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 $(-CH_2NCH_2CO_2^-)_2 > N(CH_2CO_2^-)_2 \geq O(CH_2CO_2^-)_2 > (-CH_2OCH_2CO_2^-)_2 > Ph(OCH_2CO_2^-)_2$.

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]

Table I. Thermodynamic Values of Benzene-1,2-dioxydiacetic Acid (I = 0.10 M ($NaClO_4$); T = 25.0 °C)

pK_{a_1}	pK_{a_2}	ΔH_{011}, kJ mol^{-1}	ΔH_{021}, kJ mol^{-1}	ΔS_{011}, kJ K^{-1} mol^{-1}	ΔS_{021}, kJ K^{-1} mol^{-1}
2.70	3.40	4.39	8.16	79.8	79.1

Table II. Praseodymium–Benzene-1,2-dioxydiacetate System (I = 0.10 M ($NaClO_4$); T = 25.0 °C)

A. pH Titration Data[a]

Volume of titrant, mL	pH	10^5[L]	$\bar{n}$
13.0	3.341	3.68	0.508
14.0	3.326	4.07	0.545
15.0	3.314	4.57	0.582
16.0	3.304	5.11	0.619
17.0	3.296	5.72	0.655
18.0	3.290	6.40	0.690
19.0	3.284	7.02	0.726
20.0	3.278	7.56	0.761
21.0	3.275	8.35	0.796
22.0	3.272	9.05	0.830
23.0	3.272	9.98	0.864
24.0	3.272	10.88	0.897

B. Calorimetric Data

Volume of titrant, mL	Q, mJ	$\bar{n}$
0.334	42.94	0.432
0.665	86.09	0.445
0.994	127.6	0.458
1.370	183.0	0.474
1.748	232.3	0.489
2.128	284.6	0.504
2.508	343.6	0.519
2.882	396.5	0.534
3.258	448.6	0.549
3.637	499.3	0.564
4.015	574.4	0.578
4.443	605.2	0.595
4.869	669.2	0.612
5.296	719.0	0.628
5.726	772.6	0.645
6.148	827.8	0.661
6.569	873.8	0.677
7.071	936.6	0.696
7.577	990.6	0.715
8.076	1045	0.734
8.580	1102	0.752
9.079	1147	0.771

[a] Initial volume = 40.0 mL; initial pH 4.10. $C_{Pr}{}^0$ = 0.006 92 M; $C_L{}^0$ = 0.0112 M. [b] Initial volume = 50.0 mL (40.0 mL of Pr^{3+} + 10.0 mL of L^{2-}). $C_{Pr}{}^0$ = 0.005 335 M; $C_L{}^0$ = 0.002 298 M. In the buret; $C_L{}^0$ = 0.011 49 M.

Cerium-144 and europium-(152 + 154) were obtained from Oak Ridge National Laboratory. ^{144}Ce(III) solutions were prepared by adding hydrogen peroxide to a warm acid solution of the tracer.

Procedures. All experiments were performed with aqueous solutions in which the ionic strength was 0.1 M (adjusted with sodium perchlorate). The solutions were adjusted initially to a pH of approximately 4. The pH titrations of ligand solution into metal ion solution were carried out in a glass vessel jacketed to allow a flow of water from a water bath which maintained the temperature at 25 ± 1 °C. In the titrations, the hydrogen ion concentration varied between a pH of 3.2 and 4.2 as measured with a Beckman Research pH meter (Model 1019) standardized by standard potassium hydrogen phthalate buffer of pH 4.01 ± 0.01.

The calorimetric titrations were performed using the calorimeter and the techniques described previously.[2a] The heat of dilution for the ligand solution, determined by titration of the ligand into a solution of 0.1 M sodium perchlorate, was so much smaller than the measured heats in the complexation experiments that it could be neglected in the calculations. The calorimetric titrations were performed by addition of ligand solution to the lanthanide perchlorate solutions in the calorimeter. The stability constants and the enthalpies of complexations were calculated from mass balance expressions using a least-squares treatment of the data (program LINW modified) and the CDC-6400 computer of Florida State University. In order to calculate the stability constants it was also necessary to include the acid dissociation constants of the ligand as well as the enthalpies of protonation. These values were determined by standard titration techniques using pH and calorimetric titration.

The solvent extractions were performed using the methods described in previous publications.[7] Three milliliters of an aqueous phase of the tracer and varying concentrations of the ligand were contacted with an equal volume of organic phase containing the DEHP in toluene. After equilibration, the phases were separated and counted separately in a NaI(Tl) well-type scintillation counter for the γ radioactivity of the ^{144}Ce and ^{152,154}Eu tracers.

Results

The acid dissociation constants and the stability constants were determined initially by graphical analysis[8] to ascertain their approximate values. The least-squares program was used to obtain the final values.

The dissociation constants and heats of protonation of benzene-1,2-dioxydiacetic acid are listed in Table I. Our pK_a values are somewhat different than the reported values of 2.40 and 3.45 for the successive dissociation steps.[9]

Table II is a typical set of titration data from which the thermodynamic parameters are calculated. The titration of each metal ion was performed two to five times to ensure the reliability of the data. Table III is a listing of the thermodynamic parameters obtained as average values from the titration experiments. We estimate that our standard error is 5–8% in both K_{101} and ΔH_{101} and 10–15% in K_{102} and ΔH_{102}.

In order to calculate a reliable set of values, various sets of complexes were assumed to be present in the experiments:

Table III. Thermodynamic Parameters for the Formation of the 1:1 Lanthanide–Benzene-1,2-dioxydiacetate Complexes (μ = 0.1 M ($NaClO_4$); T = 25.0 °C)

Ion	Log K_{101}	$-\Delta G_{101}{}^a$	$\Delta H_{101}{}^a$	$\Delta S_{101}{}^b$	Log K_{102}	$-\Delta G_{102}{}^a$	$\Delta H_{102}{}^a$	$\Delta S_{102}{}^b$
La	3.81	21.7	16.3	127	3.49	19.9	10.0	100
Ce	4.16[c]	23.7			3.42 (3.45)	19.5		
Pr	4.36	24.9	14.4	132	3.33 (2.99[d])	19.0	6.32	85
Nd	4.45	25.4	17.2	141	3.20	18.2		
Sm	4.57	26.1	11.3	126	2.91	16.6	3.9	69
Eu	4.60 (4.52)	26.2	14.7	138	2.85 (2.69[d])	16.3	1.8	61
Gd	4.48	25.6	13.6	131	2.59	14.8		
Tb	4.30	24.6	19.7	149	2.35	13.4		
Dy	4.26	24.3	20.2	149				
Ho	4.11	23.5	23.9	159				
Er	3.92	22.4	26.9	165				
Tm	3.94	20.8	35	179				
Yb	4.02	22.9			(1.84[d])	(7.7)		
Lu	4.04	23.1	32.4	186				
Y	3.78	21.6	24.3	154				

[a] In kJ mol^{-1}. [b] In kJ K^{-1} mol^{-1}. [c] Same value by solvent extraction, ( ) solvent extraction results. [d] NMR results ref 10.

Table IV. Comparison of Thermodynamic Parameters of Complexation of Some Dicarboxylate Ligands and Sm(III) or Eu(III)

Ligand (ref)	Ionic strength, M	$-\Delta G$, kJ mol^{-1}	ΔH, kJ mol^{-1}	ΔS, kJ deg^{-1} mol^{-1}	$\delta\Delta H$
1. Acetate (ML) (12)	2.0	11.6	6.1	59	
2. Acetate (ML_2) (12)	2.0	18.8	12.1	103	
3. Malonate (1)	1.0	18.2	14.5	110	
(1)	(0.1	25.9	13.8	133)	
4. Thiodiacetate (3)	1.0	16.6	11.4	94	0
5. Iminodiacetate (3)	1.0	36.8	−3.7	111	~−17
6. Oxydiacetate (3)	1.0	31.5	−3.3	95	−16
7. Ethylenedithiodiacetate (4)	1.0	13.3	12.3	86	0
8. Ethylenedioxydiacetate (4)	1.0	28.9	1.6	102	−11
9. Ethylenediaminediacetate (4)	1.0	46.8	−12.2	117	−25
10. Benzene-1,2-dioxydiacetate	0.1	25.4	17.2	141	
	1.0	18.3 (est)	16.2 (est)	116 (est)	+3
11. Furoate (14)	2.0	9.5	6.4	53	

ML; ML + ML_2; ML + ML_2 + MHL; ML + ML_2 + MHL_2. For our experimental conditions, calculations of acceptable values of stability constants were obtained assuming only ML (Dy–Lu) or ML and ML_2 (La–Tb); however, this does not preclude the existence of small amounts of MHL and/or ML_2 in all our titrations.

The β_{101} stability constants of the cerium and europium complexes calculated from the solvent extraction experiments agreed well with those from the pH titrations. The β_{102} constant of the cerium complex also agreed well in the two types of experiment. However, we could not calculate a value of the stability constant for the second complex for europium from the solvent extraction data even though the ligand concentration range would seem to have been sufficient to do so.

Discussion

Suzuki et al.[9] have shown that the values of log K_1 of the complexes of benzene-1,2-dioxydiacetate with divalent cations exhibit a maximum for cation radii between 0.9 and 1.0 Å. These authors interpret this as due to the steric rigidity of the ligand which favors cations of this size. In Figure 1 we have plotted our values for the lanthanides (curve A) as well as the values for divalent cations (curve B). The agreement seems to support the proposal of Suzuki et al. The steady decrease in the log K_2 values with cation atomic number for the lanthanides also could be interpreted as reflecting significant steric effects. The steric arguments for the divalent cations are consistent with the lack of a maximum in the log K_1 values of their monodentate acetate[11] complexes (curve C) and a shift of the maximum to ~0.75 Å for their more flexible hexadentate EDTA[11] complexes (curve D). We find that the lanthanide complexes exhibit a maximum in log K_1 at 0.95 Å for the acetates[12] (curve E) but no maximum for EDTA[13] (curve F). The absence of a maximum for EDTA is consistent with the divalent cation–EDTA system, but the presence of a maximum in curve E at r_+ ~0.95 Å for acetate complexing raises doubts about the validity of interpreting the maximum at the same position in curves A and B as due to steric rigidity.

Figure 2 is a plot of ΔG_{101} as a function of total ligand basicity (i.e., $\sum pK_a$) for a number of Sm(III) or Eu(III) complexes. Our benzene-1,2-dioxydiacetate data were obtained in ionic media of 0.1 M in order to allow direct comparison with the data of Suzuki et al. In order to allow comparison with the other complexes in Figure 2 we have adjusted our data to 1.0 M ionic strength as follows. Based on the relative values for the malonate complexing at 0.1 and 1.0 M we estimate ΔH_{101} (0.1 M) to be 1 kJ less than ΔH_{101} (1.0 M) and ΔS_{101} is reduced by the same ratio as for malonate (i.e., 110/133). These estimated values of ΔH_{101} (17 kJ mol^{-1}) and ΔS_{101} (116 kJ K^{-1} mol^{-1}) are used to obtain ΔG_{101} (1.0 M). The ΔG, ΔH, and ΔS values for the complexes included in Figure 2 are listed in Table IV. The slope of the ΔG vs.

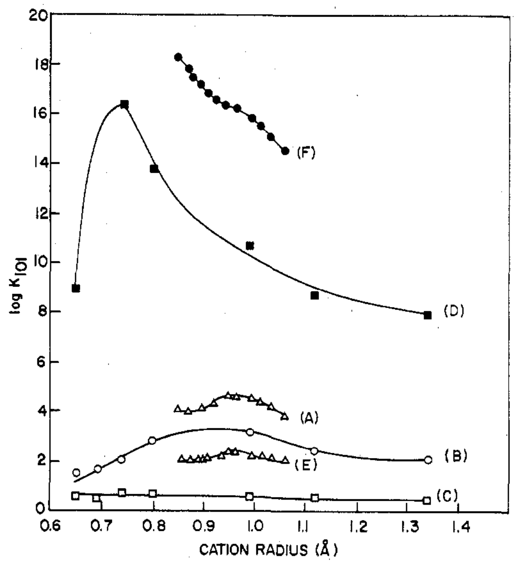

Figure 1. The relationship between cationic radius and log K_{101} for divalent cations (curves B, C, and D) and trivalent lanthanides (A, E, F) with acetate (C, E), EDTA (D, F), and benzene-1,2-dioxydiacetate (A, B).

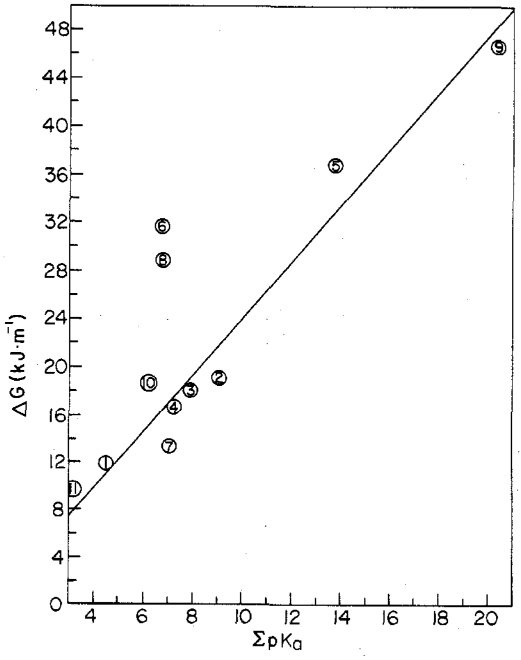

Figure 2. The variation of the free energy of complexation of Sm(III) or Eu(III) as a function of the sum of the pK_a values of the ligands. See Table IV to relate the numbers with the ligands.

$\sum \mathrm{p}K_\mathrm{a}$ correlation in Figure 2 is the same as that reported previously for a series of monocarboxylate complexes.[2] While many of the complexes fit the correlation satisfactorily, a few do not. To discuss these, we must consider Table IV in some detail.

We note in Table IV that there is relatively little variation in the ΔS values (for the same ionic strength of 0.1 M)—100 ± 15. This suggests that the net structural effects may be rather similar in all these complexes. Since the diacetate complex is included, it is reasonable that the major entropy effect in all cases involves the effect of the association of the cation with two carboxylate groups. In other words, if chelation includes metal–sulfur, metal–nitrogen, or metal–oxygen (ether) interaction, this has little entropy effect.

Grenthe and Gardhammar[4] proposed that complexation of lanthanides by $\mathrm{S(CH_2CO_2)_2^{2-}}$ and $\mathrm{(-CH_2SCH_2CO_2)_2^{2-}}$ involved one carboxylate group and no Ln–S interaction. From Figure 2 we believe that both carboxylate groups are coordinated since $\sum(\mathrm{p}K_{\mathrm{a}_1} + \mathrm{p}K_{\mathrm{a}_2})$ provides the correlation; however, the interaction with the S atoms must be negligible by the same correlation. On the other hand, we see that the correlation is poor for the analogous ether–oxygen complexes, indicating appreciable Ln···O interaction. In fact, from this curve we see that the basicity of the ether–oxygen must be in the order: (a) $\mathit{O}\mathrm{(CH_2CO_2)_2^{2-}}$ > (b) $\mathrm{(-CH_2}\mathit{O}\mathrm{CH_2CO_2)_2^{2-}}$ > (c) $\mathrm{Ph(}\mathit{O}\mathrm{CH_2CO_2)_2^{2-}}$ > (d) furoate. The ether oxygen in furoate has such a low basicity that the lanthanide cations do not coordinate with it. The deviation of the oxygen–ligand complexes from the correlation could be due to structural effects; however, this does not seem likely when the ΔS_{101} values in Table IV are compared. The displacement of the dithio complex (no. 7 in Figure 2) from the correlation may reflect structural effects, consistent with its lower ΔS_{101} (note that if the entropy were 95 kJ $\mathrm{m^{-1}}$, the ΔG would fit the correlation).

This observed order of basicity is the expected one. The ether oxygens in (b) should be less basic than that of (a) due to a weaker inductive effect. In (c) the basicity should be less than in (b) due to the electron-withdrawing effect of the phenyl ring. The ether oxygen in furoate is even less basic as the nonbonding electrons of the oxygen are intimately involved in the π system.

As noted, the values of the entropies of formation, ΔS_{101}, of the ML complexes (Table IV) have a rather narrow range of values when compared at the same ionic strength. The similarity in values of ΔS_{101} for formation of $\mathrm{Sm(OAc)_2^+}$ (with two separate carboxylate ligands), $\mathrm{Sm(malonate)^+}$, $\mathrm{SmS(CH_2CO_2)_2^+}$, $\mathrm{Sm(-CH_2SCH_2CO_2)_2^+}$ (all with bidentate chelation via two carboxylate groups), $\mathrm{SmN(CH_2CO_2)_2^+}$, $\mathrm{SmO(CH_2CO_2)_2^+}$, $\mathrm{Sm(-CH_2NCH_2CO_2)_2^+}$, $\mathrm{Sm(-CH_2OCH_2CO_2)_2^+}$, and $\mathrm{SmPh(OCH_2CO_2)_2^+}$ (tridentate or tetradentate chelation via two carboxylate groups and one or two N or O donors) indicates that the entropy primarily reflects similar solvation changes upon complexation by the two carboxylate groups in all these complexes. If, as seems to be the case, each carboxylate group has the same effect whether in acetate or in a tetradentate ligand, we can, perhaps, assume a similar effect in the enthalpy; i.e., each carboxylate interaction produces a similar enthalpy contribution.

Based on the values for malonate, the mono- and dithiodiacetates, and the biacetate, $\mathrm{ML_2}$, we can estimate that the entropy effect of two carboxylate groups is 95 ± 10 kJ $\mathrm{K^{-1}\,mol^{-1}}$ while the enthalpy effect is 12.5 ± 1.5 kJ $\mathrm{mol^{-1}}$. Using 13 kJ $\mathrm{mol^{-1}}$ for ΔH^1, we obtain $\delta\Delta H$ ($=\Delta H_{101} - \Delta H^1$) in Table IV. The $\delta\Delta H$ is a relative measure of the interaction of the S, N, and O atoms with the lanthanides and, hence, is a measure of the basicity of these donor atoms. In a similar analysis, Grenthe[15] has estimated values of $\delta\Delta H$ of −15, −15, and −29 kJ for the differences in affinities of ether oxygen and aliphatic and aromatic nitrogen relative to ether sulfur. The $\delta\Delta H$ values indicate that the thio donors do not interact while the order of basicity of the italic N and O donors is: $\mathrm{(-CH_2}\mathit{N}\mathrm{CH_2CO_2)_2^{2-}} > \mathit{N}\mathrm{(CH_2CO_2)_2^{2-}} \geq \mathit{O}\mathrm{(CH_2CO_2)_2^{2-}} > \mathrm{(-CH_2}\mathit{O}\mathrm{CH_2CO_2)_2^{2-}} > \mathrm{Ph(}\mathit{O}\mathrm{CH_2CO_2)_2^{2-}}$.

The success of this approach encourages us to use Figure 2 to obtain estimates of the "true" total $\sum \mathrm{p}K_\mathrm{a}$ values of the oxy ligands. Subtracting the $\sum(\mathrm{pK_{a_1} + pK_{a_2}})$ from these total values, we get these estimates for the oxy donor atoms:

	$\Sigma \mathrm{p}K_\mathrm{a}$	$\mathrm{p}K_\mathrm{a}$/oxygen
$\mathit{O}\mathrm{(CH_2CO_2)_2^{2-}}$	~6.6	6.6
$\mathrm{(-CH_2}\mathit{O}\mathrm{CH_2CO_2)_2^{2-}}$	~5.4	2.7
$\mathrm{Ph(OCH_2CO_2)_2^{2-}}$	~1.5	0.8

An NMR study of the ^{1}H and ^{13}C shifts in benzene-1,2-dioxydiacetate induced by paramagnetic lanthanide ions has confirmed the interpretation of the thermodynamic data that the ether oxygen is involved in the complexation.[10] In the 1:1 complex the Ln···O (ether) distances are 2.1–2.2 Å which compares well with Ln···O bond distances in crystals.

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Registry No. Benzene-1,2-dioxydiacetic acid, 5411-14-3; $\mathrm{[La(Ph(OCH_2CO_2)_2)]^+}$, 63765-23-1; $\mathrm{[Ce(Ph(OCH_2CO_2)_2)]^+}$, 63765-24-2; $\mathrm{[Pr(Ph(OCH_2CO_2)_2)]^+}$, 63765-25-3; $\mathrm{[Nd(Ph(OCH_2CO_2)_2)]^+}$, 63765-26-4; $\mathrm{[Sm(Ph(OCH_2CO_2)_2)]^+}$, 63765-27-5; $\mathrm{[Eu(Ph(OCH_2CO_2)_2)]^+}$, 63765-28-6; $\mathrm{[Gd(Ph(OCH_2CO_2)_2)]^+}$, 63765-29-7; $\mathrm{[Tb(Ph(OCH_2CO_2)_2)]^+}$, 63765-30-0; $\mathrm{[Dy(Ph(OCH_2CO_2)_2)]^+}$, 63765-31-1; $\mathrm{[Ho(Ph(OCH_2CO_2)_2)]^+}$, 63765-32-2; $\mathrm{[Er(Ph(OCH_2CO_2)_2)]^+}$, 63765-33-3; $\mathrm{[Tm(Ph(OCH_2CO_2)_2)]^+}$, 63765-34-4; $\mathrm{[Yb(Ph(OCH_2Co_2)_2)]^+}$, 63765-35-5; $\mathrm{[Lu(Ph(OCH_2CO_2)_2)]^+}$, 63765-36-6; $\mathrm{[Y(Ph(OCH_2CO_2)_2)]^+}$, 63765-37-7.

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