best defined redox chemistry of any class of multiply bonded dimetal species.[1] The only conversions that remain to be accomplished are shown by dashed lines in Scheme I. These await the one-electron chemical reduction of $[Re_2Cl_6(PR_3)_2]^-$ to $[Re_2Cl_6(PR_3)_2]^{2-}$, a transformation that has so far defied our attempts.

**Acknowledgment.** Support from the National Science Foundation (Grant No. CHE82-06117) is gratefully acknowledged. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered to the American Chemical Society, for partial support of this research.

**Registry No.** $[(C_5H_5)_2Co][Re_2Cl_6(PEt_3)_2]$, 93806-21-4; $[(C_5H_5)_2Co][Re_2Cl_6(P\text{-}n\text{-}Pr_3)_2]$, 93806-23-6; $[(C_5H_5)_2Co][Re_2Cl_6(PMePh_2)_2]$, 93806-25-8; $[(C_5H_5)_2Co][Re_2Cl_6(PEtPh_2)_2]$, 93806-27-0; $[(C_5H_5)_2Co][Re_2Cl_5(PMePh_2)_3]$, 93841-95-3; $[Re_2Cl_5(PMePh_2)_3]PF_6$, 93806-29-2; $Re_2Cl_4(PMePh_2)_4$, 93806-30-5; $[(C_5H_5)_2Co][Re_2(O_2CC_3H_7)_4Cl_2]$, 93806-31-6; $[(C_5H_5)_2Co][Re_2(O_2CCMe_3)_4Cl_2]$, 93806-33-8; $[(C_5H_5)_2Co][Re_2(O_2CC_6H_5)_4Cl_2]$, 93806-35-0; $[Re_2Cl_6(PEt_3)_2]^{2-}$, 93806-36-1; $[Re_2Cl_6(P\text{-}n\text{-}Pr_3)_2]^{2-}$, 93806-37-2; $[Re_2Cl_6(PMePh_2)_2]^{2-}$, 93806-38-3; $[Re_2Cl_6(PEtPh_2)_2]^{2-}$, 93806-39-4; $[Re_2Cl_5(PMePh_2)_3]^+$, 93806-28-1; $Re_2Cl_6(PEt_3)_2$, 19584-31-7; $Re_2Cl_6(P\text{-}n\text{-}Pr_3)_2$, 41021-44-7; $Re_2Cl_6(PMePh_2)_2$, 55661-11-5; $Re_2Cl_6(PEtPh_2)_2$, 55661-10-4; $Re_2Cl_5(PMePh_2)_3$, 55450-43-6; $Re_2Cl_5(PEt_3)_3$, 61840-74-2; $Re_2(O_2CC_3H_7)_4Cl_2$, 15654-30-5; $Re_2(O_2CCMe_3)_4Cl_2$, 15654-33-8; $Re_2(O_2CC_6H_5)_4Cl_2$, 15654-34-9; $(n\text{-}Bu_4N)_2Re_2Cl_8$, 14023-10-0; $Re_2Cl_6(P\text{-}n\text{-}Bu_3)_2$, 38832-70-1; $Re_2Cl_6(PMe_2Ph)_2$, 92359-79-0; $[(C_5H_5)_2Co]$, 1277-43-6.

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# Complexation of *o*-Phenylenediaminetetraacetic Acid with Some Bivalent First-Row Transition-Metal Ions in Aqueous Solution

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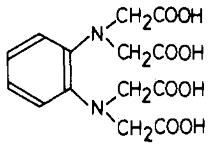
Potentiometric and spectrophotometric studies have been carried out on the complexation of *o*-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (PhDTA, $H_4L$) with some transition-metal ions in aqueous solution at 25 °C and at an ionic strength of 1 M ($NaClO_4$). The studied metal ions include manganese(II), iron(II), cobalt(II), nickel(II), copper(II), and zinc(II). The usual pH titration method gave satisfactory results for the formation constants $K_{ML}$ for manganese(II) and iron(II), but this was not the case for the other transition metals, whose complexes do not dissociate to an appreciable extent even at pH as low as 2. Therefore copper-selective and mercury electrodes were used to monitor free metal ion concentration in a ligand buffer containing an excess of a second metal ion. Spectrophotometric measurements resulted in an equilibrium constant for a relevant exchange reaction, from which $K_{ML}$ was also obtained. Reduced basicity of the nitrogen atom in PhDTA is reflected in the formation constants of its complexes, which are lower than those of the corresponding EDTA and CyDTA complexes. However, the conditional formation constants of PhDTA complexes become the highest when these complexes are reacted in the acid region. This is due to the lower basicity of the ligand and the formation of diprotonated PhDTA complexes. The logarithmic formation constants of PhDTA complexes are linearly related with those of CyDTA complexes.

Considerable efforts have been devoted to improve the complexing ability of amino polycarboxylates such as ethylenediaminetetraacetic acid (EDTA) by increasing the number of donor atoms or by introducing some groups into the skeleton.[1-3] Although the gauche character of the chelate ring is usually retained in a variety of EDTA derivatives, substitution of the phenylene group for the ethylenic backbone leads to the planar configuration of the N–C–C–N moiety and decreases the basicity of two nitrogen atoms.[4,5] Complexation of *o*-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (**1**) has been, however, little investigated, in spite of the interesting features expected from such structural and electronic modifications. This may be partly due to the considerable difficulty in synthesizing this ligand with chloroacetic acid.[6] The purpose of the present paper is to describe an experimental study on the complexation of this ligand with some divalent transition-metal ions in an aqueous solution.



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## Experimental Section

**Reagents.** *o*-Phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (1,2-phenylenedinitrilotetraacetic acid, abbreviated as PhDTA or $H_4L$) was prepared according to the method of McCandlish et al.[5] with slight modifications.[7] The reaction mixture was monitored with a combination electrode to maintain the constant pH of the solution.

Triethylenetetramine (trien, Wako, technical grade) was distilled at 160 °C under reduced pressure. The distillate (200 g) was dissolved in 700 g of ethanol, and concentrated hydrochloric acid was added dropwise. 2,2′,2″-Triaminotriethylamine (tren) precipitated first when 100 $cm^3$ of the acid was added. Then a mixture of tren and trien was obtained after 360 $cm^3$ of acid was added. Further addition of hydrochloric acid (570 $cm^3$) and ethanol (100 $cm^3$) gave a white crystal of trien·4HCl. Identification of compounds was carried out by the carbon-13 NMR method. trien·4HCl was recrystallized by dissolving the product in a small quantity of hot water (60 °C), followed by addition of cool ethanol.[8] This procedure was repeated three times, and then the Volhard determination of chloride was applied, resulting in a value of purity of 99.43% for trien·4HCl.

Sodium and other metal perchlorates were prepared by reacting metal carbonates with or by dissolving 99.99% metals in 60% perchloric acid (Wako Pure Chemical Industries), and they were recrystallized two or three times from water.[9] All other chemicals used were of reagent grade.

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(1) (a) Schwarzenbach, G. *Helv. Chim. Acta* **1946**, *29*, 1338. (b) Schwarzenbach, G. *Adv. Inorg. Chem. Radiochem.* **1961**, *3*, 257–285.

(2) Chaberek, S.; Martell, A. E. "Organic Sequestering Agents"; Wiley: New York, 1959.

(3) Anderegg, G. In "Coordination Chemistry"; Martell, A. E., Ed., Van Nostrand Reinhold: New York, 1971; ACS Monogr. 168, pp 427–490.

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

(5) McCandlish, E. F. K.; Michael, T. K.; Neal, J. A.; Lingafelter, E. C.; Rose, N. J. *Inorg. Chem.* **1978**, *17*, 1383.

(6) Otozai, K.; Kato, I. *Jpn. Anal.* **1959**, *8*, 259.

(7) Anal. Calcd for $C_{14}H_{16}O_8N_2$: C, 49.42; N, 8.23; H, 4.74. Found: C, 49.52; N, 8.25; H, 4.74.

(8) Utsuno, S., private communication on the method for purifying trien.

(9) Nakasuka, N.; Makimura, K.; Kajiura, H. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3749.

0020-1669/85/1324-0010$01.50/0

**Equipment.** Measurements were carried out at 25.0 ± 0.1 °C and at an ionic strength of $I = 1.00$ M ($NaClO_4$),[10] unless otherwise noted. Electrochemical measurements were done by using a Corning 130 pH meter or an Orion Model 701A Ionalyzer. The accuracy was 0.1 mV. We utilized a Metrohm EA 109 glass electrode, a DKK copper-selective electrode (Denki Kagaku Keiki), and/or a J-tube mercury electrode,[11] together with a Merohm EA 404 calomel electrode, which contained a saturated sodium chloride solution. A 0.01 M $HClO_4$ solution ($I = 1$ M in $NaClO_4$) was used as a pH standard. A Horiba 6028-10T combination pH electrode was used with a Hitachi-Horiba M-5 pH meter for the ligand synthesis.

The UV-visible spectrophotometric measurements were made with a Union Giken SM-401 or a Carl Zeiss Model PMQ II spectrophotometer. The NMR spectra were obtained on a JEOL JNM-PMX60 or a JEOL JNM-FX90QE FT spectrometer for proton and on a JEOL JNM-FX60 FT spectrometer for carbon-13. IR spectra were recorded on a JASCO IRA-3 spectrophotometer. The mass spectra were obtained with a Hitachi M-80 double-focusing mass spectrometer. The thermogravimetric measurements were carried out with a Shimadzu DT-30 thermal analyzer. X-ray powder spectra were recorded with a Rigaku Denki X-ray diffractometer, Model D-3F. Elemental analysis was performed by the microanalytical section at the Faculty of Agriculture, Nagoya University. Data were processed on FACOM M 382 at the Nagoya University Computation Center.

## Results

**(1) Properties of PhDTA.** The carbon-13 NMR spectra of PhDTA showed five sharp peaks in deuterium oxide: 59.7 ($CH_2$ in carbomethoxy group; relative intensity 2), 126.8 and 130.0 (benzene CH; each 1), 145.8 (benzene CN; 1), 179.9 ppm (carboxy CO; 2). The $^1H$ NMR spectra in $D_2O$ were identical with those of the experiments by McCandlish and others[5] except for chemical shifts.[12]

In the molecular ion region the protonated molecule ($MH^+$) appeared at $m/z$ 341 as the base peak in the SI mass spectrum.

Although IR spectra of a product were in agreement with the aforementioned experiments (denoted as spectra A) in most cases, vibrational spectra were slightly different from the authentic ones (spectra A) occasionally on recrystallization from water (denoted as spectra B), in that new peaks appeared at 1420, 960, and 760 $cm^{-1}$ in spectra B whereas the peaks seen in spectra A at 1305, 1290, and 750 $cm^{-1}$ disappeared. Thermogravimetric analysis of both types of compounds showed the absence of hydrated water. In each case the ligand was stable and maintained the same weight up to 210 °C, where it decomposed without giving a definite melting point. $^1H$ NMR, $^{13}C$ NMR, elemental analysis,[7] and protonation constants gave identical results for both products. Moreover, normal spectra A were observed when the product from water was recrystallized from acetone in turn. Therefore, the curious behavior may be interpreted in terms of the difference in packing on crystallization from different solvents. This was confirmed by an X-ray powder diffraction study, which showed entirely different patterns for the products from the two solvents.

When an undried product was dissolved in acetone and placed over concentrated sulfuric acid in a desiccator for days, white large cubic crystals appeared. This compound gives well-defined $^1H$ NMR spectra in $D_2O$ and IR spectra (see Figure S1; supplementary material). The former is identical with those of PhDTA, except for an acetone peak. Comparison of the integrated areas indicated a composition of PhDTA·2(acetone), which was confirmed by alkalimetry. The diacetone adduct weathered into powder in a few days and returned to PhDTA when exposed to air.

Purification of the ligand is easily achieved by recrystallizing the diacetone adduct from water. The product no longer contained acetone, and an acid–base titration showed a purity of over 99.5%, although repeated recrystallization from acetone alone gave a purity of no more than 98.5%.

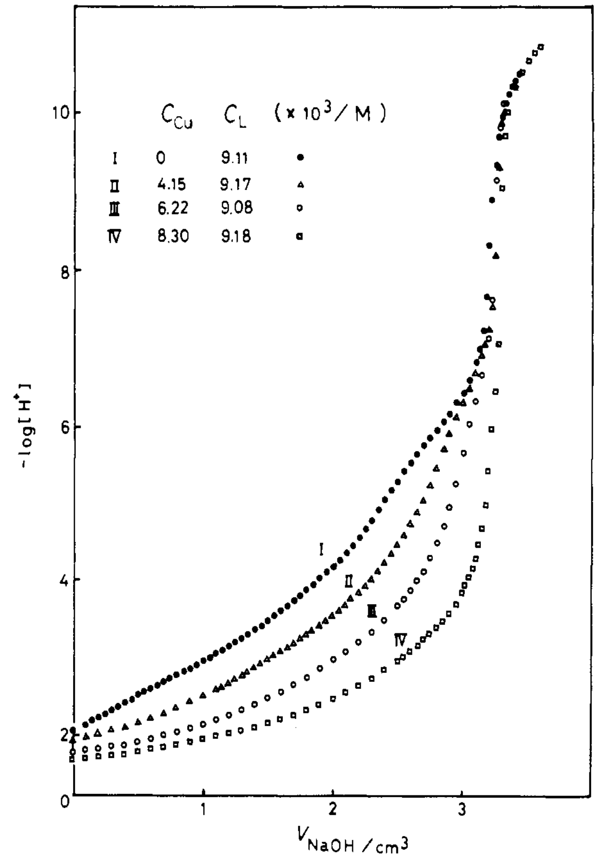

**Figure 1.** Titration of PhDTA with a 1.139 M NaOH solution in the absence and in the presence of copper(II) perchlorate. Total concentrations of copper(II) ion and PhDTA: (I) $C_{Cu} = 0$, $C_L = 9.11 \times 10^{-3}$ M; (II) $C_{Cu} = 4.15 \times 10^{-3}$ M, $C_L = 9.17 \times 10^{-3}$ M; (III) $C_{Cu} = 6.22 \times 10^{-3}$ M, $C_L = 9.08 \times 10^{-3}$ M; (IV) $C_{Cu} = 8.30 \times 10^{-3}$ M, $C_L = 9.18 \times 10^{-3}$ M.

**(2) Formulation of Equilibria.** The stepwise protonation of the PhDTA anion $L^{4-}$ is expressed as

$$K_i = [H_iL]/[H_{i-1}L][H^+] \qquad (1)$$

The charge for a species will be omitted at times except that for $H^+$ for simplicity. As will be discussed later, PhDTA forms only a 1:1 complex with a metal ion $M^{2+}$; the formation constant is defined by

$$K_{ML} = [ML]/[M][L] \qquad (2)$$

Protonation of the metal complex ML is formulated as

$$K^H_{MH_iL} = [MH_iL]/[MH_{i-1}L][H^+] \qquad (3)$$

The average number of protons bound to a ligand $\bar{q}$ is defined as

$$\bar{q} = (\sum_q q[H_qL] + \sum_q q[MH_qL])/C_L \qquad (4)$$

where $C_L$ is the total concentration of the ligand. Calculated $\bar{q}$ values are compared with experimental ones resulting from pH metric data to give relevant formation constants.

**(3) Protonation of the Ligand.** Application of a least-squares technique to the results from usual pH titrations (Figure 1) produced four protonation constants, $K_1$–$K_4$, for PhDTA, which are summarized in Table I. Addition of perchloric acid to a ligand solution showed further protonation in a highly acid region, where allowance should be made for the liquid-junction potential. The measured emf ($E$) of the cell is given by

$$E = E° + s \log [H^+] + E_j \qquad (5)$$

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[10] 1 M = 1 mol dm$^{-3}$.

[11] Reilley, C. N.; Porterfield, W. W. *Anal. Chem.* **1956**, *28*, 443.

[12] The reported values are 4.0 and 7.06 ppm downfield from *tert*-butyl alcohol,[5] whereas we found a singlet at 4.35 ppm and an octet including two sharp peaks centered at 7.2 ppm from DSS on 60- and 90-MHz spectrometers.

Table I. Protonation Constants of PhDTA and Related Compounds (log $K_i$)

| | log $K_i$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | $i = 1$ | $i = 2$ | $i = 3$ | $i = 4$ | $T$/°C | $I$/M | ref |
| PhDTA | 6.41 | 4.61 | 3.53 | 3.00 | 25 | 1.0 | this work[a] |
| PhDTA | 6.7 | 4.8 | 3.7 | 2.9 | 30 | 0.1 | 4 |
| EDTA | 8.85 | 6.28 | 2.3 | 2.2 | 20 | 1.0 | 13b |
| CyDTA | 9.30 | 5.87 | 3.52 | 2.41 | 20 | 1.0 | 13b |

[a] Determined potentiometrically; $10^2C_L = 1.11, 1.21, 1.25$, and 1.50 M (see text).

where $E°$ is the emf at unit hydrogen ion concentration in the absence of the liquid-junction potential, $s$ is the Nernstian slope, and $E_j$ is the liquid-junction potential at the calomel electrode. In this work the slope $s$ was determined as 59.15 mV, from the data over a pH range 2.0–3.5. Deviation from linearity was observed between $E$ and $-\log [H^+]$ at pH <2. This may be attributed to a change in $E_j$ as a function of hydrogen ion concentration, and $E_j$ conformed to

$$E_j/s = 0.0498[H^+] - 0.0348[H^+]^2 \qquad (6)$$

Gran plots gave a value of $pK_w = 13.75$ at $I = 1$ M in $NaClO_4$.

The experimental value of $\bar{q}$ passes through the point $\bar{q} = 4.5$ at $-\log [H^+] = 0.7$, and increases to >5 with increasing hydrogen ion concentration. This indicates that log $K_5$ is somewhat less than 0.7 (Figure S2; supplementary material).

The ligand shows three absorption maxima at 231 nm ($\epsilon = 1.1 \times 10^4$ $M^{-1}$ $cm^{-1}$), 256 nm (shoulder, $\epsilon = 5.8 \times 10^3$ $M^{-1}$ $cm^{-1}$), and 295 nm ($\epsilon = 1.6 \times 10^3$ $M^{-1}$ $cm^{-1}$) at $-\log [H^+] = 2.2$ ($10^4C_L = 4.96$ and 5.69 M). At a pH less than 4.0, the intensities of these peaks change without appreciable shift of the wavelength. Absorbance at 295 nm decreases monotonically with hydrogen ion concentration to become nonabsorbing at $C_H$ less than 1 M. The change in absorbance was consistent with log $K_5 = 0.4$ and log $K_6 = 0.3$, when plotted as a function of $-\log [H^+]$.[13]

**(4) Complex Formation. Alkalimetry.** PhDTA solutions were titrated with sodium hydroxide in the presence of metal perchlorates, as illustrated in Figure 1. Analysis of titration curves gave the values of formation constants for ML as well as protonation constants for the complex, in the case of manganese(II) and iron(II). In the usual titration procedure for the latter, a very small quantity of oxygen present oxidized the iron(II) complex to give a brown solution. Thus, the solid ammonium iron(II) sulfate (Mohr's salt) was introduced into a ligand solution,[14] which was deoxygenated previously with nitrogen passed through an iron(II)–EDTA or a pyrogallol aqueous solution.[15]

For the other transition metals, direct determination of the formation constant $K_{ML}$ from titration curves was unsuccessful, since the complexation of PhDTA in excess was so complete that the free metal ion was down to an extremely low level of concentration even at a pH as low as 2.[16]

In such a case, however, the protonation constant of ML is readily determined from the mean number of protons bound to a complex ML, $\bar{n}_H$, defined as

$$\bar{n}_H = \sum_n n[MH_nL]/\sum_n[MH_nL] = \sum_n n[MH_nL]/C_M \qquad (7)$$

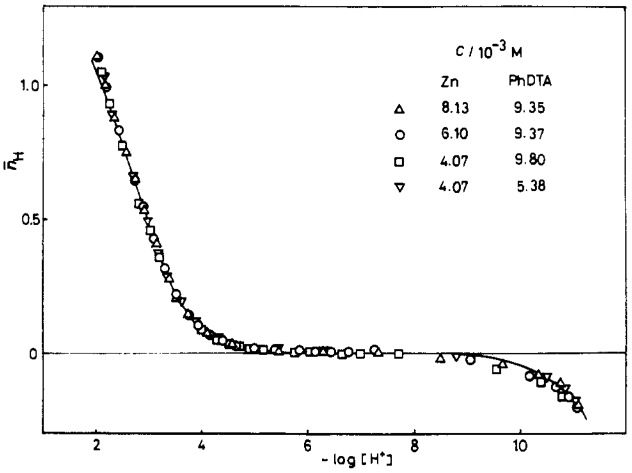

**Figure 2.** Average number of protons bound to the zinc(II)–PhDTA complex as a function of pH. The solid curve was calculated by use of the constants shown in Table II.

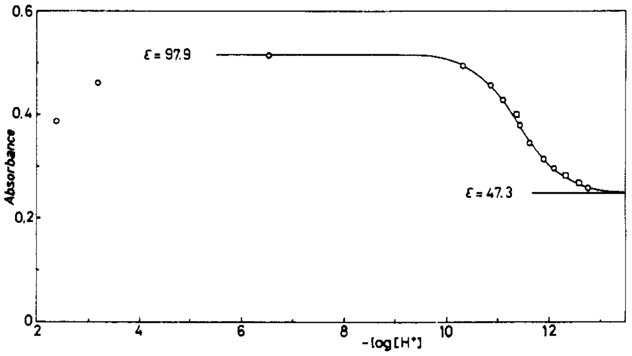

**Figure 3.** Spectrophotometric determination of the deprotonation constant of the copper(II)–PhDTA complex. $C_{Cu} = 5.269 \times 10^{-3}$ M, and $C_L = 5.545 \times 10^{-3}$ M. A least-squares technique yields the solid curve and the hydrolysis constant (see text).

Experimental values of $\bar{n}_H$ are plotted as a function of $-\log [H^+]$, which is illustrated in Figure 2 for zinc(II). The experimental points fall on a single line, irrespective of concentrations of the metal and the ligand.

Values of $\bar{n}_H$ exceed unity as the pH is lowered, which indicates the formation of the diprotonated species $MH_2L$. Protonation constants were evaluated by the curve-fitting method.[17] These values were further refined by data processing with ACREF[16] at a constant value of $K_{ML}$ that had been determined by the ion-selective electrode method described below.

Hydrolysis of metal complexes is evident from negative $\bar{n}_H$ values at higher pH, as illustrated in Figure 2, and the hydrolysis constant was approximately evaluated by a similar curve-fitting method. Since deprotonation begins only at an elevated pH where the glass electrode works less satisfactorily, the hydrolysis constant thus determined is accompanied by a considerable error, which may amount to 0.5 (see Table II).

The copper complex undergoes a change in color as the pH is varied, and it was analyzed as a function of pH. The least-squares technique gave a more accurate value of the hydrolysis constant, log $K^H{}_{CuL} = 11.40 \pm 0.04$ ($2\sigma$), as shown in Figure 3.

**Use of a Copper-Selective Electrode.** Although a copper ion electrode is said to respond linearly to pCu to as low a concentration as $10^{-19}$ M in a solution metal buffered with triethylenetetramine (trien)[18] or ethylenediamine (en),[19] this was

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(13) (a) Lagrange, J.; Lagrange, P. *Bull. Soc. Chim. Fr.* **1972**, 13. (b) Anderegg, G. *Helv. Chim. Acta* **1967**, *50*, 2333.

(14) Skochdopole, R.; Chaberek, S. *J. Inorg. Nucl. Chem.* **1959**, *11*, 222.

(15) Studies on the protonation of sulfate ion (B) resulted in log $K_1 = 1.05 \pm 0.02$ ($2\sigma$) at $I = 1$ M ($NaClO_4$). Titration of Mohr's salt gave log $K_{FeB} = 1.87 \pm 0.02$. Examination of the titration curves for PhDTA, by itself and in the presence of ammonium perchlorate, indicated no interaction between the ligand and ammonium ion, which was also confirmed by the identical electronic spectra of PhDTA in both cases.

(16) Existence of dimeric species such as $M_2L$ or a higher complex $ML_2$ was disproved under the present experimental conditions by data processing using a Fortran program ACREF: Cromer-Morin, M.; Scharff, J. P.; Martin, R. P. *Analusis* **1982**, *10*, 92.

(17) Rossotti, F. J. C.; Rossotti, H. "The Determination of Stability Constants"; McGraw-Hill: New York, 1961.

(18) Heijne, G. J. M.; van der Linden, W. E. *Anal. Chim. Acta* **1978**, *96*, 13.

(19) Avdeef, A.; Zabronsky, J.; Stuting, H. H. *Anal. Chem.* **1983**, *55*, 298.

Table II. Formation Constants of Metal Complexes (log $K$)

| | Mn | Fe | Co | Ni | Cu | Zn | $T$/°C | $I$/M | remarks[a] |
|---|---|---|---|---|---|---|---|---|---|
| | | | | log $K_{ML}{}^{n}$ | | | | | |
| PhDTA | | | 13.18* | 13.48* | 15.21* | 12.89* | 25 | 1.0 | Cu; *b* |
| | 11.4 | | | 13.1 | | 12.9 | 25 | 1.0 | Hg; *c* |
| | 11.37* | 12.2* | | | | | 25 | 1.0 | pH; *d* |
| | | | 13.11 | | 15.29 | | 25 | 1.0 | sp; *e* |
| EDTA | 14.04 | 14.22 | 16.31 | 18.62 | 18.80 | 16.50 | 20 | 0.1 | *f, g* |
| CyDTA | 16.78 | 18.20 | 18.92 | 19.68 | 21.30 | 18.68 | 20 | 0.1 | *f-h* |
| | | | | log $K^{H}{}_{MHL}$ | | | | | |
| PhDTA | 2.29 | 2.41 | 2.52 | 3.32 | 3.04 | 2.96 | 25 | 1.0 | pH; *d* |
| EDTA | 3.1 | 2.75 | 3.0 | 3.2 | 3.0 | 3.0 | 20 | 0.1 | *f, i* |
| CyDTA | 2.8 | | 2.9 | | 3.1 | 2.9 | 20 | 0.1 | *f* |
| | | | | log $K^{H}{}_{MH_2L}$ | | | | | |
| PhDTA | 1.7 | | 1.2 | 0.9 | 1.8 | 1.3 | 25 | 1.0 | pH; *d* |
| | | | | log $K^{H}{}_{ML}$ | | | | | |
| PhDTA | 11.5 | | 12 | 11.5 | 11.4 | 11.7 | 25 | 1.0 | pH; *d, j* |
| EDTA | | | 12.92 | 13.34 | 11.35 | 11.5 | 25 | 1.0 | *k-m* |

[a] Cu, Hg, pH, and sp stand for the methods of copper ion selective electrode, mercury electrode, pH titration, and spectrophotometry, respectively. [b] $C_{Cu} = 5.25 \times 10^{-3}$ M, $C_N = (0.489 - 3.88) \times 10^{-2}$ M, $C_L = (0.738 - 1.202) \times 10^{-2}$ M. [c] $C_{Hg} = (0.109 - 1.63) \times 10^{-4}$ M, $C_L = (0.213 - 3.53) \times 10^{-3}$ M, $C_M = (2.07 - 9.14) \times 10^{-4}$ M. [d] $C_M = (4.0 - 8.2) \times 10^{-3}$ M, $C_L = (5.2 - 9.4) \times 10^{-3}$ M. [e] $C_{Co} = (0.801 - 1.202) \times 10^{-2}$ M, $C_{Zn} = (0.8128 - 0.1626) \times 10^{-2}$ M, $C_L = 1.272 \times 10^{-2}$ M; $C_{Cu} = 4.120 \times 10^{-3}$ M, $C_{Ca} = 2.310 \times 10^{-2}$ M, $C_L = 4.166 \times 10^{-3}$ M, $C_{trien} = 4.144 \times 10^{-3}$ M. [f] Schwarzenbach, G.; Gut, R.; Anderegg, G. *Helv. Chim. Acta* 1954, *37*, 937. [g] Bond, J.; Jones, T. I. *Trans. Faraday Soc.* 1959, *55*, 1310 (25 °C, 0.1 M; for the Fe(II) complexes of EDTA and CyDTA). [h] Starý, J. *Anal. Chim. Acta* 1963, *28*, 132 (20 °C, 0.1 M; for Ni-CyDTA). [i] Borggaard, O. K. *Acta Chem. Scand.* 1972, *26*, 393 (for FeH(edta)). [j] These values are evaluated by fitting potentiometric data to the normalized curve (Figure 2). In the case of Cu-PhDTA, log $K^{H}{}_{Cu} = 11.40$* has been obtained by the spectrophotometric method (see text). [k] Bhat, T. R.; Krishnamurthy, M. *J. Inorg. Nucl. Chem.* 1963, *25*, 1147 (spectrophotometric method, except for Zn(II)). [l] Kula, R. J. *Anal. Chem.* 1965, *37*, 989 (34-38 °C; $I$ = ?; NMR method; only for Zn(II)). [m] Converted from the original data, assuming that p$K_w = 13.75$. [n] An asterisk indicates the best formation constant in this study.

not the case with PhDTA, possibly for the same reason as for the case with EDTA.[18,20] Copper(II) ion concentration was, however, successfully measured with a copper(II) ion selective electrode in a ligand buffer[21] containing an excess of a second metal perchlorate.[22]

Let us consider the following exchange reaction:

$$\mathrm{Cu} + \mathrm{NL} \rightleftharpoons \mathrm{N} + \mathrm{CuL} \tag{8}$$

where N is another metal ion.

$$K_{ex} = \frac{[\mathrm{N}][\mathrm{CuL}]}{[\mathrm{Cu}][\mathrm{NL}]} = \frac{K_{CuL}}{K_{NL}} \tag{9}$$

So long as $K_{NL} < K_{CuL}$ and any complexes do not dissociate to an appreciable extent, the free copper(II) concentration is given by[23]

$$[\mathrm{Cu}] = \frac{C_{Cu}(C_{Cu} + C_N - C_L)K_{NL}\alpha_{NL(H)}}{(C_L - C_{Cu})K_{CuL}\alpha_{CuL(H)}} \tag{10}$$

under the following conditions:

$$C_{Cu} < C_L < C_{Cu} + C_N \tag{11}$$

$\alpha_{NL(H)}$ and $\alpha_{CuL(H)}$ are side-reaction coefficients taking into account the protonation of the complexes NL and CuL.[24]

As evident from eq 10, pCu remains constant in a pH range where the protonation of both complexes is negligible. This is illustrated in Figure 4, which gives the value of pCu = 7.54 for a ligand buffer containing calcium(II) ion. The formation constant of the copper complex was determined as log $K_{CuL}$ = 15.21, with the help of this value and log $K_{CaL}$ = 8.27, which had been obtained by the pH titration method.[25]

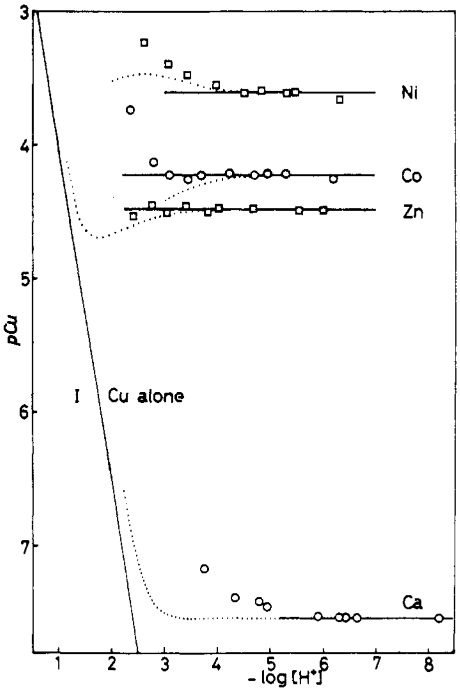

**Figure 4.** pCu-pH diagram for determination of the formation constant of a metal-PhDTA complex NL. The dotted line is yielded by taking into account the dissociation of CuL and the protonation constants of both complexes CuL and NL. The pH-dependent solid curve I is calculated for a system containing the ligand and copper(II) ion alone.

The formation constant of NL, in turn, can be determined by the use of eq 10 with a knowledge of $K_{CuL}$. In this manner, formation constants were estimated for the PhDTA complexes of bivalent cobalt, nickel, and zinc ions (Table II). The electrode

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(21) Tanaka, M. *Anal. Chim. Acta* **1963**, *29*, 193.

(22) (a) Nakano, T.; Suzuki, Y. *Nippon Kagaku Kaishi* **1980**, 1485. (b) Yuchi, A.; Wada, H.; Nakagawa, G. *Anal. Chim. Acta* **1983**, *149*, 209.

(23) (a) Schmid, R. W.; Reilley, C. N. *J. Am. Chem. Soc.* **1956**, *78*, 5513. (b) Reilley, C. N.; Schmid, R. W. *Anal. Chem.* **1958**, *30*, 947.

(24) Ringbom, A. "Complexation in Analytical Chemistry"; Interscience: New York, 1963.

(25) Kunimatsu, M., unpublished results.

potential and the pH were measured for a solution containing copper(II) and other metal perchlorates as well as PhDTA, which had been left at least overnight in order to ensure the establishment of equilibria.

**Use of the Mercury Electrode.**[23] A mercury electrode was also utilized as an indicator of pL in ligand buffers. Potential data were treated in a manner quite similar to that for the copper-selective electrode described above. Mercury(II) ion oxidizes the electrode to form mercury(I) ion in such amounts that a correction should be applied by taking into account the formal disproportionation constant $K_{\rm disp}$

$$\mathrm{Hg^{2+} + Hg(l) \rightleftharpoons Hg_2^{2+}} \qquad (12)$$

$$K_{\rm disp} = [\mathrm{Hg_2^{2+}}]/[\mathrm{Hg^{2+}}] = 96 \qquad (25\ ^\circ\mathrm{C}, I = 1\ \mathrm{M}) \qquad (13)$$

$K_{\rm disp}$ was obtained by extrapolation from the original data,[26] and a formation constant was first determined for Hg–PhDTA as log $K_{\rm HgL} = 17.38 \pm 0.05$. Ideally, pHg should increase gradually with pH to give a plateau in the ligand buffer region.[23] This was virtually the case for manganese(II), and the value log $K_{\rm MnL} = 11.4$ thus obtained compares favorably with that of 11.37 from the titration method. With the other metals examined, however, the electrode was no longer stable at pH higher than 3, and this was especially the case for copper(II). Thus the gradual increase in potential in an acid region was interpreted in terms of formation of protonated complexes (cf. eq 10), and the curve-fitting method gave approximate formation constants, which are summarized in Table II. Cobalt(II) ion did not give any stable and reproducible potential, which is consistent with the report on EDTA complexes.[23]

**Spectrophotometry.** Another method for determining an extremely large equilibrium constant is given by a displacement reaction.[2,27] Triethylenetetramine (trien) chelates copper(II) ion very strongly but calcium(II) ion poorly.[28] Moreover the Cu–trien complex absorbs at 580 nm, while Cu–PhDTA absorbs quite differently at 740 nm. Addition of sodium hydroxide augments absorbance at 580 nm but diminishes it at 740 nm, showing an isosbestic point at 666 nm for a solution containing Cu(II), Ca(II), PhDTA, and trien. Analysis of changes in pH and in absorbances according to Schwarzenbach and Freitag[27] with some modification gave the equilibrium constant for the exchange reaction

$$\mathrm{CuL + trien \rightleftharpoons Cu(trien) + L} \qquad (14)$$

from which $K_{\rm CuL}$ is obtained (Table II). Application of the displacement method to nickel(II) was unsuccessful because of minor changes in pH and spectra.

Cobalt(II)–PhDTA complexes are relatively intense in color, and therefore optical measurements of the competition of cobalt(II) ion with zinc(II) ion for PhDTA give information about the exchange reaction under the experimental conditions

$$C_{\rm Co}, C_{\rm Zn} < C_{\rm L} < C_{\rm Co} + C_{\rm Zn} \qquad (15)$$

Precipitation in a less acid solution confined the use of data to the acid region alone. The following relationships hold:

$$C_{\rm Co} = [\mathrm{Co}] + [\mathrm{CoL}] \qquad C_{\rm Zn} = [\mathrm{Zn}] + [\mathrm{ZnL}]$$

$$C_{\rm L} = [\mathrm{CoL}]\alpha_{\rm CoL(H)} + [\mathrm{ZnL}]\alpha_{\rm ZnL(H)}$$

$$A = (\epsilon(\mathrm{Co}))[\mathrm{Co}] + \epsilon_0[\mathrm{CoL}] + \epsilon_1[\mathrm{CoHL}] + \epsilon_2[\mathrm{CoH_2L}] \qquad (16)$$

where $\epsilon_i$ is the molar extinction coefficient of $\mathrm{CoH}_i\mathrm{L}$.

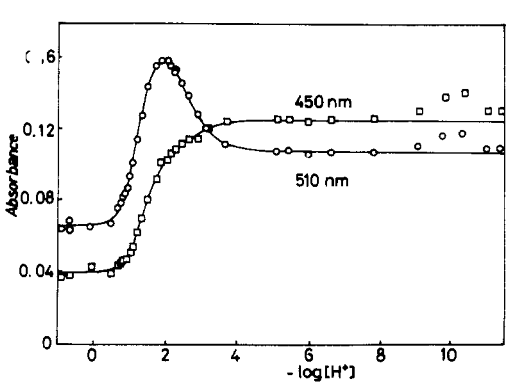

**Figure 5.** Change in absorbance of Co(II)–PhDTA chelates with pH. $C_{\rm Co} = 1.202 \times 10^{-2}$ M, and $C_{\rm L} = 1.364 \times 10^{-2}$ M. A calculation yields the solid line together with the molar extinction coefficients: $\epsilon$(Co) = 2.33 $\mathrm{M^{-1}\ cm^{-1}}$ (450 nm), 5.03 (510); $\epsilon$(CoL) = 10.27, 8.80; $\epsilon$(CoHL) = 8.3, 14.4; $\epsilon(\mathrm{CoH_2L})$ = 7.0, 15.1. Marked deviation of experimental points may be attributed to the oxidation of cobalt(II) by oxygen in the alkaline region and to the oxidation of the ligand in acid solution.

Since the molar extinction coefficients, the protonation constants, and therefore the $\alpha$ coefficients are all known in advance (see Figure 5), the remaining problem is to evaluate the concentrations of Co, Zn, CoL, and ZnL. The four stoichiometric relationships were solved by a numerical method to give the concentrations of four species, which led to log $K_{\rm CoL} = 13.11 \pm 0.17$ ($2\sigma$) as a mean value of formation constants from the optical measurements at five wavelengths, based on log $K_{\rm ZnL} = 12.89$.

## Discussion

**Properties of PhDTA.** The protonation constants of PhDTA agree reasonably well with those obtained by Grimes et al.,[4] allowing for the difference in temperature and ionic strength. This ligand shows a drastic decrease in the basicity of two nitrogen atoms, compared with EDTA and CyDTA, as expected from the electron-withdrawing effect of the benzene ring. Nevertheless, the effect is less pronounced in PhDTA than in (phenylimino)diacetic acid, for which log $K_1 = 5.04$ (at 25 °C, $I = 1.0$ M ($\mathrm{NaClO_4}$)).[29] Electron withdrawing is centered at one nitrogen atom in the latter, whereas it is divided into two nitrogen atoms in the former. Substituton of the phenylene group does not produce any appreciable effect on the basicity of carboxylate oxygens, $K_3$ and $K_4$.

Microscopic equilibria should be taken into consideration, in view of the overlap of $K_2$, $K_3$, and $K_4$. The second protonation may take place on the nitrogen atom and on a carboxylate oxygen, although the latter makes a minor contribution. The macroscopic constant $K_2$ is the sum of microscopic ones $k^{\rm N}_2$(amino) and $k^{\rm O}_2$(carboxylate). Since log $k^{\rm O}_2$ is at most 3.5, log $k^{\rm N}_2$ is greater than 4.57, which is not appreciably different from the macroscopic constant log $K_2$.

Although the present study is in essential agreement with the literature,[4-6] there have been found some contradictions for the properties of PhDTA.[30] This is reasonably interpreted in terms of adduct formation, since the misleading acetone adduct may not be readily distinguishable from the parent compound. It seems rather curious that the acetone adduct should be formed from the aqueous acetone solvent rather than from the anhydrous solvent. Such a paradoxical example has been known in relation to tetrahydropapaverine.[31] This is solvated by methanol on recrystallization from an aqueous methanol solution, whereas it does

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(26) (a) Schwarzenbach, G.; Anderegg, G. *Helv. Chim. Acta* **1957**, *40*, 1773. (b) Heitanen, S.; Sillén, L. G. *Ark, Kemi* **1956**, *10*, 103.

(27) Schwarzenbach, G.; Freitag, E. *Helv. Chim. Acta* **1951**, *34*, 1492, 1503.

(28) The poteniometric titration method gave the protonation constants of trien: log $K_1 = 10.157 \pm 0.011$; log $K_2 = 9.615 \pm 0.010$; log $K_3 = 7.222 \pm 0.008$; log $K_4 = 3.877 \pm 0.009$ ($2\sigma$). Examination of the titration curves indicates that log $K_{\rm ML} = 21.19$ and log $K^{\rm H}{}_{\rm MHL} = 3.23$ for copper complexes and that the interaction of trien with calcium(II) ion is negligibly weak (log $K_{\rm ML} = 0.7$).

(29) Nakanishi, Y., unpublished results.

(30) In an early paper,[6] some properties of the product are described: A large crystal changes from transparent to white, followed by decomposition, when exposed to air. It glides about on water. Thus, PhDTA was thought to be subject to sublimation rather than weathering. In the course of the present study, however, these properties are found to be true for the acetone adduct rather than for the ligand itself.

(31) Goldschmiedt, G. *Monatsh. Chem.* **1898**, *19*, 327.

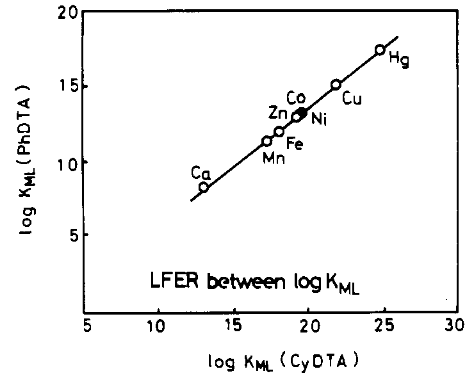

**Figure 6.** Linear free energy relationship among the formation constants of metal complexes for PhDTA and CyDTA.

not contain methanol on recrystallization from the pure methanol.

**Transition-Metal Complexes.** The formation constants of ML complexes are compatible with the so-called Irving–Williams order as well as the formation constants of the complexes of EDTA and CyDTA. For the same metal, the formation constant of M–PhDTA is always lower than those of the other two ligands, owing to the lower electron density on the nitrogen atoms. The effective coordinating ability $K'_{\mathrm{ML}}$ of PhDTA exceeds, however, that of another ligand at pH <5 in the case of manganese(II) for example

$$K'_{\mathrm{ML}} = \frac{[(\mathrm{ML})']}{[\mathrm{M}][\mathrm{L}']} = \frac{[\mathrm{ML}] + [\mathrm{MHL}] + [\mathrm{MH_2L}]}{[\mathrm{M}]([\mathrm{L}] + [\mathrm{HL}] + ... + [\mathrm{H_6L}])} = K_{\mathrm{ML}}\alpha_{\mathrm{ML(H)}}/\alpha_{\mathrm{L(H)}} \quad (17)$$

Since the side-reaction coefficient $\alpha_{\mathrm{L(H)}}$ of PhDTA is the smallest among those of related compounds and the diprotonated complex is formed favorably in the case of PhDTA, $K'_{\mathrm{ML}}$(PhDTA) becomes the highest at lower pH.[24,32] This is a unique feature of PhDTA, which may provide a potential analytical method for metal ions, especially in an acid solution.

Deviation of pCu from a constant value in Figure 4 may be caused by the dissociation of CuL as well as the protonation of metal complexes at lower pH. Exact examination of these effects on pCu gives a theoretical curve, as shown by the dotted line. When $K_{\mathrm{NHL}}{}^{\mathrm{H}} < K_{\mathrm{CuHL}}{}^{\mathrm{H}}$,[24] it passes through a minimum and then approaches curve I calculated for the system consisting of the ligand in excess and Cu(II) ion alone. Protonation of NL promotes dissociation of the copper chelate, whereas protonation of CuL suppresses the concentration of free copper(II) ion, as is expected from eq 10.

In all cases, however, the electrode potential shows a gradual departure from the calculated curve in the positive direction at lower pH. The DKK copper-selective electrode works most satisfactorily near pH 6, and it shows a positive deviation of potential in a lower pH range. It, however, functions reasonably well at considerably higher concentrations of free copper(II) ion even in the acid solution. Thus experimental values of potential (experimental pCu) conform to the calculated curve up to pH 4 for the transition metals. On the contrary, they begin to deviate at pH as high as 5, for the calcium(II)–ligand buffer where the free copper(II) ion concentration is greatly reduced.

The diprotonated species $\mathrm{MH_2L}$ is present in an appreciable quantity for PhDTA, as compared with reactions involving other amino polycarboxylates. This fact may be related to the considerable strain built up in a PhDTA complex, especially because of the planar structure including the two nitrogens.

Construction of a Dreising model shows that the two carboxylate oxygen atoms bond readily to the central metal ion, particularly on a position perpendicular to the plane including the phenylenediamine moiety (R ring).[33] The third oxygen may coordinate without great bending of bonds (G ring) but the fourth cannot without some distortion from the octahedral structure, which was demonstrated by the X-ray study on the Co(II) compound.[5]

As is the case for other pairs of ligands, the linear free energy relationship (LFER) holds well among formation constants of M–PhDTA and M–CyDTA (Figure 6). Because this is not the case for PhDTA and EDTA complexes, geometric similarity and rigidness of PhDTA and CyDTA may be responsible for the LFER.

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**Registry No.** 1, 40774-59-2.

**Supplementary Material Available:** IR spectrum of PhDTA·2acetone (Figure S1) and the plot of $\bar{q}$ against −log [H$^+$] for PhDTA in the acid region (Figure S2) (2 pages). Ordering information is given on any current masthead page.

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[32] Calculated values of the conditional formation constants for manganese(II) complexes: 5.5 (PhDTA), 3.4 (EDTA), 4.6 (CyDTA) at pH 2; 8.2, 5.6, 7.4 at pH 4; 10.8, 11.7, 9.3 at pH 6; 11.3, 11.7, 14.0 at pH 8, respectively.

[33] Weakliem, H. A.; Hoard, J. L. *J. Am. Chem. Soc.* **1959**, 81, 549.