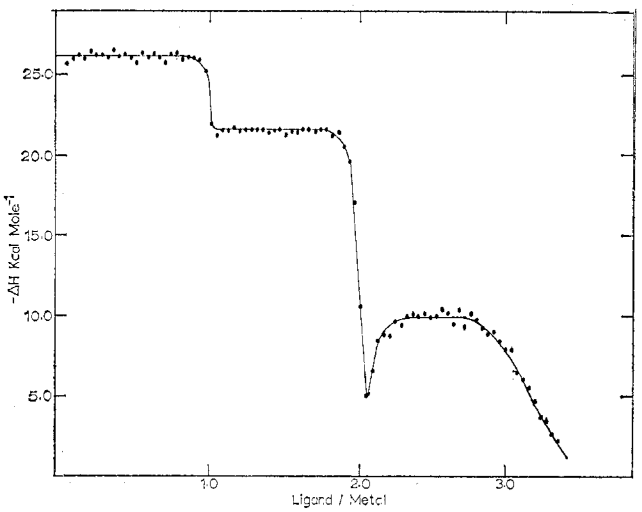

Figure 2.—Enthalpy curve for the formation of $Gd(dien)_n(ClO_4)_3$.

The stepwise enthalpies of complexation, ΔH_n, were obtained from the enthalpy at a plateau on the titration curve and are presented in Table IV. The constant value of ΔH_n at a given ligand to metal ion mole ratio indicates that the increment of diethylenetriamine reacts nearly quantitatively to form a single complex species, characteristic of the ligand to metal ion mole ratio at which the increment is added. This behavior is further proof that the stepwise formation constants are both large and well separated. Unfortunately, a nearly quantitative reaction of an increment to form a single complex species precludes the possibility of calculating the stepwise formation constants from the enthalpy curves by a rather accurate iterative procedure.[20]

TABLE IV
ENTHALPIES OF COMPLEXATION OF LANTHANIDE PERCHLORATES AT 23°

Ln^{3+}	Enthalpy change,[a] kcal mol⁻¹ $-\Delta H_1$	$-\Delta H_2$	$-\Delta H_3$
La^{3+}	23.8	19.8	13.1
Pr^{3+}	24.6	20.8	12.6
Nd^{3+}	25.6	20.9	11.5
Sm^{3+}	25.7	21.2	10.7
Gd^{3+}	26.1	21.5	9.9
Dy^{3+}	27.2	22.2	6.9
Er^{3+}	28.1	23.5	6.2
Yb^{3+}	27.4	22.7	6.1

[a] Deviation ±0.3 kcal mol⁻¹. All enthalpy data were corrected for heat of solution of diethylenetriamine. The conductance data are strong evidence for constancy of ionic strength in the perchlorate system and the values are related to an ionic strength of 0.024 M $Ln(ClO_4)_3$.

The monotonic decrease in ΔH_3 values with decreasing metal ion size clearly demonstrates the presence of a steric effect upon coordination of the third molecule of diethylenetriamine. The decrease in ΔH_3 offers a quantitative measure of the steric effect in these high-coordinate complexes as a function of metal ion radius. The large difference observed in ΔH_3 values for Gd^{3+} and Dy^{3+} may indicate that steric factors are decisive in preventing the isolation of the tris chelates of the heavier lanthanide nitrates.

The unusual minimum which occurs in all the enthalpy curves at the 2:1 ligand to metal ion mole ratio is apparently due to a trace quantity of moisture in the system. Addition of 0.01 ml of water to the system increases the number of abnormally low ΔH values, thereby significantly broadening the dip observed in this region of the curve. Water reacts with a strongly basic amine to form hydroxide ion, which will compete with diethylenetriamine for the metal ion. In a calorimetric titration of a lanthanide ion with ethylenediamine, interference by water is observed upon the addition of the first increments of ligand.[21] Thus it is difficult to understand why this interference should occur *precisely* at the 2:1 ligand to metal ion mole ratio with diethylenetriamine.

An enthalpy curve for the titration of neodymium nitrate is given in Figure 3. The curve is characterized by two plateaus, demonstrating the formation of a mono and a bis chelate. The absence of a third plateau is further proof that the tris chelate is thermodynamically unfavorable relative to the bis chelate in acetonitrile solutions of the nitrate salts. The effect of coordinated nitrate in lowering the effective positive charge of the

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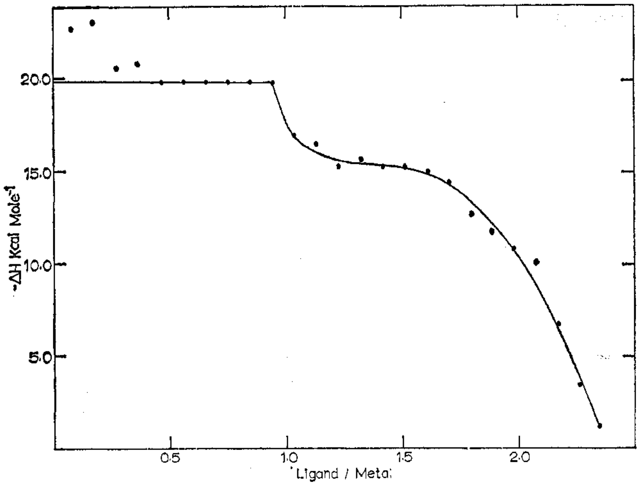

Figure 3.—Enthalpy curve for the formation of $Nd(dien)_n(NO_3)_3$.

metal ion is reflected in the lower enthalpy changes ($\Delta H_1 = -19.8$, $\Delta H_2 = -15.4$ kcal mol^{-1}) observed for neodymium nitrate compared with neodymium perchlorate (Table IV).

TABLE V

TOTAL ENTHALPIES OF COMPLEXATION FOR ETHYLENEDIAMINE AND DIETHYLENETRIAMINE CHELATES OF LANTHANIDE PERCHLORATES

Ln^{3+}	Total enthalpy change, kcal mol^{-1}		
	$-\Delta H_c(en)$	$-\Delta H_c(dien)$	Difference
La^{3+}	57.6	56.7	0.9
Pr^{3+}	59.9	58.0	1.9
Nd^{3+}	60.4	58.0	2.4
Sm^{3+}	60.7	57.6	3.1
Gd^{3+}	60.9	57.5	3.4
Dy^{3+}	60.1	56.3	3.8
Er^{3+}	63.4	57.8	6.6
Yb^{3+}	66.1	56.2	9.9

The total enthalpies of complexation, ΔH_c, for the formation of tetrakis-ethylenediamine chelates[13] and tris-diethylenetriamine chelates are given in Table V. The total enthalpy of complexation is less for the tris-diethylenetriamine chelates for each lanthanide ion, even though it involves formation of nine metal–nitrogen bonds compared to only eight for the tetrakis-ethylenediamine chelates. Furthermore, the difference in ΔH_c increases with decreasing metal ion radius, indicating the presence of greater steric repulsions in the tris-diethylenetriamine chelates. Since the nitrogen atoms in each of these ligands are expected to be of comparable donor strength, a comparison of ΔH_c values provides a quantitative measure of the difference in the steric requirements of these two ligands in high-coordinate complexes, as a function of metal ion radius.

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Preparation and Properties of Lanthanide Chelate Complexes

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Compounds of five types have been synthesized: $M(dpm)_3$ [M = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu]; $M(dpm)_3py$ [M = same 12 metals]; $M(dpm)_3dipy$ [M = same first 11 metals, not Lu]; $M(dpm)_3phen$ [M = same first 11 metals, not Lu]; and $Ce(dpm)_4$ [where dpm = dipivaloylmethane, py = pyridine, dipy = α,α'-dipyridyl, phen = 1,10-phenanthroline]. They have been characterized by their thermal (melting point, dta, tga), spectral (ir, visible, uv), and magnetic (susceptibility, Weiss constant) properties and are under investigation as proton nmr shift reagents.

Introduction

The recently reported[1] discovery that the pyridine adduct of tris(dipivaloylmethanato)europium(III), $Eu(dpm)_3(py)_2$, could be used as a proton nmr shift reagent for cholesterol prompted us to begin the preparation of a series of analogous lanthanide complexes with the same bulky bidentate β-keto enolate ligand with all of the available lanthanide ions. We wanted to explore more fully the potential of the various $4f^n$ systems as shift reagents for a variety of organic molecules and to see if we could determine and understand the specific characteristics which produce the best shift reagents. More recent reports have established that (1) $Eu(dpm)_3$ itself (*i.e.*, without the pyridine molecules appended) is even better than the dipyridine adduct,[2] (2) the analogous praseodymium compound, $Pr(dpm)_3$, induces proton nmr shifts[3] of the opposite sign of those reported for $Eu(dpm)_3$ and also much larger than those reported for $Eu(dpm)_3$, (3) Eu(III), Gd(III), and Ho(III) cations will serve as nmr structural probes in several biological systems,[4] (4) when $Eu(dpm)_3$ serves as the shift reagent for adamantan-1- and -2-ol, the mechanism of deshielding involves interaction *both* through space (pseudocontact shift) and through bonds (contact shift),[5] and (5) $Eu(dpm)_3$ may be used as a shift reagent for a steroid and a triterpene.[6]

We have now prepared 47 compounds of the types $M(dpm)_3$ (M = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), $M(dpm)_3py$ (M = same 12 metals), M-

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