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Observations on the Rare Earths. LXXIX.[1] The Syntheses and Properties of Ethylenediamine Chelates of the Tripositive Lanthanide Ions

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Received October 3, 1968

Under carefully controlled experimental conditions and with maintenance of completely anhydrous systems, the direct reaction of ethylenediamine with a lanthanide(III) salt in acetonitrile yields solid compounds of the stoichiometric compositions $Ln(en)_3X_3$ and $Ln(en)_4X_3$, where X = NO_3, Cl, Br, or ClO_4. Infrared data establish coordination by the anion in several of the solid complex compounds. Although the 20% decrease in metal ion radius across the lanthanide series does not affect the number of ethylenediamine molecules bonded to an Ln^{3+} ion, the space available for coordination by an anion is affected, and selectivity in terms of anion size is demonstrated. The result is variation in total coordination number of the cation from 9 to 8.

Significant differences in complexation between the lanthanide ions and the d-type transition metal ions are suggested by the existence of far fewer characterized complex derivatives of the former.[2,3] Effective shielding of the 4f orbitals of the lanthanide ions by the $5s^25p^6$ octet precludes the existence of strongly covalent cation–ligand interaction and accounts for the substantially electrostatic bonding indicated by the recorded magnetic, spectral, and rapid ligand-exchange properties of these complex species. Furthermore, there is for a given lanthanide ion a variability of coordination number that appears to be dictated by cationic size and electrostatic forces of attraction and repulsion rather than by bond orientation.[3]

Of the ligands forming complexes with the lanthanide ions, the majority, by a wide margin, contain oxygen-atom donor sites in their molecular structures. Nitrogen donors are well characterized only in association with oxygen donors in anionic species such as the polyaminepolycarboxylates and 8-quinolinolates[2], or, to a more limited extent, in cationic species such as the pyramidone chelates.[1] Although these complexes are isolable from aqueous media, observations that under comparable conditions strongly basic amines yield difficultly soluble hydrous oxides or hydroxides and that weakly basic amines are apparently unreactive have prompted the assumption that lanthanide complexes derived from neutral ligands that are pure nitrogen donors are thermodynamically unstable.

The problem of synthesis using aqueous media, however, is one of comparative donor availability and donor strength. Prevention of precipitation of a hydroxide of solubility product[4] *ca.* 10^{-19} to 10^{-24} $mol^4\ l.^{-4}$ would require large thermodynamic stability for an amine–lanthanide ion complex.[5] Interaction with a weakly basic donor species would occur only by displacement of strongly bonded water molecules from the aquo cation. That both solvated 1,10-phenanthroline[6,7] and bipyridyl[8–11] complexes of the type $LnX_3 \cdot 2L$ (L = *o*-phen, bipy) have been isolated from 95% ethanol indicates that the Ln^{3+}–N bond is stable in the absence of a strongly competitive donor. In each of these species, a coordination number in excess of 6 is achieved by bonding to anions and solvent molecules. Only when the weakly coordinating perchlorate ion is present could the unsolvated tetrakis chelates be obtained.[12]

In a previous communication,[13] we reported that the strongly basic amine ethylenediamine forms both tris and tetrakis chelates with the tripositive lanthanide ions under rigorously anhydrous conditions. In the present paper, a complete list of the isolated compounds, the methods of preparation, and a description of properties are given. Infrared data are used to indicate the presence or absence of coordinated anions, the total coordination number of the lanthanide ion in a given species, and the variation in coordination number as a function of crystal radius of the cation.

Experimental Section

Materials.—The lanthanide oxides, all of 99.9% purity or better, were obtained largely from American Potash and Chemical Corp. Anhydrous nitrates were prepared by direct reaction of the oxides with liquid nitrogen(IV) oxide.[14] Hydrated chlorides,

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[1] Part LXXVIII: L. J. Sauro and T. Moeller, *J. Inorg. Nucl. Chem.*, **30**, 953 (1968).

[2] T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrús, G. R. Feistel, and W. J. Randall, *Chem. Rev.*, **65**, 1 (1965).

[3] T. Moeller, E. R. Birnbaum, J. H. Forsberg, and R. B. Gayhart, "Progress in the Science and Technology of the Rare Earths," Vol. 3, L. Eyring, Ed., Pergamon Press, New York, N. Y., 1968, pp 61–128.

[4] T. Moeller and H. E. Kremers, *J. Phys. Chem.*, **48**, 395 (1944).

[5] S. P. Sinha, "Complexes of the Rare Earths," Pergamon Press, New York, N. Y., 1966, pp 25–27.

[6] F. A. Hart and F. P. Laming, *Proc. Chem. Soc.*, 107 (1963); *J. Inorg. Nucl. Chem.*, **26**, 579 (1964); **27**, 1605 (1965).

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[8] N. I. Lobanov and V. A. Smirnova, *ibid.*, **8**, 2208 (1963).

[9] V. Carassiti, A. Seminara, and A. Seminara-Musumeci, *Ann. Chim.* (Rome), **54**, 1025 (1964).

[10] S. P. Sinha, *Spectrochim. Acta*, **20**, 879 (1964).

[11] F. A. Hart and F. P. Laming, *J. Inorg. Nucl. Chem.*, **27**, 1825 (1965).

[12] S. S. Krishnamurthy and S. Soundararajan, *Z. Anorg. Allgem. Chem.*, **348**, 309 (1966).

[13] J. H. Forsberg and T. Moeller, *J. Am. Chem. Soc.*, **90**, 1932 (1968).

[14] T. Moeller, V. D. Aftandilian, and G. W. Cullen, *Inorg. Syn.*, **5**, 37 (1957).

bromides, and perchlorates were obtained by treating the appropriate acid with excess amounts of the oxides, filtering, and evaporating to dryness. The anhydrous chlorides and bromides were then obtained by standard dehydration techniques.[15] The anhydrous perchlorates were prepared by slowly heating the hydrates at 1.0 mm, as suggested by Thompson.[16] Hydrated perchlorates of the lighter lanthanides lost water readily at 200° without significant hydrolytic decomposition. With the heavier lanthanides, however, the 250° temperature required for complete dehydration caused hydrolytic conversion of about half of the hydrated compound to an insoluble product. The anhydrous perchlorate was easily removed by extraction with anhydrous acetonitrile. Aliquots of solutions of the anhydrous salts in acetonitrile were analyzed by dilution with water and titration with ethylenediaminetetraacetate, using xylenol orange as indicator.

Reagent grade acetonitrile was dried and purified by distillation from phosphorus(V) oxide. Ethylenediamine was dried by distillation from metallic sodium. Anhydrous deuterated ethylenediamine was prepared by a reported procedure.[17]

Synthesis of Complex Species.—All manipulations were carried out in a drybox under an atmosphere of dry nitrogen. Each compound $Ln(en)_nX_3$ ($X^- = NO_3^-, Cl^-, Br^-, ClO_4^-$; $n = 3, 4$) was prepared by direct reaction of ethylenediamine with a 2-mol quantity of the anhydrous lanthanide salt in anhydrous acetonitrile. Ethylenediamine (16 mmol for $n = 4$; 6 mmol for $n = 3$) was dissolved in acetonitrile and the solution was added dropwise to the well-stirred lanthanide salt solution. Precipitation of the product occurred immediately when $X^- = NO_3^-$, Cl^-, or Br^-, but a completely stoichiometric product was obtained only after the suspension was heated under reflux for 12 hr. This procedure was particularly necessary with the chlorides and bromides because of the reduced solubilities of the anhydrous salts in acetonitrile. When $X^- = ClO_4^-$, crystallization could be initiated only by evaporation of the solution nearly to dryness in a current of dry nitrogen. No tris complexes were obtained when $X^- = ClO_4^-$. Deuterated analogs were prepared similarly. All products were hygroscopic crystalline powders that underwent rapid hydrolytic decomposition in contact with atmospheric moisture.

A complete list of complexes and typical microanalytical data are given in Table I. The fact that the list does not contain the complete series of lanthanide ions with each anion does not mean that the missing species cannot be isolated. The chloride and bromide salts were isolated only for use in infrared studies, and no attempt was made to prepare the complexes for the entire series. The perchlorate salts were used exclusively for calorimetric studies, and only a few of these species were isolated to prove their existence in the solid state. The nitrate salts represent the most complete series, with the exclusion of only the cerium(III), promethium(III), thulium(III), and lutetium(III) compounds. The last three were excluded because of their scarcity, and cerium(III) nitrate was excluded because of the difficulty of preparing this compound free from cerium(IV). There is no doubt that the tetrakis chelates of these metal ions could also be prepared to complete the series.

The tris chelates for metal ions lighter than Gd^{3+} and heavier than Ho^{3+} could not be prepared by application of the general procedure in the case of the nitrate salts. With the lighter cations, nonstoichiometric species formulated as $Ln(en)_2(NO_3)_3 \cdot (CH_3CN)_x$ ($x < 0.5$) were obtained. The analyses of the compounds isolated for the Er^{3+} and Yb^{3+} ions indicate the formulation $Ln(en)_{3.5}(NO_3)_3$.

Infrared Measurements.—Infrared spectra in the region 4000–650 cm^{-1} were obtained with a Perkin-Elmer Model 521 grating instrument that had been calibrated with polystyrene film. Acetonitrile solutions of the complexes were contained in 1-mm sodium chloride cavity cells. Nujol and hexachlorobutadiene mulls were supported between sodium chloride plates. Infrared spectra in the region 700–300 cm^{-1} were obtained with a Beckman Model IR5A prism instrument equipped with cesium bromide optics. Nujol mulls were supported between polyethylene plates.

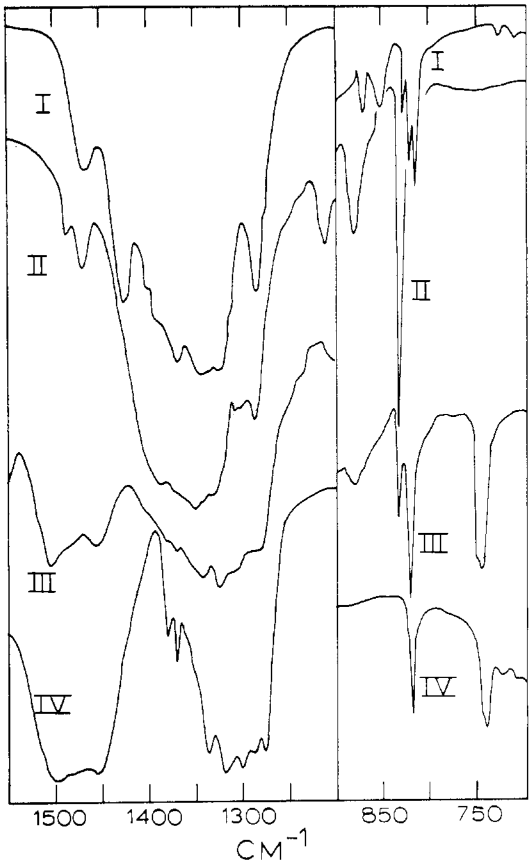

Figure 1.—Infrared spectra of $Ln(en)_n(NO_3)_3$ species in the region of nitrate absorptions: I, $[Ln(en)_4NO_3](NO_3)_2$; II, $[Ln(en)_4](NO_3)_3$; III, $[Ln(en)_3(NO_3)_2]NO_3$; IV, $[Nd(en)_2(NO_3)_3] \cdot 0.4CH_3CN$.

Results and Discussion

The inclusion or lack of inclusion of an anion in the coordination sphere, as indicated in Table I, was based upon interpretations of infrared data.

The infrared spectra of the nitrate-containing chelates in the regions of nitrate absorption are depicted in Figure 1. The spectrum of each of the specific complexes of a given class was identical with that chosen to represent that class. Assignments of the nitrate bands recorded in Table II are based upon the two possible symmetry types, D_{3h} (free NO_3^- ion) and C_{2v} (coordinated NO_3 group).[18,19] The assignments of ethylenediamine absorptions in this region are included to allow identification of all observed bands. Of the allowed bands, the 1030-cm^{-1} band of the C_{2v} symmetry could not be identified because of strong absorptions by the NH (or ND) groups of the coordinated ethylenediamine molecule. The data indicate that all of

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[15] M. D. Taylor, *Chem. Rev.*, **62**, 503 (1962).

[16] L. C. Thompson, private communication.

[17] A. Sabatini and S. Califano, *Spectrochim. Acta*, **16**, 677 (1960).

[18] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p 178.

[19] B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc.*, 4222 (1957).

TABLE I

COMPOUNDS PREPARED AND TYPICAL ANALYTICAL DATA

General formulation[a]	Ln for compounds prepared	Typical anal						
			% C		% H		% Ln	
		Ln	Calcd	Found	Calcd	Found	Calcd	Found
$[Ln(en)_4(NO_3)](NO_3)_2$	La–Sm (≠Ce, Pm)	Nd	16.84	16.71	5.65	5.81	25.28	25.18
$[Ln(en)_4](NO_3)_3$	Eu–Yb (≠Tm)	Gd	16.46	16.26	5.52	5.59	26.94	27.35
$[Ln(en)_3(NO_3)_2]NO_3$	Gd–Ho	Gd	13.76	13.67	4.62	4.51	30.03	29.97
$[Ln(en)_4Cl]Cl_2$	La, Nd	Nd	19.57	19.42	6.57	6.55	29.38	29.55
$[Ln(en)_4]Cl_3$	Sm, Gd, Er	Er	18.69	18.75	6.27	6.21	32.54	32.41
$[Ln(en)_3Cl_2]Cl$	Gd, Er	Gd	16.23	15.53	5.40	5.60	35.42	35.82
$[Ln(en)_4Br]Br_2$	La	La	15.52	15.47	5.21	5.26	22.44	22.40
$[Ln(en)_4]Br_3$	Nd, Gd	Nd	15.39	15.10	5.16	5.22	23.11	23.65
$[Ln(en)_3Br_2]Br$	Gd	Gd	12.48	12.72	4.17	4.49	27.24	27.06
$[Ln(en)_4](ClO_4)_3$	La, Pr, Nd	Nd	14.08	14.06	5.18	5.18	21.12	20.49

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

TABLE II

ASSIGNMENT OF INFRARED ABSORPTIONS OF NITRATES

Assignment	ν, cm^{-1}			
	$[Ln(en)_4(NO_3)](NO_3)_2$	$[Ln(en)_4](NO_3)_3$	$[Ln(en)_3(NO_3)_2]NO_3$	$[Nd(en)_2(NO_2)_3]\cdot 0.4CH_3CN$
$\nu_3(NO_3)$ (D_{3h})	1345	1350	1345 sh	. . .
$\nu_2(NO_3)$ (D_{3h})	829	832	832	. . .
$\nu_1(NO_3)$ (C_{2v})	?	. . .	1325	1320, 1300
$\nu_4(NO_3)$ (C_{2v})	1428	. . .	1505	1500
$\nu_6(NO_3)$ (C_{2v})	820, 815	. . .	815	815
$\nu_3(NO_3)$ (C_{2v})	725 (?)	. . .	740	740
CH_2 scissors	1465	1485, 1470	1458	1455
CH_2 wag	1370	1385	1370	1380, 1370
CH_2 twist	1285	1305, 1285	1285	1300, 1275
NH_2 wag	. . .	. . .	. . .	1338

the tris chelates and the tetrakis chelates of only the lighter lanthanide ions contain both coordinated and ionic nitrate groups. The rather low frequency (band at 1430 cm^{-1}) of the coordinated nitrate group in the tetrakis chelates indicates only small distortion from D_{3h} symmetry and thus weak coordination.[20] This circumstance is predictable in terms of the steric crowding that results from the inclusion of another group in the coordination sphere. Only the largest Ln^{3+} ions are capable of so accommodating the nitrate group without loss of an ethylenediamine molecule. It is significant that the nitrate group has sufficient donor strength that the ethylenediamine groups "make room" for it in the coordination spheres of these cations.

The 830-cm^{-1} band and the broad shoulder at 1345-cm^{-1} in the spectra of the tris chelates indicate the presence of D_{3h} nitrate groups. Inasmuch as there are both types of nitrate groups in both the tris and the lighter tetrakis compounds, it is not unreasonable to assign *two* C_{2v}-type groups to a tris molecule and *one* to a tetrakis molecule, as was done in Table I.

The disappearance of the 1428- and 815-cm^{-1} bands in the spectra of the tetrakis chelates of the heavier lanthanides indicates the absence of C_{2v} nitrate groups in these compounds. It is apparent that as the radius of the Ln^{3+} ion decreases, crowding in the coordination sphere is too large to allow accommodation of the extra group.

The infrared spectra of the species formulated as $[Ln(en)_{3.5}](NO_3)_3$ (Ln = Er, Yb) are identical with those of the tetrakis nitrates of these two cations. That these compounds are not mixtures of tris and tetrakis chelates is indicated by the observation that the spectrum of a true equimolar mixture of the holmium tris and tetrakis compounds shows the presence of C_{2v} nitrate groups. The alternative explanation for this stoichiometry requires dimerization through bridging by ethylenediamine molecules. Unfortunately, the reduced solubility of these species made molecular weight determination impossible.

A species of compositional formulation $Nd(en)_2(NO_3)_3\cdot 0.4CH_3CN$ was obtained in an attempt to prepare a tris-ethylenediamine chelate of neodymium. Strong absorptions at 1500 and 1300 cm^{-1}, together with a single band at 815 cm^{-1}, indicated the presence of only C_{2v}-type nitrate groups. The relatively narrow band at 1320 cm^{-1}, as compared with the broad absorptions shown by the tris species in this region, is further proof that the latter species contain nitrate groups of both C_{2v} and D_{3h} symmetries.

It is impossible on the basis of infrared measurements alone to determine whether the C_{2v}-type nitrate group is uni- or bidentate. Bidentate behavior, at least in the tetrakis chelates, appears to be sterically improbable. If the coordinated NO_3 group is unidentate, the

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(20) J. R. Ferraro, *J. Mol. Spectry.*, **4**, 99 (1960).

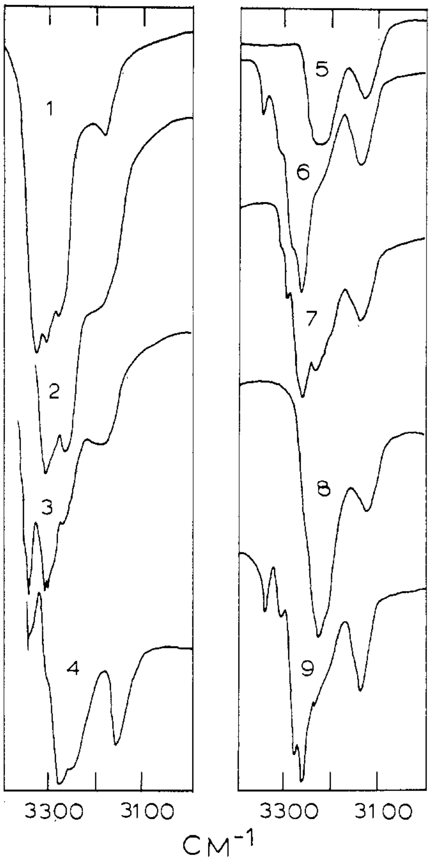

Figure 2.—Infrared spectra of $Ln(en)_nX_3$ species in the NH stretching region: 1, $[Ln(en)_4(NO_3)](NO_3)_2$; 2, $[Ln(en)_4](NO_3)_3$; 3, $[Ln(en)_3(NO_3)_2]NO_3$; 4, $[Ln(en)_4Cl]Cl_2$; 5, $[Ln(en)_4]Cl_3$; 6, $[Ln(en)_3Cl_2]Cl$; 7, $[Ln(en)_4Br]Br_2$; 8, $[Ln(en)_4]Br$; 9; $[Ln(en)_3Br_2]Br$.

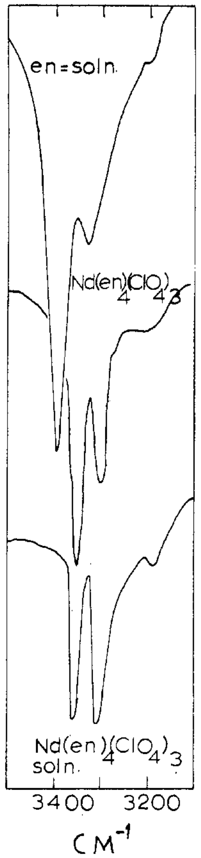

Figure 3.—Effect of coordination and of the ClO_4^- ion upon NH stretching frequencies.

lighter tetrakis chelates exemplify nine-coordination and all of the tris and the heavier tetrakis chelates exhibit eight-coordination. The Raman spectra of the solids should be useful in distinguishing between uni- and bidentate nitrate groups.[21,22]

Alterations in the NH stretching frequency in the infrared spectra of amine complexes of d transition metal ions have been described frequently and reviewed in detail for ammine species.[23] This frequency is decreased when the amine molecule is bonded to a metal ion, and the magnitude of the shift to a lower frequency is enhanced by increase in the positive charge of the metal ion,[24] covalency in the metal–nitrogen bond,[24] and thermodynamic stability of the complex.[25] Hydrogen bonding between the anion present and the proton in the NH group also decreases the NH stretching frequency, and the magnitude of the observed shift depends on the size of the anion and decreases as $Cl^- > Br^- > NO_3^- > ClO_4^-$.[25]

Typical infrared spectra in the NH stretching region are shown in Figure 2. The observed modes showed the expected shift upon deuteration ($\nu_{NH}/\nu_{ND} = 1.35$ (obsd) *vs.* 1.37 (calcd)), indicating them to be free of coupling. The effect of coordination on the NH stretching frequency was determined by comparing data for the $Ln(en)_4(ClO_4)_3$ species with those for free ethylenediamine in acetonitrile solutions (Figure 3). That the $Ln(en)_4^{3+}$ ions are not extensively dissociated in this solvent and that the perchlorate ion does not compete with ethylenediamine as a ligand were shown by calorimetric evaluation of enthalpies of complexation.[26] On this basis, a decrease of 40 cm^{-1} is a reasonable value to show the effect of coordination to ethylenediamine. Anion effects resulting from ion-pair formation involving the large complex cation and the perchlorate anion in dilute solutions (0.01 *M*) are expected to be small. This 40-cm^{-1} shift is smaller than the 100–150-cm^{-1} shifts noted for d-type species.[27] The NH stretching frequencies for the tetrakis perchlorates were identical for Nujol mull and solution measurements, thus indicating the lack of effect of the ClO_4^- ion on this mode.

The corresponding modes for the nitrate, chloride,

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[21] J. R. Ferraro, A. Walker, and C. Cristallini, *Inorg. Nucl. Chem. Letters*, **1**, 25 (1965).

[22] J. R. Ferraro, C. Cristallini, and I. Fox, *J. Inorg. Nucl. Chem.*, **29**, 139 (1967).

[23] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963, p 143.

[24] G. F. Svatos, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **77**, 6159 (1955).

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[26] J. H. Forsberg and T. Moeller, *Inorg. Chem.*, **8**, 889 (1969).

[27] F. A. Cotton in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, pp 362–368.

TABLE III

FAR-INFRARED SPECTRAL DATA

Compound	Assignment, cm^{-1}		
	NH_2 rock	Ring def	ν_{Ln-N}
$[Nd(en)_4NO_3](NO_3)_2$	606 s	476 s, 457 sh	360 w
$[Dy(en)_4](NO_3)_3$	640 s, 606 s	488 s, 460 sh	369 w
$[Gd(en)_3(NO_3)_2]NO_3$	621 s, 592 sh	486 s, 463 sh	378 w
$[Nd(en)_4Cl]Cl_2$	633 sh, 612 s, 540 w	498 s, 477 s, 423 s	359 w
$[Gd(en)_4]Cl_3$	670 s, 635 s, 595 m, 577 m	500 s, 485 s	364 w
$[Gd(en)_3Cl_2]Cl$	675 s, 620 sh, 599 s	517 s, 502 sh, 472 s, 453 sh	392 w, 372 w, 456 w
$[La(en)_4Br]Br_2$	625 s, 605 s, 586 s, 525 s	463 s, 448 sh	345 w
$[Gd(en)_4]Br_3$	647 s, 625 s, 612 s, 562 w	490 s, 474 s, 455 sh	358 w
$[Gd(en)_3Br_2]Br$	655 s, 610 sh, 601 s, 568 sh	512 s, 470 s, 450 sh	392 w, 370 w, 354 w
$[Nd(en\text{-}d_4)_4NO_3](NO_3)_2$	555 sh, 540 s, 530 sh	450 sh, 405 sh, 383 s	
$[Gd(en\text{-}d_4)_3(NO_3)_2]NO_3$	565 sh, 547 s, 535 sh	464 s, 407 s, 370 sh	340 sh
$[Nd(en\text{-}d_4)_4Cl]Cl_2$	545 s	422 sh, 410 s, 392 s	308 w
$[Gd(en\text{-}d_4)_4]Cl_3$	575 sh, 555 s	476 w, 437 s, 417 s, 399 s, 380 sh	331 w
$[La(en\text{-}d_4)_4Br]Br_2$	535 s, 524 sh	402 s, 379 s, 370 sh	317 w
$[Nd(en\text{-}d_4)_4]Br_3$	570 sh, 550 s	426 s, 407 s, 390 s, 368 sh	325 w

and bromide salts (Figure 2) are displaced additionally to lower frequencies in the order $\nu_{ClO_4^-} > \nu_{NO_3^-} > \nu_{Cl^-} \sim \nu_{Br^-}$—the order expected in terms of hydrogen bonding.

In addition, the NH stretching modes for a series of complexes containing the same anion show one marked change as the crystal radius of the Ln^{3+} ion decreases. It is apparent from Figure 2 (spectra 1 and 2) that addition of nitrate ion to the coordination sphere in the tetrakis chelates increases the frequency of this band. Spectrum 1 also shows the presence of an additional band. The effect of coordination by the nitrate ion is even more apparent with the tris complexes (Figure 2, spectrum 3). The larger number of bands observed when the nitrate group is coordinated indicates an overlapping of two nonequivalent sets of NH stretching frequencies. The observed increase in frequency of one set may be a result of repulsion between the coordinated anion and the NH dipole[28] or of poorer hydrogen bonding with that anion. The changes in NH and NO_3 spectra both occur at the Eu^{3+} ion.

A similar change in NH stretching modes occurs with the chloride salts. Although the broad absorptions appear at lower frequencies than with the nitrates, there is a high-frequency band at 3330 cm^{-1} in the spectrum of the tetrakis chelate of lanthanum or neodymium (Figure 2, spectrum 4). This band corresponds to the high-frequency band in the spectra of tetrakis chelates containing coordinated nitrate groups. The complicated spectra of these species again indicate overlap of nonequivalent NH modes. The high-frequency band disappears, and the spectra are simplified for tetrakis chelates of the heavier, and smaller, Ln^{3+} ions (Figure 2, spectrum 5). Both the high-frequency band and more complicated absorptions are characteristic of the spectra of the tris chelates of the heavier Ln^{3+} ions (Figure 2, spectrum 6). By analogy to the nitrate series, these changes probably result from entry of the chloride ion into the coordination sphere. Thus both the lighter tetrakis chelates and all of the tris chelates contain coordinated chloride, whereas the heavier tetrakis chelates contain only ionic chloride. Chloride ion is apparently forced out of the coordination sphere in the tetrakis chelates at the Sm^{3+} ion. Again there is a correlation with crystal radius since the smaller oxygen atom of the nitrate group can remain coordinated with the Sm^{3+} ion but not with the smaller Eu^{3+} ion.

The NH spectra of the bromides are similar to those of the chlorides (Figure 2, spectra 7–9) except that they indicate coordination by the bromide ion in the tetrakis series only with the La^{3+} compound. The ability of the anion to enter the coordination sphere thus decreases in the expected order $NO_3^- > Cl^- > Br^-$ as the radius of the Ln^{3+} ion decreases. Apparently a small change in the cationic radius can alter significantly the size of the available "hole" when the coordination sphere contains four ethylenediamine molecules. The coordination sphere in any of the tris chelates can accommodate any of these anions.

There are no changes in the NH stretching frequencies when the anion is perchlorate. Characteristic absorption at 1110 cm^{-1} and the absence of a strong band at 932 cm^{-1} indicate the presence of only ClO_4^- ions of T_d symmetry.[29] The absence of displacements in the NH stretching frequencies in these spectra supports the argument that these changes in other spectra are due to coordination by the anion.

Variations in the NH stretching region are accompanied by changes in the NH rocking region (Table III). The number and frequencies of the bands observed for this region depend both on the anion present and whether the anion is in the coordination sphere. The NH rocking frequencies are expected to increase as the strength of hydrogen bonding increases.[25] That this change is characteristic of the species here described is evidenced by the appearance of the higher frequency bands in the spectra of the halides. A

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(28) G. W. Watt and D. S. Klett, *Inorg. Chem.*, **5**, 1278 (1966).

(29) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

TABLE IV

METAL–NITROGEN STRETCHING MODE

	$\nu_{\text{Ln–N}}$ cm^{-1}	
Ln	$Ln(en)_4(NO_3)_3$	$Ln(en)_3(NO_3)_3$
La	354	
Pr	357	
Nd	360	
Sm	365	
Eu	366	
Gd	369	378
Tb	371	380
Dy	372	383
Ho	373	383
Er	376	
Yb	381	

complete interpretation of this spectral region cannot be made without a normal-coordinate analysis, since deuteration studies indicated that the NH rocking modes are strongly coupled ($\nu_{NH}/\nu_{ND} = 1.125$ (obsd) *vs.* 1.37 (calcd)). The ring deformation modes are also strongly coupled, as indicated by their substantial displacements (*ca.* 100 cm^{-1}) upon deuteration.

Data for the far-infrared spectra (700–300 cm^{-1}) for several representative complexes are summarized in Table III. The assignments of NH rocking and ring deformation modes follow those made for ethylenediamine complexes of some d transition metal ions.[30] Although metal–nitrogen stretching modes are assigned to the 600–500-cm^{-1} region for the d species,[31] both the weaker metal–nitrogen bonding and the large mass of the Ln^{3+} ion suggest that this mode will occur at a lower frequency for the lanthanide–ethylenediamine complexes. Accordingly, the band at 380–350 cm^{-1} was assigned to one of the possible Ln–N stretching modes. Table IV shows the variation in this mode across the lanthanide series for nitrate-containing species.

This assignment is reasonable when compared to the 250–200-cm^{-1} assignment for the same mode for the lanthanide–bipyridyl complexes.[32] The metal–nitrogen stretching frequency should be somewhat higher for the ethylenediamine chelates since ethylenediamine is a stronger base. The observed gradual change in frequency of this mode as the crystal radius of the Ln^{3+} ion changes is expected. This band is present in the spectra of all of the complexes, and its position is nearly independent of the anion present. The small shift to lower frequency (20–60 cm^{-1}) for the halides probably reflects a combination of increased mass when the ND_2 group is present and coupling of the Ln–N stretching mode to ring deformation modes. The corresponding band cannot be found in the spectra of the deuterated nitrate complexes because of strong ring deformation modes in this region. This mode lies at 10 cm^{-1} higher for the tris chelates. If the assignment is correct, replacement of a strong ligand by a weaker one increases the over-all metal–nitrogen interaction and overcomes any reduction in charge on the cation by the coordinated anion.

The low Ln–Cl and Ln–Br bond orders and the large mass of a given Ln atom suggest that the corresponding Ln–X stretching frequencies lie below the range of the instrument used (300 cm^{-1}). The d transition metal–halogen stretching modes are in the 300–400 cm^{-1} region.

Although the 20% decrease in crystal radius from the ion La^{3+} to the ion Lu^{3+} does not affect the number of ethylenediamine groups that can bond to the Ln^{3+} ion, the additional space available for coordination by an anion is affected, and selectivity in terms of anion size results. Thus there is a variation of total coordination number from 9 to 8 among the tripositive lanthanide ions.

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