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Thermodynamic and NMR Studies on the Complexation of Lanthanoid(III) Ions with *o*-Phenylenediamine-*N,N,N′,N′*-tetraacetate in Aqueous Solutions

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The complex formation of *o*-phenylenediamine-*N,N,N′,N′*-tetraacetate (PhDTA, H_4L) with trivalent lanthanoid ions (M^{3+}) in aqueous solutions has been studied at a temperature of 25.0±0.2 °C and an ionic strength of 1.0 M in $NaClO_4$ by potentiometry, calorimetry, and ^{1}H and ^{139}La NMR. The formation constant, K_{ML}, of 1 : 1 PhDTA complexes increases monotonically with the atomic number of the central metal ions ($\log K_{ML}=11.39$ for La, and 16.26 for Lu), showing the tetrad effect and a linear free energy relationship with the formation constant of CyDTA complexes. The change in entropy increases gradually with increasing atomic number, as is the case for EDTA. The large change in entropy ($\Delta S^{\circ}_{ML}\approx 257$—$329\ J\ K^{-1}\ mol^{-1}$) overweighs the endothermicity ($\Delta H^{\circ}_{ML}=5.4$—$14.6\ kJ\ mol^{-1}$) of the complexation. The NMR study indicated that the La–PhDTA complex has four acetate groups with an identical magnetic environment and a lanthanum nucleus with higher electric symmetry in comparison with the corresponding EDTA and CyDTA complexes.

Modification of EDTA (ethylenediamine-*N,N,N′,N′*-tetraacetic acid) has been attempted by increasing the number of chelate rings, by changing the number of atoms in a chelate ring, by introducing functional groups to the chelate ring and so on.[1] The substitution of phenylene group for its ethylenic backbone leads to *o*-phenylenediamine-*N,N,N′,N′*-tetraacetic acid (PhDTA), which has been found to coordinate with metal ions very strongly in aqueous solutions, despite the poor basicity of its nitrogen atoms.[2–4] Thereby beryllium(II) was titrated successfully with PhDTA,[5] and crystallographic studies have shown that PhDTA complexes have a structure that the central metal ion is on the plane of the phenylene group.[6,7] Such a steric peculiarity may lead to appearance of AB patterns for acetate methylene signals of proton NMR, irrespective of the lifetime of metal-ligand bonds. We were thus attracted to the measurement of the thermodynamic stability of a series of lanthanoid complexes and NMR spectra of La(III) and Lu(III) complexes with PhDTA to obtain information concerning the structure and bonding.

Experimental

Materials. PhDTA (H_4L) and perchlorates of sodium(I) and copper(II) were prepared and analyzed as described previously.[3] Lanthanoid(III) perchlorate solutions were prepared by dissolving the respective lanthanoid(III) oxides (Wako, >99.9%) in aqueous solutions of reagent grade perchloric acid. The concentrations of hydrogen ion and lanthanoid ions were determined by the Gran method,[8] and by complexometry (pH 5—6 by use of xylenol orange as an indicator[1]), respectively. Lanthanoid(III) complexes were prepared by adding a ligand solution in slight excess (10% on the molar scale) to the respective metal ion solutions, followed by adjusting the pH to 6—7. The solution mixture was warmed before adding ethanol in large excess, and left standing until crystals appeared. Deuterium oxide (Wako, 99.75%) was used as received for the NMR measurement.

Potentiometry. Potentiometric titrations were carried out as described previously[3] at 25.0±0.2 °C and at an ionic strength of 1.0 M[9] ($NaClO_4$). A couple of Metrohm EA109T glass–AG9100 calomel electrodes was used to measure the pH of solutions with a Metrohm 605 pH-meter to a precision of 0.1 mV. The copper(II) ion activity was measured with a DKK copper(II) ion selective electrode in combination with a Metrohm EA440 double-junction Ag–AgCl electrode on a Corning 130 pH-meter. The solution pH was carefully adjusted in order to avoid the protonation or the hydrolysis of copper(II) and lanthanoid(III) complexes. The total concentration of a metal ion ($C_M\approx 10^{-2}$ M) was chosen in such a way that it was lower than that of PhDTA, C_L, in the pH titrations, and they are summarized in Table S1. The autoprotolysis constant was determined as $pK_w=13.75$ from the titrations of perchloric acid with sodium hydroxide (experimental Nernstian slope of the glass electrode=58.7 mV/pH). Potentiometric data were processed by use of Fortran program based on the non-linear least-squares technique with a FACOM 382 computer at the Computation Center, Nagoya University.

Calorimetric Measurements. Calorimetry was done with a Tokyo-Riko Model MP-111 twin-type conduction calorimeter, as described elsewhere.[10] The respective lanthanoid perchlorate solutions were delivered with two motor-driven piston burets (Metrohm, Multi-Dosimat 655) simultaneously to the ligand solution (pH ca. 7) and to the reference solution (without ligand), equilibrated thermally in advance.

NMR Measurements. Crystals of a lanthanoid(III) complex were dissolved in D_2O, to which lithium perchlorate was added with the view of measuring below 0 °C. NMR spectra were measured on a JEOL JNM-GX 270 FT NMR spectrometer operating at 270 MHz, and its probe was thermostated at an appropriate temperature.

Results and Discussion

Refinement of the Protonation Constants of PhDTA. Repeated crystallization of the ligand resulted in further

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** The supplementary material (Tables S1 and S2, Figures S1 and S2) is deposited as Document No. 9000 at the Office of the Ediotr of Bull. Chem. Soc. Jpn.

purification (99.4%), which permitted us to refine its logarithmic stepwise protonation constants (log $K_i = \log([H_iL]/[H_{i-1}L][H^+])$ for H_iL with 2σ) from potentiometric data; HL (6.404±0.003), H_2L (4.605±0.004), H_3L (3.531±0.006), H_4L (2.984±0.006). They are in good accord with our previous results,[3] and with those obtained by other groups,[2,11] with allowance made for a certain difference in experimental conditions.

Complex Formation of PhDTA with Lanthanoid(III) Ions. Potentiometric titration of a solution containing the lanthanum(III) and PhDTA ions with sodium hydroxide led to a formation constant, K_{ML}, corresponding to the following reaction

$$M^{3+} + L^{4-} \rightleftarrows ML^-; \quad K_{ML}$$

$$K_{ML} = [ML^-]/[M^{3+}][L^{4-}] \tag{1}$$

with log K_{LaL}=11.39 (when M=La). M^{3+} and L^{4-} represent a lanthanoid(III) ion and PhDTA in a free form, respectively. This type of pH-metry was applicable to the determination of K_{ML} for the La(III)-PhDTA alone, owing to its relatively low constant. As was the case for the divalent transition metal ions,[3] however, a direct method using a glass electrode did not permit us to estimate the formation constant of the other lanthanoid(III) complexes with accuracy due to the high potency of complexation of PhDTA. Accordingly, we applied the ligand buffer method[3,12] to these systems by adding copper(II) ion instead of calcium(II) ion,[3] and we were able to determine the constants successfully with a copper(II) ion selective electrode.

When a copper(II) ion concentration is measurable, the formation constant K_{ML} for a lanthanoid complex, ML, may be calculated according to Eq. 2 on the basis of the following exchange reaction[3]

$$M^{3+} + CuL^{2-} \rightleftarrows Cu^{2+} + ML^-$$

$$K_{ML} = \frac{[Cu^{2+}]\,(C_L - C_{Cu} + [Cu^{2+}])\,K_{CuL}}{(C_{Cu} - [Cu^{2+}])\,(C_{Cu} + C_M - C_L - [Cu^{2+}])} \tag{2}$$

where C_X denotes the total concentration of a component X (X=Cu, M, or L). K_{CuL} is the formation constant for the copper (II) complex, CuL. In general, it should be necessary to take into consideration the protonation and the hydrolysis of the complexes CuL and ML, respectively. The protonation to these PhDTA complexes, however, was only seen at pH's lower than 3, and the hydrolysis of the lanthanoid(III) ion was detected only at pH>7 in the analysis of potentiometric data of lighter lanthanoid ions including La(III). Thus the free copper(II) ion concentration remained constant in a certain range of pH, as can be seen from the horizontal parts in Fig. 1. The value of the Cu-PhDTA complex, log K_{CuL}=15.21,[3] was used as the standard for the calculation of the formation constant from the exchange reaction. The formation constants thus obtained are summarized in Table 1, from which it is seen that the formation constant of the lanthanum(III) complex agrees completely with that determined by

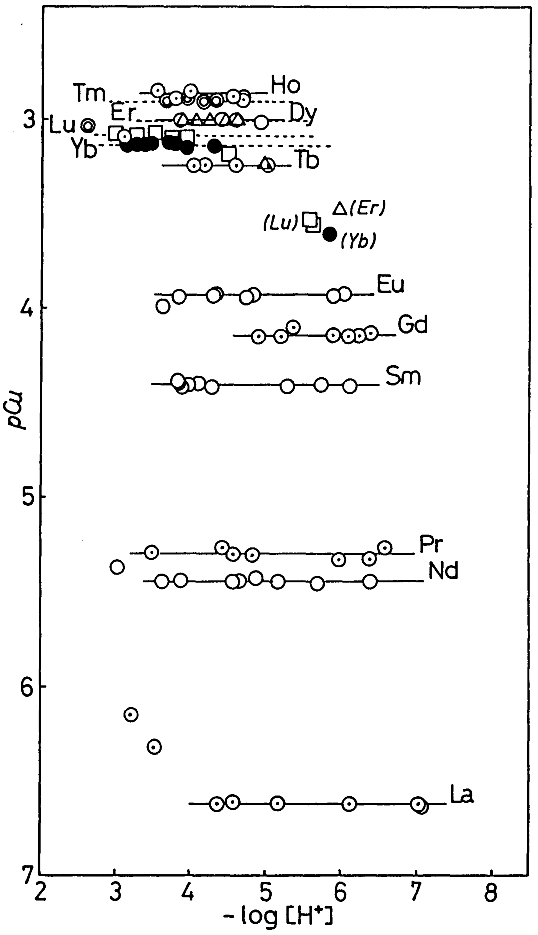

Fig. 1. Determination of the formation constants of PhDTA complexes based on the pCu-pH diagram.

Table 1. The Formation Constant (log K_{ML}) Obtained by the Ligand Buffer Method, the Corresponding Thermodynamic Quantities from Calorimetry, and the Protonation Constant (log K_{MHL}) from pH-Metry of Lanthanoid(III)-PhDTA Complexes[a)]

Ion	log K_{ML}	ΔH°_{ML}	ΔS°_{ML}	log K_{MHL}
La	11.39(2)[b)]	11.7(3)	257(2)	1.81(3)
Pr	12.26(4)	13.5(3)	280(2)	1.54(4)
Nd	12.63(2)	13.5(4)	287(2)	1.43(2)
Sm	13.35(3)	13.7(8)	301(4)	1.34(5)
Eu	13.65(4)	14.3(5)	309(3)	1.14(6)
Gd	13.89(4)	14.6(2)	315(2)	
Tb	14.46(3)	12.3(2)	318(2)	
Dy	14.89(3)	11.6(1)	324(1)	
Ho	15.18(5)	9.6(3)	323(2)	
Er	15.55(6)	8.4(3)	326(2)	
Tm	15.87(4)	6.7(3)	326(2)	
Yb	16.06(4)	5.3(3)	325(2)	
Lu	16.26(5)	5.4(3)	329(2)	

a) Values at 25 °C and 1.0 M ($NaClO_4$). Experimental errors at the least significant digits shown in parentheses. Units: in ΔH°_{ML} in kJ mol^{-1} and ΔS°_{ML} in J K^{-1} mol^{-1}. b) The pH-metry gave also the same value of log K_{ML}=11.39.

potentiometry.

The formation constant log K_{ML} increases monotonically with increasing atomic number, which may be interpreted as usual in terms of increasing charge density caused by the lanthanide contraction. Plotting of these constants reveals the so-called gadolinium break,[13] and also the tetrad[14] or the double-double effect.[15] The logarithmic formation constants of the PhDTA complexes show the "inclined W",[13] when plotted against the total angular momenta of the lanthanoid(III) ions for the groups La–Pr–Nd, Sm–Eu–Gd, Gd–Tb–Dy–Ho, and Er–Tm–Yb–Lu,[13,16,17] as is the case for the complexes of EDTA[18] and CyDTA (cyclohexanediamine-*N,N,N',N'*-tetraacetate).[18]

The linear free energy relationship (LFER) holds for this trivalent series among the formation constants of PhDTA and CyDTA complexes (Fig. 2), but the slope of the straight line (ca. unity) differs slightly from that of the divalent[3] and monovalent metal ions.

Protonation to a metal complex, ML, could readily be estimated from the analysis of potentiometric data for lighter lanthanoids (Table 1), as was the case for the very stable complexes of divalent transition metal ions:[3]

$$\mathrm{ML}^- + \mathrm{H}^+ \rightleftarrows \mathrm{MHL}: \qquad K_{\mathrm{MHL}}.$$

$$K_{\mathrm{MHL}} = [\mathrm{MHL}]/[\mathrm{ML}^-][\mathrm{H}^-]. \qquad (3)$$

The protonated species of heavier lanthanoid complexes, however, was not formed enough to decide their equilibrium constant with accuracy. The protonation constants obtained for the PhDTA complexes are smaller than those of the corresponding complexes with EDTA (e.g. log K_{LaHL}=2 at 25 °C, 0.1 M)[18] and CyDTA (e.g. log K_{LaHL}=2.24 at 20 °C, 0.1 M).[19] It should also be noted that the protonation constant of PhDTA (log K_4=2.984) is larger than log K_4 for the other two ligands (2.2 for EDTA and 2.41 for CyDTA at 20 °C 1.0 M ($\mathrm{NaClO_4}$),[20] and 2.40 for CyDTA 20 °C and 0.1 M ($\mathrm{KNO_3}$)[19]).

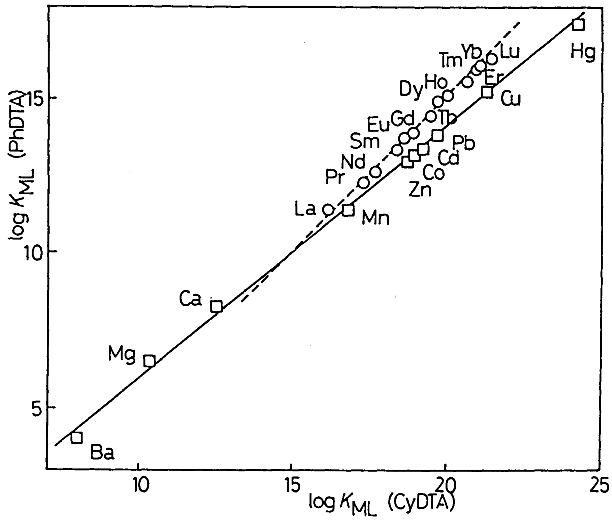

Fig. 2. LFER between the logarithmic formation constants for the metal complexes of PhDTA and CyDTA.[18]

The lower value of a lanthanoid(III)–PhDTA complex indicates protonation to the oxygen atom of a carboxylate group complexed to lanthanoid(III) ion and complexation of all the four carboxylate groups to the central metal ion, since the protonation constant of the complexes of most divalent metal ions, log K_{MHL}, is usually about 3 for EDTA and CyDTA.[18,21] In fact Hoard et al. have found that a hydrogen atom is carried by a carboxylate group complexed by the $\mathrm{La^{3+}}$ ion in the complex $\mathrm{La(Hedta)(H_2O)_4}$ (coordination number CN=

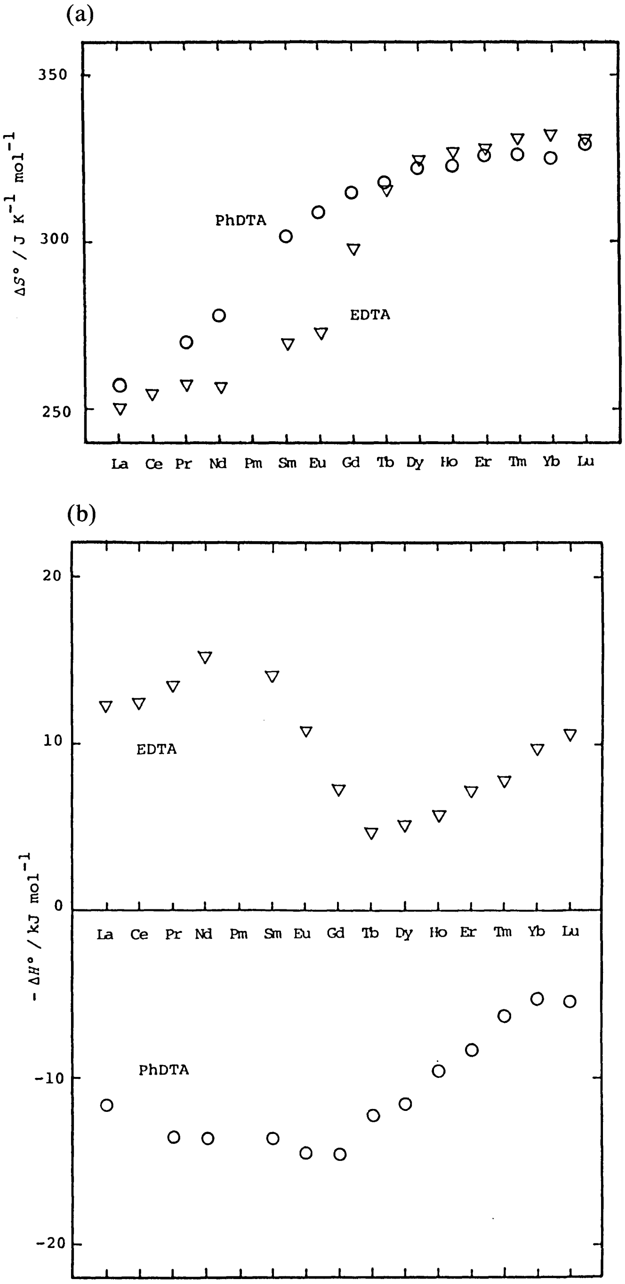

Fig. 3. Comparison of the thermodynamic quantities for the complex formation of lanthanoid(III) ions with PhDTA and EDTA.[23] (a) Change in entropy; (b) Change in enthalpy.

10) from X-ray crystallography.[22] In this case protonated Hedta acts as a hexadentate ligand, and the binding mode may be schematized as La–O–CR–OH (R is the residual part of EDTA). A similar situation has also been found for $Zn(H_2phdta)(H_2O)$, where one proton is bonded to an oxygen atom of the carboxylate group that is dissociated, and the other proton is carried by the unbonded carbonyl oxygen of the carboxylate group that is complexed to zinc ion, though Hphdta acts as a pentadentate ligand.[7b)]

Thermodynamic Quantities of Complexation as Determined by Calorimetry. Calorimetric studies led to the changes in enthalpy (ΔH°_{ML}) and in entropy (ΔS°_{ML}) of complexation of PhDTA corresponding to Eq. 1, and they are compared with those of EDTA[23] in Fig. 3a and 3b. The ΔS°_{ML} values increase linearly with the reciprocal ionic radii for the PhDTA complexes of lighter lanthanoids down to gadolinium, reaching a plateau in common with EDTA complexes. Spedding et al. have demonstrated that the coordination number of hydrated lanthanoid(III) ions decreases from 9 to 8 around Gd, from the measurements of the partial molal volume[24] and the X-ray diffraction of lanthanoid(III) solutions.[25] Kanno and Hiraishi have drawn the same conclusion from the change in frequency of the totally symmetric stretching vibrations of aqua lanthanoid(III) ions in Raman spectroscopy.[26] Hoard et al. have found that $K[La(edta)(H_2O)_3]\cdot 5H_2O$ has also a CN=9.[27] Choppin and Graffeo have studied the complexation of propionic and isobutyric acids and interpreted the gadolinium break in terms of the decrease in hydration number, on the basis of the variation of the entropy change in the series.[28]

The ΔH°_{ML} value remains almost constant up to Gd for PhDTA, while showing a sinusoidal variation for EDTA.[23] Interestingly, the reaction of PhDTA with the lanthanoid(III) ions is greatly endothermic, while that of EDTA is exothermic. The former endothermicity may readily be explained in terms of the reduced basicity at the nitrogen atoms of PhDTA.[3,4] In spite of the endothermicity, the lanthanoid(III)–PhDTA complexes are very stable, owing to the great change in entropy.

Proton NMR Studies of La(III) and Lu(III) Complexes. Day and Reilley have studied some EDTA complexes with diamagnetic metal ions by the ^1H NMR technique, and classified the lability of metal-ligand bonds as follows:[29]

a) The lifetimes of both the metal–oxygen (M–O) and the metal–nitrogen (M–N) bonds are short. Accordingly, the acetate methylene protons are made equivalent magnetically, which leads to the appearance of one resonance peak alone (e.g. Pb(II)–EDTA, apart from the isotope effects[29a)]).

b) The lifetimes of both the M–O and the M–N bonds are long. The two methylene protons on a given acetate group will be in different magnetic environments and yield AB splitting patterns (e.g. inert Co(III)–EDTA complex[29a)]).

c) The lifetime of the M–O bond is short, while that of the M–N bond is long. Only one resonance peak is expected for the ethylenic protons of an EDTA complex. However, the two acetate protons are no more equivalent, which leads to an AB splitting pattern (e.g. Cd(II)–EDTA[29a,30)]).

In the case of CyDTA complexes, the interconversion of the conformation (chair–chair) of the cyclohexane ring is necessary to average the magnetic environment of the acetate groups when the lifetime of the M–N bond is long, but it will be averaged only insufficiently because of its slow interconversion.[29b)]

For PhDTA complexes, however, the two nitrogen donor atoms and the central metal ion are fixed on a plane in common with the phenylene group to give rise to a planar five-membered chelate ring.[6,7] Accordingly, the two methylene protons of an acetate group will not experience averaging of their magnetic environment through conformational interconversion of the diamine backbone as seen in the EDTA complex, so far as the M–N bond life is sufficiently long. This steric peculiarity may lead to the appearance of several sets of AB patterns for the acetate methylene protons in PhDTA and CyDTA complexes, irrespective of the lifetime of the M–O bonds, depending on their structural symmetry.

For the La(III)–EDTA complex, we observed a typical AB pattern of the methylenic protons with a coupling constant $J_{AB}=16.5$ Hz (Fig. S1). Lowering of the experimental temperature to 5.4, −4.6, and −9.9 °C caused a gradual broadening of the methylene quartet compared to the HDO signal, while raising to 62 °C did not produce such broadening (Table S2). These findings provide evidence for the long lifetime of the M–N bonds, and the La–EDTA complex may be classified as c) stated above.

Nieboer studied proton NMR (60 MHz, 75 °C) of the same complex, reporting that a methylene singlet broadened at lower temperature to split into a doublet below 10 °C.[31] Thus La(III)–EDTA was thought to have acetate groups free from complexation to the metal ion. The same author studied also the Eu(III)–EDTA complex to report the appearance of the AB pattern of the methylene protons (60 MHz, 75 °C).[31] We could not find any spectra other than the HDO signal for the Eu(III)–EDTA system, and this fact may be justified by

Table 2. Resonance Line Widths at the Half-Height ($\Delta\nu_{1/2}$) and Chemical Shifts (δ) of ^{139}La NMR Spectra for the Lanthanum(III) Complexes of PhDTA, EDTA, and CyDTA at 334 K

	$\Delta\nu_{1/2}$/Hz	$\delta^{a)}$/ppm	C_{La}/M	C_L/M	$-\log[H^+]$
EDTA	6200	170	0.025	0.025	5.5
PhDTA	3400	160	0.025	0.025	4.5
CyDTA	7800	180	0.025	0.025	5.5

a) Chemical shift vs. the aqua La^{3+} ion.

the paramagnetism of Eu(III). Ryhl has observed the methylene singlet for La^{3+}-EDTA (60 MHz, 45 °C) to suggest the lability of both the M–N and M–O bonds, while observing an AB quartet for Lu^{3+}-EDTA (J_{AB}=17.1 Hz).[32] Choppin et al. have also found a singlet (though broader than that of the free ligand) in the proton NMR spectra (90 MHz, 30 °C), insisting the short life of both the M–O and M–N bonds.[33] The discrepancies between their findings and ours may readily be resolved by taking into consideration that we used an NMR spectrometer with a higher resolution (270 MHz), which permitted us to observe the splitting of the methylene signal into a quartet.

The La(III)–PhDTA complex showed also an AB pattern (J_{AB}=16.0 Hz) of the methylenic protons in ^{1}H NMR spectra (Fig. 4), although the free ligand alone displayed a sharp singlet. Therefore, only one type of magnetic environment should be present in the La(III)–PhDTA system, i.e. the four acetate groups are in the identical magnetic environment. A trigonal prismatic polyhedron[6,7] may be a possible structure of the La–PhDTA complex which accounts for this finding. Any broadening of the signals was not observed between −3.3 and 60 °C, which indicates a sufficiently long lifetime of the La–N bonds. Nevertheless, the lifetime of the La–O bonds can not be estimated from the present data alone.

The methylene signals split into two AB patterns (J_{AB}=16.4 Hz, Fig. S2) in the proton NMR spectra of the La(III)–CyDTA complex, which is indicative of the presence of two different types of magnetic environments for the acetate groups. The lifetimes of the La–N bonds should be sufficiently long, because the width of the signals did not increase with increasing temperature between −2.9 and 61.1 °C, although nothing can be concluded about the La–O bonds.

Similar spectra were observed also for the lutetium(III) complexes of these three ligands. Both the EDTA and PhDTA complexes showed only one AB pattern for the acetate group, while the CyDTA complex exhibited two sets of AB patterns. The broadening of signal was not observed for any of these complexes in the temperature range of 0 to 60 °C. It indicates again the long lifetime of the Lu–N bond of these three complexes,[33] while the lifetime of the Lu–O bond is difficult to estimate. Nevertheless, it may be safely concluded that the Lu(III)–PhDTA complex has a high symmetry, and the four acetate groups are almost identical from a viewpoint of the magnetic environment, as is the case for the La(III) complex.

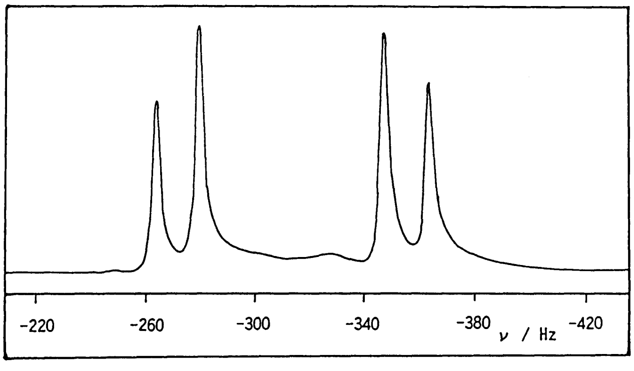

Fig. 4. The AB splitting pattern of the acetate methylenic protons in ^{1}H NMR spectra for La(III)–PhDTA at 5.6 °C. The resonance frequency on the abscissa was measured in Hz relative to HDO.

La-139 NMR Studies of the Complexes of PhDTA and Related Ligands. The lanthanum-139 nucleus has a spin of I=7/2 and a relatively high electric quadrupole moment, which produces broad resonance lines as a consequence of quadrupolar relaxation.[34,35] In Table 2 are summarized experimental resonance linewidths at the half height ($\Delta\nu_{1/2}$) of ^{139}La NMR spectra for the complexes of the three ligands. For a complex undergoing rapid tumbling in solution, the linewidth of a quadrupolar nucleus may be expressed by the following equation:[35]

$$\Delta\nu_{1/2}=\frac{3\pi^2(2I+3)}{10I^2(2I-1)}\left(\frac{e^2q_{zz}Q}{h}\right)^2\left(1+\frac{a^2}{3}\right)\tau_c, \tag{5}$$

where $e^2q_{zz}Q/h$ is the quadrupolar coupling constant, Q the nuclear quadrupole moment, q_{zz} the largest component of the electric field gradient at the nucleus, a the asymmetry parameter for q, and τ_c the correlation time. Under conditions of rapid tumbling,

$$\tau_c=\tau_R. \tag{6}$$

The rotational correlation time τ_R can be approximated by the Stokes diffusion equation:

$$\tau_R=4\pi r^3\eta/3kT, \tag{7}$$

where r is the radius of a rigid sphere tumbling in a solvent of viscosity η.

The viscosity η may not be expected to change so much from one sample to another, and then the difference in τ_R between the complexes should primarily reflect the difference in r^3. Thus the linewidth will depend on the symmetry of La complexes and their differences in volume.

Geraldes and Sherry have interpreted the larger line width of La–CyDTA than La–EDTA in terms of a more symmetric ligand field as well as a smaller size of the latter complex.[35] As evident from Table 2, the La(III)–PhDTA complex has a $\Delta\nu_{1/2}$ value conspicuously smaller than the other two complexes. Since the molar volume of the complexes increases in the order of EDTA<PhDTA≤CyDTA.[36] Consequently, the lanthanum nucleus in the PhDTA complex should have a symmetry considerably higher than that in the EDTA complex. In view of the conclusion of Geraldes and Sherry, the PhDTA complex must have the highest electric symmetry among the three La(III) complexes. The high electric symmetry of the PhDTA complex is consistent with the high structural symmetry as proved

by the proton NMR study. Since La(III)–EDTA has been proved to be in the trigonal prismatic structure in the solid state as a first approximation,[27] the La(III)–PhDTA complex is expected to have a more symmetric structure in solution.

Supplementary Material Available. Composition of the sample solutions for the potentiometric titrations for the determination of the formation constant of lanthanoid(III) complexes with PhDTA (Table S1), temperature variation of the half-height linewidths ($\Delta\nu_{1/2}$) of the ^{1}H NMR spectra for the lanthanum(III) and lutetium(III) complexes of EDTA, PhDTA, and CyDTA (Table S2), temperature variation of the methylenic proton signals in proton NMR spectra of La(III)–EDTA (Fig. S1), and comparison of the ^{1}H NMR spectra of CyDTA alone and its lanthanum(III) complexes in deuterium oxide solution at ambient temperature (Fig. S2).

References

1) R. Přibil, "Analytical Applications of EDTA and Related Compounds," Pergamon, Braunschweig (1972).

2) J. H. Grimes, A. J. Huggard, and S. P. Wilford, *J. Inorg. Nucl. Chem.*, **25**, 1225 (1963).

3) N. Nakasuka, M. Kunimatsu, K. Matsumura, and M. Tanaka, *Inorg. Chem.*, **24**, 10 (1985).

4) K. Matsumura, N. Nakasuka, and M. Tanaka, *Inorg. Chem.*, **26**, 1419 (1987).

5) N. Nakasuka, K. Takahashi, and M. Tanaka, *Anal. Chim. Acta,* **207**, 361 (1988).

6) E. F. K. McCandlish, T. K. Michael, J. A. Neal, E. C. Lingafelter, and N. J. Rose, *Inorg. Chem.*, **17**, 1383 (1978) (Co(II) complex).

7) a) N. Nakasuka, S. Azuma, C. Katayama, M. Honda, J. Tanaka, and M. Tanaka, *Acta Crystallogr., Sect. C,* **41**, 1176 (1985) (Mn(II)); b) S. Azuma, N. Nakasuka, and M. Tanaka, *ibid.*, **42**, 673 (1986) (Zn(II)); c) N. Nakasuka, S. Azuma, and M. Tanaka, *ibid.*, **42**, 1482 (1986) (Cu(II)); d) N. Nakasuka, S. Azuma, and M. Tanaka, *ibid.*, **42**, 1736 (1986) (Cd(II)); e) N. Nakasuka and M. Shiro, *ibid.*, **45**, 1487 (1989) (Mg(II)).

8) G. Gran, *Analyst,* **77**, 661 (1952).

9) Non-SI unit: 1 M=1 mol dm^{-3}.

10) N. Nakasuka, Y. Natsume, and M. Tanaka, *Inorg. Chem.*, **29**, 147 (1990).

11) A. Mederos, J. V. Herrera, J. M. Felipe, and M. L. Quesada, *An. Quim.*, **80**, 281 (1984).

12) T. Nakano and Y. Suzuki, *Nippon Kagaku Zasshi,* **1980**, 1485.

13) S. P. Sinha, "Structure and Bonding," Springer, Berlin (1976), Vol. 30, p. 1.

14) D. F. Peppard, G. W. Mason, and S. Lewey, *J. Inorg. Nucl. Chem.*, **31**, 2271 (1969).

15) I. Fidelis and S. Siekierski, *J. Inorg. Nucl. Chem.*, **33**, 3191 (1971).

16) L. J. Nugent, *J. Inorg. Nucl. Chem.*, **32**, 3485 (1970).

17) S. P. Sinha, *Helv. Chim. Acta,* **58**, 1978 (1975).

18) G. Schwarzenbach, R. Gut, and G. Anderegg, *Helv. Chim. Acta,* **37**, 937 (1954).

19) T. Moeller and T. M. Hseu, *J. Inorg. Nucl. Chem.*, **24**, 1635 (1962).

20) G. Anderegg, *Helv. Chim. Acta,* **50**, 2333 (1967).

21) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publications No. 17 (1964); No. 25 (1971), The Chemical Society, London.

22) M. D. Lind, B. Lee, and J. L. Hoard, *J. Am. Chem. Soc.*, **87**, 1611 (1965).

23) J. L. MacKey, J. E. Powell, and F. H. Spedding, *J. Am. Chem. Soc.*, **84**, 2047 (1962).

24) F. H. Spedding, M. J. Pikal, and B. O. Ayers, *J. Phys. Chem.*, **70**, 2440 (1966).

25) A. Habenschuss and F. H. Spedding, *J. Chem. Phys.*, a) **70**, 2797 (1979); b) **73**, 442 (1980).

26) H. Kanno and J. Hiraishi, a) *Chem. Phys. Lett.*, **75**, 553 (1980); b) *J. Phys. Chem.*, **86**, 1488 (1982).

27) J. L. Hoard, B. Lee, and M. D. Lind, *J. Am. Chem. Soc.*, **87**, 1612 (1965).

28) G. R. Choppin and A. J. Graffeo, *Inorg. Chem.*, **4**, 1254 (1965).

29) a) R. J. Day and C. N. Reilley, *Anal. Chem.*, **36**, 1073 (1964); b) *idem, ibid.*, **37**, 1326 (1965).

30) J. L. Sudmeier and C. N. Reilley, *Inorg. Chem.*, **5**, 1047 (1966).

31) E. Nieboer, "Structure and Bonding," Springer, Berlin (1975), Vol. 32, p. 1.

32) T. Ryhl, *Acta Chem. Scand.*, **26**, 4001 (1972).

33) P. A. Baisden, G. R. Choppin, and B. B. Garrett, *Inorg. Chem.*, **16**, 1367 (1977).

34) R. K. Harris, "Nuclear Magnetic Resonance Spectroscopy," Pitman, London (1983).

35) C. F. G. C. Geraldes and A. D. Sherry, *J. Magn. Reson.*, **66**, 274 (1986).

36) In the liquid state, the molar volume V°=179.6 Å^3/molecule for cyclohexane, while V°=146.6 Å^3/molecule for benzene. Compare the molar volume 460 Å^3/molecule for K[Fe(H$_2$O)phdta]·2H$_2$O[37] with 383.4 Å^3/molecule for K[Fe(H$_2$O)edta]·H$_2$O,[38] and 513.4 Å^3/molecule for Ca$_{1/2}$[Fe(H$_2$O)cydta]·4H$_2$O.[39]

37) M. Mizuno, S. Funahashi, N. Nakasuka, and M. Tanaka, *Inorg. Chem.*, **30**, 1550 (1991).

38) X. Solans, M. Font-Altaba, and J. Garcia-Oricain, *Acta Crystallagr., Sect. C,* **40**, 635 (1984).

39) G. H. Cohen and J. L. Hoard, *J. Am. Chem. Soc.*, **88**, 3228 (1966).