September, 1992] *Bull. Chem. Soc. Jpn.*, ***65***, *2333—2337 (1992)* 2333

Thermodynamic Studies on the Complexation of *o*-Phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate with Divalent Cadmium, Mercury, and Lead Ions in Aqueous Solutions

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(Received March 6, 1992)

Potentiometric studies have been carried out on the complexation of *o*-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate (phdta, L^{4-}) with the cadmium and lead ions (M^{2+}) in aqueous solutions at 25±0.1 °C and I=1.00 M ($NaClO_4$). The ligand buffer method was successfully applied to the determination of the formation constant ($M^{2+}+L^{4-}=ML^{2-}$: K_{ML}) by use of Cd and Pb ion-selective electrodes. This method gave $\log K_{ML}=13.37$ for CdL and 13.89 for PbL. Calorimetry and potentiometry gave the values of enthalpy and entropy of complexation ($-\Delta H^\circ$/kJ mol^{-1}=18.9, ΔS°/J K^{-1} mol^{-1}=193 (CdL); 34.8, 149 (PbL); and 50.6, 165 (HgL), respectively). Thermodynamic parameters of the protonation to ML were also examined for the PhDTA complexes of these and some divalent transition metal ions. The metal complexes are classified into two categories according to the thermodynamic parameters: A) Mn^{2+}, Cd^{2+}, and Pb^{2+} ($-\Delta H^\circ_{MHL}=-1.1$—1.1 kJ mol^{-1}; $\Delta S^\circ_{MHL}=43$—49 J K^{-1} mol^{-1}). B) Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ($-\Delta H^\circ_{MHL}=8.0$—11.3 kJ mol^{-1}; $\Delta S^\circ_{MHL}=18$—37 J K^{-1} mol^{-1}). The smaller value of $-\Delta H^\circ_{MHL}$ for A has been interpreted in terms of simple protonation to a carboxylate oxygen in the complex ML, with any acetate group not being dissociated. The entire process of protonation for B, however, may be composed of two steps: i) Detachment of one carboxylate group from the metal ion, followed by the hydration resulting in $M(L')(H_2O)^{2-}$, where L′ represents a ligand anion with a free carboxylate group. ii) Protonation to an oxygen atom of the detached carboxylate group.

The basicity of amines is highly sensitive to the resonance effect, as illustrated by the fact that aniline has about a million times weaker basicity than that of aliphatic amines.[1] Similar phenomena have also been found for *o*-phenylenediamine[2] and *o*-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (phdtaH_4),[3] in comparison with ethylenediamine and ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (edtaH_4), respectively. The second protonation is endothermic for the phenylene nitrogen atom of the former two ligands,[3] while this is not the case for most of the common amines.

PhDTA has logarithmic protonation constants (6.41 and 4.61)[4] considerably smaller than EDTA (8.85 and 6.24)[5] for the nitrogen protonation and this has been interpreted in terms of the electron-withdrawing effect of the benzene ring on the basis of a calorimetric evidence.[3] The change in enthalpy of complexation of PhDTA is also more endothermic than that of EDTA, whereas the change in entropy is almost identical for the complexation of these two chelating agents with transition metal ions[3] and lanthanoid ions.[6]

Another interesting feature of PhDTA is the planarity of the chelate ring of its metal complexes, and the heptacoordinate Fe(III)-PhDTA complex has a two-fold axis passing through the Fe(III) and the oxygen atom of the hydrated water, bisecting the aforementioned chelate ring.[7] The corresponding EDTA complex has, however, only a pseudo two-fold axis.[8] The cadmium(II) ion is octacoordinated in its PhDTA complex in the solid state,[9] although the heptacoordination is commonly observed for the Cd–EDTA complexes studied to the present.[10–13] We have studied the complexation of PhDTA with several kinds of metal ions in solution, and found that thermodynamic parameters depend not only on the geometry but also on the electronic structure of the central metal ions.[3,4,6,7,14,15] The present paper describes the measurement of the thermodynamic properties of complexation of PhDTA with the cadmium(II), mercury(II), and lead(II) ions, because they are large in size and have the filled d shell. Calorimetric study was also done on the protonation to complexes of metal ions which included also some divalent transition metal ions, and a comparison is made between the thermodynamic parameters of their protonation.

Experimental

Materials. *o*-Phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (H_4L) and sodium perchlorate were prepared and purified as previously described.[3] Cadmium(II) and lead(II) perchlorates were prepared by dissolving the respective reagent grade metal nitrates in aqueous perchloric acid, followed by recrystallization from the water. The hydrogen ion concentration in a given metal perchlorate solution was determined by use of the Gran method.[4,6] The divalent metals were analyzed complexometrically (BT for Cd and XO for Pb as indicators). Perchlorates of mercury(II) and divalent transition metals were prepared and analyzed as described elsewhere.[4]

Electrochemical Measurements. All thermodynamic measurements were carried out at a temperature of 25.0±0.1 °C and at an ionic strength of 1.00 M in $NaClO_4$ (Non-SI unit: 1 M=1 mol dm^{-3}). A pair of Metrohm EA109T glass-AG9100 calomel electrodes and an Orion digital ionalyzer were used to measure the change in pH to a precision of 0.1 mV. The metal ion activity was measured with an Orion cadmium 94-48A, a DKK cadmium type 7120 or an Orion lead 94-82 ion selective electrode. Each was combined with a Metrohm EA440 double-junction Ag–AgCl electrode. All potentiometric data

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were processed through a Fortran program ACREF[16] on a FACOM 382 computer at the Computation Center, Nagoya University.

Calorimetric Measurements. Calorimetry was performed with a Tokyo-Riko Model MP-111 twin-type conduction calorimeter. The sample and reference solutions, thermally preequilibrated in the calorimeter, were simultaneously titrated with a metal perchlorate solution (for studying complexation) or a perchloric acid one (for studying protonation). The evolved heat was evaluated by comparing the surface under a curve traced with a Tokyo-Riko CU-228 recorder. The change in enthalpy was calibrated by the standard heat of acid-base neutralization ($\Delta H^\circ = -57.2$ kJ mol^{-1}).[17]

Results and Discussion

The Formation Constants of PhDTA Complexes with Cadmium(II) and Lead(II) Ions. Interaction of a metal ion, M^{2+}, with the ligand anion, L^{4-}, is formulated as follows

$$M^{2+} + L^{4-} \rightleftharpoons ML^{2-}. \tag{1}$$

Direct use of a glass electrode (pH-metry) did not, however, permit determination of a formation constant, K_{ML}, corresponding to Eq. 1, due to the complete reaction of PhDTA with Cd^{2+} and Pb^{2+}, as observed in our previous studies on the complex formation of the transition metal[4] and lanthanoid ions.[6] Accordingly, we applied the ligand buffer concept[17] to the evaluation of the equilibrium constant by using cadmium and lead ion-selective electrodes, respectively. Although these electrodes responded linearly to the free metal ion concentration down to approximately 10^{-6} M in the absence of a ligand, its presence lowers greatly the detection limit.[4,6,18] As illustrated in Fig. 1, the free Cd^{2+} concentration remained constant over a wide range of pH,[4,6] when Ca^{2+} was added in excess. The formation constant of Cd-PhDTA, K_{CdL}, was evaluated on the basis of $\log K_{CaL} = 8.27$.[4] The Pb(II) ion-selective electrode behaved similarly, and the results for both metal complexes are summarized in Table 1, along with the data for zinc(II) and mercury(II) from the previous study.

The stepwise protonation constant, K_{MH_jL}, for a metal complex can readily be estimated by processing the pH-metric data according to the following equation

$$H^+ + MH_{j-1}L \rightleftharpoons MH_jL \; (j = 1, 2). \tag{2}$$

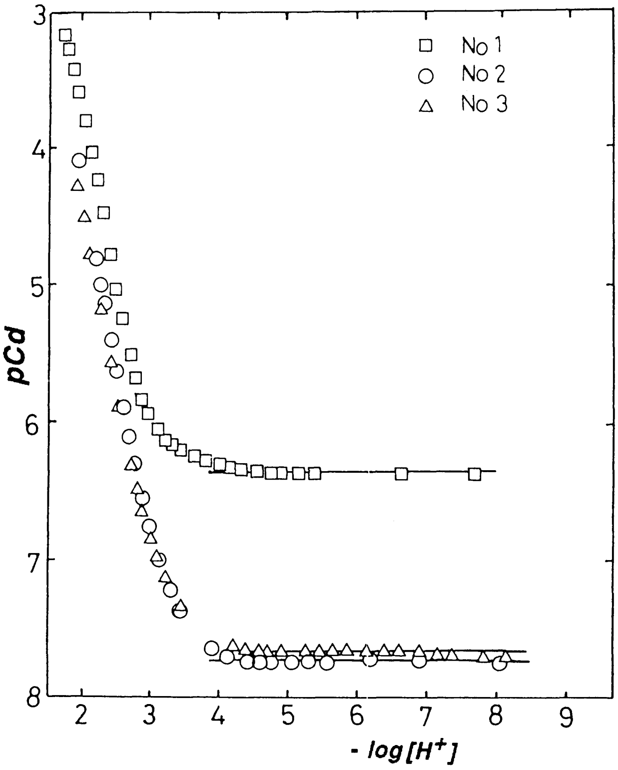

Fig. 1. The diagram of pCd as a function of $-\log[H^+]$ used to determine the formation constant of the Cd-PhDTA complex. The total concentrations of Cd, Ca, and PhDTA for the experiments were as follows: No. 1 (square) $10^3\,C_{Cd}/M = 7.281$, $10^3\,C_{Ca}/M = 9.189$, $10^3\,C_L = 8.393$ (calcud $\log K_{CdL} = 13.37$); No. 2 (circle) 3.642, 3.062, 5.490 (calcd $\log K_{CdL} = 13.39$); No. 3 (triangle) 3.642, 6.123, 7.208 (calcd $\log K_{CdL} = 13.36$).

Table 1. Thermodynamic Parameters for the Formation of the 1:1 PhDTA Complex ML Compared with the Corresponding EDTA Complex

Metal	$\log K_{ML}$	$-\Delta G^\circ_{ML}$ kJ mol^{-1}	$-\Delta H^\circ_{ML}$ kJ mol^{-1}	ΔS°_{ML} J K^{-1} mol^{-1}
PhDTA[a]				
Zn	12.89	73.6	−4.1	260
Cd	13.37 (2)	76.3(1)	18.9 (6)	193 (3)
Hg	17.38 (5)	99.2 (3)	50.6 (25)	165 (9)
Pb	13.89 (4)	79.3 (2)	34.8 (8)	149 (3)
EDTA[b]				
Zn	16.50	92.6	20.3	247
Cd	16.46	92.3	37.9	186
Hg	21.80	122.3	79.1	149
Pb	18.04	101.2	37.9	157

a) This work (25 °C, 1 M ($NaClO_4$)), except for the thermodynamic parameters of Zn (Ref. 3) and the $\log K_{HgL}$ value (Ref. 4). Experimental errors for the least significant digits are given in parentheses. b) Ref. 19 (20 °C, 0.1 M (KNO_3)).

The formation constant, K_{ML}, was treated as fixed at the value obtained by the ion-selective electrode method in the computer refinement of the protonation constants. The second protonation constant (j=2) could also be determined for the cadmium(II) complex, but poor solubility of $\mathrm{PbH_2L}$ prevented determination of the corresponding constant.

Thermodynamic Parameters for the Formation of the Complex ML. The calorimetric titrations gave the thermodynamic quantities for the complex formation of the Cd(II), Hg(II), and Pb(II) ions. They are summarized in Table 1, together with the corresponding values of EDTA.[19] Although the reaction of PhDTA is less exothermic than that of EDTA for a given metal ion, the ΔH° values of the two ligands vary in parallel. The change in entropy ΔS° also varies in a parallel manner, but the numerical value is almost the same for a given metal ion. An exception is found for lead(II), where the value for EDTA is larger than that of PhDTA. The value of ΔS° is usually a monotonic function of the ionic radius, r_{i}, as has been confirmed for PhDTA[6] and EDTA[20] complexes of the lanthanoid(III) ions. Since $\mathrm{Pb^{2+}}$ (r_{i}=1.20 Å) is larger than $\mathrm{Hg^{2+}}$ (r_{i}=1.10 Å) in size, the former ion should have a smaller ΔS° value than the latter. This is indeed the case for the PhDTA complexes, although not for the EDTA complexes, as can be seen in Table 1.

Thermodynamic Parameters of the Protonation to the Complexes. The change in enthalpy of protonation to a metal complex ML was determined by measuring the heat evolved during the titration of solutions containing the metal perchlorate and the ligand with perchloric acid. The $\Delta H^{\circ}_{\mathrm{MHL}}$ was evaluated on the basis of the concentrations of the protonated species present, calculated by use of the appropriate formation constants. This was accomplished after a correction was applied for the heat due to other side reactions such as the ligand protonation, the neutralization of the hydroxyl ion, and the complex dissociation. The thermodynamic parameters of the protonation were also determined for the PhDTA complexes with several divalent transition metal ions, and for the second protonation of the Cd–PhDTA complex (j=2 in Eq. 2).

The divalent metal ions can be classified into two categories according to the thermodynamic parameters of the corresponding PhDTA complexes

A) $\mathrm{Mn^{2+}}$, $\mathrm{Cd^{2+}}$, and $\mathrm{Pb^{2+}}$ ($-\Delta H^{\circ}_{\mathrm{MHL}}=-1.1$—1.1 kJ mol^{-1}; $\Delta S^{\circ}_{\mathrm{MHL}}$=43—49 J K^{-1} mol^{-1}).

B) $\mathrm{Co^{2+}}$, $\mathrm{Ni^{2+}}$, $\mathrm{Cu^{2+}}$, and $\mathrm{Zn^{2+}}$ ($\Delta H^{\circ}_{\mathrm{MHL}}$=8.0—11.3 kJ mol^{-1}; $\Delta S^{\circ}_{\mathrm{MHL}}$=18—37 J K^{-1} mol^{-1}).

Any ion of Category A is large (r_{i}=0.80—1.20 Å), and the change in enthalpy of protonation is nearly zero. Since the $\Delta H^{\circ}_{\mathrm{i}}$ values for stepwise ligand protonation to carboxylate oxygen atoms of PhDTA are very samll ($-\Delta H^{\circ}_{\mathrm{i}}$/kJ mol^{-1}=3.5 ($i$=3) and 0.8 ($i$=4); ΔS°/J K^{-1} mol^{-1}=56 (i=3) and 55 (i=4)),[3] the protonation can be simply thought of as occurring at a carboxylate oxygen in the complex ML, with any acetate group not being dissociated. This is the case for the solid La(III)–EDTA complex, where the acid hydrogen is carried by an oxygen atom of the carboxylate group directly complexed by $\mathrm{La^{3+}}$.[21]

It might be possible to interpret these parameters in terms of direct protonation to the oxygen atom belonging to a free carboxylate group not complexed by the contral metal ion. This implies that a carboxylate group is

Table 2. Thermodynamic Parameters for the Protonation to the Metal Complex ML

Metal	Ionic rad. Å	log K_{MHL}	$-\Delta G^{\circ}_{\mathrm{MHL}}$ kJ mol^{-1}	$-\Delta H^{\circ}_{\mathrm{MHL}}$ kJ mol^{-1}	$\Delta S^{\circ}_{\mathrm{MHL}}$ J K^{-1} mol^{-1}
PhDTA[a)					
Mn	0.80	2.29	13.1	0.2 (9)	43 (4)
Co	0.72	2.52	14.4	9.0 (3)	18 (2)
Ni	0.69	3.32	19.0	8.0 (1)	37 (1)
Cu	0.72	3.04	17.4	8.7 (5)	29 (3)
Zn	0.74	2.96	16.9	11.3 (16)	19 (6)
Cd	0.97	2.33	13.3	−1.1 (16)	48 (6)
Pb	1.20	2.39	13.6	1.1 (14)	49 (6)
CdH[b)	0.97	2.03	11.6	7.2 (9)	15 (5)
EDTA[c)					
Mn	0.80	3.1	17.6	5.0	42
Co	0.72	3.0	17.2	7.9	29
Ni	0.69	3.2	18.4	7.5	38
Cu	0.72	3.0	17.2	8.4	29
Zn	0.74	3.0	17.2	9.2	25
Cd	0.97	2.9	16.7	1.7	50

a) This work (25 °C, 1 M ($\mathrm{NaClO_4}$)), except for the log K_{MHL} values of the transition metal complexes (Ref. 4). b) Parameters for the second protonation (log $K_{\mathrm{MH_2L}}$) corresponding to Eq. 2 (j=2) for the cadmium(II) complex. c) Ref. 19 (20 °C, 0.1 M ($\mathrm{KNO_3}$)). d) Experimental errors for the least significant digits are given in parentheses.

dissociated in the complex ML and that phdta^{4-} acta as a pentadentate ligand. Higginson and Samuel evaluated tha proportions of the monoaqua pentadentate complex from spectrophotometric measurements.[22] They were found to be 24% for Co(II), 25% for Ni(II), 38% for Cu(II), and ca. 30% for Pb(II) in the case of EDTA complexes, on the assumption that every metal ion has a coordination number of six. On the other hand, McCandlish et al. studied the protonation equilibrium of the Co(II)–PhDTA complex in aqueous solutions by electronic and infrared spectroscopies, and concluded that the complex is practically hexadentate (at least 97%).[23] They ascribed the instability of the pentadentate form to the planarity of the phenylenediamine backbone. Moreover, the assumption of Higginson and Samuel of hexacoordination appears to be somewhat doubtful for the large lead(II) ion, in view of the crystallographic results of the Pb–EDTA complex, in which the lead(II) ion is octacoordinated.[24] The infrared spectra of D_2O solutions of Pb(II)–EDTA have only one ν(C–O) band, which has been attributed to ionically bonded carboxylate groups.[25] Accordingly, the Pb–PhDTA complex should be present almost as a hexadentate complex. In fact, the relatively large value of $-\Delta H^{\circ}_{\mathrm{MnL}}$ of the complexation has been well accounted for by the heptacoordination of Mn^{2+} of the Mn–PhDTA complex in aqueous solutions. This explanation has been reinforced by an X-ray crystallographic study of this complex.[26]

In the Cd–PhDTA crystal, the cadmium(II) ion is fully coordinated by PhDTA and has two additional water molecules, resulting in octacoordination.[9] This finding is consistent with the interpretation of the partial molar volume data of the EDTA complexes with divalent cations including Cd^{2+}.[27,28] Accordingly, the hydration environment will only be partly destroyed, resulting in a relatively small value of $\Delta H^{\circ}_{\mathrm{MHL}}$, when protonation on the complex of a larger metal ion occurs (category A).

On the other hand, the metal ion of Category B has a large value of $-\Delta H^{\circ}_{\mathrm{MHL}}$. This can no longer be interpreted in terms of only the protonation to a carboxylate oxygen of the complex ML. The entire process of protonation may be composed of two steps, as illustrated in Fig. 2, and described as follows:

i) Detachment of one carboxylate group from the metal ion, followed by hydration as

$$\mathrm{ML^{2-} + H_2O \rightleftharpoons M(L')(H_2O)^{2-}}, \tag{3}$$

where L′ represents a ligand anion with a free carboxylate group.

ii) Protonation to an oxygen atom of the detached carboxylate group as

$$\mathrm{M(L')(H_2O)^{2-} + H^+ \rightleftharpoons M(HL')(H_2O)^-}. \tag{4}$$

The first hydration process can have a large enthalpy change, $-\Delta H^{\circ\mathrm{W}}_{\mathrm{ML'w}}$, (estimated as ca. 20 kJ mol^{-1} by extrapolating from the plot of $-\Delta H^{\circ}_{\mathrm{ML}}$ for Mn–PhDTA).[3] The second process can have a small change of enthalpy change, $-\Delta H^{\circ\mathrm{H}}_{\mathrm{MHL}}$, which will not be very different from the value for the ligand (carboxylate) protonation. Process (3) can be characterized by a negative change in entropy due to the hydration and separation of charges in M and L′. The ligand protonation has a value of ΔS°_{i}=55—56 J K^{-1} mol^{-1} (i=3, 4),[3] and therefore the smaller value of $\Delta S^{\circ}_{\mathrm{MHL}}$ can be taken as reasonable. The second protonation leading to CdH_2L can be classified as Category B, according to the corresponding thermodynamic parameters. The diprotonated species can probably no longer keep the coordination structure without the dissociation of a carboxylate group, due to strain. Accordingly, one acid hydrogen atom should be carried by a dissociated carboxylate group and the other by an undissociated group. This point has been illustrated in X-ray crystallographic studies of the diprotonated PhDTA complex ZnH_2L[29] and the diprotonated Ni–EDTA complex[30] in the solid state.

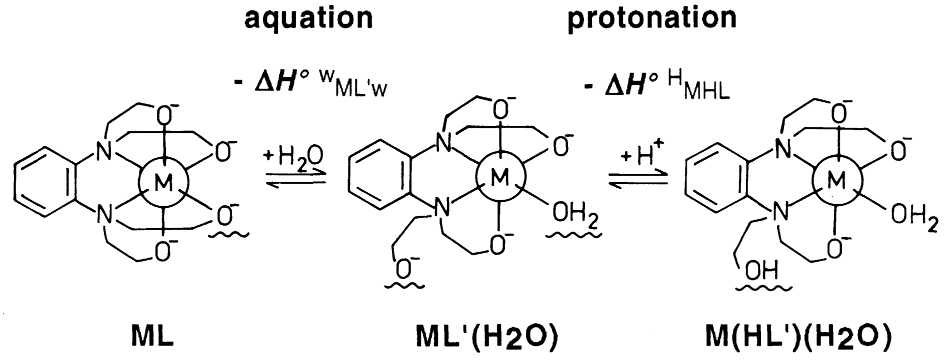

Fig. 2. Schematic diagram illustrating the two-step protonation (Category B). The first step is the detachment of a carboxylate group, followed by hydration (characterized by $-\Delta H^{\circ\mathrm{w}}_{\mathrm{ML'w}}$, w denoting a water molecule). The second step is the simple protonation to the free carboxylate group, forming a pentadentate protonated complex (characterized by $-\Delta H^{\circ\mathrm{H}}_{\mathrm{MHL}}$).

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