Studies of Ethylenediamine Complexes of the Lanthanide(III) Perchlorates Using Nuclear Magnetic Resonance Spectroscopy

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Complexes of ethylenediamine with the tripositive lanthanide ions have been studied in anhydrous acetonitrile solution by nuclear magnetic resonance spectroscopy. The variation of the isotropic shift, ΔH_0, for the tetrakis complexes as a function of atomic number is reported. A contact mechanism is apparently responsible for the shift in the lighter rare earths, cerium through holmium, whereas a pseudocontact shift is responsible for the shift in the remainder of the series. Experimental verification of the prediction that $g_\perp = 0$ for the even-electron ions is obtained. Calculation of geometric factors for a dodecahedral and a square-antiprismatic coordination geometry indicates that either model can be used to explain the experimental ratio of the proton shifts.

The reports of nuclear magnetic resonance (nmr) studies with paramagnetic lanthanide complexes have multiplied rapidly in recent years due primarily to the discovery of the effectiveness of the tetramethylheptanedione (thd and several fluorinated analogs) complexes as "shift reagents."[2] The mechanism responsible for the isotropic shifts observed in these studies is generally attributed to a pseudocontact interaction. The evidence for this lies primarily with the agreement of the ratios of the observed shifts with the ratios of the calculated geometric factors, $(3 \cos^2 \theta - 1)/r^3$. Several reports have appeared of a change in the sign of the observed isotropic shifts upon using the praseodymium "shift reagent" complex instead of the europium complex.[3-5] Such changes in sign are assumed to be due to variations in the anisotropy of the Lande g factor from metal ion to metal ion. Reports on the variation of the isotropic shift across the *entire* lanthanide series have been limited to a very few papers.[6-9] In this paper we should like to report the variation in isotropic shift across the series observed for the tetrakis(ethylenediamine) complexes of the tripositive lanthanide ions.

Experimental Section

All solutions for the nmr studies were prepared using anhydrous reagent grade acetonitrile (Baker), distilled from phosphorus(V) oxide, and anhydrous reagent grade ethylenediamine (Baker), distilled *in vacuo* from barium oxide (Baker). The solutions were prepared in a drybox purged with dried nitrogen gas. All glassware was flamed prior to insertion into the drybox to remove adsorbed water. Samples of rare earth oxides with a purity of greater than 99.9% were provided by Molybdenum Corp. of America and the American Potash and Chemical Corp.

Hydrated lanthanide perchlorates and chlorides were prepared by dissolving a stoichiometric amount of the appropriate oxide in concentrated $HClO_4$ and HCl (Baker "reagent"), respectively, and evaporating to dryness on a rotary evaporator. The hydrated perchlorate salts were made anhydrous in one of two ways: (1) direct stepwise heating *in vacuo* to 300°; (2) refluxing an acetonitrile solution of the hydrated perchlorate through a Soxhlet extractor packed with Linde 4A molecular sieves.[10]

The first method was satisfactory for the lighter lanthanide salts.[11] The heavier salts, however, partially decomposed at the high temperatures necessary to dry them to an insoluble material (probably $LnOCl$). A third method was attempted which involved the reaction of anhydrous $LnCl_3$ with anhydrous $AgClO_4$ in acetonitrile. The anhydrous $LnCl_3$ for this reaction was prepared by the stepwise heating of an intimate mixture of the hydrated lanthanide chloride and NH_4Cl (Baker "reagent").[12] Since in the presence of chloride ion an insoluble $Ln(en)_4Cl_3$ salt precipitates,[13] the anhydrous solutions of $Ln(ClO_4)_3$ prepared in this fashion were made up with a very slight excess of $AgClO_4$. However data obtained from solutions prepared in this manner were not reproducible. By far the better method was no. 2. Solutions prepared this way did not precipitate hydroxy species upon addition of ethylenediamine for several days, if carefully dried glassware (including nmr tubes) was used. The results reported for the heavier lanthanide ions were obtained from anhydrous solutions prepared by method 2.

Solutions for an nmr experiment were prepared by adding appropriate amounts of a stock lanthanide perchlorate solution and anhydrous ethylenediamine with Hamilton syringes into a volumetric flask followed by dilution to volume with anhydrous acetonitrile. The concentration of metal ion in the stock solution was determined by titration with Baker "reagent" grade ethylenediaminetetraacetic acid (EDTA) using Xylenol Orange (Baker "indicator") as an indicator in an acetate (pH 6) buffer.[14]

The nmr spectra were measured using a Varian A-60A nmr spectrometer at probe temperature (~39°). Acetonitrile was used as an internal reference.

Results and Discussion

The isotropic shifts induced by the paramagnetic, tripositive lanthanide ions (except for promethium) in the NH_2 and CH_2 protons of ethylenediamine were recorded over a range of metal ion concentrations. Only single NH_2 and CH_2 resonances were observed at all concentrations, indicative of fast exchange with excess ligand on the nmr time scale. A typical plot of nmr shift *vs.* concentration of metal ion for the europium(III) ion is shown in Figure 1. The standard deviation associated with the least-squares plot of

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(11) No explosions occurred upon heating the hydrated $Ln(ClO_4)_3$ salts to 300° to dehydrate them. However a small explosion occurred with $Dy(ClO_4)_3$ after it was dried when a steel spatula was used to loosen the caked, anhydrous salt from the glass drying flask. The explosion was sufficient to break the flask and burn two small holes in the rubber gloves of the drybox. No injury was sustained. It appeared that a small amount of grease from the flask's joint was responsible. Striking the anhydrous salt with a steel hammer produced no detonation. Caution is definitely advised when working with these anhydrous salts in the solid state.

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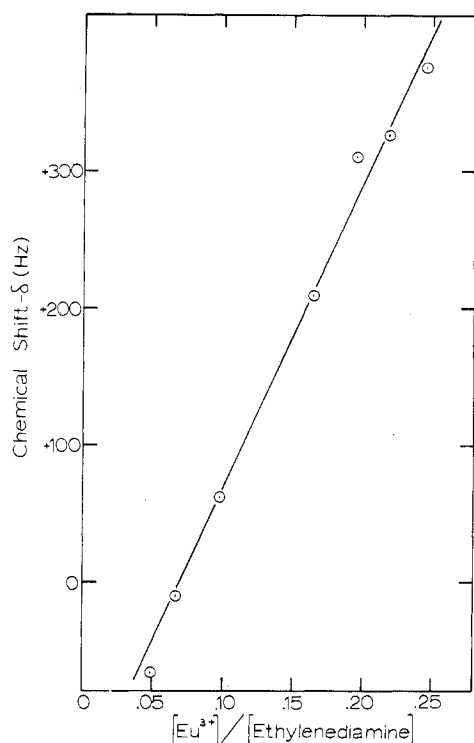
Figure 1. A plot of δ_{obsd} *vs.* [Eu^{3+}] for the CH_2 proton of ethylenediamine (en) in acetonitrile; [en] = 0.748 *M*. δ_{obsd} is reported in hertz from tetramethylsilane.

Figure 2. A plot of ΔH_0 *vs.* atomic number for the NH_2 (○) and CH_2 (△) protons of ethylenediamine complexed to the lanthanide(III) ions. ΔH_0 is calculated for the tetrakis complex and is the chemical shift difference between the paramagnetic en-Ln^{3+} complex and the diamagnetic en-La^{3+} (or -Lu^{3+}) complex. A negative value of ΔH_0 indicates a downfield shift of the resonance with respect to the lanthanum complex.

the data is small for neodymium and the lighter lanthanides. Similar plots made for the heavier lanthanide ions have larger standard deviations, which is probably due to broadening induced by the longer spin relaxation times of these ions.[15] The most severe broadening occurs with gadolinium(III), which, due to its being an S-state ion, has the longest spin relaxation time of the lanthanides. The ligand concentration used for these ions was increased to allow a spectrum to be measured over a range of metal ion concentrations. For gadolinium only the direction of the nmr shifts could be obtained.

Earlier work done with the ethylenediamine complexes of the lanthanide ions indicated that, in the presence of the perchlorate anion, 4:1 ethylenediamine complexes are formed in acetonitrile as a solvent.[13,16] No higher complex could be isolated in the solid state nor detected in solution by calorimetry.[16] In the presence of excess ligand and fast chemical exchange the observed shift due to the paramagnetic ion, ΔH_{obsd},[17] is related to the concentration of complex in solution by eq 1, where m_m and m_l are the total number of
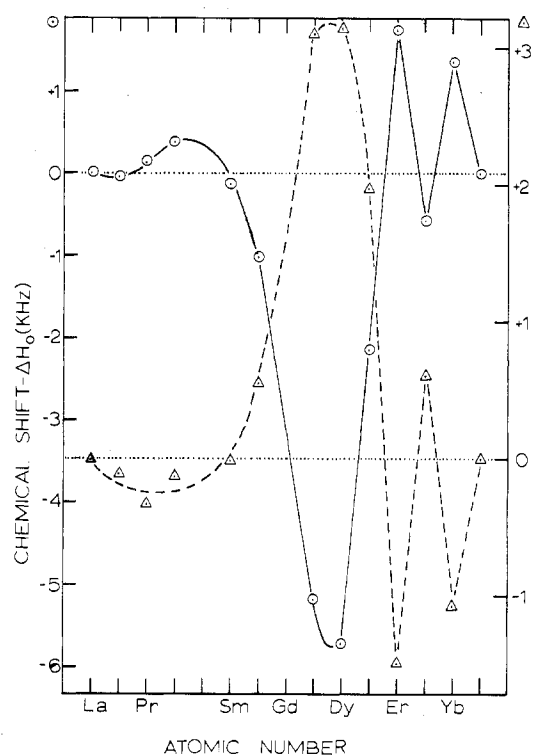
$$\Delta H_{obsd} = nm_m/m_l\Delta H_0 \qquad (1)$$

moles of metal ion and ligand, respectively, ΔH_0 is the shift that would be observed for the pure complex, and *n* has a value of 4, since these are tetrakis complexes. A plot of ΔH_{obsd} *vs.* the metal ion concentration at a fixed ligand con-

Table I. Values of $g_L - 1$, *J*, ΔH_0, and $\Delta H_0/g_L(g_L - 1)J(J + 1)$ for the Ethylenediamine Complexes of the Lanthanide Ions

Ln	$g_L - 1$[a]	*J*	ΔH_0,[b] Hz		$\Delta H_0/g_L(g_L - 1)J(J + 1)$	
			NH_2 proton	CH_2 proton	NH_2 proton	CH_2 proton
Ce	$-^1/_7$	$^5/_2$	−41	−102	+38	+95
Pr	$-^1/_5$	4	+120	−336	−38	+105
Nd	$-^3/_{11}$	$^9/_2$	+353	−135	−72	+27
Sm	$-^5/_7$	$^5/_2$	−135	−7	+75	+4
Eu	$^1/_2$	1	−1011	+558	−674	+372
Gd	1	$^7/_2$	−[c]	+		
Tb	$^1/_2$	6	−5196	+3102	−165	+98
Dy	$^1/_3$	$^{15}/_2$	−5780	+3149	−204	+111
Ho	$^1/_2$	8	−2161	+1975	−96	+88
Er	$^1/_4$	$^{15}/_2$	+1745	−1486	+114	−97
Tm	$^1/_5$	6	−547	+609	−67	+75
Yb	$^1/_7$	$^7/_2$	+1312	−1079	+509	−418

[a] W. Low, *Solid State Phys., Suppl.*, No. 2 (1960). [b] The isotropic shift, ΔH_0, is the chemical shift difference between the paramagnetic en-Ln^{3+} complex and the diamagnetic en-La^{3+} (or -Lu^{3+}) complex. Negative shifts represent a downfield proton shift. [c] Only the direction of the shift could be detected for the protons of ethylenediamine complexed to gadolinium(III).

centration should be linear if only a single complex species is present. This is indeed the case for all the lanthanide complexes studied above a 4:1 ligand to metal ion mole ratio. The value of the isotropic shift for the 4:1 complex, ΔH_0, was obtained by the extrapolation of the above linear least-squares plots to the 4:1 mole ratio. The values for the isotropic shifts for the series of lanthanide ions are reported in Table I. In Figure 2 these values for the isotropic shifts of the NH_2 and CH_2 protons are plotted *vs.* atomic number.

Two of the ions, praseodymium and neodymium, were

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(17) Z. Luz and R. G. Shulman, *J. Chem. Phys.*, **43**, 3750 (1965). ΔH_0 is the difference in resonance position between the protons of ethylenediamine in the presence of a paramagnetic lanthanide ion and either the lanthanum(III) or lutetium(III) ion, depending upon its position in the series. In any case the effect of the diamagnetic cations on the proton resonances of ethylenediamine was small.

studied below a 4:1 mole ratio. As the ratio drops below 4, the direction of the isotropic shift for the NH₂ protons changes from plus to minus for both ions. The shift for the CH₂ protons remains negative but the slope of the line becomes much greater, indicating that the 3:1 complex has a larger negative shift than the 4:1 complex. A rough estimate for the isotropic shifts (ΔH_0) for the 3:1 ethylenediamine complex of praseodymium(III) are $\Delta H_0(NH_2) \approx$ −500 Hz and $\Delta H_0(CH_2) \approx$ −1050 Hz. There are large uncertainties in the magnitude of the shifts (±50 Hz) due to line broadening. However the break in the isotropic shift *vs.* metal to ligand ratio plot at the 4:1 mole ratio for both protons is sharp and in excellent agreement with the calorimetry reported earlier,[15] suggesting that the 4:1 species is the only complex in solution above a 4:1 mole ratio.

The variation in sign of the isotropic shift of the ethylenediamine protons in the 4:1 complexes as a function of atomic number is of interest. Considering the CH₂ proton, the shift is negative for cerium through samarium whereupon it becomes positive at europium. The shift remains positive in sign up to and including holmium and then becomes negative for erbium, positive for thulium, and finally negative for ytterbium. The NH₂ shifts follow an essentially similar pattern but have opposite signs for each lanthanide ion except for cerium and samarium where both the NH₂ and CH₂ protons exhibit negative shifts.

The mechanism responsible for the observed shifts can be an isotropic contact interaction, an anisotropic pseudocontact interaction, or some combination of the two. The isotropic shifts reported by Lewis, *et al.*, for the ¹⁷O resonance of H₂O in aqueous solutions of the tripositive lanthanide ions followed a sinusoidal dependence on atomic number.[6] The lighter lanthanides, cerium through samarium, shifted the ¹⁷O resonances to lower frequency while the heavier lanthanide ions, europium through ytterbium, shifted the ¹⁷O resonances to higher frequency. This variation with atomic number was attributed to an isotropic contact interaction *via* 6s orbital participation in covalent bonding. The treatment of a contact shift for the ¹⁷O resonance of water by Lewis, *et al.*, indicates that the shift can be expressed by the equation

$$(\Delta H_0)_i/H = (2\pi\beta A_i/3kT\gamma_n)[g_L(g_L - 1)J(J + 1)] \tag{2}$$

where A_i is the hyperfine coupling constant, g_L is the Lande g factor, and the other symbols have their usual meaning. Thus the change in the sign of the shift at europium coincides with the change in sign of the $(g_L - 1)$ term.

The sign dependence of the resonance shifts of the CH₂ proton of ethylenediamine on atomic number is in excellent agreement with the values for $(g_L - 1)$ shown in Table I for cerium through holmium. The sign of the CH₂ shift changes at europium from minus to plus just as the ¹⁷O shift of water. In addition the direction of the proton shifts in the presence of the gadolinium(III) ion is consistent with the shifts observed for the nearest neighbor ions. Since gadolinium(III) is an S-state ion and the shifts observed must result from an isotropic contact mechanism, it follows that the similar shifts observed for the nearby ions also result from a contact mechanism. Lewis, *et al.*,[6] suggested that the ratio $\Delta H_0/g_L(g_L - 1)J(J + 1)$ should be roughly a constant if only a contact mechanism is present; *i.e.*, A_i is roughly the same for all the tripositive lanthanide ions (see eq 2). Reuben and Fiat have calculated values of A_i for the aquo complexes of most of the lanthanide series which are quite close to each other, indicating that this may be the case.[8]

The values for this ratio shown in Table I for the CH₂ proton of ethylenediamine range from 4 (Sm) to 372 (Eu), with most of the values clustered around 100. The value for europium may be significantly off since the first and second excited states are populated at room temperature.

The resonance shifts of the NH₂ protons of ethylenediamine have the opposite sign from those of the CH₂ protons with the exception of cerium and samarium. This is consistent with a contact mechanism as the source of the nmr shifts since electron density is usually transmitted between nitrogen and carbon atoms in amines *via* a polarization mechanism which causes the signs of the isotropic shifts to be opposed for protons on adjacent carbon and nitrogen atoms.[18]

The fact that for the tetrakis complexes of cerium and samarium the NH₂ and CH₂ shifts have the same sign indicates that, in addition to a contact mechanism, a pseudocontact mechanism must be present in this system. The large scatter in the values of $\Delta H_0/g_L(g_L - 1)J(J + 1)$ for the NH₂ protons for the lighter lanthanides also suggests that a pseudocontact shift may be making an important contribution here (Table I). The possibility that both mechanisms are in fact operating is not surprising if we consider that the isotropic shifts of the *proton* resonance of water induced by the lanthanides does not follow any regular pattern as a function of atomic number.[8] Reuben and Fiat ascribed these random shifts to the dipolar pseudocontact interaction.

The tris(ethylenediamine) complexes of praseodymium and neodymium exhibit negative isotropic shifts for both the NH₂ and the CH₂ protons. The geometry of these complexes in solution is uncertain since acetonitrile may also be coordinating which would result in a seven- or possibly eight-coordinate complex. The bonding in the complexes should be similar and hence the signs of the resulting contact shifts in the tris complexes should be unchanged from the signs of the shifts in the tetrakis complexes. Thus the change in the sign of the isotropic shift of the NH₂ protons from positive in the tetrakis complex to negative in the tris complex is almost certainly due to the change in the geometry in going from one complex to the other. This change in geometry results in an increase in the pseudocontact shift which is negative for both protons and which is greater than the contact shift, so that a negative shift is seen for both NH₂ and CH₂ protons of the tris complex.

The isotropic shift originating from the dipolar interaction has been described for "liquids" (correlation time for tumbling is larger than the electron spin relaxation time, $\tau \gg T_1e$) by McConnell and Robertson.[19] For an axial complex

$$(\Delta H_0)_i/H = -f(g)[\beta^2 J(J + 1)/45kT](3 \cos^2 \theta_i - 1)/r_i^3 \tag{3}$$

where r_i is the distance from the metal ion to the ith proton and θ_i is the angle the distance vector makes with the principal axis of the complex. The term f(g) is a measure of the anisotropy of the complex and is described by

$$f(g) = (3g_{\parallel} + 4g_{\perp})(g_{\parallel} - g_{\perp}) \tag{4}$$

where $g_{\parallel}$ and $g_{\perp}$ are the parallel and perpendicular components of the g tensor with respect to the principal axis of the complex.

There are two observations which necessitate deviation

(18) R. S. Milner and L. Pratt, *Discuss. Faraday Soc.*, 34, 88 (1962).
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from assuming that only a simple contact interaction is responsible for the shifts in the tetrakis complexes. One, mentioned earlier, is that the isotropic shifts of the NH_2 and CH_2 protons of cerium and samarium have the same sign. The second is the alternation of signs that occurs with the very end of the lanthanide series, erbium through ytterbium. Equation 3 contains two terms which could conceivably change sign from one lanthanide to another, the "geometric factor" $(3 \cos^2 \theta - 1)/r^3$ and $(g_\parallel - g_\perp)$.

The presence of both a contact and pseudocontact shift operating can explain the deviation in sign for the NH_2 proton of ethylenediamine when complexed to cerium and samarium. For these two cases (as well as possibly for neodymium and europium) there may be a pseudocontact mechanism operating whose sign is negative at the NH_2 proton position. Owing to the angle factor, $3 \cos^2 \theta - 1$, or the distance factor, r^3, the shifts of the NH_2 and CH_2 protons are not equal and in this case it appears that the pseudocontact contribution is greater for the NH_2 proton. This overcomes the positive shift produced by the contact mechanism for the NH_2 proton. Variations in the geometry of the tetrakis complex with ionic radius across the lanthanide series may also affect the magnitude of the pseudocontact contribution from ion to ion, causing a greater deviation from pure "contact" shifts to be observed for some ions than others.

The alternation in the sign of the shifts in going from erbium to ytterbium is more difficult to explain. It has been suggested that in principle $g_\perp$ should be 0 for all lanthanide ions with an even number of electrons.[20,21] If $g_\perp$ is greater than $g_\parallel$ in these complexes for the heavy lanthanide ions, then a change in sign will be observed when $g_\perp = 0$ for every other ion. A similar alternation in sign was observed for the thd complexes of the lanthanides, although no explanation was offered.[22] This model would very nicely explain the alternation in sign from erbium to ytterbium for either the NH_2 proton or the CH_2 proton, but not apparently for both. We have previously ascribed the fact that the NH_2 and CH_2 protons are shifted in opposite directions to a contact mechanism. If we make the reasonable assumption that the contact shift of the NH_2 and CH_2 protons in the presence of erbium is similar to the shifts found for holmium, -2231 and $+1820$ cps, respectively, then it is clear that no overlying pseudocontact shift of the same sign for both protons can yield a net shift of $+1675$ and -1641 cps for erbium. Thus in order to explain the alternation in sign of the NH_2 and CH_2 proton shifts the pseudocontact shift itself must have an opposite sign for the NH_2 proton compared to the CH_2 proton.

One explanation for the above difficulty is that the molecular axis of the complexes is such that the distance vectors for the NH_2 and CH_2 protons form angles (θ) with the axis such that $3 \cos^2 \theta - 1$ has an opposite sign for the two different protons. If we consider the most likely coordination polyhedra for octacoordinate lanthanide ions, a square antiprism and an irregular dodecahedron, we can calculate the ratios of the geometric factors, $(3 \cos^2 \theta - 1)/r^3$, for the NH_2 and CH_2 protons. For the square-antiprismatic arrangement a model was constructed using an M–N bond distance of 2.8 Å and a gauche conformation for the ethylenediamine ring, and the principal molecular axis was

Table II. Values for the Angles (θ) and the Distances $(r)^a$ for a Square-Antiprismatic Ethylenediamine–Lanthanide Complex[b]

NH proton	θ, deg	r, Å	CH proton	θ, deg	r, Å
1	42	3.2	1	104	3.4
2	49	3.1	2	108	4.5
3	132	3.3	3	83	3.4
4	137	3.3	4	77	4.5

[a] The metal–nitrogen distance is assumed to be 2.8 Å. [b] The plane determined by the metal ion and both nitrogens of the ethylenediamine is roughly parallel to the principal molecular axis.

Table III. Calculated Geometric Factors for a Square-Antiprismatic Ethylenediamine–Lanthanide Complex

NH proton	$10^3(3 \cos^2 \theta - 1)/r^3$	CH proton	$10^3(3 \cos^2 \theta - 1)/r^3$
1	+20.02	1	−20.94
2	+9.73	2	−7.85
3	+9.57	3	−24.30
4	+16.75	4	−9.29
Av	+14.02		−15.60

assumed to coincide with the fourfold axis of the square antiprism. The ethylenediamine molecule can span coordination sites such that the rings formed are aligned roughly parallel or perpendicular to the principal molecular axis. If perpendicular (*i.e.*, if the ethylenediamine spans two sites in a square face), then the distance vectors to the CH_2 and NH_2 protons will form roughly identical angles with the molecular axis, resulting in the same rather than opposite sign for the two proton shifts. However, if the rings are parallel to the principal axis (*i.e.*, the ethylenediamine spans two sites in a triangular face), then the geometric factors obtained from the model are quite different. Table II lists the angles and distances taken from the model for the eight protons of an ethylenediamine bound to the metal ion.

Using the values listed in Table II the geometric factor, $(3 \cos^2 \theta - 1)/r^3$, was calculated for each proton. These results were averaged over the four NH protons and four CH protons. The calculated geometric factors are shown in Table III.

The results for the square antiprismatic geometry (Table III) indicate that the shifts of the NH_2 and CH_2 protons should be equal in magnitude but opposite in sign, which is in excellent agreement with the experimental data for the lanthanides holmium through ytterbium. It is interesting to note that for the other lanthanides with the exception of the four lightest lanthanides the NH_2:CH_2 shift ratio is 2:1 or greater. This ratio seems to agree with a contact mechanism since the NH_2 proton would have the shorter through-bond distance.

Analogous results can be obtained for a dodecahedral coordination geometry, assuming that the ethylenediamine forms a ring which is aligned parallel to the principal molecular axis of the dodecahedron.[23] Again if the ethylenediamine ring should be perpendicular to the principal axis, the angle factors would be identical resulting in a prediction of the same sign for the NH_2 and CH_2 proton shifts. Table IV shows the calculation of the geometric factors for a dodecahedral coordination geometry. On this basis the square-antiprismatic and dodecahedral coordination geometries are indistinguishable.

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(21) T. H. Siddall, III, W. E. Stewart, and D. G. Karraker, *Inorg. Nucl. Chem. Lett.*, 3, 479 (1967).

(22) N. Ahmad, N. S. Bhacca, J. Selbin, and J. D. Wander, *J. Amer. Chem. Soc.*, 93, 2564 (1971).

(23) The D_{2d} symmetry of an irregular dodecahedron should not have $g_x = g_y \neq g_z$ as is required for McConnell's relationship. However since these complexes are not rigid structural entities, the rapid equilibrium between the two sets of binding sites in the xy plane should average to a single (noncubic) ring. The result is that a pseudo fourfold axis should exist in analogy with the square antiprism.

Table IV. Values for the Angles (θ) the Distances (r)^a and the Calculated Geometric Factors for a Dodecahedral Ethylenediamine-Lanthanide Complex^b

NH proton	θ, deg	r, Å	$10^3(3\cos^2\theta -1)/r^3$	CH proton	θ, deg	r, Å	$10^3(3\cos^2\theta -1)/r^3$
1	35	3.2	+30.91	1	70	3.8	−11.83
2	40	3.2	+23.22	2	66	4.7	−5.32
3	128	3.2	+4.18	3	93	3.6	−21.24
4	120	3.2	−7.63	4	93	4.5	−10.87
Av			+12.67				−12.32

^{a} The metal–nitrogen distance is assumed to be 2.8 Å. Variations of ±0.5 Å do not significantly affect the ratio of the NH$_2$ to CH$_2$ proton shifts. ^{b} The plane determined by the metal ion and both nitrogens of the ethylenediamine contains the principal molecular axis.^{23}

Thus it appears that for the ethylenediamine complexes of the lanthanide ions in acetonitrile solution a contact mechanism is the dominant factor in the proton shifts of the lighter members of the series, cerium–dysprosium, while a pseudocontact mechanism predominates in the heavy members of the series, holmium–ytterbium. A pseudocontact shift is apparently present for the lighter lanthanides as reflected by the $\Delta H_0/g_L(g_L - 1)J(J + 1)$ ratios for the NH$_2$ protons; however, the magnitude of this shift is not sufficient to distort the sinusoidal curve obtained for the CH$_2$ proton shifts as a function of atomic number (Figure 2). The apparent increase in the magnitude of the pseudocontact shift at holmium may result from the lantha-

nide contraction. The effect of the contraction is twofold. It could cause a distortion of the geometry in such a manner as to increase the anisotropy of the g tensor giving rise to a larger pseudocontact shift for the heavier and smaller members of the lanthanide series. In addition the geometric factor could be significantly altered due to a change in coordination geometry. For example, ethylenediamine may preferentially span sites in the square face of a square antiprism for the lighter lanthanides producing pseudocontact shifts of the same sign for the NH$_2$ and CH$_2$ protons. As the radii of the ions get smaller, the preferred coordination geometry could change such that the ethylenediamine molecule spans two sites in a triangular face (Table III). Of course several other geometrical possibilities exist which could cause such a change as a function of ionic radii.

Electron Spin Resonance and Electronic Structures of Vanadyl Bis(maleonitriledithiolene) and Vanadium Tris(maleonitriledithiolene)

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The electron spin resonance spectra of magnetically dilute vanadyl bis(maleonitriledithiolene) and of vanadium tris(maleonitriledithiolene) oriented in single crystals of diamagnetic hosts have been analyzed. The data are interpreted in terms of molecular orbital descriptions of the electronic structures of the complexes. A reassignment of the ground state of vanadium tris(maleonitriledithiolene) is proposed.

Introduction

Recently, there has been considerable interest in complexes in which a transition metal is coordinated by sulfur.^{1} Insofar as the complexes exhibit low-energy d–d transitions, the thioorganic chelating groups can be classified as "weak field" ligands in the crystal field sense. On the other hand, the complexes are often very stable and can undergo a series of one-electron-transfer reactions. Two models have been proposed to explain the properties. Gray and his collaborators^2 preferred a more ionic model in which a metal cation stabilizes a sulfur ligand radical system, while Davison and his collaborators^3 have suggested extensive mixing between the metal d orbitals and the ligand π system. It is clearly of interest to

probe the electronic structures of these complexes in more detail. Apart from the interest from the viewpoint of inorganic chemistry, there is the possibility that coordination of transition metals by sulfur may be important in systems of biological significance, for example, in non-heme iron proteins.

Complexes which have doublet ground states are particularly amenable to study by electron spin resonance, (esr), although the assignment of a ground state on the basis of esr data may not be a trivial operation, particularly if there is a high degree of covalent bonding. In the great majority of cases studied the esr data have been obtained from samples in fluid solutions and in rigid glasses and in the latter situation often indicate axial symmetry in the complex, although the true symmetry is strictly lower. It seemed desirable to study the anisotropies in more detail, and in this paper we present data for two oriented complexes, vanadyl bis(maleonitriledithiolene), VO(mnt)$_2^{2-}$, and vanadium tris(maleonitriledithiolene), V(mnt)$_3^{2-}$. The anisotropies of the g ten-

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