profiles in sufficient detail due to the lack of suitable UV laser lines. We cannot therefore assess quantitatively the importance of *B*-term scattering for the nontotally symmetric modes of these tetraiodide species, although we might reasonably expect it to be small in view of the large separation of the first two excited states.

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Nuclear Magnetic Resonance Studies of Lanthanide Dicarboxylate Complexes in Solution

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^{1}H NMR and ^{13}C shift data were measured for complexes of La(III), Pr(III), Eu(III), and Yb(III) with ethylene-1,2-dioxydiacetate (EDODA), ethylene-1,2-dithiodiacetate (EDSDA), and ethylene-1,2-diaminodiacetate (EDDA). In the EDSDA complexes, the data indicate that the sulfur atoms do not participate in bonding to the lanthanide cations. Both carboxylate groups bind to Pr and Eu, but only a single carboxylate group interacts with Yb. The EDDA and EDODA complexes are tetradentate with long-lived Ln–N bonds in LnEDDA but short-lived Ln–O(ether) bonds in LnEDODA.

Introduction

A thermodynamic study of the complexation of lanthanide cations by ethylene-1,2-dioxydiacetate (EDODA) and the analogous ethylene-1,2-dithiodiacetate (EDSDA) and ethylene-1,2-diaminodiacetate (EDDA) has been reported by Grenthe and Gardhammar.[1] Similar studies were reported from this laboratory for complexing by benzene-1,2-dioxydiacetate (BDODA)[2] The data for BDODA, EDODA, and EDDA were interpreted as reflecting tetradentation by the ligand involving the amino and the ether oxygen donors. However, the thio ligand EDSDA formed weaker complexes which indicated a probable lack of involvement of the thio donors in bonding to the lanthanide cations.

The tetradentation of the BDODA complexes was confirmed by a study of the ^{1}H and ^{13}C nuclear magnetic resonance spectra of the ligand when complexed by the paramagnetic ions Pr(III), Eu(III), and Yb(III).[3] From analysis of the induced shifts, internuclear distances and angles in the complex could be calculated. The ML complex had a planar chelate ring with metal–oxygen distances of 2.2 ± 0.1 Å for both ether oxygen and carboxylate oxygen donors.

In this paper we report on a study of the ^{1}H and ^{13}C NMR spectra of the complexes of EDODA, EDDA, and EDSDA with the same three paramagnetic lanthanides (i.e., Pr, Eu, and Yb). The purpose of the study was to obtain information on the structure of the complexes in solution with particular regard to the question of the participation of the ether oxygen, the nitrogen, and the sulfur atoms in the coordination of the ligands to the metals. Our earlier study of BDODA complexes had shown that the three paramagnetic ions, Pr(III), Eu(III), and Yb(III), were a satisfactory set for obtaining insight into such structural details of complexes in solution.

If we assume axial symmetry, the lanthanide-induced dipolar shift ($\Delta\delta$) can be described by the McConnel–Robertson equation[4,5] (1), where r is the distance between the metal and
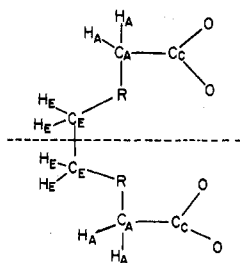
$$\Delta\delta = C(3\cos^2\theta - 1)/r^3 \qquad (1)$$

the nucleus being observed, θ is the angle which the principal magnetic axis makes with a line drawn from the metal to the nucleus, and C is a proportionality constant for a given complex. Obviously, the $\cos^2$ function leads to a zero shift for $\theta = 54°\ 44'$.

A major question in the application of the LIS theory involving eq 1 to calculations of ligand structure involves the requirement of axial symmetry. The details of structure are known for relatively few lanthanide complexes in solution. However, invariance in shift ratios with several lanthanide ions is used as a satisfactory test for axial symmetry.[6,7] Horrocks[8] has discussed the question of the apparent presence of "effective" axial symmetry in solution complexes while Pennington and Cavanaugh have demonstrated the use of the LIS theory even for such flexible, dynamic complexes as those formed by benzoic acids.[9]

In order to use the shifts in the McConnel–Robertson equation, it is necessary also to ascertain that the experimental shifts are purely dipolar or to correct for any contact contribution. This can be achieved usually by using more than one paramagnetic lanthanide ion since the relative contribution of the two mechanisms[10,11] to the observed shift is different for different cations. However, if the lanthanide ions form complexes with the same structure and the shifts are purely dipolar, the shift ratio should be constant irrespective of the particular nucleus measured. In isostructural complexes of Pr(III), Eu(III), and Yb(III), the Pr(III)-induced dipolar shift is of opposite sign from that of the shifts of Eu(III) and Yb(III). In such complexes, the absolute magnitude of the dipolar shifts decreases in the sequence Yb(III) > Pr(III) > Eu(III).

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R = O, S or NH

Figure 1. Labeling scheme for EDRDA ligands.

Table I. Proton and Carbon Shifts for Ethylene-1,2-dioxydiacetic Acid, Ethylenediamine-1,2-diacetic Acid, and Ethylene-1,2-dithiodiacetic Acid[a]

ligand	H_A	H_E	C_C	C_A	C_E
EDODA acid	4.23	3.80	107.6	3.54	1.01
EDDA acid	3.73	3.52	104.1	−17.00	−23.48
EDSDA acid	3.44	2.92	108.1	−33.27	−35.16
Na-EDODA	4.01	3.7	...	...	...
Na-EDDA	3.70	3.51	112.42	−14.55	−19.23
Na-EDSDA	3.25	2.82	112.0	−30.66	−35.09

[a] In ppm downfield from DSS and dioxane for the proton and carbon resonances, respectively.

Experimental Section

Ethylene-1,2-dithiodiacetic acid was prepared by refluxing 1,2-dichloroethane with β-mercaptoacetic acid and sodium hydroxide in 25% aqueous alcohol.[12] The product was isolated by distilling the alcohol, cooling the solution, and acidifying with concentrated HCl. The EDSDA was purified by recrystallization from water.

Ethylene-1,2-dioxydiacetic acid was prepared by oxidation of triethylene glycol with nitric acid at ∼75 °C.[13] Purification of the product was achieved by recrystallization from acetone.

Ethylenediamine-*N,N'*-diacetic acid (La Mont Laboratories) was purified by recrystallization from water.

All solutions were prepared in D_2O. Solutions of lanthanide perchlorates were prepared from corresponding oxides (American Potash and Chemical Corp.) by treatment with analytical grade $HClO_4$. Stock solutions of the ligands were prepared by dissolving the corresponding acids in NaOD. The purity of the ligands was checked by NMR. Samples for NMR measurements of the complexes were prepared by mixing weighted amounts of standardized metal and ligand solutions.

The proton NMR spectra were obtained by using either a Varian A-60 spectrometer or a Bruker HX-270 high-resolution spectrometer. The carbon-13 spectra were recorded on the 270-MHz spectrometer operating at 67.905 MHz. For the ^{13}C spectra the protons were decoupled. The probe temperature was maintained at 25 °C in the proton measurements and in the range 30–35 °C in the carbon measurements. Sodium 4,4-dimethyl-4-silapentanesulfonate (DSS) and dioxane were used as internal standards for the proton and carbon spectra, respectively.

Results

The labeling scheme used in the following discussion is shown in Figure 1. The results of measurement of the proton and carbon resonances of the three ligands in D_2O solutions of their acid and their sodium salt are listed in Table I. All resonances were singlets in these systems. If we compare the data in Table I, we see that the oxygen ligand has the largest downfield shifts while the thio ligand has the largest upfield shifts. Nucleus C_C is an exception to this. The electronegativity of the R group in the acid form $(CH_2RCH_2CO_2H)_2$ is in the same order as the downfield shifts, i.e., O > N > S.

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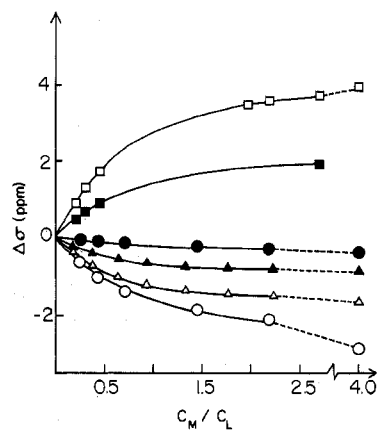(14) P. Letkeman and A. E. Martell, *Inorg. Chem.*, **18**, 1284 (1979).

Figure 2. Proton shifts induced in EDSDA by Pr(III), Eu(III), and Yb(III) as a function of the C_M:C_L ratios: Pr(III), □ and ■; Eu(III), △ and ▲; Yb, ○ and ●; H_E, ■, ▲, and ●; H_A, □, △, and ○.

Table II. Limiting Shifts for the Complex ML_i in the Complex Formation of Ethylene-1,2-dioxydiacetate, Ethylene-1,2-dithiodiacetate, and Ethylenediaminediacetate with La^{3+}, Pr^{3+}, Eu^{3+}, and Yb^{3+} [a]

	H_A	H_E	C_C	C_A	C_E
[LaEDODA]⁺	...	...	...	...	...
[PrEDODA]⁺	5.64	−16.16	22.2	18.4	−33.5
[EuEDODA]⁺	−4.38	9.37	−17.2	−13.1	20.7
[YbEDODA]⁺	...	27.5	...	−29.7	...
[LaEDSDA]⁺	0.02	0.04	...	...	...
[PrEDSDA]⁺	3.90	2.00	...	...	...
[EuEDSDA]⁺	−1.67	−0.87	43	−38.7	−1.3
[YbEDSDA]⁺	−2.41	−0.37	...	...	...
[LaEDDA]⁺	0.03	0.02	...	...	...
[Yb(EDDA)₂]⁻	−4.8	−17.1	...	...	...
	−13.8	−21.6			

[a] Shifts in ppm; positive values represent downfield shifts.

In the range pH 4–5 of the sodium salt solutions, EDDA exists as H_2L with both nitrogen atoms protonated. Since the protonation of the nitrogen atoms affects the ^1H and ^{13}C shifts more than protonation of carboxylate groups does,[14] we observe similar shifts for acid and the sodium salt solutions of EDDA.

Figure 2 shows the proton shifts induced by Pr(III), Eu(III), and Yb(III) in EDSDA as a function of C_M:C_L ratios. In this case the solutions were all at pH 4 while the total ligand concentration varied in the range 0.03–0.07 M. Similarly, spectra of solutions of constant pH and varying C_M:C_L ratios were measured for the three ligands with each metal ion. Problems of solubility, multiplicity of solution species, etc. placed limits on the spectra which could be measured and on the extent of their analysis. Stability constants were used to calculate the concentrations of M, ML, and/or ML_2 species at each M:L ratio. From the variation of net shift with the M:ML_i ratios, limiting shifts for ML_i could be ascertained. For EDODA and EDSDA, these limiting shifts could be determined for the 1:1 complex while, for EDDA, that of the 1:2 complex was obtained. The limiting shifts calculated are listed in Table II.

The observation of single, sharp peaks in the solutions of EDSDA and EDODA in which only Ln^{3+} and LnL^+ species were present reflects fast exchange of the ligand on the NMR time scale. Peaks in the EDODA systems were broader than in the EDSDA solutions, indicating faster exchange in the EDSDA complexes.

The ratios between the Eu(III)- and Pr(III)-induced shifts in the EDSDA complexes are −0.43 and −0.44 for both the H_A and H_E protons, respectively. This provides good evidence that these shifts can be treated as purely dipolar. However, the ratios of the Yb(III) to Pr(III) shifts are −0.6 (H_A) and

−0.2 (H_E). The sequence of absolute magnitude of shifts is Pr > Yb > Eu which may reflect contact contributions to the Yb shifts and/or a lack of structural identity between YbL and the analogous Pr(III) and Eu(III) complexes. However, for the EDODA complexes, the average of the ratio of the Eu(III)-, Pr(III)-, and Yb(III)-induced shifts for each nucleus observed is 0.7:−1:1.7. (The shift values are scaled by setting the Pr(III)-induced shifts equal to −1.) The constancy of the ratios and the order of the absolute magnitudes are consistent with essentially completely dipolar nature of all the shifts.

In the EDDA solutions, the ratio $C_M:C_L$ was always less than 0.5 (pH 7–8). The result was that the metal ion was present always as the ML_2 complex. The complexes studied gave quite different results. For the Yb(III) system well-resolved spectra were obtained showing separate peaks for protons in the free and in the complexed ligand, indicating slow ligand exchange relative to the NMR time scale. In addition to the two singlet resonances observed in the free ligand, four resonances of equal intensity were seen in the spectra of the Yb(III) complex. Two broader, more upfield resonances (at 13.60 and 18.08 ppm upfield from DSS, respectively) were assigned to the H_E protons and two sharper resonances (at 1.14 and 10.10 ppm) to the H_A protons. For the Eu–EDDA solutions at low $C_M:C_L$ ratios (<0.1), separate peaks could be observed for the protons in the free ligand and for those in the complexed ligand, with those for the complex being quite broad. All proton resonances in the complex were in the range 2–8 ppm upfield from DSS, but the width prevented precise location. No proton resonances could be observed for the Pr(III)–EDDA solutions. An addition of a very small amount of Pr(III) to a ligand solution caused a disappearance of the two resonances, showing that the rate of ligand exchange in the Pr(III) complex is fast. For ML_2, the rate of ligand exchange must increase in the sequence Yb(III) < Eu(III) < Pr(III). This is consistent with the results of Grenthe and Gardhammar,[1] which showed that the stability of the lanthanide complexes with EDDA increases markedly with increasing atomic number of the lanthanide ion.

Discussion

The nonrigidity of the ligands and the relatively few nuclei observed in the spectra limit the information which can be deduced about the geometric structures of the complexes. The two proton shifts measured for the EDSDA and EDDA systems allow only qualitative discussion of those complexes. The metal ion can, in principle, be coordinated to these ligands in several ways which give rise to different shift patterns. For example, (i) if the metal is coordinated to the R groups as well as to the carboxylate groups (tetradentation), the shifts of nuclei H_E and C_E should be large and/or should be in the direction opposite from that of the shifts of nuclei H_A, C_A, and C_C (on the assumption that the "effective" magnetic axis is along the dotted line in Figure 1). Alternately, (ii) the metal ion may be coordinated to the ligand through only the two carboxylate groups. In such a complex, the shift of H_A would be in the same direction as that of H_E and the ratio of the magnitude of the two shifts would be larger than in the first case. Finally, (iii) we can consider the case where the metal ion is coordinated to only one carboxylate group. Then the shift of H_A should be much larger than that of H_E. The magnitude of the shifts is expected to decrease for these three possibilities in the order (i) > (ii) > (iii) due to the increase of metal–proton and metal–carbon distances.

For the EDSDA complexes, the shifts are small with that of H_A in the same direction but larger than that of H_E. This

leads us to conclude that the sulfur atoms do not participate in the bonding to the lanthanide ions. The same conclusion had been deduced from the thermodynamic data.[1,2] A further conclusion can be reached from the observations that the two Yb(III)-induced shifts are much smaller than would be expected from the Pr(III)- and Eu(III)-induced shifts while the difference between the H_A and H_E shifts is much larger for YbL than it is for PrL and EuL. These differences are consistent with a structural change in the YbL complex compared to the case of the PrL and EnL complexes. More specifically, the shifts suggest that in the complexes with the larger ions, Pr(III) and Eu(III), both carboxylate groups of the ligand are at least partly coordinated to the metal while in the complex with Yb(III) only one of the carboxylate groups is coordinated. The entropies of complexation[1] provide some support for such a change in the coordination. The difference in the ΔS of formation between the ML complexes of the light and of the heavy lanthanides is about 40 J K^{-1} mol^{-1} for EDODA and EDDA but only about half of that for EDSDA. Grenthe and Gardhammar concluded from the small stability constants that EDSDA is bonded by only a singlet carboxylate group throughout the lanthanide series. However, the NMR data suggest a model of weak interaction between lanthanide and both carboxylates of the ligand in the light lanthanides and interaction with only one carboxylate in the heavier lanthanides.

For the EDODA complexes, the magnitude and relative signs of the shifts (e.g., H_E and C_E in opposite direction from H_A, C_A, and C_C) are evidence for bonding by the lanthanides to the ether oxygens as well as to the carboxylate groups. The related benzenedioxydiacetate complexes were found to have the ether oxygens bonded to the lanthanide cations.[3] Grenthe and Gardhammar[1] also concluded from their thermodynamic data that the ether oxygens in EDODA were bonding to the lanthanides.

For the 1:2 EDDA complexes, the slow ligand exchange as well as the magnitude of the shifts observed in the Yb(III) system strongly suggests that the metal is coordinated to the amino as well as to the carboxylate groups of the ligand. In this case, the H_E resonances should show larger shifts than the H_A resonances. This has led us to assign the resonances at 18.08 and 13.60 ppm upfield from DSS to H_E protons while the two at 1.14 and 10.10 ppm are assigned to H_A protons. The observance of resonance doublets for these protons is related to a relatively long lifetime for the metal–nitrogen bonds compared to that for the metal–carboxylate bonds.[15] The observance of only singlets for H_A and H_E resonances in Ln–EDODA complexes means that the lanthanide–ether oxygen bond is shorter lived than the lanthanide–nitrogen bond in the Ln(EDDA)$_2$ complexes. The formation of Ln(EDDA)$_2^-$ which involves tetradentation implies a coordination number of 8 for the lanthanides. CN = 8 has been shown to exist in the Ln(BDODA)$_2^-$ complexes, and CN = 8 and possibly even >8 has been implied from many other studies of lanthanide complexes.

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