portunity to transfer fluorine to the chromium before dissociating. In this way we can rationalize the high reactivity of CrN_3^{2+} with fluorine as well as the formation of CrF^{2+} as the major reaction product.

To form $CrNO^{2+}$ from CrN_3^{2+}, it is necessary for the nitrogen bound to the chromium to add what is formally a neutral oxygen atom

$$CrN_3^{2+} + [O] \rightarrow CrNO^{2+} + N_2$$

The process is formally similar to the addition of an oxygen atom to water to form hydrogen peroxide. NMR studies of HOF suggest that the molecule may have a charge distribution approximating $^{1/2+}H\cdots O\cdots F^{1/2-}$.[16] Hence, its oxygen atom is already neutral, whereas the oxygen atom in OF_2 is probably positive, and the oxygen atoms in HNO_2 and HOCl are almost certainly negative. Furthermore, microwave spectroscopy has shown the H–O–F bond angle to be an unusually acute 97°,[17] which gives the molecule a geometric configuration that should be especially favorable to the transfer of an oxygen atom with formation of HF. The corresponding bond angles in OF_2 and HOCl are both around 103°.[18,19] Finally, the large bond energy of HF makes the reaction

$$HOF \rightarrow HF + O$$

much less endoergic than the analogous reactions of HOCl and OF_2, and should make it much easier for HOF to transfer an oxygen atom. All three of these factors probably contribute to making hypofluorous acid a remarkably effective oxygen atom donor, and they can account for the ease with which HOF transfers O to H_2O to form H_2O_2 and to CrN_3^{2+} to form $CrNO^{2+}$.

It is interesting that reactions 8 and 9 become competitive with reactions 2 and 1, respectively, at about the same concentration of CrN_3^{2+}. This means that the *relative* reactivities of CrN_3^{2+} and H_2O are about the same toward F_2 as they are toward HOF.

We see from Table I that Rh^{3+}, like Cr^{3+}, is unreactive toward F_2 and HOF. Experiments with RhN_3^{2+} similar to those with CrN_3^{2+} reported here might prove interesting, although the synthesis of the rhodium azido complex has never been reported.

All in all, the work that we have reported provides a fairly consistent picture of the interaction of fluorine and HOF with aqueous solutions. Much of the chemistry that takes place when fluorine is introduced into an aqueous solution probably can be attributed to HOF. However, many reducing agents are able to react directly with F_2, and in favorable cases the direct reaction can lead to a product that may be distinguished from the product of the reaction with HOF.

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Registry No. F_2, 16984-48-8; HOF, 14034-79-8; $(H_2O)_5CrClO_3^{2+}$, 54566-83-5; $(H_2O)_5CrNO^{2+}$, 14951-34-9; $(H_2O)_5CrCl^{2+}$, 14404-08-1; $(H_2O)_5CrBr^{2+}$, 26025-60-5; $(H_2O)_5CrN_3^{2+}$, 18517-09-4; OF_2, 7783-41-7; HOCl, 7790-92-3; H_2SO_5, 7722-86-3.

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Nuclear Magnetic Resonance Study of the Structure in Solution of Lanthanide Complexes with Benzene-1,2-dioxydiacetate

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The induced shifts of ^1H and ^{13}C nuclei in the ligand benzene-1,2-dioxydiacetate complexed by Pr^{3+}, Eu^{3+}, and Yb^{3+} have been measured. From the ratios of the shifts, the relative extent of contact and dipolar contributions to the shifts has been estimated. The dipolar shifts were used with the McConnell–Robertson equation to calculate the internuclear distances and angles of 1:1 and 1:2 complexes.

Introduction

The application of lanthanide chelates as shift reagents in the NMR spectra of organic molecules is well established as a useful tool for investigating structural features of complex molecules.[1-4] Providing the observed shifts are dipolar the lanthanide shift data have the potential for quantitative structure determination. Unfortunately, the observed shifts are often composed of a mixture of dipolar and contact shifts, but by using more than one lanthanide ion, the contact contribution can be estimated.[5-7] Pr(III), Eu(III), and Yb(III) provide a satisfactory trio of paramagnetic ions as (a) they span the lanthanide series, (b) they induce relatively little line broadening (because of a combination of short electron-spin relaxation times and moderate magnetic anisotropies), (c) they give rise to shifts with different relative amounts of contact contribution, and (d) Pr(III) causes shifts in the opposite direction from those induced by Eu(III) and Yb(III).

The observed lanthanide induced shift is not only a function of the geometry of the complex but also of its concentration and stoichiometry. By studying how the induced shifts vary with the metal:ligand ratio, we can determine the stability constants of the complexes present. In systems where stability constants are known from potentiometric titration, comparisons can serve as a check on the NMR analysis.

A study of the thermodynamics of complexation between lanthanide cations and benzene-1,2-dioxydiacetate has indicated that the ether oxygens are involved in the tetradentate chelation.[8] The symmetry and the rigidity as well as the number of different protons and carbons made this a promising complex to study by NMR.

Experimental Section

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 $HClO_4$. Concentrations were determined by EDTA titrations using xylenol orange as the end-point indicator. A stock solution of sodium benzene-1,2-dioxydiacetate was prepared by dissolving the corresponding acid (Aldrich Chemical) in NaOD. Samples for NMR measurements were prepared by mixing weighted amounts of standardized metal and ligand solutions. The pD of the prepared samples were in the range 4.0–4.5.

The proton NMR spectra were obtained by using either a Bruker HX-90 or a Bruker HX-270 high-resolution spectrometer both equipped with Nicolet Fourier transform computer. 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. In the proton measurements the probe temperature was maintained at 25 °C, while, due to the decoupling, the temperature in the carbon measurements was a little higher, generally in the range 32–36 °C. Sodium 2,2-dimethyl-2-silapentanesulfonate (DSS) and dioxane (~0.5%) were used as internal standards for the proton and carbon spectra, respectively.

Data Analysis

In the NMR spectra, only single resonances were observed for the analogous protons and carbon atoms indicating rapid exchange between free and complexed ligand. The thermodynamic study[8] had indicated the formation of ML and ML_2 complexes for the conditions of our experiments. Accordingly, the observed isotropic shifts relative to that of the free ligand are given by

$$\Delta\delta_{\text{obsd}} = \Delta\delta_{\text{M1}}\frac{[\text{ML}]}{C_\text{L}} + \Delta\delta_{\text{M2}}\frac{2[\text{ML}_2]}{C_\text{L}} \qquad (1)$$

where C_L is the total ligand concentration and [ML], $\Delta\delta_{M1}$ and $[ML_2]$, $\Delta\delta_{M2}$ are respectively the equilibrium concentrations and limiting shifts of the first and second complex.

The equilibrium constants and the limiting shifts have been calculated by a least-squares computer program (a modification of program PSCNT[9]) which minimizes the error square sum

$$U(K_\text{i}, \Delta\delta_\text{i}) = \Sigma(\Delta\delta_{\text{obsd}} - \Delta\delta_{\text{calcd}})^2 \qquad (2)$$

The input data are the values of $\Delta\delta_{obsd}$, the total concentrations of metal and ligand, and initial guesses of the equilibrium constants, K_i, and the limiting shifts, $\Delta\delta_i$.

Provided that the dipolar limiting shifts of the complexes are known and the complexes have effective axial symmetry, the McConnell–Robertson equation[10-12] can be used to obtain structural information. The equation is

$$\Delta\delta_\text{i} = C(3\cos^2\theta - 1)/r^3 \qquad (3)$$

where C is a constant for a given lanthanide and temperature, r is the distance of the nucleus i from the metal ion, and θ the angle between $\vec{r}$ and the principal magnetic symmetry axis. Note that a zero shift will be obtained for $\theta = 54° 44'$. This equation can give information on the geometry of the complex from the ratio of the shifts for different nuclei. In order to orient a ligand with a known geometry to a lanthanide, at least six limiting shifts have generally to be known as it takes three polar coordinates to fix the position of the lanthanide ion, two additional angles to define the main magnetic axis orientation, and one signed value for the proportionality constant in eq 3. If the number of limiting shifts determined is larger than six, additional information on the structure of the complex may be obtained. The calculations were performed for the lanthanide ions placed systematically in different positions. At each lanthanide position the variable term $(3\cos^2\theta - 1)/r^3$ was evaluated for all i protons and carbon atoms. This set of numbers was then scaled by least squares against the observed shifts $\Delta\delta_{oi}$ to yield a set of calculated shifts $\Delta\delta_{ci}$. In order to assess the correspondence between the observed and calculated values an agreement factor R was calculated as

$$R = [\sum_\text{i} w_\text{i}(\Delta\delta_{\text{oi}} - \Delta\delta_{\text{ci}})^2]^{1/2}$$

where the weighting factor, w_i, was chosen as 1 or $1/\Delta\delta_{oi}$ (vide infra). The position of the lanthanide ion giving the lowest R factor was taken as the "best" one. The structural calculations were made by the computer program MOLMEC.[13]

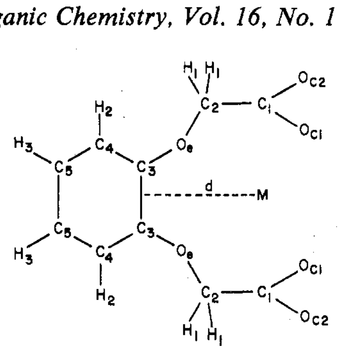

Figure 1. The numbering system for the benzene-1,2-dioxydiacetate.

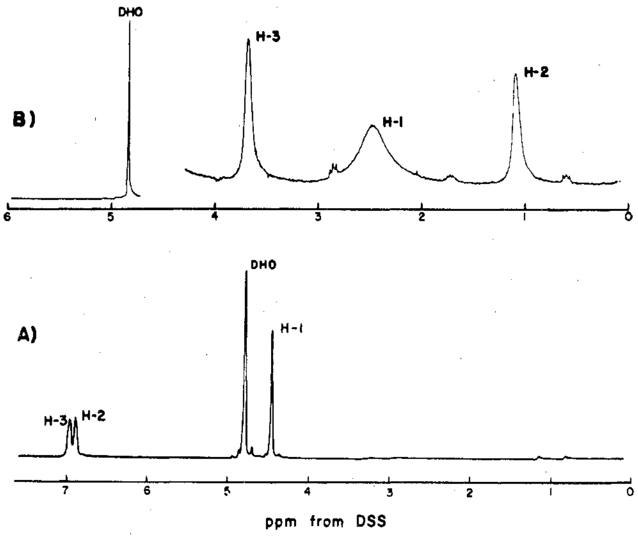

Figure 2. The ^1H NMR spectrum of (A) the free benzene-1,2-dioxydiacetate ligand and (B) the ligand in the presence of Pr(III) when $C_M/C_L = 0.5$. The resonances are relative to DSS standard.

Results and Discussion

In the following discussion we use the numbering scheme of Figure 1.

Proton Spectra. Three proton resonances are observed for the benzene-1,2-dioxydiacetate anion in solution (Figure 2a) corresponding to the proton pairs labeled H_1, H_2, and H_3. H_2 and H_3 are partly resolved doublets with H_3 slightly more downfield. Addition of La^{3+} caused small downfield shifts

Table I. Log K_2 Values Obtained from Proton Shifts for the Formation of Benzene-1,2-dioxydiacetate Complexes of Pr^{3+}, Eu^{3+}, and Yb^{3+}

		No. of obsn	Δ,[a] ppm	Log K_2[b]
Pr	H_1	16	0.12	2.99 ± 0.14
	H_2	17	0.07	2.99 ± 0.15
	H_3	21	0.08	3.00 ± 0.15
Eu	H_1	12	0.04	2.68 ± 0.17
	H_2	12	0.04	2.66 ± 0.20
	H_3	12	0.03	2.72 ± 0.21
Yb	H_1	23	0.09	1.84 ± 0.08

[a] Δ = average value of the differences ($\Delta\delta_{obsd} - \Delta\delta_{calcd}$). [b] 95% confidence limits. [c] $K_2 = [ML_2]/[ML][L]$.

while the paramagnetic lanthanide ions Pr^{3+}, Eu^{3+}, and Yb^{3+} gave sizable shifts downfield as well as upfield. The spin doublets of H_2 and H_3 collapsed in the lanthanide solutions. The shifts induced by Pr^{3+}, Eu^{3+}, and Yb^{3+} are presented in Figure 3.

The resonances were generally sharper in solutions containing mainly only one ligand species than in solutions containing a mixture of different ligand species. For the Eu^{3+} system all three proton resonances of the ligand gave fairly sharp peaks over the whole C_M/C_L range studied. For the Pr^{3+} system the H_3 peak was sharp for all solutions used while the H_1 resonance, narrow at low C_M/C_L ratios, broadened considerably at $C_M/C_L > 0.5$. The reverse holds for the H_2 resonance which was not observable at low C_M/C_L ratios. For the Yb^{3+} system the H_1 peak was present in the spectra of all solutions although the peak was broad in the range $0.2 < C_M/C_L < 0.9$. In this range the H_2 and H_3 resonances disappeared completely due to line broadening.

Attempts to calculate K_1 and K_2 gave large uncertainties so we used the K_1 values from ref 8 and calculated values of K_2 (Table I) and of the limiting shifts (Table II) using a model of 1:1 and 1:2 complexation. The average of the differences between observed and calculated shifts was in no case larger than 0.12 ppm. The values of K_2 agree satisfactorily with those determined by potentiometry.[8]

Carbon-13 Spectra. Figure 4 gives the ^{13}C spectrum of the free ligand, showing five peaks. The calculated limiting shift values for ^{13}C are given in Table II. The shift values for the first complex were obtained from spectra of solutions with high C_M/C_L ratios (>2) in which range all the ligand exists as ML. Limiting shifts for the ML_2 complex were obtained from spectra of solutions with $0 < C_M/C_L < 0.4$. The C_1 and C_3 resonances exhibited lower intensity due to longer relaxation times. With the addition of La^{3+}, these two resonances gave upfield shifts and the C_2, C_4, and C_5 resonances gave downfield shifts which agreed with prediction.[14,15] A measurement of precise limiting shifts for the second complex in the Yb^{3+} system turned out to be impossible due to line broadening which also reduced the accuracy of determination of the limiting shifts for the C_1 and C_3 resonances of the YbL

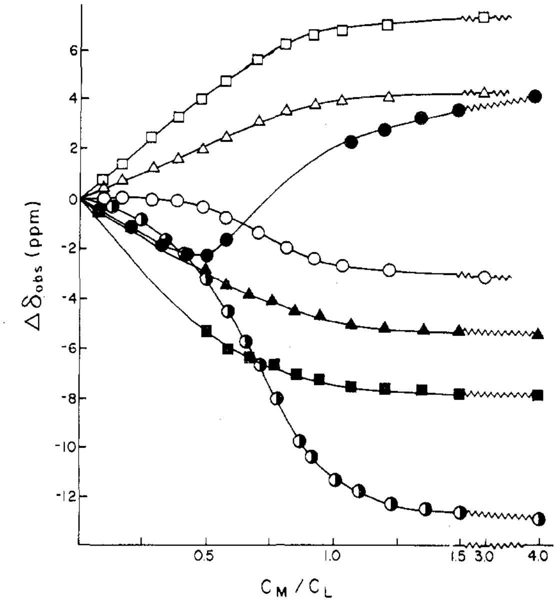

Figure 3. The paramagnetic induced shifts for the protons of benzene-1,2-dioxydiacetate; the total metal and ligand concentrations were in the range 0.03–0.15 M. Shifts for the H_1 resonances are given by circles, H_2 by squares and H_3 by triangles. Eu(III) shifts are given by ○, □, △; Pr(III) shifts by ●, □, ▲; and Yb(III) shifts by ◑.

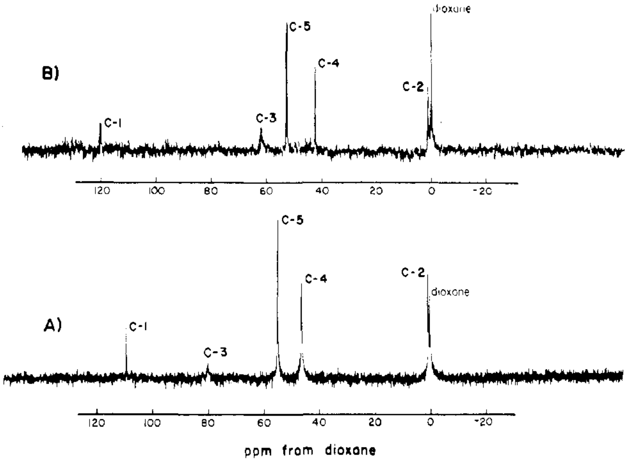

Figure 4. The carbon-13 spectrum of (A) the free benzene-1,2-dioxydiacetate ligand and (B) the ligand in the presence of Pr(III) when $C_M/C_L = 0.5$. The resonances are relative to dioxane standard.

Table II. Limiting Shifts for the First and Second Benzene-1,2-dioxydiacetate Complexes of La^{3+} Pr^{3+}, Eu^{3+}, and Yb^{3+}[a-c]

	H_1	H_2	H_3	C_1	C_2	C_3	C_4	C_5
				First Complex				
La	0.29	0.27	0.21	−0.60	3.05	−1.91	0.92	1.91
Pr	4.08	−7.91	−5.57	39.0	14.8	−38.7	−10.08	−6.92
Eu	−3.22	7.28	4.26	−26.2	−12.4	18.0	5.45	7.58
Yb	−12.92	21.16	15.67	−154	−32.1	102.1	35.6	29.0
				Second Complex				
La	0.28	0.26	0.20	−0.80	2.80	−1.84	0.79	1.83
Pr	−3.09	−5.83	−3.03	13.9	0.65	−26.3	−6.08	−3.60
Eu	0.01	4.45	2.16	−18.0	−5.50	10.0	2.97	5.08
Yb	0.36						27.2	19.9

[a] The free ligand (deprotonated) exhibited proton resonances at 4.50, 6.92, and 6.97 ppm (downfield from DSS) and carbon resonances at 109.60, 0.60, 80.24, 46.36, and 55.07 ppm (downfield from dioxane) for H_1-H_3 and C_1-C_5, respectively. The limiting shifts are given relative to these resonances (shifts in ppm). [b] Positive values = downfield shifts. [c] The errors of the shifts are generally less than 0.1 ppm or 2% (see also text).

Table III. Corrected Limiting Shifts, $\Delta\delta^*$, for the First and Second Benzene-1,2-dioxydiacetate Complexes of Pr^{3+}, Eu^{3+}, and Yb^{3+} [a]

	H_1	H_2	H_3	C_1	C_2	C_3	C_4	C_5
				First Complex				
Pr	3.79	−8.18	−5.78	39.6	11.8	−36.8	−11.00	−8.83
Eu	−3.51	7.01	4.05	−25.6	−15.5	19.9	4.53	5.67
Yb	−13.21	20.89	15.46	−153	−35.1	104.0	34.7	27.1
				Second Complex				
Pr	−3.37	−6.09	−3.23	14.7	−2.15	−24.5	−6.87	−5.43
Eu	−0.27	4.19	1.96	−17.2	−8.30	11.8	2.18	3.25
Yb	0.08						(26.4)	(18.1)

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

complex. In the Pr^{3+} and Eu^{3+} systems there was a moderate line broadening, which, however, did not significantly reduce the precision of the shift values determined.

Determination of Geometry. The diamagnetic contribution to the limiting shifts introduced by the paramagnetic lanthanide ions was determined by using the diamagnetic complexes of La(III) recorded in Table II. The similarity in the shifts of the LaL and LaL_2 complexes indicates that the geometry of the ligands in the two complexes is very similar. The corrected paramagnetic lanthanide induced shifts, $\Delta\delta^*$, are given in Table III and were used in the structure calculations.

In order to use the limiting shifts in the McConnell–Robertson equation, it is necessary to ascertain that the experimental shifts are purely dipolar or to correct them for contact contributions. The proton shifts induced by paramagnetic lanthanides are usually entirely dipolar[1,16] while for carbon shifts, the contact mechanism is often more important.[2,17] The different lanthanide ions induce different relative contributions of the two mechanisms.[18,19] The contact shift contribution is expected to be smallest for Yb^{3+}, about 2.5 times larger for Pr^{3+}, and slightly over 20 times larger for Eu^{3+}.[7,20] Providing Pr^{3+}, Eu^{3+}, and Yb^{3+} form complexes with the same structure, which is likely, the shift ratio should be constant irrespective of the particular nucleus measured if the shifts were purely dipolar. If, however, a nucleus has a significant contact interaction, the ratio of the shifts for that nucleus will be different, with the Eu^{3+} shift value the most sensitive. The differences in radii of the three cations can lead to small variations in bond distances and angles. Small changes of the angle θ in the range $50° < \theta < 60°$ produce pronounced effects on the induced chemical shifts.[1] Since H_1 and C_2 values of θ in this critical range (vide infra), these two nuclei are unreliable probes for contact/dipolar analysis and are not considered. As we see from Table III, for the other nuclei the average of the ratio of the limiting shifts of the Eu^{3+}, Pr^{3+}, and Yb^{3+} systems is 0.68:−1:2.86 and 0.6:−1:3.6 for the first and second complex, respectively (the shift values scaled by setting the Pr^{3+} induced shifts = −1). It is only the Eu^{3+} induced C_4 shifts that markedly deviate in the shift ratios. (The two deviating carbon shifts are not included in the calculation of the average shift ratios given above.) Thus it can be concluded that the dipolar interaction is dominant for all nuclei and an analysis of the shift ratios shows that the contact shift terms for Pr^{3+} and Yb^{3+} do not in any case exceed some 10% of the total shift. These shifts therefore can be used with confidence for structural calculations.

The observed shifts show that the lanthanide benzene-1,2-dioxydiacetate complexes have C_2 symmetry as the same shift was obtained for the pairs of analogous atoms such as C_1, etc. We therefore located the lanthanide ion in the symmetry plane which allowed two parameters, one angle for locating the metal ion, and one angle for the magnetic axis, to be kept constant throughout the calculations. As the temperature in the carbon measurements was a little higher than in the proton measurements, we have chosen to use different values for the *C* parameter in eq 3 for the two different nuclei.[21] For each complex the proton *C* parameter was generally found to be 5–15% larger than the corresponding carbon parameter, which is expected from the temperature differences.

From this discussion and that in the Data Analysis section, we see that we have nine adjustable parameters—the three angles above and the six parameters relating to the polar coordinates, the magnetic axis, and the proportionality constant. There might seem to be a problem since we have only eight observables (Table III). However, due to the symmetry of the ligand, the eight shifts correspond to two nuclei each so Table III records 16 observations.

The ligand consists of a benzene ring with a rigid framework and two flexible oxyacetate groups. Bond distances and bond angles in the benzene-1,2-dioxydiacetate for the structure calculations were taken from standard data[22] and/or from ref 23. An approximate location of the lanthanide ion relative to the benzene ring was determined by using the shifts of the protons and carbons in the benzene ring. When the shifts of the nuclei in the oxyacetate groups were included a variation of the values of the angles C_4–C_3–O_e, C_3–O_e–C_2, and O_e–C_2–C_1 was performed.

First Complex. All the shifts of Pr^{3+} and Yb^{3+} were used in the structure calculations but for Eu^{3+} only the proton shifts were employed since the contact interaction for the carbon shifts is nonnegligible. The calculations showed that the lanthanide ions are located in the plane of the ligand with the fits between observed and calculated shifts dependent on the values of the angles C_4–C_3–O_e, C_3–O_e–C_2, and O_e–C_2–C_1. From contour maps of the error square sum vs. the angles C_4–C_3–O_e and C_3–O_e–C_2, the combination of these two angles giving the "best" fit was obtained. For Pr^{3+} and Yb^{3+} this was followed by a variation of the value of the angle O_e–C_2–C_1. Table IV lists the results for sets of angles giving the "best" fits. The accuracy of the distances and bond angles in Table IV is estimated to be within 0.05–0.10 Å and 3–4°, respectively.[24]

The errors in bond distances and angles of the benzene-1,2-dioxydiacetate ligand were not considered in the estimate of errors of distances and angles in the complexes. The bond distances in the ligand obtained from literature sources are certainly very accurate as are the angles in the benzene ring. No other assumptions of the ligand structure were made as the bond angles of the oxyacetate groups were determined from the shift data. Thus the errors given (estimated from the fit of the shift data) should roughly correspond to the total errors.

The values of the angle C_4–C_3–O_e found in this study are very much the same as the value, 125°, found for potassium benzene-1,2-dioxydiacetate.[23] For the angle C_3–O_e–C_2, on the other hand, the lanthanide values are considerably higher than the value, 118°, found in the potassium salt structure. Some representative metal–ligand atom distances, calculated from the data sets giving the "best" fits, are given in Table V. In order to determine the metal–carboxyl oxygen bond distances the orientation of the carboxyl groups have to be known. In

Table IV. Parameters Giving "Best" Fits and Corresponding Differences between Observed and Calculated Shifts[a]

	PrL	EuL	YbL	PrL_2	EuL_2
d, Å	3.00	2.95	2.92	3.65	3.45
$\angle C_4-C_3-O_e$, deg	124	125	125	128	130
$\angle C_3-O_e-C_2$, deg	133	130	134	113	125
$\angle O_e-C_2-C_1$, deg	105	109[b]	105	109	109[b]
	% error	% error	% error	% error	Abs error, ppm
H_1				3.5	0.01
H_1	3	−2	−0.5	3.5	0.01
H_2	0.5	8.5	−2	5.5	0.28
H_3	5	−5.5	7	−10.5	−0.52
C_1	5		(36)[c]	11	
C_2	7		2.5	(−52)[d]	
C_3	−7		−14	10	
C_4	−10.5		−3	−20	
C_5	15		19	5	

[a] Errors given are either relative errors, $100(\Delta\delta_{obsd} - \Delta\delta_{calcd})/\Delta\delta_{obsd}$, or absolute errors, $(\Delta\delta_{obsd} - \Delta\delta_{calcd})$. [b] Not varied. [c] Value in parentheses was omitted due to large experimental uncertainty. [d] Value in parentheses was omitted due to the small magnitude of the shift.

Table V. Selected Distances in the Lanthanide-Benzene-1,2-dioxydiacetate Complexes, Calculated from the Data Sets Giving the "Best" Fits. $M-O_c$ Distances Are Given for Various Torsion Angles of the Carboxyl Groups around the C_1-C_2 Axis

	PrL	EuL	YbL	PrL_2	EuL_2
$M-O_e$, Å	2.20	2.15	2.10	2.65	2.45
$-H_1$	3.70			4.25	
$-H_2$	4.90			5.45	
$-H_3$	6.45			7.10	
$-C_1$	2.60			3.15	
$-C_2$	3.00			3.55	
$-C_3$	3.10			3.70	
$-C_4$	4.45			5.05	
$-C_5$	5.45			6.10	

		Torsion of the carboxyl group[a]				
		0°	20°	45°	60°	90°
PrL	$M-O_{C_1}$	1.70	1.80	2.10	2.35	2.90
	O_{C_2}	3.80	3.75	3.55	3.40	2.90
PrL_2	$M-O_{C_1}$	2.30	2.40	2.70	2.95	3.50
	O_{C_2}	4.40	4.35	4.15	4.00	3.50

[a] The torsion angle = 0° when the oxygen atoms are in the ligand plane.

potassium benzene-1,2-dioxydiacetate the two carboxyl oxygen atoms are approximately in the same plane as the rest of the ligand. The same orientation is less likely to occur in the lanthanide complexes as it gives unreasonably short $M-O_{C1}$ distances (~1.7 Å)(vide infra). However, a rotation of the carboxylic groups around the C_1-C_2 axis is probable and metal–carboxyl oxygen distances for some selected torsional angles are listed in Table V. A compilation[25] of structures of lanthanide complexes shows that in carboxylate complexes with both coordinated ether and carboxyl oxygen atoms the two different lanthanide oxygen distances are similar although the lanthanide–carboxyl oxygen distance is generally the shorter one. A 45° rotation of the carboxyl groups from the plane gives $M-O_{C1}$ bond distances of the same magnitude as the metal–ether oxygen distances (Table V). The $M-O_c$ distances also depend on the values of the three angles determined. As each of these values has an uncertainty of 3–4°, the $M-O_c$ distances cannot be determined as accurately as the other distances. Lanthanide oxygen bond distances in solid compounds are generally in the range 2.45 ± 0.3 Å with higher coordination numbers resulting in longer distances.

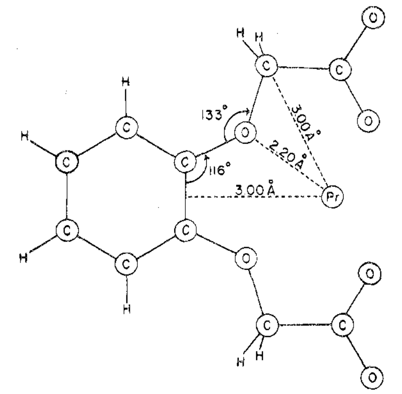

Figure 5. The structure of the ML complex. Angles and distances given refer to the Pr(III) complex.

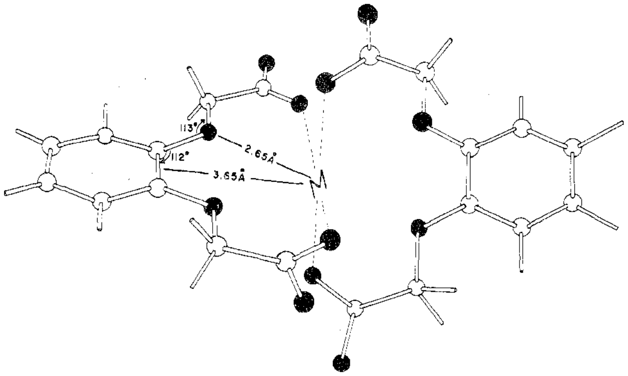

Figure 6. The structure of the ML_2 complex. Angles and distances given refer to the Pr(III) complex.

The data in Table V indicate strongly that the ether oxygens are bonded to the lanthanide ions. The $M-O_e$ distances found are relatively short which is to be expected as the ligand occupies only four of the available coordination sites, the rest being occupied by H_2O. Also, it is likely that, for ionic compounds, bond distances in solution are shorter than in solids. Figure 5 shows the structure of the ML complex.

Second Complex. Structure calculations were made for the Pr^{3+} complex, where all shifts were employed, and for the Eu^{3+} complex where only the proton shifts were used. The two ligands give rise to the same shifts which could result from both ligands having the same structure relative to the metal, from rapid exchange or from rapid conformational changes. The following discussion is not dependent on which of these is the basis of the identity of the shifts for both ligands in ML_2. The least-squares calculations showed that the lanthanide ion is located in the plane of each of the two ligands. From contour maps of the error square sum vs. the angles $C_4-C_3-O_e$ and $C_3-O_e-C_2$ the "best" fits in Table IV were obtained. The errors in the d distance and the bond angles are estimated to be much the same as those for the first complex.[24]

Table V lists some selected interatomic distances in the Pr^{3+} complex calculated from the set of data giving the "best" fit. Metal–carboxyl oxygen distances have been calculated for various torsional angles of the carboxyl groups. The results indicate that the carboxyl oxygens are in the same plane as the rest of the ligand since reasonable $M-O_{C1}$ bond distances are obtained with this orientation. Figure 6 shows the ML_2 complex.

The metal–ether oxygen distances are considerably longer in the second complex than in the first but the distances do not exclude bonding through the ether oxygens in ML_2 although the bonding should be weaker.

The lanthanide ions are located in the plane of each of the two ligands but the shift data do not give information on the angle between the ligand planes. It seems probable that the planes are perpendicular as this minimizes the mutual repulsion.

The structure of ML_2 exhibits two striking differences from that of ML in the longer bond distances and the smaller value of the angle $C_3–O_e–C_2$. These differences may be explained by the mutual repulsion of the carboxyl groups of the ligands in the ML_2 complex. Also, a decrease of the bond strength between the lanthanide ions and the ether oxygens would result in a decrease of the relatively high values of the $C_3–O_e–C_2$ angle of the ML complex.

In the structural study of potassium benzene-1,2-dioxydiacetate it was found that the potassium ion lies between a pair of twofold related ligand molecules. Both the ether and carboxyl oxygens are coordinated to the potassium ion, with K–O distances between 2.75 and 2.92 Å. The potassium ion is located 1.55 Å from the planes of the two adjacent ligands. Thus the increase in size and/or decrease in charge density of the metal in going from the trivalent lanthanide ions ($r \simeq$ 1 Å) to K^+ (r = 1.33 Å) causes a structural change with the cation moving out of the ligand plane. For both types of cations, however, the metal is coordinated to the ether oxygens as well as to the carboxyl oxygens.

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Registry No. LaL^+, 63765-23-1; PrL^+, 63765-25-3; EuL^+, 63765-28-6; YbL^+, 63765-35-5; LaL_2^-, 63797-25-1; PrL_2^-, 63797-24-0; EuL_2^-, 63797-23-9; YbL_2^-, 63797-22-8; benzene-1,2-dioxydiacetate, 63783-93-7; ^{13}C, 14762-74-4.

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Thermodynamic Properties of Lanthanide Complexes with Benzene-1,2-dioxydiacetic Acid

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The free energies, enthalpies, and entropies of complexation of lanthanide ions by benzene-1,2-dioxydiacetate have been determined by potentiometry, calorimetry, and solvent extraction. Comparison of the entropy values with those of analogous complexes involving bi-, tri-, and tetradentate diacetate ligands gives an entropy change of ca. 95 ± 10 kJ K^{-1} mol^{-1} per carboxylate group. This correlation was used to obtain a relative measure of the Lewis basicity of the other ligand donor sites (oxo, imino, thio). The lanthanide cations do not interact with the thio donors while the order with the oxo and imino donors is $(-CH_2\mathit{N}CH_2CO_2^-)_2 > \mathit{N}(CH_2CO_2^-)_2 \geq \mathit{O}(CH_2CO_2^-)_2 > (-CH_2\mathit{O}CH_2CO_2^-)_2 > Ph(\mathit{O}CH_2CO_2^-)_2$.

Previous studies in this laboratory of the complexation of trivalent lanthanides by simple dicarboxylate ligands such as malonate[2a] and maleate[2b] have demonstrated the effect of chelate ring size. Grenthe and his co-workers have studied lanthanide complexation by more complicated dicarboxylate ligands such as oxydiacetate and ethylenedioxydiacetate as well as the thio and imino analogues of these ligands.[3,4] We have extended these studies to the benzene-1,2-dioxydiacetate complexes in order to investigate more fully the effects of ring size and ligand basicity in lanthanide complexation. Potentiometric and calorimetric titration were used to determine the free energy and enthalpy changes on complexation. These values were checked by solvent extraction measurements of cerium and europium complexation.

Experimental Section

Reagents. All chemicals were reagent grade. Sodium perchlorate and benzene-1,2-dioxydiacetic acid were recrystallized twice from water. Diethylhexylphosphoric acid was purified[5] for the solvent extraction experiments; the other reagents were used without further purification. The concentrations of acid solutions were determined by titration using potassium hydrogen phthalate as the standard. Stock solutions of the lanthanides were prepared by dissolving known amounts of the metal oxides in perchloric acid.

The concentrations of the lanthanide solutions were determined from EDTA titration using xylenol orange as indicator. The hydrogen ion concentrations of each solution were determined from the pH values and assuming 0.83 as the activity coefficient of the hydrogen ion.[6] Methods of preparing solutions of constant ionic strength for titration have been described in previous publications.[2]