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COMPLEXES OF LANTHANIDE (III) IONS WITH NITROGEN DONOR LIGANDS

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CONTENTS

ABBREVIATIONS

acac	acetylacetonate
benz	benzoate
dbm	dibenzoylmethide
dien	diethylenetriamine
diket	diketonate
dimp	4,4′-dimethyl-2,2′-dipyridyl
dipy	2,2′-dipyridyl
dpm	dipivaloylmethane
en	ethylenediamine
Hsal, sal	salicylate
Ln	lanthanide
Pc	phthalocyanine
phen	1,10-phenanthroline
pic	picoline
pn	1,2-propanediamine
terpy	terpyridyl
thd	2,2,6-tetramethyl-heptane-3,5-dione
TPT	2,4,6-tri-α-pyridyl-1,3,5-triazine
tren	β,β′,β″-triaminotriethylamine
trien	triethylenetetramine
TTA	thenoyltrifluoroacetone

A. INTRODUCTION

Although coordination chemistry of the trivalent lanthanide ions has expanded rapidly in the last twenty years, the majority of complexes studied have been derived from strongly chelating anionic ligands with oxygen donor sites[1,2]. Prior to 1964, nitrogen coordination was well characterized only in association with oxygen donors, as exemplified by the polyaminepolycarboxylates and 8-quinolinolates. The observation that cationic complexes derived from N-donors could not be isolated from aqueous media prompted the assumption that Ln^{3+}–N interactions were necessarily weaker than Ln^{3+}–O interactions.

The conspicuous absence of these species in aqueous solution dictates a significant difference in coordinating tendency of lanthanide ions and *d*-type transition metal ions. This difference may be attributed to effective shielding of the lanthanide 4*f* orbitals by the $5s^2 5p^6$ octet, precluding the existence of strongly covalent metal–ligand interactions. Thus metal–ligand bonding in lanthanide complexes is substantially electrostatic, as corroborated by magnetic, spectral and kinetic data[3]. Thus it is not surprising that the species isolable from aqueous media are derived from anionic donors, in which strong electrostatic bonding with the metal ion is possible. The fact that complexes derived from neutral N-donors could not be isolated prompted the assumption that these species were thermodynamically unstable in aqueous solution.

However, the problem of synthesizing complexes in aqueous media is one of comparative donor availability and donor strength. Complexation of a weakly basic N-donor could occur only by displacement of strongly bonded water molecules. The calculated enthalpy of hydration[4] (-800 to -900 kcal.mole^{-1}) is indicative of the strength of the Ln^{3+}–H_2O interaction. In addition, the large excess of solvent molecules makes it even more difficult for the relatively small number of N-donors to compete effectively.

Strongly basic N-donors, which might otherwise be expected to form strong metal–nitrogen bonds, generate a sufficient concentration of hydroxide ion by interaction with water to precipitate the highly insoluble lanthanide hydroxides[5] (K_{sp} ca. 10^{-19}–10^{-24} mole^4. l^{-4}). Prevention of hydroxide precipitation would require the formation of an amine complex possessing extensive thermodynamic stability[6].

It is apparent that the ability of lanthanide ions to coordinate with neutral N-donors could best be evaluated in non-aqueous media of moderate polarity. Since 1964, a number of cationic or neutral complexes containing N-donor ligands have been isolated utilizing non-aqueous solvent media. Calorimetric measurement of the enthalpies of complexation of several N-donors (see p. 218) with the lanthanide ions in acetonitrile provides quantitative evidence for considerable thermodynamic stability of lanthanide complexes based solely upon nitrogen coordination. The fact that complexes derived from N-donors have coordination numbers of eight or nine is perhaps indicative of a stronger Ln^{3+}–N interaction than previously assumed.

It is now well established that coordination numbers greater than six are favored in lanthanide systems[3]. The variation in coordination number (six to twelve) observed in lanthanide complexes may be attributed to steric factors and electrostatic forces of attraction and repulsion, rather than bond orientation by the well-shielded 4*f* orbitals of the metal ion. Thus the relatively large size of the lanthanide ions (La^{3+} = 1.061 Å, Lu^{3+} = 0.848 Å) generally allow accommodation of more than six donor atoms in the coordination sphere.

This review is concerned with lanthanide complexes derived from neutral nitrogen donors, with primary emphasis upon the characterization of these species with respect to coordination number (usually greater than six), bonding, molecular geometry, and thermodynamic and kinetic stability. Sections of the review are devoted to an extensive discussion of the fluorescence, NMR, infrared and thermodynamic data utilized in the characterization of these species.

B. SYNTHESIS OF COMPLEX SPECIES

(i) Complexes derived from weakly basic N-donors

The isolation of the first lanthanide complexes derived from the weakly basic nitrogen donors 1,10-phenanthroline and 2,2'-dipyridyl was reported[7-9] in 1963. Complexes derived from these ligands and other related species are summarized in Table 1. These species are most commonly obtained by treating warm ethanolic solutions of a hydrated lanthanide salt with excess ligand.

The number of neutral ligands coordinated to the lanthanide ion depends primarily upon the coordinating ability of the anion present. When the anion is a strongly chelating 1,3-diketonate or acetate, only mono-substituted complexes are obtained, indicating the inability of the weakly basic amine to displace a strongly coordinated anion from the coordination from the coordination sphere. However, addition of a bidentate phenanthroline or dipyridyl group to the tris-diketone complexes demonstrates expansion of the lanthanide coordination sphere, indicative of significant Ln^{3+}—N interaction. That dipyridyl and phenanthroline enter the coordination sphere of the $Ln(thd)_3$ chelates (thd = 2,2,6,6-tetramethyl-3,5-heptane-3,5-dione)[121] perhaps best exemplifies the ability of lanthanide ions to form high-coordinate complexes, in view of the bulky nature of the diketonate ligand. Proof of Ln—N bonding is found in the crystal structure[47] of $[Eu(acac)_3\,phen]$ (see p. 201), in which the Ln^{3+} ion is eight-coordinate, with a slightly distorted square antiprismatic arrangement of O- and N-donor atoms.

Kertes and Kassierer have determined the stepwise enthalpy, entropy and free energy changes for the addition of dipyridyl to several $Ln(TTA)_3\,2H_2O$ chelates (TTA = thenoyltrifluoroacetone) in chloroform solution by direct titration calorimetry[122]. The shapes of the thermograms suggest that two complexes, $Ln(TTA)_3\,(dipy)_n$ ($n = 1, 2$), coexist in equilibrium. Since the enthalpy change associated with the complexation reaction is a measure of the difference between the metal—dipyridyl and metal—water bond energies, the large, exothermic enthalpy changes observed (12.47—29.14 kcal.mole^{-1}) provide quantitative proof of a significant Ln^{3+}—N interaction in these species.

Bis-phenanthroline and dipyridyl complexes are obtained when the anion is chloride, nitrate or salicylate (Hsal)[7-20,28-30]. Excess ligand does not yield the tris species. In each of these species, a coordination number greater than six is achieved by bonding to the anions and solvent molecules. Ten-coordination in the species $[La(dipy)_2\,(NO_3)_3]$ has been

TABLE 1
Complexes with weakly basic amines

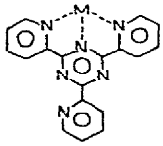
Formula	Designations	Ref.
$Ln(phen)_2X_3 \cdot (H_2O \text{ or } C_2H_5OH)_n$	$X = Cl, NO_3, SCN, SeCN; n = 0-5$	7–20
$Ln(dipy)_2X_3 (H_2O \text{ or } CH_3OH)_n$	$X = Cl, NO_3, SCN, SeCN; n = 0-2$	9, 13–15, 20–25
$Ln(dipy)_3X_3$	X = SCN, SeCN	(13–15), 21
$Ln(phen)_3X_3$	X = SCN, SeCN	13–15, 18
$Ln(phen)_4(ClO_4)_3$		26
$[Ln(phen)_3(ClO_4)_2] ClO_4$		27
$[Ln(phen)_2X_2] X$	X = salicylate, benzoate, *p*-hydroxybenzoate	28–30
$Ln(dimp)_2Cl_3(H_2O)_2$		25
$Ln(terpy) X_3 (H_2O)_n$	$X = Cl, Br, NO_3; n = 0-3$	31–35
$Ln(terpy)_2X_3$	$X = Cl, Br, ClO_4$	36, 37
$Ln(terpy)_3(ClO_4)_3$		36
$Ln(diket)_3phen$		31, 38–40, 121
$Ln(diket)_3dipy$		31, 38, 121
$Ln(diket)_3terpy$		31
$Ln(diket)_3B_2$	B = pyridine, picoline, quinoline	41, 42
$[Ln(TPT)(NO_3)_3H_2O]$		43
$[Ln(TPT)_2(ClO_4)_2] ClO_4$		43
$[Ln(TPT)_3] (ClO_4)_3$		43
$Ln(TPT)Cl_3 \cdot (H_2O)_n$	$n = 3-5$	44
$LnL_2(NO_3)_3$	L = 4,4'-dibutyl-2,2'-bipyridine, 5,5'-dibutyl-2,2'-bipyridine	45
$LnL_2(NO_3)_3 \cdot (H_2O)_n$	L = 4,4'-dipyridyl; $n = 2-6$	46
LnPcX	X = Cl, formate	123, 124
$LnPc_2H$		125, 126, 128

verified[48] by a crystal structure determination (see p. 201). Although the weakly basic N-donors do not displace the NO_3^- and Cl^- anions from the coordination sphere, *two* phenanthroline and dipyridyl ligands are accommodated in the coordination sphere owing to the small steric requirements of the anions. Only one terpyridyl group is accommodated in the coordination sphere of the nitrate salts, perhaps indicative of the greater steric requirements of this tridentate ligand, although bis-terpyridyl chelates are obtained with chloride and bromide salts. Infrared and fluorescence data indicate displacement of an anion from the coordination sphere of the salicylate chelates, resulting in formation of an eight-coordinate species $[LnL_2(Hsal)_2]$ Hsal.

Tris-phenanthroline and dipyridyl complexes are obtained when the anion is thiocyanate or selenocyanate[13–15, 18–21]. The infrared spectra of the $LnL_3(SeCN)_3$ species indicate coordinated selenocyanate groups (through N) only, suggesting formulation of a nine-coordinate species[13]. The analogous $LnL_3(NCS)_3$ species are likely to be nine-coordinate also, although the infrared data do not prove conclusively the coordination of the thiocyanate group[18,21].

Maximum coordination by the neutral donor is obtained when the anion is the weakly coordinating perchlorate. Thus both the eight-coordinate[26] $Ln(phen)_4(ClO_4)_3$ and nine-coordinate[36] $Ln(terpy)_3(ClO_4)_3$ species have been isolated. The crystal structure of the tris-terpyridyl complex (see p. 201) verifies the formation of nine metal–nitrogen bonds[49].

Infrared data indicate that all the nitrate groups are coordinated[43] in the 2,4,6-tri-α-pyridyl-1,3,5-triazine (TPT) chelates, $[Ln(TPT)(NO_3)_3H_2O]$. The proposed coordination sites of the ligand in these species are



Inclusion of water in the coordination sphere gives a seven-coordinate complex. However, with perchlorate salts, the nine-coordinate $[Ln(TPT)_3]$ $ClO_4)_3$ species are obtained[43].

Mono-phthalocyanine complexes, LnPcX, have been obtained[123,124] by the direct reaction of lanthanide chlorides and formates with o-phthalonitrile at 250–300°C. Kirin et al.[125,126] prepared species formulated as $[LnPc]^+[Ln(Pc)_2]^-$ by reacting lanthanide acetates with o-phthalonitrile at 280°C. The existence of both a cationic and an anionic complex species was verified by electrophoresis experiments in dimethylformamide[125]. The mono and bis complexes were separated on a column of Al_2O_3 and isolated as the LnPcCl and $Ln(Pc)_2H$ species, respectively. A ferrocene-type structure has been proposed for the bis complex, based upon the results of spectroscopic studies[127,128].

(ii) Complexes derived from strongly basic N-donors

Solid adducts of anhydrous lanthanide chlorides with ammonia and several monodentate amines have been prepared[50–52]. These species are generally obtained by reacting the gaseous amine directly with the anhydrous salt. The stoichiometries of the adducts, e.g. $LnCl_3 \cdot (NH_3)_n$ ($n = 1–8$), $LnCl_3 \cdot (CH_3NH_2)_n$ ($n = 1–5$), were established by absorption techniques on a vacuum line. However, the coordination number in these solid adducts is not known with certainty, and neither has the existence of these species as thermodynamically stable complexes in solution yet been established.

TABLE 2
Complexes with strongly basic amines

Formula[a]	Designations	Ref.
$[Ln(en)_4NO_3](NO_3)_2$	Ln = La–Sm (≠ Ce, Pr)	53, 54
$[Ln(en)_4](NO_3)_3$	Ln = Eu–Yb (≠ Tm)	53
$[Ln(en)_3(NO_3)_2]NO_3$	Ln = Gd–Ho	53
$[Ln(en)_4Cl]Cl_2$	Ln = La, Nd	53, 60
$[Ln(en)_4]Cl_3$	Ln = Sm–Lu	53, 60
$[Ln(en)_3Cl_2]Cl$	Ln = Gd, Er	53, 60
$[Ln(en)_4Br]Br_2$	Ln = La	53
$[Ln(en)_4]Br_3$	Ln = Nd, Gd	53
$[Ln(en)_3Br_2]Br$	Ln = Gd	53
$[Ln(en)_4](ClO_4)_3$	Ln = La, Pr, Nd	53
$[Ln(pn)_4NO_3](NO_3)_2$	Ln = La, Nd	57
$[Ln(pn)_4](NO_3)_3$	Ln = Gd, Er	57
$[Ln(pn)_3(NO_3)_2]NO_3$	Ln = La, Nd, Gd, Er	57
$[Ln(pn)_4](ClO_4)_3$	Ln = La, Nd, Gd	57
$Ln(pn)_4Cl_3$	Ln = La, Nd	57
$[Ln(dien)_3](NO_3)_3$	Ln = La, Pr, Nd, Sm, Gd	55
$[Ln(dien)_2(NO_3)_2]NO_3$	Ln = La, Pr, Nd, Sm, Gd, Dy, Er, Yb	55
$[Ln(tren)_2NO_3](NO_3)_2$	Ln = La, Pr, Nd	56
$[Ln(tren)_2](NO_3)_3$	Ln = Sm, Eu, Gd, Dy, Er, Yb	56
$[Ln(tren)(NO_3)_3]$	Ln = La, Pr, Nd, Sm, Gd, Dy, Er, Yb	56
$[Ln(tren)_2](ClO_4)_3$	Ln = La, Pr, Nd, Gd, Er	58
$[Ln(trien)_2](NO_3)_3$	Ln = Pr, Nd, Eu	59
$[Ln(trien)_2](ClO_4)_3$	Ln = La, Pr, Nd, Sm, Gd, Tb, Ho	59

[a] Coordination sphere dictated by infrared and conductivity data.

Complexes derived from several polydentate amines are listed in Table 2. All of these species have been obtained by the reaction of the anhydrous lanthanide salt with the ligand in acetonitrile. These compounds are obtained as crystalline powders and possess considerable thermal stability, but limited hydrolytic stability; they are rapidly hydrolyzed upon exposure to the atmosphere.

In contrast to the behavior observed with weakly basic nitrogen donors, high-coordinate complexes containing only nitrogen atoms in the coordination sphere may be obtained with strongly basic donors, even in the presence of strongly coordinating anions such as nitrate and chloride. Calorimetric measurements (see p. 218) of the enthalpies of ligation established the thermodynamic stability of these complexes in solution[55,56,61].

C. MOLECULAR STRUCTURES

Several papers concerning possible geometries of coordination polyhedra in high-coordinate complexes have appeared recently[62–67]. Lanthanide complexes serve as ideal models in providing information on preferred ground state geometries, since the observed geometry of the complex is that which minimizes Coulombic repulsions within the constraints imposed by the ligands.

Al-Karaghauli and Wood determined the crystal and molecular structure of the bis-bipyridyl complex, $La(bipy)_2(NO_3)_3$ (Fig. 1)[48,129]. All three nitrate ligands are bidentate, resulting in a ten-coordinate complex. The coordination polyhedron (C_2 symmetry) is derived from one of the possible models described for decacoordination, the bicapped dodecaheron with D_2 symmetry. The three metal–oxygen bond lengths are equal, averaging 2.605 Å, while the two metal–nitrogen bond lengths are 2.665 Å (N_1) and 2.648 Å (N_2). Distortion from the idealized bicapped dodecahedron may be attributed to the constraints imposed by the chelating ligands.

The crystal and molecular structure of tris-(2.2′, 6′, 2″-terpyridyl)europium(III) perchlorate (Fig. 2) showed that the metal ion was nine-coordinate with overall C_2 symmetry[49]. The coordination polyhedron most closely resembles an idealized *s*-tricapped trigonal prism (D_3 symmetry), with slight distortions from D_3 symmetry being caused by non-planarity of the ligands. The most important contribution to the distortions is thought to be intra-ligand lone pair interactions. Thus a rotation as well as slight bending of both terminal pyridine rings about the inter-ring C–C bonds is observed, moving the nitrogen lone pairs as far apart as possible. The Eu^{3+}–N bond lengths lie in the range 2.57–2.62Å.

The crystal and molecular structure of tris(acetylacetonato)- (1,10-phenanthroline)euro-

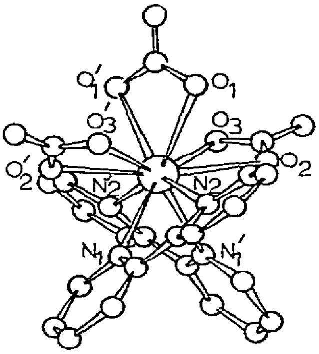


Fig. 1. Molecular structure of $La(bipy)_2(NO_3)_3$. Reprinted with permission of the authors and The American Chemical Society from A.R. Al-Karaghauli and J.S. Wood, *J. Amer. Chem. Soc.*, 90 (1968) 6548.

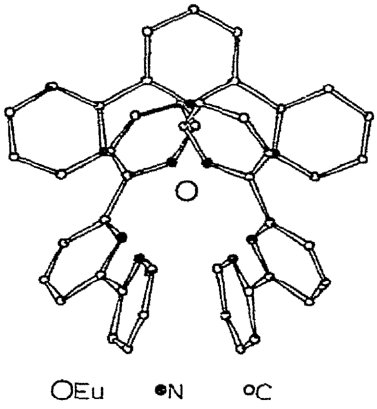


Fig. 2. Molecular structure of $Eu(terpy)_3(ClO_4)_3$. Reprinted with permission of the authors and The Chemical Society from G.H. Frost, F.A. Hart, C. Heath and M.B. Hursthouse, *Chem. Commun*, (1969) 1421.

pium(III) indicates the metal ion is coordinated to eight ligand atoms which forms a distorted square antiprism[47]. The Eu—O bond distances average 2.397 Å and the two Eu-N bond distances average 2.643 Å. The symmetry around the europium ion is approximately C_s with the ligands spanning the square (s) edges of the polyhedron.

The structure of tris(2, 2, 6, 6-tetramethyl-heptane-3,5-dionato)-bis(4-picoline) holmium(III), $Ho(thd)_3(4\text{-}pic)_2$, contains an eight-coordinate metal ion with a coordination polyhedron closely resembling a square antiprism[68]. The picoline ligands are situated at apices of opposite square faces as far removed as possible. The crystal symmetry is C_2, with one chelate ring spanning a lateral (l) edge and the other two spanning s edges. The Ho—O bond distance averages 2.27 Å with an Ho—N bond distance of 2.53 Å.

D. ELECTRONIC FLUORESCENCE SPECTRA

Weissman[69] first observed that direct excitation of the organic moiety in certain lanthanide complexes resulted in fluorescence characteristic of the intra-4f transition of the metal ion. A later discovery that such systems have potential laser activity[70–78] prompted an extensive investigation of the fluorescence properties of these complexes. Fluorescence spectra provide valuable information relating to coordination numbers, nature of bonding and symmetry in lanthanide complexes.

Although several mechanisms for metal—ion fluorescence in lanthanide complexes have been reported[79–84], that of Whan and Crosby[72] (Fig. 3) appears most reasonable, based upon interpretation of several studies. Direct excitation of the ligand moiety ($S \rightarrow S_0$) is followed by a non-radiative intersystem crossing, forming a ligand triplet (T_1, T_2). The ligand triplet may phosphoresce ($T_1 \rightarrow S_0$) or lose energy by a non-radiative transfer to the lanthanide ion. When the latter process occurs, the excited lanthanide ion can lose its energy by either a radiative (fluorescence) process or a series of non-radiative processes as depicted in Fig. 3.

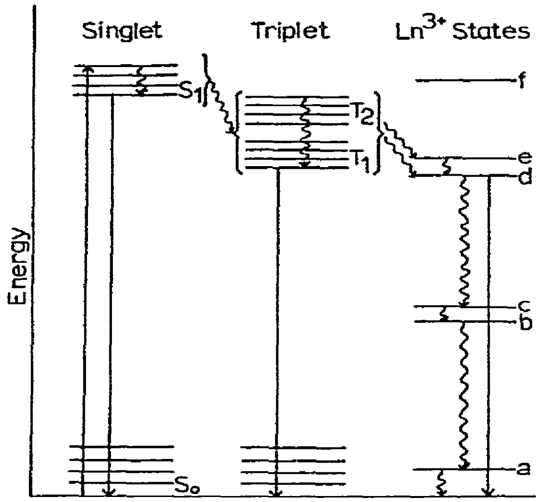


Fig. 3. Schematic energy-level diagram showing paths for loss of energy from a ligand excited state. Radiative transitions →; non-radiative transitions ⇝. Reprinted with permission of the authors and Academic Press, Inc., New York, from R.E. Whan and G.A. Crosby, *J. Mol. Spectrosc.*, 8 (1962) 315.

Consistent with this mechanism, Whan and Crosby have classified complexes of the lanthanide ions into three categories[72] based upon their fluorescence properties. The first category includes complexes of La^{III}, Gd^{III} and Lu^{III}, which exhibit no metal-ion fluorescence. Intra-4*f* transitions are not possible for the La^{III} (f^0) and Lu^{III} (f^{14}) ions. The lowest-lying excited state of Gd^{III} (32,000 cm^{-1}) lies above the triplet energy levels of the ligands investigated, precluding energy transfer from ligand to metal and subsequent metal-ion fluorescence. The second category includes complexes of Sm^{III}, Eu^{III}, Tb^{III} and Dy^{III}, which exhibit strong metal-ion fluorescence. Each of these ions has an excited state which lies close in energy to the triplet energy level of the ligands studied. The third category includes complexes of Pr^{III}, Nd^{III}, Ho^{III}, Er^{III}, Tm^{III} and Yb^{III}, which exhibit weak metal-ion fluorescence. Each of these metal ions possesses several closely spaced energy levels, thus increasing the probability of a non-radiative transition as a consequence of the need to dissipate a smaller amount of energy.

The line-like emission spectra of trivalent lanthanide ions result from intra-4*f* transitions of predominantly electric dipole character, although magnetic dipole radiation is often jointly responsible for the line intensity. For a free ion, electric dipole transitions between states of the same $4f^n$ configuration are strictly forbidden. Thus the observed spectra must be explained in terms of interactions caused by the ligand field that mixes in higher energy states of opposite parity. This mixing can be brought about by the removal of the center of symmetry in the ion, or by vibronic coupling in the case of centrosymmetric complexes.

Since electrons in the 4*f* orbitals are well shielded from the ligand field by the intervening $5s^25p^6$ octet, the order of perturbations for a lanthanide ion is crystal field < spin—

orbit coupling < interelectronic repulsions. Utilizing the Russell–Saunders coupling scheme, the effect of the ligand field is to remove the J-degeneracy of the various $^{2S+1}L_J$ terms, thus giving rise to fine structure associated with an emission line. The extent to which the degeneracy is removed depends upon both the strength and symmetry of the ligand field.

The only restriction on ΔJ governing electric dipole transitions between different J states is $\Delta J \leqslant 6$, although, for an even number of electrons, transitions from $J =$ even to $J =$ odd states are usually weak[120]. Magnetic dipole transitions are governed by the selection rule, $\Delta J = 0, \pm 1$, except $J = 0 \rightarrow J = 0$. Ligand field mixing of J states could produce weak magnetic dipole transitions with $\Delta J \geqslant 2$. However, the $\Delta J = 0, \pm 1$ rule is generally satisfied[120].

The small splittings that characterize certain lanthanide emission lines are useful for establishing, by a group theoretical method, the local site symmetry of the metal ion in the complex. $\mathrm{Eu^{III}}$ chelates are often studied in preference to other lanthanides, since the low J values of the strongest emission lines ($^5D_J \rightarrow {}^7F_{J'}, J = 0, 1; J' = 0, 1, 2$) give rise to a smaller number of closely spaced energy levels than is observed with most other lanthanide ions. Transitions from the $^5D_0$ state are particularly useful for interpretations of site symmetry, since the emitting state ($J = 0$) cannot be split by the ligand field. Thus transitions from $^5D_0$ to the various F_J states are generally well separated, and transitions to a particular J manifold are often well resolved. The number of electric dipole allowed ($\Delta J \leqslant 6$) and magnetic dipole allowed ($\Delta J = 0, \pm 1$) transitions in commonly encountered non-centrosymmetric symmetries for the $^5D_0 \rightarrow {}^7F_{J'}$ ($J' = 0$–4) transitions of $\mathrm{Eu^{III}}$, as predicted from group theory, are presented in Table 3. Transitions from $J = 0 \rightarrow J = 1$ are expected to have predominantly magnetic dipole character.

Hart and co-workers have interpreted the fluorescence spectrum of $\mathrm{Eu(terpy)_3(ClO_4)_3}$ (Fig. 4, Table 4) in terms of slightly distorted D_3 symmetry about the metal ion[36]. This interpretation is in agreement with the molecular structure of the complex, as subsequently determined by X-ray crystallography[49] (see p. 201). The rather small splitting observed (4 Å) for the E component of the $^5D_0 \rightarrow {}^7F_1$ transition indicates a comparatively small distortion from D_3 symmetry, since the usual magnitude of crystal-field splitting of an individual component is 40 Å in this spectral region. Thus the small splitting is reasonably assigned to a second-order effect arising from the non-coplanarity of the three pyridine rings.

Butter et al. have interpreted the fluorescence spectrum of $\mathrm{Eu(phen)_2(NO_3)_3}$ in terms of a D_2 site symmetry for the metal ion[85]. This assignment appears quite reasonable, based upon the D_2 symmetry observed in the crystal structure of the analogous dipyridyl chelate[48], $\mathrm{La(dipy)_2(NO_3)_3}$.

Strong fluorescence has been observed[23,32,34,35] for the dipyridyl, phenanthroline, and terpyridyl chelates of $\mathrm{Eu^{III}}$, $\mathrm{Tb^{III}}$, $\mathrm{Dy^{III}}$ and $\mathrm{Sm^{III}}$. Based upon the observation that little increase in fluorescence intensity occurs upon lowering the temperature from 300°K to 78°K, Sinha et al. concluded that non-radiative relaxation of the excited metal ion through vibrational effects is not the main factor in determining fluorescence yields in complexes derived from N-heterocycles. They attribute the quantum yields to a "bottleneck" in the energy transfer from the aromatic ligand to the $4f$ levels of the metal ion[86].

TABLE 3

Splitting of ^7F_J levels and activity[a] of $^5D_0 \rightarrow {}^7F_J$ transitions[b] of Eu$^{\text{III}}$ in non-centrosymmetric ligand fields

Symmetry	$J=0$			$J=1$			$J=2$			$J=3$			$J=4$		
	Γ^c	ED	MD	Γ	ED	MD	Γ	ED	MD	Γ	ED	MD	Γ	ED	MD
O	A_1	−	−	T_1	+	+	E	−	−	A_2	−	−	A_1	−	−
							T_2	−	−	T_1	+	+	E	−	−
										T_2	−	−	T_1	+	+
													T_2	−	−
T_d	A_1	−	−	T_1	−	+	E	−	−	A_2	−	−	A_1	−	−
							T_2	+	−	T_1	−	+	E	−	−
										T_2	+	−	T_1	−	+
													T_2	+	−
D_4	A_1	−	−	A_2	+	+	A_1	−	−	A_2	+	+	$2A_1$	−	−
				E	+	+	B_1	−	−	B_1	−	−	A_2	+	+
							B_2	−	−	B_2	−	−	B_1	−	−
							E	+	+	$2E$	+	+	B_2	−	−
													$2E$	+	+
D_3	A_1	−	−	A_2	+	+	A_1	−	−	A_1	−	−	$2A_1$	−	−
				E	+	+	$2E$	+	+	$2A_2$	+	+	A_2	+	+
										$2E$	+	+	$3E$	+	+
D_{3h}	A'_1	−	−	A'_2	−	+	A'_1	−	−	A'_2	−	+	A'_1	−	−
				E'	−	+	A'_2	−	+	E'	+	−	$2E'$	+	−
							E'	+	−	A''_1	−	−	A''_1	−	−
							E''	−	+	A''_2	+	−	A''_2	+	−
										E''	−	+	E''	−	+
D_{2d}	A_1	−	−	A_2	−	+	A_1	−	−	A_2	−	+	$2A_1$	−	−
				E	+	+	B_1	−	−	B_1	−	−	A_2	−	+
							B_2	+	−	B_2	+	−	B_1	−	−
							E	+	+	$2E$	+	+	B_2	+	−
													$2E$	+	+

TABLE 3 (continued)

Splitting of ${}^7F_J$ levels and activity[a] of ${}^5D_0 \rightarrow {}^7F_J$ transitions[b] of $\mathrm{Eu^{III}}$ in non-centrosymmetric ligand fields

Symmetry	$J=0$			$J=1$			$J=2$			$J=3$			$J=4$		
	Γ^c	ED	MD	Γ	ED	MD	Γ	ED	MD	Γ	ED	MD	Γ	ED	MD
D_2	A	−	−	B_1	+	+	$2A$	−	−	A	−	−	$3A$	−	−
				B_2	+	+	B_1	+	+	$2B_1$	+	+	$2B_1$	+	+
				B_3	+	+	B_2	+	+	$2B_2$	+	+	$2B_2$	+	+
							B_3	+	+	$2B_3$	+	+	$2B_3$	+	+
C_{4v}	A_1	+	−	A_2	−	+	A_1	+	−	A_2	−	+	$2A_1$	+	−
				E	+	+	B_1	−	−	B_1	−	−	A_2	−	+
							B_2	−	−	B_2	−	−	B_1	−	−
							E	+	+	$2E$	+	+	B_2	−	−
													$2E$	+	−
C_{3v}	A_1	+	−	A_2	−	+	A_1	+	−	A_1	+	−	$2A_1$	+	−
				E	+	+	$2E$	+	+	$2A_2$	−	+	A_2	−	+
										$2E$	+	+	$3E$	+	+
C_{3h}	A'_1	−	+	A'	−	+	A'	−	+	A'	−	+	A'	−	+
				E''	−	+	E'	+	−	E'	+	−	$2E'$	+	−
							E''	−	+	$2A''_2$	+	−	$2A''$	+	−
										E''	−	+	E''	−	+
C_{2v}	A_1	+	−	A_2	−	+	$2A_1$	+	−	A_1	+	−	$3A_1$	+	−
				B_1	+	+	A_2	−	+	$2A_2$	−	+	$2A_2$	−	+
				B_2	+	+	B_1	+	+	$2B_1$	+	+	$2B_1$	+	+
							B_2	+	+	$2B_2$	+	+	$2B_2$	+	+
C_4	A	+	+	A	+	+	A	+	+	A	+	+	$3A$	+	+
				E	+	+	$2B$	−	−	$2B$	−	−	$2B$	−	−
							E	+	+	$2E$	+	+	$2E$	+	+
C_3	A	+	+	A	+	+	A	+	+	$3A$	+	+	$3A$	+	+
				E	+	+	$2E$	+	+	$2E$	+	+	$3E$	+	+
C_2	A	+	+	A	+	+	$3A$	+	+	$3A$	+	+	$5A$	+	+
				$2B$	+	+	$2B$	+	+	$4B$	+	+	$4B$	+	+

TABLE 3 (continued)

Splitting of ^7F_J levels and activity of $^5D_0 \rightarrow {}^7F_J$ transitions[b] of Eu$^{\text{III}}$ in non-centrosymmetric ligand fields

Symmetry	$J=0$			$J=1$			$J=2$			$J=3$			$J=4$		
	Γ[c]	ED	MD	Γ	ED	MD	Γ	ED	MD	Γ	ED	MD	Γ	ED	MD
C_s	A'	+	+	A'	+	+	$3A'$	+	+	$3A'$	+	+	$5A'$	+	+
				$2A''$	+	+	$2A''$	+	+	$2A''$	+	+	$4A''$	+	+

[a] Strong magnetic dipole transition expected only for $^5D_0 \rightarrow {}^7F_1$ transition. The $^5D_0 \rightarrow {}^7F_J$ (J = odd) transition is usually weak for electric dipole.

[b] $^5D_0 \rightarrow {}^7F_0 \sim 5800$ Å, $^5D_0 \rightarrow {}^7F_1 \sim 5900$–$5960$ Å, $^5D_0 \rightarrow {}^7F_2 \sim 6100$–$6200$ Å, $^5D_0 \rightarrow {}^7F_2 \sim 6500$ Å, $^5D_0 \rightarrow {}^7F_4 \sim 6870$–$7030$ Å.

[c] Abbreviations and symbols: Γ, irreducible representation; ED, electric dipole allowed transition; MD, magnetic dipole allowed transition.

The efficiency of energy transfer is expected to depend upon the metal–nitrogen bond length as well as the degree of covalency in the metal–ligand bond. Thus Sinha[25] observed an overall enhancement of fluorescence intensity in the europium complex, Eu(dimp)$_2$Cl$_3$, derived from the methyl-substituted dipyridyl chelate, 4,4′-dimethyl-2,2′-dipyridyl (dimp). This observation is accounted for in terms of a more efficient energy transfer, resulting from a decrease in the metal–nitrogen bond length due to increased electron density at the donor sites of the methyl-substituted ligand. Analogous effects have been observed by

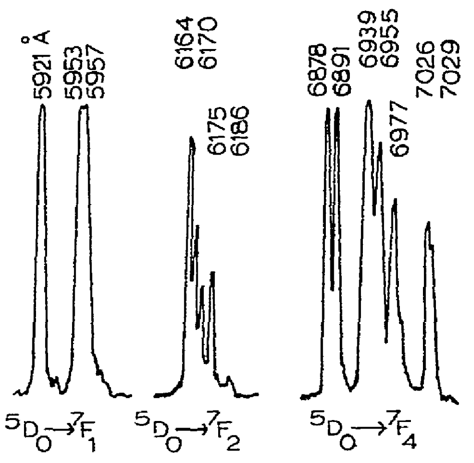


Fig. 4. Fluorescence spectrum of Eu(terpy)$_3$(ClO$_4$)$_3$. Reprinted with permission of the authors and Pergamon Publishing Co., Oxford, from D.A. Durham, G.H. Frost and F.A. Hart, *J. Inorg. Nucl. Chem.*, 31 (1969) 833.

TABLE 4
Assignment of transitions in Eu(terpy)$_3$(ClO$_4$)$_3$ based upon D_3 symmetry

$^5D_0$	Ligand field split components in D_3	Transitions allowed to:	Assignments (A)
$^7F_4$	$2A_1 + A_2 + 3E$	$A_2 + 3E$	7029, 7026 (E) 6977 (A_2) 6955, 6939 (E) 6891, 6878 (E)
$^7F_3$	$A_1 + 2A_2 + 2E$	$2A_2 + 2E$	Transition very weak; singlet only at 6499
$^7F_2$	$A_1 + 2E$	$2E$	6186, 6175 (E) 6170, 6164 (E)
$^2F_1$	$A_2 + E$	$A_2 + E$	5921 (A_2) 5957, 5953 (E)
$^7F_0$	A_1	None	Transition absent

Filipescu et al.[87] in the substitution of electron-donating groups on the aromatic rings of the dibenzoylmethide group in Eu(dbm)$_3{}^{3+}$, and the opposite effect (decrease in fluorescence intensity) upon substitution of electron-withdrawing groups.

Sinha and Butter[30] interpreted the fluorescence spectra of the bis-phenanthroline-tris-carboxylate europium(III) complexes (Eu(phen)$_2$(sal)$_3$, Eu(phen)$_2$ benz; sal = salicylate, benz = benzoate) in terms of eight-coordinate species, with metal-ion site symmetries D_2 and C_{2v} respectively.

E. INFRARED STUDIES

Infrared data have proved quite useful for distinguishing between coordinated and non-coordinated ligands through group theoretical interpretations based upon symmetry changes occurring upon coordination of a ligand. Thus assignments of the nitrate ion absorptions, based upon the two possible symmetry types, D_{3h} (free nitrate) and C_{2v} (coordinated nitrate) help define the coordination sphere of several complexes listed in Tables 1 and 2. The D_{3h} nitrate group has three infrared allowed transitions (A_2'', 831 cm^{-1}; E', 1390 cm^{-1}; E', 790 cm^{-1}) and an additional transition (A_1', 1050 cm^{-1}) observed only in Raman spectra. Coordination of a nitrate group to a metal ion lowers its site symmetry to C_{2v}, resulting in six infrared active bands (A_1, 1030 cm^{-1}; B_2, 810 cm^{-1}; B_1, 1480–1530 cm^{-1}; A_1, 1290 cm^{-1}; A_1, 740 cm^{-1}; B_1, 713 cm^{-1}). A distinction between bidentate and monodentate nitrate coordination cannot be made on the basis of infrared data alone, since the nitrate group has C_{2v} symmetry in both instances.

The infrared spectra of the bis-dipyridyl[88] and phenanthroline[89] complexes,

$[LnL_2(NO_3)_3]$, have been interpreted in terms of all nitrate groups being coordinated. This interpretation has been verified by a crystal structure determination (see p. 201) in the case of the dipyridyl chelates. Thus it is likely that the analogous phenanthroline complexes are also ten-coordinate, because of the similar steric requirements of the phenanthroline and dipyridyl molecules.

Infrared studies of complexes derived from the strongly basic N-donors ethylenediamine, 1,2-propanediamine, diethylenetriamine and β,β',β''-triaminotriethylamine clearly establish that the amine is capable of replacing the nitrate group in the coordination sphere[53,55–57]. Thus the species formulated as $[Ln(en)_3(NO_3)_2]NO_3$, $[Ln(pn)_3(NO_3)_2]NO_3$ and $[Ln(dien)_2(NO_3)_2]NO_3$ exhibit absorptions corresponding to both D_{3h} and C_{2v} nitrate groups. In addition, the mono-tren chelate, $[Ln(tren)(NO_3)_3]$ gives peaks corresponding only to coordinated nitrate groups. However, the spectra of the species formulated as $[Ln(en)_4](NO_3)_3$ (Ln = Eu–Yb), $[Ln(pn)_4](NO_3)_3$ (Ln = Eu–Yb), $[Ln(dien)_3](NO_3)_3$ and $[Ln(tren)_2](NO_3)_3$ (Ln = Sm–Yb) give bands corresponding only to free nitrate groups, indicating displacement of this anion from the coordination sphere upon coordination of an additional molecule of amine.

The spectra of the tetrakis-ethylenediamine and bis-β,β',β''-triaminotriethylamine (tren) chelates of the larger lanthanide ions show absorptions corresponding to both C_{2v} and D_{3h} nitrate groups[53,56]. The rather low frequency (1428 cm^{-1} and 1420 cm^{-1} respectively) of the B_1 mode indicates a small distortion from D_{3h} symmetry and weak coordination. Steric considerations favor formulations with one coordinated nitrate group, i.e. $[Ln(en)_4NO_3](NO_3)_2$ and $[Ln(tren)_2NO_3](NO_3)_2$. In each series of complexes, the decreasing ionic radius of the metal ion across the lanthanide series results in displacement of the coordinated nitrate group. However, nitrate displacement does not occur at the same metal ion in each system. In the series of ethylenediamine chelates, displacement occurs between samarium and europium, whereas in the series of tren chelates, displacement occurs before samarium. This may be attributed to greater steric crowding in the bis-tren chelates, created by the accommodation of two additional ethylene groups in the coordination sphere. No evidence was observed for nitrate coordination in the more sterically hindered nine-coordinate tris-diethylenetriamine chelates[55].

The effect of coordination upon the N–H stretching frequencies of an amino group is observed by comparing data for free ethylenediamine and complexed ligand, as in $Ln(en)_4(ClO_4)_3$, in acetonitrile[53]. On this basis, a decrease of 40 cm^{-1} in the N–H stretching frequency is observed upon coordination, a much smaller shift than is typically found for amine complexes of d-type transition metals[90] (100–150 cm^{-1}). The corresponding modes for the nitrate, chloride and bromide salts (Fig. 5) are displaced additionally to lower frequencies in the order $\nu_{ClO_4^-} > \nu_{NO_3^-} > \nu_{Cl^-} > \nu_{Br^-}$, which is the order expected in terms of a decrease due to hydrogen bonding between the anion and NH_2 protons[91].

Changes in the nitrate regions of absorption corresponding to nitrate coordination are accompanied by alterations in the N–H stretching region (Fig. 5). In general, a larger number of bands is observed upon nitrate coordination, as clearly demonstrated in the mono-

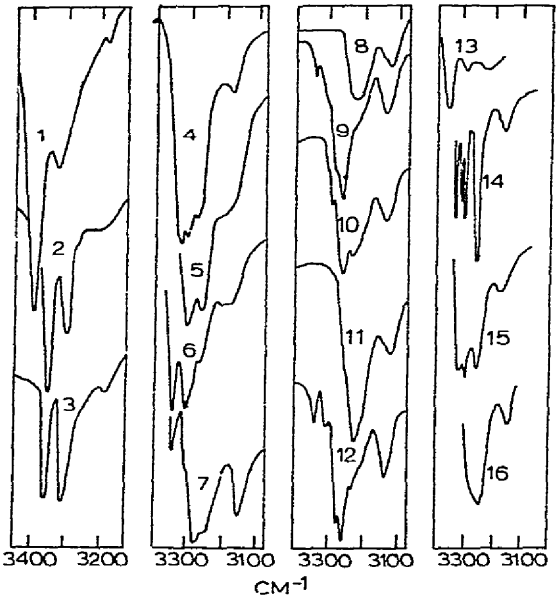


Fig. 5. Infrared spectra of Ln(en)$_n$X$_3$ and Ln(tren)$_n$X$_3$ species in the NH stretching region: 1, free en (soln.); 2, Nd(en)$_4$(ClO$_4$)$_3$; 3, Nd(en)$_4$(ClO$_4$)$_3$ (soln.); 4, [Ln(en)$_4$NO$_3$] (NO$_3$)$_2$: 5, [Ln(en)$_4$] (NO$_3$)$_3$; 6, [Ln(en)$_3$(NO$_3$)$_2$] NO$_3$; 7, [Ln(en)$_4$Cl] Cl$_2$; 8, [Ln(en)$_4$] Cl$_3$; 9, [Ln(en)$_3$Cl$_2$] Cl; 10, [La(en)$_4$Br]-Br$_2$; 11, [Ln(en)$_4$] Br$_3$; 12, [Ln(en)$_3$Br$_2$] Br; 13, free tren; 14, [Ln(tren) (NO$_3$)$_3$]; 15, [Ln(tren)$_2$NO$_3$]-(NO$_3$)$_2$; 16, [Ln(tren)$_2$] (NO$_3$)$_3$. Reprinted with permission of The American Chemical Society from J.H. Forsberg and T. Moeller, *Inorg. Chem.*, 8 (1969) 883 and J.H. Forsberg, T.M. Kubik, T. Moeller and K. Gucwa, *Inorg. Chem.*, 10 (1971) 2656.

tren chelate, in which five bands are resolved, compared with the bis chelates, in which three bands are observed. The large number of NH$_2$ bands observed upon anion coordination may be attributed to non-equivalent sets of amino groups. The increase in frequency of one set may result from repulsions between the nitrogen end of the N—H dipole and the coordinated anion[92], or poorer hydrogen bonding of the amino protons with the coordinated anions.

Similar alterations are observed in the chloride and bromide salts of the ethylenediamine chelates. By analogy with the nitrate series, these changes were attributed to entry of the anions into the coordination sphere. The ability of the anion to enter the coordination sphere decreases in the order expected based upon anion size ($NO_3^- > Cl^- > Br^-$), as the radius of the Ln^{3+} ion decreases (see Table 2).

Coordination of the perchlorate ion (T_d symmetry) lowers the site symmetry of this ion to C_{3v}, resulting in splitting of the band at 1111 cm^{-1} and intensification of a band around 927 cm^{-1}. The infrared spectra of the Ln(phen)$_3$(ClO$_4$)$_3$ chelates are interpreted in terms of both ionic and coordinated perchlorate groups[27]. However, all perchlorate groups were found to be ionic in the eight-coordinate species [Ln(en)$_4$] (ClO$_4$)$_3$ (ref. 53), [Ln(pn)$_4$] (ClO$_4$)$_3$ (ref. 57), [Ln(phen)$_4$] (ClO$_4$)$_3$ (ref. 26) and [Ln(tren)$_2$] (ClO$_4$)$_3$

(ref. 58) as well as the nine-coordinate species [Ln(terpy)$_3$] (ClO$_4$)$_3$ (ref. 36) and [Ln(TPT)$_3$] (ClO$_4$)$_3$ (ref. 43). Both ionic and coordinated groups were observed in the eight-coordinate [Ln(TPT)$_2$(ClO$_4$)$_2$] ClO$_4$ species[43].

The characteristic ring breathing mode (990 cm^{-1}) in α-substituted pyridines is shifted to higher frequency (~ 1015 cm^{-1}) upon chelation. Thus the disappearance of the free ligand band at 990 cm^{-1}, together with the appearance of a band in the 1015 cm^{-1} region, is indicative of Ln—N bond formation in the dipyridyl[23], terpyridyl[33] and 2,4,6-tri-α-pyridyl-1,3,5-triazine complexes[43]. In the last example, a small unshifted peak is present in addition to the 1015 cm^{-1} peak, suggesting that the triazine molecule is not coordinating through all potential donor sites.

The spectra of dipyridyl, terpyridyl, phenanthroline and ethylenediamine chelates have been recorded in the far infrared region. An absorption in the 200—250 cm^{-1} region is assigned to the metal—nitrogen stretching mode in the bis-dipyridyl and phenanthroline chelates[93]. A plot of the frequency of this metal—nitrogen stretch vs. e/r^2, as a measure of the polarizing power of the cation, shows a gradual increase in frequency with increasing polarizing power, with a break at Gd^{3+} and Eu^{3+} in the dipyridyl chelates and phenanthroline chelates respectively. No metal—nitrogen assignments could be made for the tripyridyl chelates, but Ln—Cl and Ln—Br stretching modes were assigned to the regions 200—260 cm^{-1} and 140—155 cm^{-1}, respectively[37].

A band in the region of 350—380 cm^{-1} was assigned to one of the possible Ln—N stretching modes in the ethylenediamine chelates[53]. This band shows a monotonic increase in frequency across the lanthanide series, indicative of stronger Ln—N bonding with decreasing metal ion radius. This band is present in all ethylenediamine complexes, and its position is nearly independent of the anion present. Although metal—nitrogen stretching modes are assigned to the 500—600 cm^{-1} region[94] for amine complexes of *d*-type transition metals, both the weaker lanthanide—nitrogen bonding and the large mass of the Ln^{3+} ion suggest that this mode should occur at a lower frequency in the lanthanide—amine complexes.

F. NUCLEAR MAGNETIC RESONANCE STUDIES

(i) Isotropic shifts

Nuclear magnetic resonance spectroscopy has proven to be a powerful investigative tool for the elucidation of structure and bonding in transition metal complexes. Prior to the discovery by Hinckley[95] that certain lanthanide complexes can be used as NMR shift reagents, relatively few NMR studies involving lanthanide complexes had been reported. The proliferation of literature[100] in this area is indicative of the considerable interest these species have attracted as shift reagents. Although several studies involving amines have been reported, the majority concern analysis of the substrate spectrum and do not include characterization of the Ln^{3+}—N interaction[96—100].

The isotropic shifts observed in the NMR spectra of paramagnetic complexes may be composed of both a Fermi contact term (through bond interaction) and a dipolar or pseudo-contact term (through space interaction). The contact shift is dependent upon the magnitude of A_N (electron–proton hyperfine coupling constant), which is related to the extent of covelency in the metal–ligand bond[101]. The dipolar shift is proportional to the product of a magnetic anisotropy factor and a geometric factor in the case of axial symmetry[102], whereas two magnetic and two geometric factors are involved for non-axial symmetry[103,104]. The dipolar shifts provide information relating to the geometrical configuration of the ligands about the metal ion.

In order to observe nuclear resonance in the presence of a paramagnetic metal ion, it is necessary that one of the conditions

$$T_1^{-1} \gg A_N \quad \text{or} \quad T_e^{-1} \gg A_N$$

be fulfilled[105], where T_1 is the electron spin relaxation time and T_e is an electron spin exchange time relating to condensed systems. The large value of T_1^{-1} for most lanthanide ions (Gd^{III} being an exception), together with the small values of A_N expected for predominantly electrostatic interactions, fulfill the first condition, allowing the observation of relatively narrow resonance lines in several lanthanide systems. The relative broadening abilities of the various lanthanides were observed to follow the order

$$\mathrm{Pr} \simeq \mathrm{Nd} \simeq \mathrm{Sm} \simeq \mathrm{Eu} < \mathrm{Yb} < \mathrm{Ho} \simeq \mathrm{Er} < \mathrm{Tm} < \mathrm{Tb} < \mathrm{Dy} < \mathrm{Gd}$$

for the methyl resonances of the 2-picoline adducts with the tris-dipivaloylmethanatolanthanide(III) chelates[100]. Although the largest isotropic shifts are generally observed in complexes of the heavier lanthanide ions, these resonances are the most severely broadened and most difficult to observe. The NMR spectra of Gd^{III} chelates are often not observed, owing to extreme line broadening by the gadolinium ion.

The simultaneous appearance of contact and dipolar interactions makes it difficult to assess the relative contribution of each to the observed isotropic shift. The well defined coordination spheres of d-type transition metal complexes in solution, together with the measured g-tensor anisotropy, provide at least a qualitative estimate of the magnitude of the dipolar shifts. However, the coordination number and geometry of a lanthanide complex in solution is dictated solely by steric factors and electrostatic forces of attraction and repulsion, rather than bond orientation by the well shielded $4f$ orbitals. As a consequence of this stereochemical non-rigidity, neither the geometry nor the coordination number of a lanthanide complex is readily predicted in solution. In addition, the g-tensor anisotropy is unknown.

Birnbaum and Moeller observed large isotropic shifts upon coordination of substituted pyridine molecules to lanthanide ions, and interpreted the shifts in terms of contact and dipolar contributions of similar magnitude but opposite sign[106]. They assumed an axially

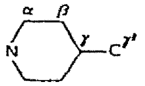
TABLE 5
Calculated pseudo-contact shifts by subtraction and by ratios of geometric factors for substituted pyridine complexes[a]

	3,5-Lutidine[b]			4-*t*-Butylpyridine[c]			4-Ethylpyridine[d]			
Type of shift	α	β	γ	α	β	γ	α	β	γ	γ′
$Nd(NO_3)_3$										
Contact shift, initial choice	−800	−189	−286	−1106	−487	−200	−1115	−492	−221	−200
δ_{comp}, calculated	+118	+32	+24	+101	0	+32	+101	0	+60	+34
Pseudo-contact shift, geometric ratio	+918	+221	+310	+1207	+487	+232	+1216	+492	+281	+234
$ND(ClO_4)_3$										
Contact shift, as for $Nd(NO_3)_3$	−800	−189	−286	−1106	−487	−200	−1115	−492	−221	−200
δ_{comp}, calculated	−148	−33	−79	−159	−118	−25	+150	−111	−18	−22
Pseudo-contact shift, subtraction	+652	+156	+207	+947	+369	+175	+965	+381	+203	+178
Pseudo-contact shift, geometric ratio	+648	+156	+218	+910	+368	+175	+925	+374	+214	+178
$Pr(NO_3)_3$										
Contact shift, above ÷ 1.18[e]	−678	−160	−242				−945	−417	−187	−170
δ_{comp}, calculated	+466	+101	+115				+448	+216	+117	+78
Pseudo-contact shift, subtraction	+1144	+261	+357				+1393	+543	+304	+248
Pseudo-contact shift, geometric ratio	+1082	+261	+366				+1290	+522	+298	+248
$Pr(ClO_4)_3$										
Contact shift, as for $Pr(NO_3)_3$	−678	−160	−242	−936	−413	−170	−945	−417	−187	−170
δ_{comp}, calculated	−255	−77	−152	−290	−203	−78	−301	−208	−85	−66
Pseudo-contact shift, subtraction	+423	+83	+90	+646	+210	+92	+644	+209	+102	+104

TABLE 5 (continued)
Calculated pseudo-contact shifts by subtraction and by ratios of geometric factors for substituted pyridine complexes[a]

	3,5-Lutidine[b]			4-*t*-Butylpyridine[c]			4-Ethylpyridine[d]			
Type of shift	α	β	γ	α	β	γ	α	β	γ	γ'
$Pr(ClO_4)_3$										
Pseudo-contact shift, geometric ratio	+345	+83	+116	+478	+193	+92	+542	+218	+125	+104

[a]



[b] Ratio of geometric factors, 4.15:1.0:1.4.
[c] Ratio of geometric factors, 5.2:2.1:1.0.
[d] Ratio of geometric factors, 3.2:2.1:1.2:1.0.
[e] In comparing the complexes of the Pr^{3+} ion with those of Nd^{3+} ion, the contact shifts were reduced by a factor of 1.18 in order to take into account the differences in average *g* value and ground state *J* value between these ions.

symmetric model and used the geometric factor $(3 \cos^2 \theta - 1)r^{-3}$ to calculate ratios of dipole shifts of the various protons on this geometrically rigid molecule (Table 5). A comparison of the calculated dipolar shift ratios with the observed shift ratios clearly indicates that the observed isotropic shift is composed of both contact and dipolar contributions. Using a method similar to that outlined by Happe and Ward[107], Birnbaum and Moeller separated the observed isotropic shift into contact and dipolar contributions. The results are presented in Table 5. Close agreement is observed between the dipolar shifts obtained by subtracting the calculated contact shift from the observed isotropic shift, and the dipolar shifts obtained using the calculated geometric factors.

The negative direction of the calculated contact shifts is consistent with a covalent interaction involving the 6*s* orbital of the lanthanide ion[109] or spin polarization of the $5s^25p^6$ octet[110].

Horrocks and Sipe[100] observed isotropic shifts of the proton resonances of 4-vinylpyridine upon coordination to the shift reagent $Ln(dpm)_3$ (dpm = dipivaloylmethane). Using a geometric factor $(3 \cos^2 \theta - 1)r^{-3}$ appropriate for axial symmetry, they found the four independent isotropic shift ratios to correlate with the ratio of the geometric factors for both upfield and downfield shifting systems. The correlation of the observed shifts with the calculated geometric factors, together with the lack of any correspondence of the observed shifts with the contact-shift pattern of 4-vinylpyridine coordinated to Ni^{II}, is indicative of the dipolar nature of these shifts.

Although the crystal structure of the analogous complex derived from 4-picoline (see p. 202) is not axially symmetric in the solid state, intramolecular rearrangements between possible structural isomers may result in an average structure in solution which approximates axiality. However, as Horrocks and Sipe point out, interpretations based upon an axially symmetric system should be accepted with certain reservations.

Hart et al. reported NMR studies involving lanthanide complexes derived from the alkyl-substituted bipyridine chelates 4,4′-di-*n*-butyl-2,2′-bipyridine and 5,5′-di-*n*-butyl-2,2′-bipyridine[111]. The isotropic shifts observed in the spectra of the paramagnetic chelates are interpreted in terms of a contribution from both contact and dipolar interactions. The attenuation of chemical shift observed along the alkyl side chain in complexes derived from both ligands was attributed to a contact mechanism. Attenuation is not expected in the case of a dipolar mechanism, since the metal-ion β-proton distance is only slightly greater than the α-proton distance (~ 7.5 Å vs. 7.2 Å), and the respective metal-ion–proton direction vectors are averaged due to rotation of the ring C_α and $C_\alpha - C_\beta$ bonds. The terminal methyl group of the 5,5′ chelates shows a larger isotropic shift than the corresponding group in the 4,4′ chelate, e.g. for Pr^{III} 53 Hz and 4 Hz, respectively. This behavior is consistent with a dipolar mechanism, since the terminal methyl group of the 5,5′ chelate approaches the metal ion more closely.

That the isotropic shift of a particular aromatic proton is nearly the same for the 4,4′ and 5,5′ chelates indicates that the two series of complexes are isostructural in solution. Although no conclusions are drawn as to the mechanism of the shifts of the aromatic proton resonances, the spectra of the diamagnetic chelates (La^{3+}, Y^{3+}, Lu^{3+}) indicate very little electron transfer between the metal ion and donor atom.

That only one set of aromatic proton resonances are observed is indicative of a rapid intramolecular exchange of chelate configuration, which averages the environment of the two non-equivalent pyridine rings. The non-equivalency of the two pyridine rings is predicted from the molecular structure observed for the analogous $Ln(dipy)_2(NO_3)_3$ species in the solid state.

Double resonance experiments establish that the two downfield resonances observed at 3.48 ppm and 7.41 ppm (referenced to TMS) in the paramagnetic complex $Nd(tren)_2^{3+}$ correspond to the two magnetically non-equivalent methylene groups[112]. The downfield position of these peaks results from isotropic shifts of 59 Hz and 452 Hz respectively. The NH_2 resonance of the coordinated ligand was not observed, presumably owing to effective relaxation by the paramagnetic ion. The fact that only two methylene resonances are observed indicates rapid intramolecular exchange and/or rapid chelate ring inversion.

A surprisingly narrow resonance line ($\Delta\nu\frac{1}{2}$ = 40 Hz) centered at 2.76 p.p.m. was observed for the paramagnetic $Gd(tren)_2^{3+}$ chelate[58]. This corresponds to an isotropic shift (referenced to the diamagnetic yttrium chelate) of only + 16 Hz. Since Gd^{III} (f^7) is an *S*-state ion, no *g*-tensor anisotropy is possible[100]. Thus no dipolar contribution to the observed chemical shift is expected. The isotropic shift observed indicates that the contact contribution to the isotropic shifts in this and other paramagnetic lanthanide–tren complexes is small. That a small contact shift is observed in this system, compared with the large contact shift reported for certain aromatic systems, may be indicative of the attenuation expected in the contact shift for a σ-bonded system.

(ii) Kinetics of ligand exchange reactions

Hart et al. have obtained kinetic data for the ligand exchange reaction

$$\mathrm{EuL_2(NO_3)_3 + L' \rightleftarrows EuLL'(NO_3)_3 + L} \tag{1}$$

in chloroform, where L = 4,4′-di-*n*-butylbipyridine, using the NMR line broadening technique in the slow exchange region[111]. The exchange was observed to be first-order, indicative of a dissociative mechanism

$$\mathrm{[EuL_2(NO_3)_3]} \xrightarrow{\text{slow}} \mathrm{[EuL(NO_3)_3]} \underset{\mathrm{L'}}{\xrightarrow{\text{fast}}} \mathrm{[EuLL'(NO_3)_3]} \tag{2}$$

The transition state parameters calculated from the temperature variation of the linewidth of a coordinated proton are $\Delta G^{\neq}(273°) = 17.6$ kcal.mole^{-1}, $\Delta H^{\neq} = 5.60$ kcal.mole^{-1} and $\Delta S^{\neq} = -40.4$ cal.deg^{-1}.mole^{-1}. The postulation of an eight-coordinate intermediate is quite reasonable, since reorganization of the coordination sphere with simultaneous exit of the ligand molecules reduces steric repulsions, stabilizing the intermediate.

Johnson and Forsberg[112] have investigated the kinetics of the ligand exchange reaction in anhydrous acetonitrile involving tren and the eight-coordinate complex $\mathrm{Nd(tren)_2^{3+}}$. Double resonance experiments establish a transfer of spin saturation (TOSS)[113] from the free ligand methylene resonances to the coordinated methylene resonance, indicative of an intermolecular exchange reaction of the type

$$\mathrm{Nd(tren)_2^{3+} + tren' \rightleftarrows Nd(tren)(tren')^{3+} + tren} \tag{3}$$

Kinetic data obtained in the slow exchange region (+40 to +80°) establish that the exchange is first-order in both complex and free ligand concentration. Thus the rate law for the bimolecular, second-order exchange is

$$\mathrm{Rate} = k[\mathrm{Nd(tren)_2^{3+}}]\ [\mathrm{tren}] \tag{4}$$

The activation parameters calculated are $\Delta H^{\neq} = 10.6 \pm 1.3$ kcal.mole^{-1}, $\Delta S^{\neq} = -15.0 \pm 4.0$ cal.deg^{-1}.mole^{-1}, $\Delta G^{\neq}(25°) = 15.1 \pm 2.5$ kcal.mole^{-1}, $k(25°) = 58.2 \pm 17.0$ l.mole^{-1}. sec^{-1}. The error limits were established by regression analysis at the 95% confidence level.

The second-order kinetics observed for this reaction indicate the simultaneous attachment of incoming and outgoing ligands. However, molecular models indicate that steric repulsions would be prohibitive in a transition state with a coordination number greater than eight. Therefore, a mechanism involving a stepwise dissociation of the coordinated ligand with a simultaneous stepwise bond formation by the incoming group was proposed.

$$\mathrm{Nd(tren)_2^{3+} + tren'} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{MN_3N'} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{MN_2N_2'} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \mathrm{MNN_3'} \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} \mathrm{Nd(tren)(tren')^{3+} + tren} \quad (5)$$

In this equation, N_x and N'_{4-x} represent the number of coordinated nitrogens in each intermediate ($\mathrm{MN}_x\mathrm{N}'_{4-x}$) for the departing and incoming ligand respectively. This mechanism allows simultaneous coordination of the two transitive ligands without requiring an increase in the coordination number of an intermediate. This mechanism was shown to be consistent with the observed rate law by applying the steady-state treatment to the intermediate $\mathrm{MN_3N'}$.

This mechanism requires that the ligand involved must possess sufficient internal flexibility to twist out of the path of the incoming ligand upon dissociation of a coordinate bond. Molecular models indicate that an ethylamine group of tren may be effectively removed from the coordination site by rotation about the C–*tert.*-N bond. The observation that second-order kinetics are exhibited by the tren exchange, in contrast to the first-order kinetics observed for the 4,4′-di-*n*-butyl-bipyridine exchange, may be due to the greater internal rigidity of the latter ligand. Although a pyridine ring may rotate about the C–C bond connecting the two rings, molecular models indicate that the coordination site remains partially blocked upon such rotation, following dissociation of the first coordinate bond. Thus coordination of the incoming group occurs after complete dissociation of the departing group.

Second-order kinetics are also observed in the exchange reaction of diethylenetriamine with the nine-coordinate complex $\mathrm{Pr(dien)_3^{3+}}$ in acetonitrile[114]. The exchange rate is ~ 10^3 times greater in this system than in the tren system, reflecting the difference in lability associated with tridentate versus tetradentate coordination by the ligand.

The determination of a ligand exchange rate by NMR in the slow exchange region involves the determination of the natural linewidth ($\Delta\nu_{\frac{1}{2}}$) of a coordinated ligand resonance[115,116]. In transition metal systems, the natural linewidth is usually obtained by extrapolation of the linear portion of a plot of log ($\Delta\nu_{\frac{1}{2}}^{\mathrm{obs}}$) vs. $1/T$ ($\Delta\nu_{\frac{1}{2}}^{\mathrm{obs}}$ is the observed linewidth measured at half height) from the region where exchange is stopped (low temperature) into the exchange region (high temperature). However, in the $\mathrm{Nd^{3+}}$–tren system, such treatment gives smaller linewidths than expected for a proton relaxation rate controlled by an $\mathrm{Nd^{3+}}$ ion. Thus it is apparent that caution must be employed in lanthanide systems when determining ($\Delta\nu_{\frac{1}{2}}$) values by extrapolation of low-temperature data.

The influence of the neodymium ion on the relaxation rate of a methylene proton of the coordinated ligand is observed in the high-temperature region of Fig. 6. Since the solution contains only the bis complex, intermolecular exchange with free ligand is not possible. Thus relatively narrow resonance lines are observed at temperatures > – 10°C, indicative of a relaxation process controlled by a neodymium ion. However, in this system as

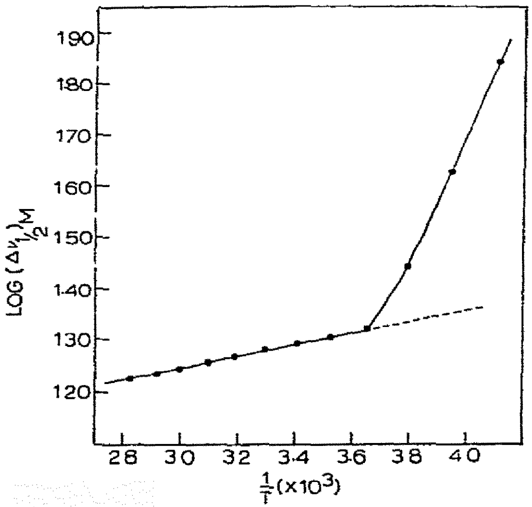


Fig. 6. Temperature variation of linewidth for a 2:1 ligand to metal ion mole ratio, $[Nd^{3+}] = 0.05$ *M*. Reprinted with permission of The American Chemical Society from M.F. Johnson and J.H. Forsberg, *Inorg. Chem.*, 11 (1972) in press.

well, excessive line broadening is observed below — 10°C. Thus it is apparent that the metal ion is not the only factor controlling the linewidth in the low temperature region. The extensive broadening observed in this region is attributed to an intramolecular exchange process relating possible structural isomers existing in solution.

G. THERMODYNAMIC STABILITY IN SOLUTION

The isolation of complexes such as those listed in Tables 1 and 2 raises a question as to the real existence of the complex species in solution, as opposed to their formation solely to satisfy the demand of crystal stability. Since all of the lanthanide complexes derived from N-donors are hydrolyzed to some extent in aqueous solution, the existence and stability of these species must be studied in non-aqueous media. Although thermodynamic stability is commonly measured in terms of formation constant data, the usual methods of evaluating formation constants are inapplicable to non-aqueous systems. However, the calorimetric measurement of stepwise enthalpies of complexation in non-aqueous media have proven quite valuable in establishing the thermodynamically stable species existing in solution[55,59,61]. Calorimetric data have also proved quite valuable in elucidating such factors as the relationship of coordination number to steric requirements of the ligand and to metal ion size.

Most of the enthalpy data reported for aqueous systems have been calculated from the temperature dependence of the formation constants. The values are small and sometimes positive[1,2], probably as a consequence of the need to displace strongly bound water molecules in the ligation process. The stability of lanthanide complexes in aqueous solution is due to the large positive entropy change (chelate effect) associated with the complexation reaction.

In contrast to the behavior in aqueous solution, the enthalpy changes associated with the complexation of ethylenediamine, diethylenetriamine, triethylenetetramine and β,β,β''-triaminotriethylamine with lanthanide perchlorates in anhydrous acetonitrile are both large and exothermic. A plot of molar enthalpy of complexation of ethylenediamine in terms of the general equation

$$\mathrm{Ln(en)}_{n-1}\,(\mathrm{CH_3CN})_x^{3+} + \mathrm{en} \rightleftarrows \mathrm{Ln(en)}_n(\mathrm{CH_3CN})_y^{3+} + (x-y)\,\mathrm{CH_3CN} \tag{6}$$

is shown in Fig. 7 for $\mathrm{Gd^{III}}$. The results for other lanthanide perchlorates are similar. Each curve is characterized by four distinct plateaux, indicating the formation of four $\mathrm{Ln(en)}_n^{3+}$ ($n = 1$–4) species in solution. The distinct breaks in these enthalpy curves are characteristic of thermodynamically stable complexes[117] in which the successive stepwise formation constant differ by 10^2–10^3. Representative enthalpy data are presented in Table 6. The stepwise formation constants (Table 7) were calculated by the method suggested by Brenner[117]. Although the treatment is subject to considerable error, the log K_n values are of the correct orders of magnitude and are useful for establishing the magnitude of thermodynamic stability which these chelates possess in solution. The stepwise formation constants, together with the molar enthalpy data, were used to calculate the stepwise entropy changes (Table 7). It is interesting to note that the entropy changes are both large and *negative* in this ligation reaction, in contrast to the large *positive* values observed in aqueous

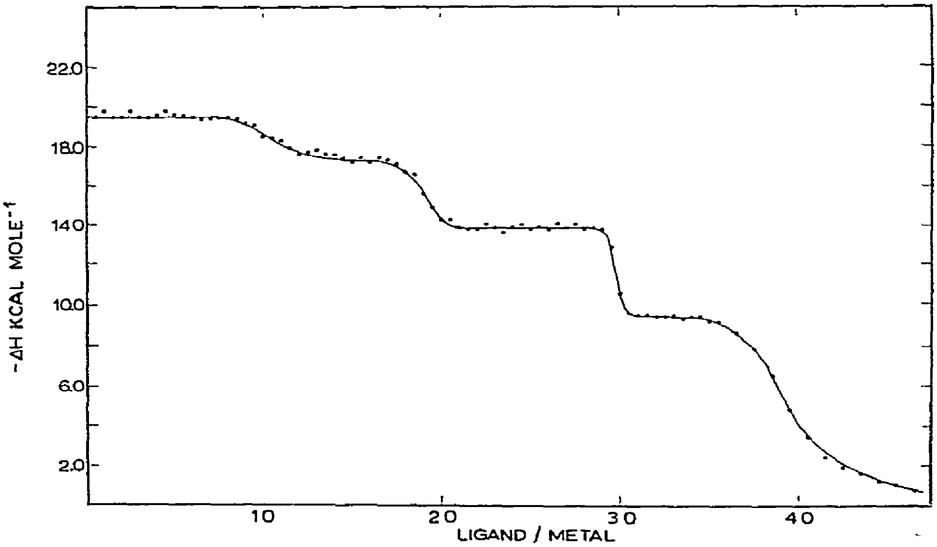


Fig. 7. Enthalpy curve for the formation of $\mathrm{Gd(en)}_n(\mathrm{ClO_4})_3$. Reprinted with permission of The American Chemical Society from J.H. Forsberg and T. Moeller, *Inorg. Chem.*, 8 (1969) 889.

TABLE 6
Enthalpies of complexation of lanthanide perchlorates at 23°C

Ln^{3+}	Enthalpy change[a] ($kcal.mole^{-1}$)						
	Ethylenediamine				Diethylenetriamine		
	$-\Delta H_1$	$-\Delta H_2$	$-\Delta H_3$	$-\Delta H_4$	$-\Delta H_1$	$-\Delta H_2$	$-\Delta H_3$
La^{3+}	17.3	15.5	13.8	11.0	23.8	19.8	13.1
Pr^{3+}	18.7	16.8	13.6	10.8	24.6	20.8	12.6
Nd^{3+}	18.8	16.9	13.8	10.9	25.6	20.9	11.5
Sm^{3+}	19.3	18.0	13.5	9.9	25.7	21.2	10.7
Eu^{3+}	19.8	18.3	13.9	9.7			
Gd^{3+}	19.5	18.0	13.9	9.5	26.1	21.5	9.9
Tb^{3+}	19.9	18.6	13.1	9.0			
Dy^{3+}	19.9	18.4	12.6	9.2	27.2	22.2	6.9
Ho^{3+}	19.9	18.2	12.7	10.0			
Er^{3+}	20.1	18.7	13.1	11.5	28.1	23.5	6.2
Yb^{3+}	20.1	18.8	14.4	12.8	27.4	22.7	6.1
Lu^{3+}	20.0	18.6	14.3	12.8			

[a] Deviation ± 0.3 kcal $mole^{-1}$. All enthalpy data are corrected for heat of solution of the ligand.

TABLE 7
Formation constant and entropy data for certain lanthanide perchlorates with ethylenediamine at 23°C

	Formation constant				Entropy change[b] ($cal.mole^{-1}.deg^{-1}$)			
	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	ΔS_1	ΔS_2	ΔS_3	ΔS_4
La^{3+}	9.5	7.5	6.2	3.3	−15.1	−18.2	−18.4	−22.1
Tb^{3+}	10.4	8.4	6.2	3.2	−19.8	−24.5	−16.0	−15.8
Yb^{3+}	11.5	9.3	6.5	3.8	−15.4	−21.1	−19.0	−25.9

[a] The deviation is ± 0.5.
[b] The deviation is ± 3.0 cal $mole^{-1}$. deg^{-1}.

solution. Thus the ethylenediamine complexes formed under these conditions are enthalpy-stabilized, emphasizing the importance of metal–nitrogen bond formation in the ligation process.

Three distinct plateaux are observed in the formation of the dien chelates[55], indicating the formation of the thermodynamically stable species $Ln(dien)_n^{3+}$ ($n = 1$–3). Representative data are depicted in Table 6. The monotonic decrease in ΔH_3 value with decreasing metal ion size clearly demonstrates the presence of a steric effect upon entry of the third diethylenetriamine molecule into the coordination sphere. The decrease in ΔH_3 offers a quantitative measure of the steric effect in these high-coordinate chelates 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 lanthanides (Table 2).

The total enthalpies of complexation, ΔH_c, for the formation of tetrakis-ethylenediamine complexes and tris-diethylenetriamine complexes are given in Table 8. The total enthalpy of complexation is less for the tris-diethylenetriamine chelates for each lanthanide ion, even though diethylenetriamine presumably involves formation of nine metal–nitrogen bonds, as 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.

Two distinct plateaux characterize the formation of the triethylenetetramine chelates, establishing the existence of the $\mathrm{Ln(trien)}_n^{3+}$ ($n = 1, 2$) species in solution[59]. A comparison of the ΔH_c values (Table 8) with the corresponding values for ethylenediamine and diethylenetriamine chelates indicates that the values for triethylenetetramine are substantially less than expected. The lower values obtained for these chelates may best be explained by the inability of this ligand to form four strong metal–nitrogen bonds, due to the strain induced in the central chelate ring upon tetradentate coordination. This effect has been noted previously in *d*-type transition metal systems[118].

The values of the total enthalpy of complexation (ΔH_c) of $Pr(ClO_4)_3$ and $Nd(ClO_4)_3$ with β,β',β''-triaminotriethylamine indicate that all four nitrogen atoms of the ligand are involved in coordination[56]. The values obtained ($\Delta H(\mathrm{Pr}) = -62.5 \pm 1.5$ kcal.mole^{-1}; $\Delta H(\mathrm{Gd}) = -60.3 \pm 1.5$ kcal.mole^{-1}) agree with the enthalpy changes corresponding to the formation of eight metal–nitrogen bonds in the tetrakis-ethylenediamine chelates[61] ($\Delta H(\mathrm{Pr}) = -59.9$ kcal.mole^{-1}; $\Delta H(\mathrm{Gd}) = -60.9$ kcal.mole^{-1}).

Molar conductivity data (Table 9) also prove useful in establishing the nature of the complex species in solution. Although the data indicate that all nitrates are coordinated to the lanthanide ion in the absence of ligand, solutions containing excess diethylenetriamine are in the range expected for 1:1 electrolytes in acetonitrile (1:1, 175 ohm^{-1}.cm^2.mole^{-1} (ref. 119); 2:1, 285 ohm^{-1}.cm^2.mole^{-1} (ref. 119); 3:1, 400 ohm^{-1}.cm^2.mole^{-1} (ref. 36). A conductance titration (Fig. 8) of $Nd(NO_3)_3$ with diethylenetriamine is characterized by a sharp increase in conductivity between the 1:1 and 2:1 ligand:metal-ion molar ratios, indicating the release of a coordinated nitrate ion in this region. The bis chelate existing in solution is formulated as $[\mathrm{Ln(dien)_2(NO_3)_2}]^+$, since the conductivities at the 2:1 ligand: metal ion molar ratio are indicative of uni-univalent electrolyte behavior. This formulation is consistent with that postulated for the solid chelates. The lack of a further large increase in conductivity beyond the 2:1 ligand:metal-ion molar ratio indicates that the third

TABLE 8
Total enthalpies of complexation for ethylenediamine, diethylenetriamine and triethylenetetramine chelates of lanthanide perchlorates

Ln^{3+}	Total enthalpy change (kcal.mole^{-1})			
	$-\Delta H_c$ (en)	$-\Delta H_c$ (dien)	$-\Delta H_a$ (trien)	Difference (dien−en)
La^{3+}	57.6	56.7	51.5	0.9
Pr^{3+}	59.9	58.0	51.9	1.9
Nd^{3+}	60.4	58.0	51.5	2.4
Sm^{3+}	60.7	57.6	52.6	3.1
Gd^{3+}	60.9	57.5		3.4
Dy^{3+}	60.1	56.3	50.9	3.8
Er^{3+}	63.4	57.8		6.6
Yb^{3+}	66.1	56.2	53.8	9.9

TABLE 9
Molar conductivities of acetonitrile solutions containing lanthanide salts and diethylenetriamine

Lanthanide salt	Λ_M (ligand:metal) (ohm^{-1}.cm^2.mole^{-1})		
	Λ_M (0:1)[a]	Λ_M (6:1)[a]	Λ_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 by 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* owing to the presence of the weak electrolyte $Ln(dien)_2(NO_3)_2^+$.

molecule of diethylenetriamine does not compete effectively against the nitrate ligands for the remaining coordination positions of the lanthanide ion.

The enthalpy curves for the titration of lanthanide nitrates with ethylenediamine[61] and diethylenetriamine[55] are characterized by two plateaux, demonstrating the formation of the mono and bis chelates. The lack of further plateaux, as observed with the perchlorate

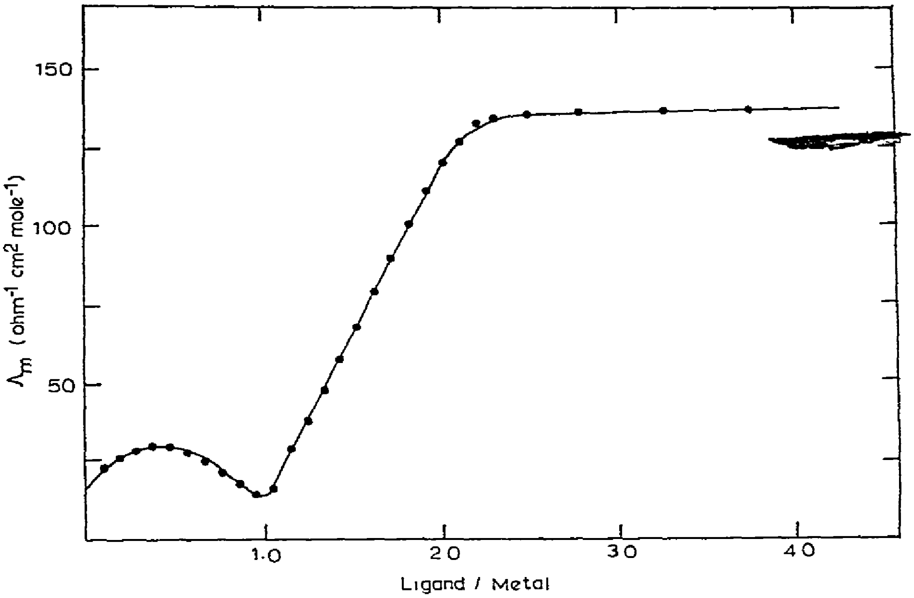


Fig. 8. Conductance titration of Nd$(NO_3)_3$ with diethylenetriamine. Reprinted with permission of The American Chemical Society from J.H. Forsberg and C.A. Wathen, *Inorg. Chem.*, 10 (1971) 1379.

salts, is further proof that in the presence of nitrate ion, the species Ln$(en)_n^{3+}$ ($n = 3, 4$) and Ln$(dien)_3^{3+}$ are thermodynamically unfavorable relative to the [Ln$(en)_2(NO_3)_3$] and Ln$(dien)_2(NO_3)_2$] NO_3 species. (The molar conductivity of perchlorate salts[55], ~400 ohm^{-1}.cm^2.mole^{-1}, indicates that the perchlorate ion does not coordinate the lanthanide ion in acetonitrile.) The effect of coordinated nitrate in lowering the effective positive charge of the metal ion is reflected in the lower enthalpy change (3–6 kcal.mole^{-1}) observed for the nitrate salts compared with the perchlorate salts.

H. SUMMARY

The use of non-aqueous solvent media has provided a means of successful synthesis of lanthanide complexes derived from several N-donors. The high coordination numbers of these species, established by determinations of molecular structure and interpretations of spectral data, are indicative of appreciable Ln^{3+}–N interaction. Calorimetric measurements of enthalpies of ligation provide quantitative evidence for considerable thermodynamic stability of lanthanide complexes based solely upon nitrogen coordination. Complexes derived from strongly basic nitrogen donors in acetonitrile are enthalpy-stabilized, emphasizing the importance of Ln^{3+}–N bond formation in the ligation reaction.

Neutral N-donors are apparently incapable of competing effectively for coordination sites with strongly coordinating anions in solution. The isolation of high-coordinate, stoichiometric complexes containing at most one nitrate or halide group in the coordination sphere may best be attributed to the greater insolubility of these species in the reaction medium, since anion displacement is not thermodynamically favorable.

Interpretations of NMR data indicate that the Ln^{3+}–N interaction is predominantly electrostatic. Thus the observed stereochemistry of a lanthanide complex may be attributed to steric factors and electrostatic forces of attraction and repulsion, rather than orientation of the metal–ligand bonds by the well shielded 4*f* orbitals of the metal ion.

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