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Thermodynamic Studies on the Protonation of *o*-Phenylenediamine-*N*,*N*,*N'*,*N'*-tetraacetate and Its Complexation with Bivalent Transition-Metal Ions in Aqueous Solutions

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Thermodynamic studies have been carried out on the protonation of *o*-phenylenediamine-*N*,*N*,*N'*,*N'*-tetraacetate (PhDTA) and on its complexation with transition-metal ions in aqueous solutions at 25 °C and at an ionic strength of 1 mol/dm^3 (NaClO$_4$). Heats of protonation at the nitrogen atoms of this ligand are greatly reduced in comparison with those of EDTA or CyDTA, and the second protonation is even endothermic ($-\Delta H_1 = 4.7$ kJ/mol and $-\Delta H_2 = -2.8$ kJ/mol). The variation in enthalpy change of complexation of PhDTA with metal ions is parallel to those of the two aforementioned ligands, $-\Delta H$ of complexation of PhDTA being lower than those of the others for a given metal ion. The complex formation is endothermic for cobalt(II) and zinc(II). On the other hand, the change in entropy of complexation ΔS is much the same as that of EDTA for a given metal ion. Therefore, the complex formation of PhDTA is especially entropy-driven. This may be interpreted in terms of the electron-withdrawing effect of the phenylene group and a steric effect arising from the planar structure of the phenylenediamine moiety.

In an attempt to clarify the effect of replacement of the ethylenic backbone in ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid (EDTA) by the phenylene ring on complex formation, potentiometric and spectrophotometric studies have been carried out on the protonation and complexation of *o*-phenylenediamine-*N*,*N*,*N'*,*N'*-tetraacetate (abbreviated as PhDTA or L^{4-}) in aqueous solutions.[1] These investigations have shown markedly reduced basicity of the nitrogen atom in this ligand: the logarithmic protonation constants are 6.41 and 4.61[1] as compared with 8.85 and 6.28 for EDTA.[2] This is reflected in the formation constants of PhDTA complexes with divalent transition-metal ions lower than those of the corresponding ones of EDTA and CyDTA (*trans*-cyclohexanediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid). Nevertheless, a PhDTA complex ML will not dissociate into the metal ion M and the ligand L, even in a strongly acid solution. Thus neither the copper(II) nor the nickel(II) PhDTA complex dissociates appreciably even at pH 2 in the presence of ligand in excess. This fact may be explained in terms of a relatively higher value of conditional formation constant[3] K'_{ML} (effective complexation ability) for PhDTA,[2] i.e., the side-reaction coefficient[3] of this ligand, relatively lower than those of the other amino polycarboxylates and the formation of protonated complexes.[2] Reduced electron density on the amino nitrogen will lead to a more endothermic reaction with metal ions. In this context calorimetric measurements were carried out as a part of thermodynamic studies on the complex formation of this type of ligand.

Experimental Section

Materials. *o*-Phenylenediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid and metal perchlorates were prepared and purified as described previously.[2] All the stock solutions of metal perchlorates contained more or less perchloric acid to avoid the hydrolysis of metal cations. The metal contents were determined complexometrically and ranged from 0.1983 to 0.2678 M (M = mol dm^{-1}).

Calorimetric Measurements. Calorimetric measurements were carried out with a Rhesca CM-502 twin-type conduction calorimeter, which was placed in a room thermostated at 25 ± 0.1 °C. The sample and reference solutions (40 cm^3 each) were thermally equilibrated before titration. Only the former contained the ligand neutralized to a pH of about 8 in advance at the total concentration $C_{\mathrm{L}} = (1.21\text{–}2.35) \times 10^{-2}$ M, and both were adjusted to an ionic strength of 1.00 M (NaClO$_4$). The same quantity of perchloric acid (0.9981 M for protonation) or metal perchlorate solution (for complexation, $<C_{\mathrm{L}}$) was added to both cells from Metrohm E274 piston burettes with an interlocking device. Differential heat evolved was detected through a direct current amplifier or with a Rhesca CIC-1 compensation caloric counter. By titration of a 0.05088 M perchloric acid solution (1.00 M NaClO$_4$) with a 1.590 M sodium hydroxide solution, the heat of neutralization was determined as $-\Delta H = 57.2$ kJ/mol. This value agrees well with the literature value (56.9 kJ/mol at 25 °C, $I = 1.0$ M NaNO$_3$).[4]

Results and Discussion

Protonation of PhDTA. Potentiometric studies have shown that the basicity of nitrogen atoms in PhDTA is considerably weaker than that of other amino polycarboxylates such as EDTA and CyDTA.[2] The stepwise protonation of a ligand is formulated as

$$\mathrm{H}^+ + \mathrm{H}_{n-1}\mathrm{L} \rightleftharpoons \mathrm{H}_n\mathrm{L} \qquad (1)$$

with

$$K_n = [\mathrm{H}_n\mathrm{L}][\mathrm{H}^+]^{-1}[\mathrm{H}_{n-1}\mathrm{L}]^{-1} \qquad (2)$$

where K_n is the stepwise protonation constant (charges are omitted for simplicity).

Thermodynamic quantities of the ligand protonation from the calorimetric measurements are given in Table I together with those of the other amino polycarboxylates. The enthalpy change was also estimated by measuring the protonation constants potentiometrically at different temperatures (the van't Hoff isochore) for reference. A small variation in equilibrium constants with temperature resulted in less accurate values of enthalpy (Table II). They may, however, be considered to be in fair agreement with the calorimetric results, if allowance is made for some discrepancy usually observed between the results from the two methods.[5,6]

Comparison of the thermodynamic quantities for PhDTA with those for the other ligands clearly shows that the decrease in basicity at the nitrogen atoms in PhDTA stems mainly from its lower heat of protonation. The first protonations of ethylenediamine (en) and *trans*-cyclohexanediamine (Cyen) are considerably exothermic ($-\Delta H_1 = 48.1$ and 48.9 kJ/mol, respectively, at infinite dilution),[7] whereas *o*-phenylenediamine (Phenen) has a much smaller value of $-\Delta H_1 = 23.2$ kJ/mol (20 °C, $I = 1$ M in KNO$_3$).[8] The second protonation is in fact endothermic for PhDTA, in contrast to the exothermicity for the other amino polycarboxylates. Although the endothermicity is quite rarely encountered in the amine protonation, the second protonation of Phenen is endothermic ($-\Delta H_2 = -25.1$ kJ/mol).[8] On the other hand, en and Cyen show a considerable exothermicity still at the

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Table I. Thermodynamic Quantities of the Protonation of Ligands

	n	$\log K_n$	$10^{-1}(\Delta H°)/$ (kJ/mol)	$10^{-2}(\Delta S°)/$ (J/(mol K))	T/°C	I/M	ref
PhDTA	1	6.41 (1)	0.47 (2)	1.07 (1)	25	1.0 ($NaClO_4$)	this work[a]
	2	4.61 (1)	−0.28 (3)	0.98 (1)			
	3	3.53 (1)	0.35 (5)	0.56 (2)			
	4	3.00 (1)	0.08 (1)	0.55 (1)			
EDTA	1	11.24	2.12	1.47	25	0	*b,c*
	2	6.3	1.69	0.76			
	3	3.11	−0.62	0.80			
	4	2.21	−0.15	0.47			
	1		2.65		25	1.0 (KNO_3)	*c*
	2		2.41				
EDTA	1	10.26	2.38	1.15	20	0.1 (KCl)	*d*
	2	6.16	1.84	0.55			
	3	2.67	−0.60	0.71			
	4	1.99	−0.07	0.41			
	5	1.55	−0.20	0.37			
EDTA	1	10.26	2.37	1.15	20	0.1 (KNO_3)	*e*
	2	6.16	1.82	0.56			
CyDTA	1	12.35	2.78	1.41	20	0.1 (KNO_3)	*e*
	2	6.12	0.86	0.88			

[a] Estimated standard deviations in the least significant digits are shown in parentheses, and the values of $\log K_n$ are cited from previous work.[1] [b] Reference 22a. [c] Reference 22b. [d] Tillotson, M. J. L.; Staveley, L. A. K. *J. Chem. Soc.* **1958**, 3613. [e] Reference 9.

Table II. Changes in Enthalpy and Entropy of Protonation, As Determined by the van't Hoff Method[a]

	$n = 1$	$n = 2$	$n = 3$	$n = 4$
$10^{-1}(-\Delta H°_n)/(\mathrm{kJ/mol})$	0.20 ± 0.06	−0.31 ± 0.09	0.26 ± 0.12	0.04 ± 0.10
$10^{-2}(\Delta S°_n)/(\mathrm{J/(K\ mol)})$	1.16 ± 0.02	0.99 ± 0.03	0.59 ± 0.04	0.56 ± 0.03

[a] Protonation constants were measured at 15, 25, and 35 °C potentiometrically. Experimental errors in ethalpy and entropy are σ values.

Table III. Thermodynamic Quantities of Complexation of Ligands

	Mn	Co	Ni	Cu	Zn
		PhDTA[a]			
$\log (K/\mathrm{M}^{-1})$	11.37	13.18	13.48	15.21	12.89
$10^{-1}(-\Delta H°)/(\mathrm{kJ/mol})$	0.33 (2)	−0.39 (6)	1.42 (7)	1.01 (5)	−0.41 (4)
$10^{-2}(\Delta S°)/(\mathrm{J/(K\ mol)})$	2.07	2.65	2.10	2.57	2.60
		EDTA[b]			
$\log (K/\mathrm{M}^{-1})$	13.80	16.31	18.62	18.80	16.50
$10^{-1}(-\Delta H°)/(\mathrm{kJ/mol})$	1.91	1.76	3.16	3.41	2.03
$10^{-2}(\Delta S°)/(\mathrm{J/(K\ mol)})$	1.99	2.52	2.49	2.44	2.47
		CyDTA[b]			
$\log (K/\mathrm{M}^{-1})$	17.43	19.57	19.68	21.95	19.32
$10^{-1}(-\Delta H°)/(\mathrm{kJ/mol})$	1.73	1.17	2.25	2.54	0.812
$10^{-2}(\Delta S°)/(\mathrm{J/(K\ mol)})$	2.74	3.35	3.00	3.33	3.42

[a] Estimated standard deviations of enthalpies are shown in parentheses for the least significant digits. [b] The thermodynamic parameters for EDTA and CyDTA are taken from Anderegg's data.[9]

second protonation (43.1 and 42.7 kJ/mol, respectively).[7] Therefore, it can safely be concluded that the endothermicity results from the electron-withdrawing effect of the phenylene group.

A question may arise about the validity of direct comparison of the results from various sources referred to different ionic media. The complication arising from the coordination of alkali-metal ions (added as a medium salt) with amino polycarboxylates will be commented on in the Appendix, together with the effects of different ionic media on values of the enthalpy of protonation.

The protonation to a carboxylate group is exothermic in the case of PhDTA, whereas it is endothermic for EDTA.[9] This is the reason the third and fourth protonation constants of PhDTA are greater than those of EDTA.

Heat of Complexation. Calorimetric results for the complexation of PhDTA with transition-metal ions are summarized in Table III, together with those of the related compounds:

$$M^{2+} + L^{4-} \rightleftharpoons ML^{2-} \quad K_{ML} \tag{3}$$

Since the calorimetric measurement was performed in the pH range of about 5–8, the 1:1 complex ML is the sole species to be considered and the contribution from protonated complexes is negligible.[2] The reaction of PhDTA is again less exothermic than those of the homologues.[9] Cobalt(II) and zinc(II) PhDTA complexes even show endothermicity. This is a rare example encountered in the transition-metal chemistry of nitrogen-containing ligands.[10] The variation of enthalpy change with metal ions is roughly parallel to those of the related compounds, as is evident from Table III. The lower formation constant of PhDTA complexes is apparently due to a smaller change in enthalpy, because the value of the entropy change of complexation is much the same as that of EDTA for a given metal ion. The relative contribution of the enthalpy term to the free energy is less important in the case of PhDTA than for EDTA or CyDTA.

Curiously, the formation of the manganese(II) PhDTA complex is more exothermic than that of cobalt(II), when viewed in the light of the ligand field theory.[11,12] This anomaly may result from

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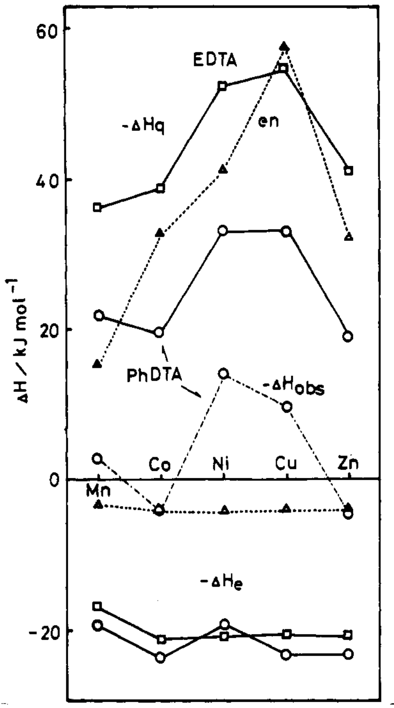

Figure 1. Observed change in the enthalpy of complexation for 1:1 PhDTA complexes ($-\Delta H_{obsd}$). Quantum-chemical ($-\Delta H_q$) and electrostatic ($-\Delta H_e$) enthalpies are as calculated from eq 5 and 6 ($p = -1$, see text). Ethylenediamine (en) complexes are chosen as reference, showing a typical behavior predicted by the ligand field theory (dotted line).[11]

the difference in hydration between the manganese(II) MnL complex and other metal complexes ML. Hence, Gurney's treatment[13] was introduced in order to take into account explicitly the effect of hydration on the thermodynamic quantities. He divided the free energy change into three parts, i.e. a long-range (electrostatic), a short-range (quantum-chemical and temperature-independent), and a cratic term. The electrostatic terms of enthalpy (ΔH_e) and entropy changes (ΔS_e) are related to the observed entropy change ΔS approximately as[14,15]

$$\Delta S_e = \Delta S + pR \ln n_w \qquad (4)$$

$$\Delta H_e = \Delta S_e(T - T_c) \qquad (5)$$

where n_w denotes the number of solvent water molecules in a unit weight of solution, p is the difference in numbers of species involved between the right- and left-hand sides in a reaction scheme, and T_c is the characteristic temperature (219 K for water).[13]

The quantum-chemical term of enthalpy change (ΔH_q) is obtainable from the observed enthalpy change ΔH:

$$\Delta H_q = \Delta H - \Delta H_e \qquad (6)$$

Calculation gives ΔH_q for $p = -1$ as illustrated in Figure 1. This value of p may be justified if we are concerned with the relative variation of the change in quantum-chemical enthalpy with different metal ions and the reaction is formulated as eq 3. In general, a certain value of p may be more appropriate than -1, if solvent melecules involved are taken into account. When the same structure is, however, assumed for all metal chelates, the same quantity of $(p + 1)RT \ln n_w$ is added to the enthalpy term, and this results in parallel displacement alone in the ordinate.

The complex formation of manganese is now more endothermic for EDTA than that of cobalt so long as the short-range force is concerned (Figure 1). However, this is not the case for PhDTA, even when the electrostatic interactions are corrected for. This suggests that the manganese(II) PhDTA complex is stabilized in comparison with octahedral complexes for some reason.

A crystal structure analysis has shown that the chelated manganese(II) ion is aquated and is heptacoordinate in the complex $(H_2O)Mn(PhDTA)Mn(H_2O)_5$.[16] In contrast, the cobalt(II) ion is hexacoordinate and is not aquated in the Co(II) PhDTA complex in the solid state.[17] Similar structures have also been found for the copper(II) and zinc(II) PhDTA complexes.[16] Thus, the heptacoordination seems to be a common feature of manganese(II) complexes with amino polycarboxylates in the solid state.[18] This may result from a larger ionic radius of this ion compared with those of other divalent transition-metal ions of the first series. Thus the manganese(II) PhDTA complex is considered to exist in either or both of the following forms: (1) seven-coordinate $Mn(H_2O)L^{2-}$ as specified by the crystal structure; (2) six-coordinate $Mn(H_2O)L^{2-}$ with L acting as a pentadentate ligand. In the former case the additional aquation gives extra exothermicity and negative entropy change if the M–L bonding remains unchanged. The latter form can be described as a result of the following transformation of a normal octahedral complex MnL

$$MnL + H_2O \rightleftharpoons MnL'(H_2O) \qquad (7)$$

where L and L′ represent a hexadentate and a pentadentate ligand, respectively. This process is an exchange of oxygen on the central ion in a rough approximation, but the release of strain applied to the chelate rings may contribute to exothermicity. The aquation reaction is also consistent with the smaller change in entropy of the manganese(II) complex than for the other transition-metal ions, a common phenomenon observed for the three ligands except for Ni^{2+} PhDTA (Table III). Hence, the present thermodynamic data point to the formation of the aquated Mn(II) PhDTA complex $MnL(H_2O)$ in the aqueous solution, with L being penta- or hexadentate.

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Appendix

Amino polycarboxylates coordinate to alkali-metal ions added as medium salts to a different extent, and the activity coefficient varies with ionic strength. The experimental enthalpy of protonation $\Delta H_{HL}(\text{exptl})$ ($=\Delta H_1$) is a mixed value of $\Delta H_{HL}(H^+ + L^{4-} \rightleftharpoons HL^{3-})$ and $\Delta H_{NaL}(H^+ + NaL^{3-} \rightleftharpoons HL^{3-} + Na^+)$. Thus

$$\begin{aligned}\Delta H_{HL}(\text{exptl}) &= (1 - r)\Delta H_{HL} + r(\Delta H_{HL} - \Delta H_{NaL}) \\ &= \Delta H_{HL} - r\,\Delta H_{NaL}\end{aligned} \qquad (A1)$$

where r is the ratio of NaL present to the total L, that is $[NaL]/([NaL] + [L])$. Charles has estimated $\Delta H_{NaL} = -1.4$ kJ/mol and $\Delta S = 13$ J/(mol K) for EDTA ($I = 1$ M, 25 °C).[19] From a linear free energy relationship, we estimate $\log K_{NaL} = 0.63$ for PhDTA,[2] if we accept 3.79 as the corresponding value for CyDTA.[20] This leads to $r = 0.81$ for PhDTA at $[Na^+] = 1$ M. Although ΔH_{NaL} is not available for PhDTA at present, it is estimated as 0.2 kJ/mol, since ΔS(PhDTA) may be equated with ΔS(EDTA) as has been mentioned above. Thus $-\Delta H_{HL}$ is thought to be practically equal to $-\Delta H_{HL}(\text{exptl})$ of PhDTA shown in Table I.

The thermodynamic protonation constant K_n^T is related to the concentration constant corrected for the complexation with sodium ion K_n^C

$$K_n^C = K_n^T y_H y_{n-1}/y_n \qquad (A2)$$

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where y_H and y_n represent the activity coefficients of the proton and a protonated species H_nL. Since the relative partial molar enthalpy $\bar{l}_i$ is generally given by

$$-\frac{\bar{l}_i}{RT^2} = \left(\frac{\partial \ln y_i}{\partial T}\right)_{P,n_j} \tag{A3}$$

partial differentiation of eq A2 with respect to temperature results in

$$\Delta\Delta H_n = \Delta H_n^{C} - \Delta H_n^{T} = \bar{l}_n - \bar{l}_{n-1} - \bar{l}_H \tag{A4}$$

where ΔH_n^{C} and ΔH_n^{T} are changes in enthalpy at a given ionic strength and at infinite dilution, respectively. The value of the right-hand side of eq A4 for PhDTA may not differ largely from that for EDTA, because both ligands are similar from an electrostatic point of view. As the complexation of potassium ion is considerably weaker than that of sodium ion,[21] it follows that $\Delta\Delta H_n(I = 1\text{–}0.1\ \text{M})/(\text{kJ/mol}) = -26.5 + 23.7 = -2.8$ from the results for EDTA[22] summarized in Table I. Hence, the intrinsic enthalpy change $-\Delta H_{HL}/(\text{kJ/mol})$ can be calculated as 1.9 (=4.7 − 2.8) for PhDTA at $I = 0.1$ M. This value may be compared more straightforwardly with that of EDTA or CyDTA at $I = 0.1$ M (KNO_3).[9] The less exothermic protonation of PhDTA is now clear.

The second protonation is less complicated, because an alkali-metal ion bonds to HL much more weakly. This is reflected in similar $-\Delta H$ values of EDTA for a potassium nitrate (24.10 kJ/mol, $I = 1$ M) and for a sodium perchlorate medium (24.14 kJ/mol, $I = 1$ M).[22]

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Electronic Structures of Cluster Compounds of MoS_4^{2-}, $Mo_3S_9^{2-}$, and $Ni(MoS_4)_2^{2-}$ by XPS Studies

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XPS studies were performed on cluster compounds $(TEA)_2MoS_4$, $(TEA)_2Mo_3S_9$, and $(TEA)_2Ni(MoS_4)_2$ (TEA = tetraethylammonium). The results are analyzed on the basis of formal charge and molecular orbital considerations. The major features of the valence band spectra of $(TEA)_2MoS_4$ and $(TEA)_2Mo_3S_9$ are in good agreement with theoretical densities of states of recent calculations using the local density pseudopotential method. However, the XPS data show that the multiple excitation process is quite significant in the simple tetrahedral MoS_4^{2-}. The XPS of $(TEA)_2Ni(MoS_4)_2$ reveals a significant difference from the XPS of the other two compounds in the top valence band, which is attributed to the additional d electrons in Ni (formally d^8) compared to Mo (formally d^2).

Introduction

The ions MoS_4^{2-}, and $Mo_3S_6^{2-}$, and $Ni(MoS_4)_2^{2-}$ belong to a large class of compounds that serve as models of active sites in molybdoenzymes[1] and for many hydrodesulfurization and hydrodenitrogenation catalysts.[2] An ultimate goal is to reach an electronic structural understanding for the nature of these chemical activities.[3–6] To this end, extensive theoretical work has been carried out recently on several Mo–S complexes[3] and transition-metal sulfide materials[4,5] to examine their bonding properties, frontier orbitals and charge distribution. In contrast, relatively little experimental work probing the electronic properties of these phenomena exists.[6,7] Here the results of experimental studies of $(TEA)_2MoS_4$, $(TEA)_2Mo_3S_9$, and $(TEA)_2Ni(MoS_4)_2$ (TEA = tetraethylammonium) are reported. These studies were performed by using X-ray photoelectron spectroscopy (XPS). Where possible, these results are directly compared with theory.

Photoelectron spectroscopy measures the distribution of the photoexcited electrons, which, in many cases, can be directly compared with the ground-state properties such as the valence band density of states (DOS). Theoretical calculations were performed by using the local density pseudopotential method for molecules as previously described.[8] In this method the electrons are represented by effective one-electron wave functions. The "average" exchange and correlation contributions are included via a one-electron exchange-correlation potential. The core electrons are represented by an angular momentum dependent pseudopotential (effective core potential), whereby only valence electrons enter the calculations. The interpretation of the results is thus as simple as in the extended Hückel theory. The method is, however, first-principle and parameter free.

Experimental Section

$(TEA)_2MoS_4$ was prepared by the metathesis reaction of $(NH_4)_2MoS_4$ with (TEA)OH in methanol solution.[9] The MoS_4^{2-} anions have a regular tetrahedral structure.[10] $(TEA)_2Mo_3S_9$ was synthesized by the thermal reaction of MoS_4^{2-} in DMF solution under anaerobic conditions.[11] The anion $Mo_3S_9^{2-}$ formally consists of two MoS_4^{2-} groups each chelating a central MoS_2^{+} ion[8] (Figure 1). $(TEA)_2Ni(MoS_4)_2$ was synthesized by the method of Callahan and Piliero.[11] It contains two

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