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Contribution from the Faculty of Science,
Nagoya University, Chikusa, Nagoya, 464-01 Japan

Complexation of Lithium and Sodium Ions with *o*-Phenylenediaminetetraacetate in Aqueous Solutions

Noriyuki Nakasuka,* Yoshihiro Natsume,
and Motoharu Tanaka

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Alkali-metal complexes are now awakening the renaissance of interest by virtue of their important roles in biological systems,[1,2] especially in transport phenomena. Though certain macrocyclic ligands, such as crown ethers and cryptands,[1,3-5] interact with alkali-metal ions very strongly, these ions bind weakly in general to most of organic substances including amino polycarboxylates.[6] Thus it is a common practice to add an alkali-metal salt as supporting electrolyte to a solution in the study of complex formation of other metal ions in order to maintain the ionic strength at a constant level. The formation constant thus determined is conditional[7] when calculated on the concentration scale, since the added salt affects the thermodynamic parameters of metal complexes through two processes. The physicochemical process determines the activity coefficient of species in solution, and the other process of complexation of the alkali-metal ion itself with a ligand produces an effect on the side-reaction coefficient.[7] This point has been discussed in the interpretation of thermodynamic data of protonation and complexation of *o*-phenylenediamine-*N*,*N*,*N'*,*N'*-tetraacetate, but no experimental data have been given.[8] In this context, the present paper reports the experimental results from potentiometric, calorimetric, and spectroscopic measurements on the protonation of this ligand and its complex formation with lithium and sodium ions in the medium of tetraethylammonium perchlorate, which may practically not interact with common ligands like amino polycarboxylates.[9]

Experimental Section

Reagents. *o*-Phenylenediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid (PhDTA, H_4L) and alkali-metal perchlorates were prepared as described previously.[8,10] Tetraethylammonium perchlorate was prepared by adding perchloric acid to an aqueous solution of tetraethylammonium bromide (Aldrich). The resultant precipitate was recrystallized twice from water (solubility ca. 0.5 M[11]) and the final product was dried in vacuo at ambient temperature.

Equipment. Measurements were carried out at 25 ± 0.1 °C and at an ionic strength $I = 0.10$ M (Et_4NClO_4), unless otherwise noted. Electrochemical measurements were made by using a Metrohm 605 pH-meter, which was connected to a Metrohm EA 109 glass electrode and either a Metrohm EA 438 silver chloride electrode with a double junction containing 0.1 M Et_4NClO_4 or an EA 404 calomel electrode. Both reference electrodes contained saturated NaCl solutions.

The protonation and complexation enthalpies were measured with a Tokyo-Riko Model MP-111 twin-type conduction calorimeter, connected to a NEC-PC9801F personal computer through an A/D converter to permit straightforward calculation of heat evolved. Alkali-metal perchlorate or perchloric acid as titrant was delivered with Metrohm 655 Dosimat buret to a ligand solution neutralized and equilibrated thermally in advance.

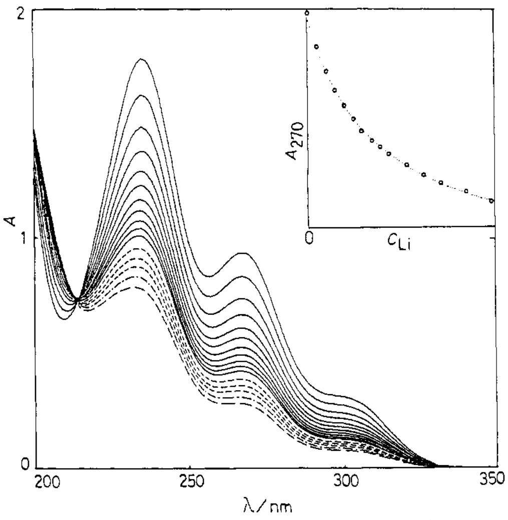

Figure 1. Change in spectra of PhDTA (1.148×10^{-4} M) on addition of 0.500 M lithium perchlorate at pH of ca. 10.5. Total lithium concentrations were varied from 0 M (top) to 0.0341 M (bottom at 270 nm). The broken lines are used only for avoiding overlap of lines. Gradual deviation from the isosbestic point is caused by the decrease in total ligand concentration with the continuously increasing volume of the lithium perchlorate solution added, and this effect was corrected for in the calculation of the formation constant and the molar extinction coefficient. The inset shows change in absorbance at 270 nm scaled as a function of total lithium concentration, and the dotted line is the curve calculated with the best fit value of $\log K_{LiL} = 1.99$.

Spectrophotometric measurement was made on a Shimadzu UV-265FW UV–visible spectrophotometer with a thermostated cell. All data were processed on a FACOM M382 computer at the Computation Center, Nagoya University.

Procedures. For potentiometry, a 0.1439 M tetraethylammonium hydroxide solution was used as titrant, and PhDTA concentrations were usually around 2×10^{-3} M. The alkali-metal perchlorate was initially added to a tetraethylammonium perchlorate solution ($C_{Li} = 3.931 \times 10^{-2}$ M and $C_{Na} = (3.1\text{–}4.2) \times 10^{-2}$ M) for the complex formation study. In the spectroscopic determination of complex formation for either metal ion, the ligand concentration and the pH were kept at about 1×10^{-4} M and higher than 10.5, respectively. Lithium ion concentration varied up to 0.03 M (see Figure 1), while a 1.00 M sodium perchlorate solution was added to the 0.1 M tetraethylammonium perchlorate solution containing PhDTA. Data for which the sodium ion concentrations were higher than 0.1 M have been discarded in the calculation of the formation constant. The calorimetric measurement was carried out in the same way as that in our previous study,[8] in which the use of a reference cell permitted us to subtract the heats of reactions other than those of interest. The calorimeter was calibrated by measuring the heat of neutralization of proton and hydroxyl ion, and we obtained $\Delta H^\circ = -57.2$ kJ mol^{-1} (25 °C, 1 M $NaClO_4$). This value compares favorably with a literature value of -57.0 kJ mol^{-1} (25 °C, 1 M $NaNO_3$).[12] A 0.100 M lithium perchlorate solution was added to 20.88 cm^3 of a 1.69×10^{-3} M PhDTA solution, which was thermally equilibrated after the adjustment of its pH to ca. 8 by adding a tetraethylammonium hydroxide solution. The heat evolved was then corrected for the heats of the first and second protonations, ΔH°_1 and ΔH°_2. A calorimetric study has been done in a similar way also for the sodium ion complexation, but the results were less reproducible than those for lithium due to the lesser extent of complex formation of sodium ion with the ligand.

Results and Discussion

Protonation of Ligands. Preliminary experiments with a glass–calomel (saturated KCl) electrode pair resulted in a Nerstian slope of 58.55 mV/pH when the NBS pH standards were used (potassium hydrogen phthalate and sodium borate), while a NaCl-saturated reference electrode was used in routine work. A

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Table I. Thermodynamic Parameters of Stepwise Protonation Constants of PhDTA[a] at 25 °C

param	K_1	K_2	K_3	K_4	medium	ref
log K_i	6.92 (2)	5.02 (2)	3.73 (1)	3.11 (1)	0.1 M Et_4NClO_4	*b*
$-\Delta H_i$	−2.3 (1)	−5.2 (1)	3.3 (3)	1.4 (3)	0.1 M Et_4NClO_4	*b*
$\Delta S_i/10^2$	1.40 (1)	1.13 (1)	0.60 (2)	0.55 (2)	0.1 M Et_4NClO_4	*b*
log K_i	6.72 (1)	4.86 (1)	3.69 (1)	3.09 (1)	0.1 M $NaClO_4$	*b*
log K_i	6.41	4.61	3.53	3.00	1.0 M $NaClO_4$	*c*
$-\Delta H_i$	4.7	−2.8	3.5	0.8	1.0 M $NaClO_4$	*c*
$\Delta S_i/10^2$	1.07	0.98	0.56	0.55	1.0 M $NaClO_4$	*c*
log K_i	6.71	4.94	3.69	2.90	0.1 M Me_4NCl	*d*

[a] Units: ΔH in kJ mol^{-1}, and ΔS in J mol^{-1} K^{-1}. Estimated standard deviations (2σ) are shown in parentheses for the least significant digit. [b] This work. [c] Reference 8. [d] Reference 13.

Table II. Thermodynamic Parameters for Alkali-Metal Complexes[a]

	PhDTA[b]			
	log K_{ML}	log K^H_{MHL}	$-\Delta H°_{ML}$[e]	$\Delta S°_{ML}/10^2$
Li^+	1.99 (1)[d]		−10.4 (5)	0.73 (2)
	2.02 (5)[c]	5.63 (8)[c]		
	2.39[i]	6.34[i]		
Na^+	0.73 (6)[d]		−9 (4)	0.4 (2)
	0.9 (2)[c]	6.6 (3)[c,d]		
	1.60[i]	6.41[i]		

	EDTA			CyDTA	
	log K_{ML}[f]	$-\Delta H°_{ML}$[g]	$\Delta S°_{ML}/10^2$[g]	log K_{ML}[h]	log K^H_{MHL}[h]
Li^+	2.43	−0.4	0.54	6.11	8.13
Na^+	1.43	5.9	0.12	4.66	9.17

[a] Units: ΔH_{ML} in kJ mol^{-1} and ΔS_{ML} in J K^{-1} mol^{-1}. Estimated standard deviations (2σ) are shown in parentheses for the least significant digit. [b] This work. [c] From potentiometry. [d] From spectrophotometry. [e] From calorimetry. [f] Reference 19 (25 °C, 0.5 M $(CH_3)_4NCl$). [g] Reference 22 (25 °C, ca. 0.05 M Cl^-). [h] Reference 20 (25 °C, 0.5 M $(CH_3)_4NOH$, polarimetry). [i] Reference 13 (25 °C, 0.1 M $(CH_3)_4NCl$, potentiometry).

0.01 M perchloric acid solution was chosen as a pH standard on the concentration scale, and pH titrations led to an autoprotolysis constant $K_w = 1.22 \times 10^{-14}$ M^2 for the 0.10 M aqueous Et_4NClO_4 medium. Liquid-junction potentials E_j were measured for a 0.10 M Et_4NClO_4 sample solution, and operationally $E_j/\text{mV} = -573[H^+]/\text{M}$. Corrections were also made for liquid-junction potentials as a function of sodium ion concentration, i.e. $E_j/\text{mV} = 33[Na^+]/\text{M}$, while lithium ion had very little effect.

Potentiometric titrations of the ligand (ca. 1.7×10^{-3} M) with tetraethylammonium hydroxide have given a series of stepwise protonation constants K_1 to K_4, which are summarized in Table I together with those of other ligands from the literature. Mederos et al. have determined the protonation constants of PhDTA in a 0.1 M tetramethylammonium chloride medium at 25 °C.[13] Their results are in fair agreement with our findings, though their constants are somewhat smaller than ours systematically.

At all protonation steps, the constants for the tetraethylammonium medium are higher than those for the sodium media, though the differences are small for the last two steps. The pH titrimetry gives a protonation constant that is rather conditional in a sense that NaL and NaHL are counted as "free L" and "monoprotonated HL", respectively. Therefore, we define the following conditional constant K_1':

$$K_1' = ([HL] + [NaHL])/[H^+]([L] + [NaL]) = K_1\,(1 + K^{Na}_{NaHL}[Na^+])/(1 + K^{Na}_{NaL}[Na^+]) \quad (1)$$

where K^{Na}_{NaHL} refers to the complexation of sodium ion with the monoprotonated ligand HL. Tetraethylammonium ion is considered practically not to coordinate to the ligand.[9]

Calculation leads to a conditional constant log $K_1' = 6.76$ at $[Na^+] = 0.1$ M, which compares with the experimental value of log $K_1 = 6.72$ at 0.1 M $NaClO_4$. This good agreement may be taken as indirect evidence for the validity of the aforementioned argument. Consequently, it follows that the constants for 0.1 M $NaClO_4$ should be intermediate between those of the Et_4NClO_4 and 1 M $NaClO_4$ media, as is indeed the case. Since sodium ion interacts very weakly with a more protonated ligand species, e.g. H_3L, the conditional constant K_3' approaches K_3.

Drastic reduction in basicity on the nitrogen atom in PhDTA is again recognized,[8,10] when the first protonation constant log K_1(PhDTA) = 6.92 is compared with log K_1(EDTA) = 10.37[6] under similar conditions. A preliminary investigation on the crystal structure of the fully protonated ligand H_4PhDTA has shown that the nitrogen atom is in a quasiplanar environment rather than in the tetrahedral one:[14] i.e., the sum of three C–N–C angles is 351°, and the N–C(benz) bond length is 1.41 Å, which is slightly shorter than the 1.45 Å usually found in the PhDTA complexes.[15-17] The latter configuration has been found in the tetraprotonated EDTA,[18] as well as in metal–PhDTA complexes so far studied.[14-17] Our crystallographic study has also shown that the two nitrogen atoms in H_4PhDTA are neither protonated nor hydrogen bonded. This is consistent with the calorimetric results summarized in Table I, which shows that the first two steps are endothermic. As we have repeatedly suggested,[8,10] the electron density on the nitrogen atoms in PhDTA is greatly reduced and they must be involved in an electronic conjugation system including the benzene ring, with some double-bond character assumed between N and C(benz).

Complex Formation. Potentiometry and spectrophotometry both gave the formation constants for lithium ion with reasonable accuracy, while the former method resulted in less accurate constants for sodium ion, due to a small change in potential. However, considerable spectral change was observed on addition of either alkali-metal ion, as is illustrated in Figure 1. Sodium ion caused only a monotonic decrease in absorbance at any wavelength observed, whereas lithium ion gave rise to an isosbestic point at 214 nm. Analysis of absorbances at 270 nm led to the formation constants of both metal complexes, as summarized in Table II. These constants are smaller than the corresponding ones for the other amino polycarboxylates,[19,20] as has already been found for transition-metal ions.[10] Our formation constants are slightly smaller than those of Mederos' group[13] except for log K^H_{NaHL}. If we take into consideration the good agreement between the two formation constants after the different methods adopted in this work, this discrepancy may tell of certain difficulty and great delicacy in determining such weak formation constants by potentiometry. The weak complexing ability forced us to add the alkali-metal ion salt to the medium at a considerably high concentration, which led to some change in the ionic strength and in the ionic composition. The formation constant, however, did not change appreciably, even when metal concentrations were varied to a considerable extent.

Another salient feature is the extraordinary high ability of the alkali-metal complexes ML to protonate. In most cases log K^H_{MHL} is 2–3 for divalent transition-metal and other metal ions that have been studied so far.[6,10,21] Hence protonation should occur at a nitrogen atom rather than at an oxygen one in this case. This is consistent with the observation that the sodium complex has a protonation constant K^H_{MHL} larger than that of the lithium complex with a larger formation constant K_{ML}. Interpretation of this phenomenon in terms of ion-pair formation rather than of complex formation may be excluded by the fact that these two complexes have different protonation constants. This is consolidated by the different modes of change in UV spectra of this

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ligand, observed on addition of the two alkali-metal ions.

Formation constants of PhDTA complexes of these alkali-metal ions are again smaller than those of the other amino polycarboxylate ligands.[6,22] Since the change in entropy is not so different among the complexes of these ligands, endothermicity is evidently responsible for the reduced reactivity of PhDTA.[8]

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Registry No. PhDTA, 40774-59-2; Na, 7440-23-5; Li, 7439-93-2.

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Contribution from the Institut de Ciència
de Materials (CSIC), C/Marti i Franques s/n,
Apartat de Correus 30102, 08028 Barcelona, Spain,
and Departament de Quimica, Universitat Autònoma
de Barcelona, Campus de Bellaterra,
Cerdanyola, 08193 Barcelona, Spain

A New Type of Macrocycle Incorporating *closo*- and *nido*-Carborane Cages: Molecular Structures of 1,2-(1,10-Dithia-4,7-dioxadecane-1,10-diyl)-1,2-dicarba-*closo*-dodecaborane and Sodium 7,8-(1,13-Dithia-4,7,10-trioxatridecane-1,13-diyl)-7,8-dicarba-*nido*-undecaborate(12)

F. Teixidor,*,† C. Viñas,‡ J. Rius,† C. Miravitlles,†
and J. Casabó‡

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One of the most differentiating characteristics of macrocycles is the existence of a cavity, which causes most of their peculiar properties. The combination of this cavity with other chemical subunits such as chelating moieties or other groups to form bi- or polycycles should form molecular species with specific features. Eventually these species could mimic not only the active site of an enzyme but also its function.

Recently, Lehn and co-workers have indicated the importance of lateral macrobicyclic cryptands as coreceptor molecules[1] based on the combination of two binding subunits, one that is chelating and the other macrocyclic, stressing the interest in having a soft, redox-active site combined with a hard Lewis acid center to activate a substrate and consequently form a cascade complex. Dinuclear macrocyclic and macropolycyclic ligands have been actively studied in recent years.[2,3]

Some of us reported earlier the synthesis and in one case the crystal structure of other macrocycles containing two 7,8-dicarba-nido-undecaborate(12) subunits, which present an anti disposition.[4] We describe here the synthesis of a new type of macrocycle that combines a "soft" 7,8-dicarba-*nido*-undecaborate(12) unit with the hard thioxa macrocycles [12]-O_2S_2 and [15]-O_3S_2. Nondegraded species and the crystal structures of sodium 7,8-(1,13-dithia-4,7,10-trioxatridecane-1,13-diyl)-7,8-dicarba-*nido*-undecaborate(12) and 1,2-(1,10-dithia-4,7-dioxadecane-1,10-diyl)-1,2-dicarba-*closo*-dodecaborane are also described.[5]

Experimental Section

Before use, *o*-carborane (I) (Dexsil Chemical Corp.) was sublimed; *o*-carborane-1,2-dithiol (II) was prepared from *o*-carborane according to the literature.[6] A 1.7 M solution of *n*-butyllithium in hexane (Fluka or Aldrich) and 1,2-bis(2-chloroethoxy)ethane (Aldrich) were used as given. 1,11-Dichloro-3,6,9-trioxoundecane was synthesized from the appropriate alcohol (tetraethylene glycol)[7] and RhCl $(PPh_3)_3$ was synthesized according to the literature.[8]

Elemental analyses were performed in our analytical laboratory by using a Perkin-Elmer 240-B microanalyzer. The ^1H NMR spectra were obtained by using a Bruker AM 400 WB instrument. IR spectra were obtained with KBr pellets on a Perkin-Elmer 240FT spectrophotometer.

Synthesis of 1,2-(1,10-Dithia-4,7-dioxadecane-1,10-diyl)-1,2-dicarba-*closo*-dodecaborane (III) and Trimethylammonium 7,8-(1,10-Dithia-4,7-dioxadecane-1,10-diyl)-7,8-dicarbaundecaborate(12) (IV). Under a dinitrogen atmosphere, the dichloride 1,2-bis(2-chloroethoxy)ethane (1.346 g, 7.2 mmol) was dissolved in degassed absolute ethanol (52 mL). Sodium hydroxide (0.578 g, 14.4 mmol) and *o*-carborane-1,2-dithiol (1.5 g, 7.2 mmol) were dissolved in 52 mL of the same solvent. By means of a syringe pump, the dichloride and the *o*-carborane-1,2-dithiolate solutions were then added simultaneously from syringes, at a rate of 4 mL h^{-1} onto refluxing degassed absolute ethanol (250 mL), contained in a round-bottom flask equipped with three condensers. To avoid the fast contact of the two reacting solutions, the syringe tubes were discharged into the lateral condensers.

After the addition, the mixture was kept stirring and refluxing for an additional 3 h period. Once the mixture was cooled to room temperature, a white solid (NaCl) was separated by filtration. The bulk of the solvent was then evaporated, and water and ethyl ether were added. The water layer was washed with more ether and kept to isolate IV and V.

Separation of 1,2-(1,10-Dithia-4,7-dioxadecane-1,10-diyl)-1,2-dicarba-*closo*-dodecaborane (III). The combined ether fractions were washed with a water/NaOH solution, discarding the aqueous phase. The ether solution was dried (anhydrous Na_2SO_4, 24 h), and evaporated to yield a yellowish oil. This was chromatographed on alumina by using ethyl ether as eluent. The solution was evaporated, and again, the oily product chromatographed as before. After partial evaporation of the solvent and on standing, white crystals of III appeared. IR (KBr): ν(C–H), 2932, 2861 cm^{-1}; ν(C–O–C), 1125 cm^{-1}; ν(B–H), 2571 cm^{-1}. MS at *m/z* (relative intensity): M, molecular peak centered at 323 (4,2%); 279 (7,9%), M – CH_2CH_2O; 234 (41,1%), M – $CH_2CH_2OCH_2CH_2O$; 207 (23,8%), M – $CH_2CH_2OCH_2CH_2OCH_2CH_2$. ^1H NMR (ppm, acetone-d_6) 3.76 (m, 2, O–CH_2), 3.60 (m, 2, O–CH_2), 2.93 (m, 2, S–CH_2). ^{13}C NMR (ppm, acetone-d_6, BB decoupled): 71.64 (s, O–CH$_2$), 70.1 (s, O–CH$_2$), 37.45 (s, S–CH$_2$). Anal. Calcd: C, 29.81; H, 6.83. Found: C, 30.0; H, 6.9.

Separation of Trimethylammonium 7,8-(1,10-Dithia-4,7-dioxadecane-1,10-diyl)-7,8-dicarbaundecaborate(12) (IV) and V. The water layer was treated with excess trimethylammonium chloride to precipitate an off-white solid (IV), which was filtered, washed with water and ether, and vacuum-dried. Yield: 1.12 g (41.6%). IR (KBr): ν(C–H) and ν(N^+–H), 3024–2865 cm^{-1}; ν(B–H), 2520 cm^{-1}; ν(C–O–C), 1117 cm^{-1}. ^1H NMR (ppm, acetone-d_6): 3.77 (m, 2, O–CH_2), 3.61 (m, 2, O–CH_2), 3.43 (s, 12, N(CH_3)$_4$), 2.95 (m, 2, S–CH_2). ^{13}C NMR (ppm, acetone-d_6, BB decoupled): 71.79 (s, O–CH$_2$), 69.95 (s, O–CH$_2$), 55.77 (t, N(CH$_3$)$_4$), 37.01 (s, S–CH$_2$). Anal. Calcd: C, 35.56; N, 3.77; H, 8.62. Found: C, 35.2; N, 3.8; H, 8.6.

If tetramethylammonium chloride is used instead of the trimethylammonium salt, tetramethylammonium 7,8-(1,10-dithia-4,7-dioxadecane-1,10-diyl)-7,8-dicarbaundecaborate(12) is obtained (V).

Synthesis of Sodium 7,8-(1,13-Dithia-4,7,10-trioxatridecane-1,13-diyl)-7,8-dicarba-*nido*-undecaborate(12) (VI). The starting procedure

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* To whom correspondence should be addressed.

† Institut de Ciència de Materials.

‡ Universitat Autònoma de Barcelona.

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