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(73) **Note Added in Proof.** The electrochemical oxidation of zinc phthalocyanine yields a paramagnetic, presumably monomeric, radical species [D. Lexa and M. Reix, *J. Chim. Phys.*, **71**, 517 (1974)].

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Contribution of the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

# New Multidentate Ligands. XIV. Aqueous Coordination Chemistry of *N*,*N*'-Bis(2-hydroxybenzyl)ethylenediamine-*N*,*N*'-bis(methylenephosphonic) Acid[1]

D. T. MacMILLAN, I. MURASE, and A. E. MARTELL*

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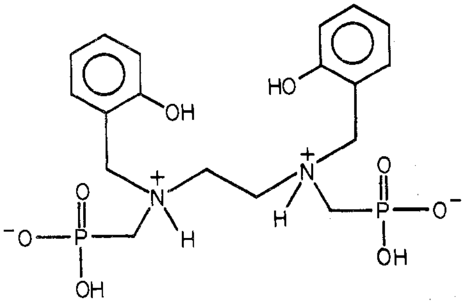
The synthesis and the metal–proton–ligand aqueous solution equilibria of the novel ligand *N*,*N*'-bis(*o*-hydroxybenzyl)-ethylenediamine-*N*,*N*'-bis(methylenephosphonic) acid (HBEDPO), $H_6L$, are described. At 25° and $\mu = 0.100$, the logarithms of the ligand protonation constants are 13.57, 11.48, 9.67, 7.24, 5.31, and 3.61 and the stability constants for the 1:1 metal chelates, $ML^{4-}$, where M = Cu(II), Ni(II), Co(II), Ca(II), and Mg(II), are respectively 24.0, 17.9, 18.0, 8.36, and 7.95 log units. In addition to the "normal" species, $ML^{4-}$, other protonated forms $MHL^{3-}$, $MH_2L^{2-}$, $MH_3L^-$ and $MH_4L$ were found to be present with Cu(II), Ni(II), and Co(II), while $MHL^{3-}$ and $MH_2L^{2-}$ are present in the Ca(II) and Mg(II) systems. The protonated Fe(III) chelate is very insoluble and dissolves only after 6 mol of base/mol of iron(III) ($a = 6$) have been added. The zinc chelate is insoluble between 1 and 4 mol of base/mol of ligand. The potentiometric data for copper and nickel show an inflection at $a = 4$ indicating essential completion of interaction with HBEDPO at that point. In contrast, cobalt(II) and zinc(II) show complete interaction, only at and above $a = 5$. Calcium(II) and magnesium(II) show the least affinity, with no interaction with the ligand below $a = 3$. The spectrophotometric study of the copper(II) and cobalt(II) systems indicates appreciable phenolate coordination with these two metal ions even below $a = 4$, indicating a structural rearrangement equilibrium involving the phenolate groups and the other metal ion coordinating groups in the ligand.

## Introduction

The recent investigation[2] of the metal-binding characteristics of *N*,*N*'-bis(2-hydroxybenzyl)ethylenediamine-*N*,*N*'-diacetic acid (HBED) shows that its affinities for many metal ions in aqueous solution are considerably higher for this ligand than for EDTA. This increase in stability has been interpreted as being the result of a very favorable arrangement of its six donor groups (two basic nitrogens, two carboxylate groups, and two *o*-phenolate groups) about the metal ion as well as the high affinity of the phenolate group for certain metal ions. EHPG (*N*,*N*'-ethylenebis(2-hydroxyphenylglycine)),[3] a structurally related ligand also containing these same six coordinating groups, shows similar high stability, although somewhat lower than that of HBED because of a less favorable steric arrangement of these donor groups. It has already been established[4,5] in these laboratories that the stability constants, upon substituting phosphonate for the carboxylate groups in EDDA (ethylenediamine-*N*,*N*'-diacetic acid) to obtain EDDPO (ethylenediamine-*N*,*N*'-bis(methylphosphonic) acid, are slightly better for copper(II) or slightly lower for nickel(II) and cobalt(II), compared to the model EDDA, even though the lowering of the basicities of the nitrogen atoms present in the ethylenediamine framework by the phosphonate groups would predict considerably lower metal ion affinities. Thus it seems that phenolate and phosphonate groups could be effective donors in multidentate ligands having suitable molecular geometry.

The present work was undertaken to combine these less conventional functional groups (*i.e.*, the phosphonate and phenolate groups) into a multidentate ligand having a sterically favorable arrangement of donor groups. The structure of the ligand meeting these objectives, *N*,*N*'-bis(*o*-hydroxybenzyl)ethylenediamine-*N*,*N*'-bis(methylenephosphonic) acid, is given by formula I. Because of structural similarity of I with HBED[2] and the fact that the latter has the highest affinity for iron(III) of any ligand previously known, the new multidentate ligand I is especially interesting because of its potential as a specific binding agent for the ferric ion.



I, *N,N'*-bis(*o*-hydroxybenzyl)ethylenediamine-*N,N'*-bis(methylenephosphonic) acid (HBEDPO, $H_6L$)

## Experimental Section

**Apparatus and Procedure.** Ligand–metal interactions were measured potentiometrically and spectrophotometrically. A Beckman Research pH meter (Model 1019) was fitted with blue glass and calomel electrodes and adjusted to read out the negative log of the hydrogen ion concentration by calibration with standard acid and titration with standard base. The deviation from calculated values in the strong acid and strong base regions (pH 2–4 and 10–12) averaged less than 0.004 log unit, and linearity in the error function was assumed for intermediate values. Temperature was maintained at 25.00 ± 0.05° by use of jacketed cells with a water-circulating constant-temperature bath. Ionic strength was kept constant by swamping the solution to 0.100 *M* in $KNO_3$. Nitrogen gas free of carbon dioxide and oxygen was passed over the solution during potentiometric measurements. All equilibrium measurements were made with the concentration 0.00200 *M* in metal and ligand. No 2:1 metal to ligand interactions were observed, since in all 2:1 cases tried the metal did not remain in solution when the pH was raised. The uv spectra were measured using a Cary 14 recording spectrophotometer with the aid of two 1.000-cm matched quartz absorption cells.

**Materials.** Reagent grade metal salts were made into stock solutions of approximately 0.025 *M* and standardized with EDTA.[6] Baker Dilut-It analytical concentrate KOH was found to be carbonate free and was standardized with potassium acid phthalate.

***N,N'*-Bis(2-hydroxybenzyl)ethylenediamine-*N,N'*-bis(methylenephosphinic) Acid (HBEDPI).** A suspension of 30 g (0.12 mol) of ethylenediamine-*N,N'*-bis(methylenephosphinic) acid (EDDPI)[4] in 180 ml of water–dimethyl sulfoxide mixture (1:1 v/v) was treated with 54 g of 20% aqueous sodium hydroxide and a clear solution was obtained. To this was added 57 g (0.27 mol) of *o*-acetoxybenzyl bromide in 300 ml of methanol, and the pH of the solution was maintained at ~9 for 1 hr at 30–40° by the dropwise addition of 20% aqueous sodium hydroxide at such a rate that the pink color of phenolphthalein indicator never persisted. After keeping the temperature at 40° for 1 additional hr, another 54 g of 20% aqueous sodium hydroxide was added and the solution was heated at 50° for 1 hr and then concentrated to ~150 ml under reduced pressure. The pH was brought to 2 by the addition of hydrochloric acid and the solution was diluted to 2 l. with water, the small amount of impurity which precipitated was removed, and the solution was allowed to stand overnight at room temperature. The resulting precipitate was filtered and washed with water and with ethanol; yield 47 g (91%).

The product was purified by dissolving it in hot aqueous sodium hydroxide, filtering, and adding hydrochloric acid to the hot filtrate to bring the pH to 2. Repeating this procedure, the pure sample was obtained as fine crystals, mp 215° dec, and was very slightly soluble in water.

*Anal.* Calcd for $C_{18}H_{26}N_2O_6P_2$: C, 50.46; H, 6.13; N, 6.54; P, 14.46. Found: C, 50.51; H, 5.99; N, 6.43; P, 14.21.

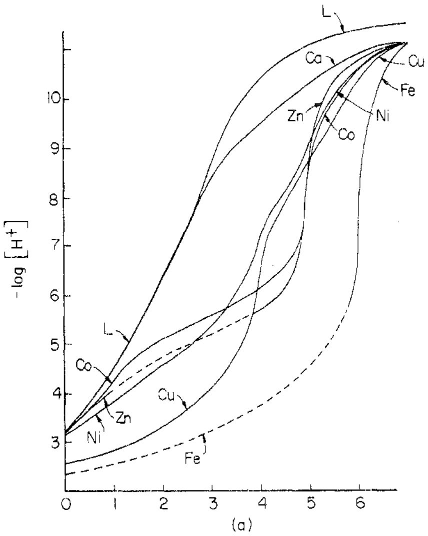


**Figure 1.** Potentiometric titration curves of various metal nitrates in the presence of equivalent quantities of HBEDPO; abscissa *a* represents moles of base added per mole of ligand present; $\mu = 0.100\,M$ $KNO_3$; $T = 25°$. "L" represents the ligand curve in the absence of metal ions.

**Table I.** Comparison of Proton Association Constants (log $K_{Hp}$) of HBEDPO with those of Structurally Similar Ligands[a]

| HBEDPO[b] | EDDPO[c] | HBED[d] |
|---|---|---|
| $K_{H_1} = 13.57\ (9)^e$ | | $K_{H_1} = 12.46$ |
| $K_{H_2} = 11.48\ (5)$ | | $K_{H_2} = 11.00$ |
| $K_{H_3} = 9.67\ (3)$ | $K_{H_1} = 10.60$ | $K_{H_3} = 8.32$ |
| $K_{H_4} = 7.24\ (4)$ | $K_{H_2} = 7.72$ | $K_{H_4} = 4.64$ |
| $K_{H_5} = 5.31\ (2)$ | $K_{H_3} = 5.75$ | |
| $K_{H_6} = 3.61\ (2)$ | $K_{H_4} = 4.58$ | |

[a] At 25° and $\mu = 0.10$ ($KNO_3$). [b] This research. [c] Reference 4. [d] References 2 and 9. [e] Values in parentheses indicate standard deviations.

***N,N'*-Bis(2-hydroxybenzyl)ethylenediamine-*N,N'*-bis(methylenephosphonic) Acid (HBEDPO).** To a suspension of 4.3 g (0.010 mol) of *N,N'*-bis(2-hydroxybenzyl)ethylenediamine-*N,N'*-bis(methylenephosphinic) acid (HBEDPI) in 200 ml of hot 50% (v/v) Ethyl Cellosolve was added 15 g of mercuric chloride in 50 ml of the same hot solvent, and the mixture was stirred on a water bath for 2 hr. Mercurous chloride was filtered off and the hot filtrate was saturated with hydrogen sulfide to remove mercury. After filtering the precipitate, the filtrate was evaporated to dryness under vacuum and the residue dissolved in dilute sodium hydroxide solution and filtered. After standing for several days, HBEDPO crystallized gradually from the filtrate. It was filtered and washed with water and with methanol; yield 2.1 g.

For further purification, the product was dissolved in alkali and filtered, and the pH of the filtrate was adjusted to ~1 with hydrochloric acid. After removal of the precipitate, pure HBEDPO crystallized gradually from the filtrate. The sample for elemental analysis was dried over $P_2O_5$ at 110° under vacuum for 5 hr.

*Anal.* Calcd for $C_{18}H_{26}N_2O_8P_2 \cdot {}^1/_2H_2O$: C, 46.05; H, 5.81; N, 5.97. Found: C, 46.22; H, 5.89; N, 5.99.

## Results

**Ligand Protonation Constants.** The ligand potentiometric equilibrium curve (L of Figure 1) shows an extended buffered zone from pH 3 to pH 11, indicating that the phosphonate deprotonation steps all overlap. A computer program developed[7] in this laboratory and described elsewhere[4] was used to calculate the first four overlapping protonation constants. The values obtained are listed in Table I and correspond to the equilibria

$$H^+ + H_{p-1}L^{(7-p)-} \rightleftharpoons H_pL^{(6-p)-}$$

$$K_{Hp} = \frac{[H_pL^{(6-p)-}]}{[H^+][H_{p-1}L^{(7-p)-}]} \qquad (1)$$

The first two protonation steps occur at very high pH in the ligand solutions, and calculations from pH measurements alone become inaccurate. Therefore the constants associated with equilibria

$$L^{6-} + H^+ \rightleftharpoons HL^{5-} \qquad K_{H_1} \qquad (2)$$

$$HL^{5-} + H^+ \rightleftharpoons H_2L^{4-} \qquad K_{H_2} \qquad (3)$$

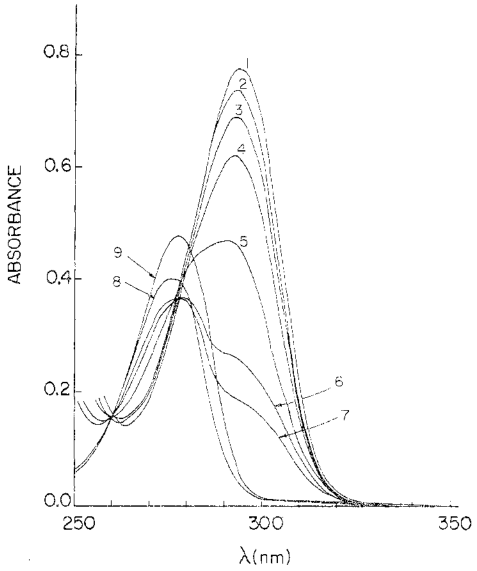


**Figure 2.** Aqueous ultraviolet spectra of HBEDPO as a function of pH: 1, 14.82; 2, 14.03; 3, 13.26; 4, 12.60; 5, 11.27; 6, 10.42; 7, 9.71; 8, 7.12; 9, 3.22. [HBEDPO] = 1.0 × $10^{-4}$ *M*.

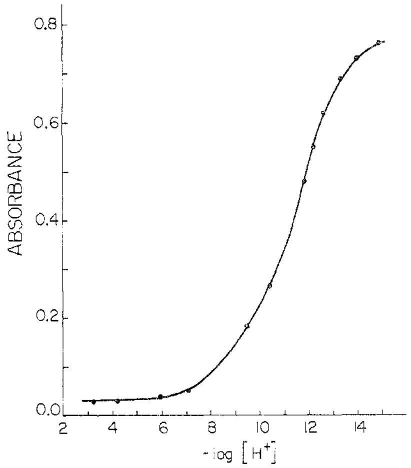


**Figure 3.** The ultraviolet absorbance of HBEDPO as a function of pH at 295 nm. [HBEDBO] = 1.0 × $10^{-4}$ *M*.

were measured spectrophotometrically.

The equilibrium involves a phenol–phenolate system, with the two species having absorption maxima at 278 and 294 nm, respectively (see Figures 2 and 3). Thus if the extinction coefficients of all of the species present in a solution of known hydrogen ion concentration are known, the total absorbance at any wavelength can be related to the two constants *via* the relations

$$E = \sum_{p=0}^{6} \epsilon_{\mathrm{H}_p\mathrm{L}}[\mathrm{H}_p\mathrm{L}] = \epsilon_{\mathrm{L}}[\mathrm{L}] + \sum_{p=1}^{6} \epsilon_{\mathrm{H}_p\mathrm{L}}[\mathrm{H}^+]^p[\mathrm{L}] \prod_{n=1}^{p} K_{\mathrm{H}n} \quad (4)$$

$$T_{\mathrm{L}} = \sum_{p=0}^{6} [\mathrm{H}_p\mathrm{L}] = [\mathrm{L}] + \sum_{p=1}^{6} [\mathrm{H}^+]^p[\mathrm{L}] \prod_{n=1}^{p} K_{\mathrm{H}n} \quad (5)$$

where $E$ is the total absorbance and $T_{\mathrm{L}}$ is the total ligand concentration.

It is expected that in the highest pH range (12.5–14.5), $[\mathrm{H}^+]^3 << K_{\mathrm{H1}}K_{\mathrm{H2}}K_{\mathrm{H3}}$, so that the eq 4 and 5 reduce to

$$E = \epsilon_{\mathrm{L}}[\mathrm{L}] + \epsilon_{\mathrm{HL}}K_{\mathrm{H1}}[\mathrm{H}^+][\mathrm{L}] + \epsilon_{\mathrm{H_2L}}K_{\mathrm{H1}}K_{\mathrm{H2}}[\mathrm{H}^+]^2[\mathrm{L}] \quad (6)$$

$$T_{\mathrm{L}} = [\mathrm{L}] + K_{\mathrm{H1}}[\mathrm{H}^+][\mathrm{L}] + K_{\mathrm{H1}}K_{\mathrm{H2}}[\mathrm{H}^+]^2[\mathrm{L}] \quad (7)$$

and

$$\epsilon_{\mathrm{HL}} = \frac{E + K_{\mathrm{H1}}E[\mathrm{H}^+] - T_{\mathrm{L}}\epsilon_{\mathrm{L}}}{T_{\mathrm{L}}K_{\mathrm{H1}}[\mathrm{H}^+]} \quad (8)$$

Since the extinction coefficient of the totally deprotonated species is known from the measurement of absorption at very high pH, $\epsilon_{\mathrm{HL}}$ and $K_{\mathrm{H1}}$ are the only unknowns in eq 8. By using absorbance values in the pH range 12.5–14.5, $K_{\mathrm{H1}}$ was varied by computer in increments of 0.01 between 13.00 and 14.00 and $\epsilon_{\mathrm{HL}}$ was calculated for each data point. The $K_{\mathrm{H1}}$ which gave the least deviation in $\epsilon_{\mathrm{HL}}$ over the pH range was chosen as the best and the average of the calculated extinction coefficients was assigned to $\epsilon_{\mathrm{HL}}$. Then $K_{\mathrm{H2}}$ was calculated directly at each data point in the pH range 10.5–12 from eq 6 and 7, and the average value was retained as the constant. These equilibrium constants are listed in Table I.

**Potentiometric Determination of Stability Constants.** Potentiometric equilibrium curves of the 1:1 ligand–metal systems investigated are shown in Figure 1. As the zinc(II) and iron(III) chelates are both insoluble in the pH range of the buffer region in which they are formed, stability constants were not calculated for these metals. The other metal ions fall into three distinct groups from the point of view of the calculations employed. The species present were all considered to be mononuclear complexes, which readily form additional protonated metal complex species, the concentrations of which increase with decreasing pH.

The copper(II) and nickel(II) curves in Figure 1 have inflections at *a* = 4, indicating that complexation by the ethylenediaminebis(methylenephosphonic) acid moiety is essentially complete at this point. For this region the stability constant calculation consisted of the usual mass and charge balance equations, including two overlapping proton association reactions, indicated by eq 9–11. The two protonation constants

$$\mathrm{H_2L^{4-} + M^{2+} \rightleftharpoons MH_2L^{2-}} \qquad K_1' \quad (9)$$

$$\mathrm{MH_2L^{2-} + H^+ \rightleftharpoons MH_3L^-} \qquad K_{1\mathrm{c}} \quad (10)$$

$$\mathrm{MH_3L^- + H^+ \rightleftharpoons MH_4L} \qquad K_{1\mathrm{d}} \quad (11)$$

were estimated from the titration curve and a value of $K_1'$ was calculated for each data point. Then $K_{1\mathrm{c}}$ and $K_{1\mathrm{d}}$ were varied in order to minimize the average deviation in $K_1'$ over the appropriate interval.

The two highest proton association constants corresponding to the reactions of the phenolate groups were treated as simple acid–base equilibria (since metal ion dissociation is not involved) and were calculated in the same manner as the ligand protonation steps. The equilibria involved are indicated by

$$\mathrm{ML^{4-} + H^+ \rightleftharpoons MHL^{3-}} \qquad K_{1\mathrm{a}} \quad (12)$$

$$\mathrm{MHL^{3-} + H^+ \rightleftharpoons MH_2L^{2-}} \qquad K_{1\mathrm{b}} \quad (13)$$

In the case of cobalt(II) and zinc(II) there are seen to be three overlapping proton dissociation steps terminating in an inflection at *a* = 5, corresponding to the formation of complexes having the composition $\mathrm{MHL^{3-}}$. The calculation of equilibrium constants was carried out by variation of the constants governing the protonation steps so as to minimize the average deviation in $K_1$ between *a* = 1 and *a* = 5. The stability constants $K_1'$, $K_{1\mathrm{b}}$, $K_{1\mathrm{c}}$, and $K_{1\mathrm{d}}$ were obtained in this way. Again, $K_{1\mathrm{a}}$ was calculated directly as an acid–base equilibrium involving no overlapping protonation reaction and no metal ion dissociation.

For calcium(II) and magnesium(II), little or no interaction was observed until beyond *a* = 3. In calculating the stability constants of these species, hydrolysis of the free metal ion was taken into account because of the high pH involved. This modification required one additional term in the proton and metal balance equations and was easily inserted into the general

Table II. Comparison of Metal–Ligand–Proton Interactions$^a$

| Ligand | Metal | log (equilibrium constants)$^b$ | | | | | |
|---|---|---|---|---|---|---|---|
| | | $K_1$ | $K_1'$ | $K_{1a}$ | $K_{1b}$ | $K_{1c}$ | $K_{1d}$ |
| HBEDPO$^c$ | Cu$^{2+}$ | 24.0 (1) | 16.09 | 9.39 | 7.75 | 4.74 | 3.41 |
| EDDPO$^d$ | | | 17.52 | | | 4.72 | 3.80 |
| HBED$^e$ | | 21.38 | 11.73 | 8.63 | 5.18 | | |
| HBEDPO$^c$ | Ni$^{2+}$ | 17.9 (1) | 10.83 | 10.02 | 7.95 | 5.53 | 4.69 |
| EDDPO$^d$ | | | 11.70 | | | 5.53 | 4.99 |
| HBED$^e$ | | 19.31 | 10.81 | 8.51 | 6.45 | | |
| HBEDPO$^c$ | Co$^{2+}$ | 18.0 (2) | 9.58 | 9.88 | 6.70 | 5.09 | 5.28 |
| EDDPO$^d$ | | | 10.23 | | | 5.98 | 5.33 |
| HBED$^e$ | | 19.89 | 9.76 | 7.77 | 5.56 | | |
| HBEDPO$^c$ | Zn$^{2+}$ | | | 10.27 | | | |
| EDDPO$^d$ | | | | | | | |
| HBED$^e$ | | 18.37 | | 8.27 | 5.99 | | |
| HBEDPO$^c$ | Ca$^{2+}$ | 8.36 (5) | 3.61 | 10.72 | 9.59 | | |
| EDDPO$^d$ | | | | | | | |
| HBED$^e$ | | 9.29 | 2.02 | 8.69 | 7.50 | | |
| HBEDPO$^c$ | Mg$^{2+}$ | 7.95 (5) | 3.04 | 11.05 | 9.10 | | |
| EDDPO$^d$ | | | | | | | |
| HBED$^e$ | | 10.51 | 2.21 | 8.15 | 7.01 | | |

[a] At 25° and $\mu = 0.10$ ($KNO_3$). [b] Unless otherwise indicated, values are within ±0.01. [c] This work. [d] Reference 4. [e] References 2 and 9.

computer program employed for the calculations described above. The hydrolysis constants[8] used for calcium(II) and magnesium(II) are

$$Ca^{2+} + OH^- \rightleftharpoons CaOH^+ \qquad \log K = 1.30 \tag{14}$$

$$Mg^{2+} + OH^- \rightleftharpoons MgOH^+ \qquad \log K = 2.50 \tag{15}$$

For these metals, the normal stability constant $K_1$ of $ML^{4-}$ (eq 16) was calculated directly, along with two successive

$$M^{2+} + L^{6-} \rightleftharpoons ML^{4-} \qquad K_1 \tag{16}$$

protonation constants, $K_{1a}$ and $K_{1b}$ (eq 12 and 13). The metal chelate formation constants and associated metal chelate protonation constants determined in this investigation are presented in Table II.

**Spectral Studies of Chelate Species.** The uv absorption spectra for the copper(II)–ligand system are shown in Figure 4 and are similar to those obtained for the cobalt(II) system. The phenolate absorption maximum of the totally deprotonated metal chelate occurs at ~287 nm, intermediate between the protonated and dissociated phenolate absorptions of the ligand in the absence of metal ions. This indicates that the phenolate oxygens are coordinated, a conclusion reinforced by the presence in the copper–ligand solution of an intense green color, also noted in the case of HBED.[2,9] Because of the overlapping nature of these bands in the uv spectra, no direct calculation was made, but the spectra (see band 5 in Figure 4) do indicate that a small but appreciable amount of coordinated phenolate species is present in the solution before the break in the potentiometric equilibrium curve at $a = 4$. Interpretation of the Co$^{II}$HBEDPO uv spectra was made difficult by the closeness of the overlapping bands as well as the overlapping of the three protonation reactions of the metal chelate.

## Discussion

**Protonation Constants.** The values of the six proton association constants found for this ligand are compared with analogous constants from EDDPO and HBED in Table I. The most reasonable scheme for the protonation of HBEDPO may be deduced from these comparisons. That the first two protonation reactions involve the phenolate oxygens—clearly the most basic sites—is shown by the uv spectral work. These constants are higher than those of the analogous ligands by 0.5–1 log unit, probably due in part to the large buildup of negative charge by the two binegative phosphonate groups. It is not unreasonable to conclude that the first two protons also stabilize the rest of the molecule relative to the other compounds listed in Table I. Such stabilization is seen in the large drop in $K_{H3}$ to almost 1 full log unit below the comparable step in EDDPO. It is noted, however, that the nitrogens in HBEDPO are much more basic than the corresponding nitrogens in HBED, as would be expected on the basis of the greater negative charge of the former ligand. The unexpectedly large differences in $K_{H3}$ for these two ligands may be due to a structural effect such as greater tendency for six-membered hydrogen-bonded ring formation between the phenol hydrogen and the amine site of HBED. It is then necessary that the fourth, fifth, and sixth association steps of HBEDPO correspond to protonation of the remaining nitrogen and the alternate phosphonate sites. In these reactions, a small decrease in basicity relative to that of EDDPO is again seen to have taken place.

**Metal Chelates of HBEDPO.** Just as there were three methods used for the calculation, the ligand–metal interactions can be divided into three groups: copper(II) and nickel(II), cobalt(II) and zinc(II), and calcium(II) and magnesium(II). The complex formed with iron(III) is quite stable. The iron(III) chelate of HBEDPO did not hydrolyze even at extremely high pH and the fact that at low pH there was a marked depression of the pH titration curve through $a = 6$ gives qualitative evidence of the high stability of the complex. The other complexes are compared with the parent compound EDDPO and with the analogous ligand HBED, in Table II.

Copper(II) and nickel(II) seem to form tetracoordinate chelates with this ligand, as evidenced by the inflection at $a = 4$ in the titration curves. Subsequent raising of the pH brings on additional interaction with the metal, not as strong as in HBED, but still strong enough to lower the first and second proton association constants appreciably. Little can be said yet as to the extent of the participation of the various donor groups in the coordinate bonding of the metal in the fully deprotonated chelate. One question arises, however, as to which of the groups are donors in the original tetracoordinate complex. The uv data for the copper complex as a function of pH (Figure 4) indicate that indeed there is some phenolate bonding at pH values below 6.5 ($a = 4$).

The comparable chelate proton association constants corresponding to the HBEDPO equilibria

$$MH_2L^{2-} + H^+ \rightleftharpoons MH_3L^-$$

$$MH_3L^- + H^+ \rightleftharpoons MH_4L$$

are nearly equal for HBEDPO and EDDPO in both the copper and nickel systems. This indicates that these proton equilibria probably involve the phosphonate groups. The formation of the phenolate complex at low pH (*i.e.*, below $a = 4$) would have to be explained by a tautomerization reaction not involving overall loss or gain of a proton, such as is indicated by the microscopic equilibrium II ⇄ III. This type of equilibrium seems to be needed in order to explain the data, if the electronic spectra have been interpreted correctly. Indeed, the very existence of this novel type of equilibrium may have been brought about by the mutual charge repulsion of the two strongly binegative groups positioned fairly close to the coordinated metal ion (formula II). Rearrangement of ligand donor groups to give III would seem to relieve partially the coulombic repulsions within the complex. The calculation of $K_X$ would be very interesting; however, it could not be carried out since the uv data were not suited to quantitative treatment (the absorption maxima of II, III, and IV are too close).

As more base is added (from $a = 4$ to $a = 6$ in the equilibrium curve), the pH becomes sufficiently high to assist in the dissociation of a proton from the remaining uncoordinated phenolic group, converting II to IV, in which both phenolate donor groups are seen to be coordinated. The phosphonates are shown uncoordinated, but it may well be that both (or at

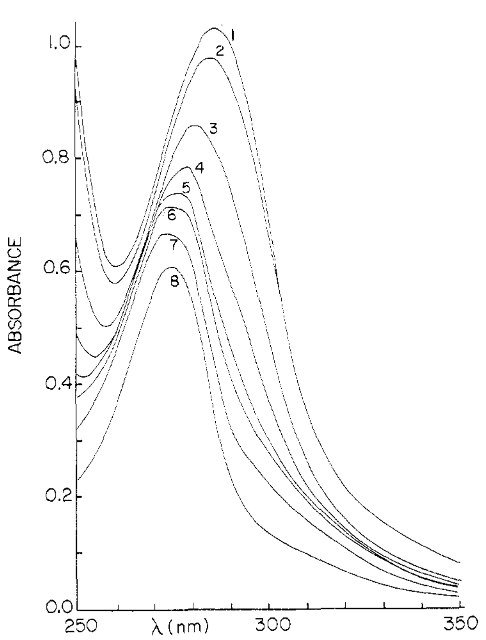
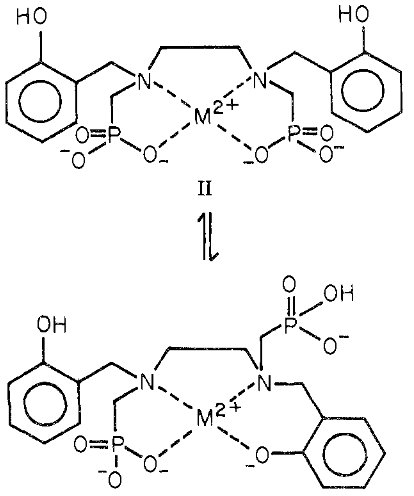


**Figure 4.** Uv spectra of (HBEDPO)Cu$^{II}$, at 1 × 10$^{-4}$ $M$ in each component, measured as a function of pH: 1, 11.19; 2, 10.13; 3, 8.86; 4, 7.75; 5, 6.97; 6, 5.32; 7, 4.03; 8, 3.01.



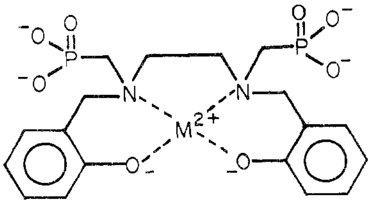
II

III

$$K_x = \frac{[III]}{[II]}$$

possible tautomeric forms of diprotonated HBEDPO, $MH_2L^{2-}$ (HBEDPO = $H_6L$)

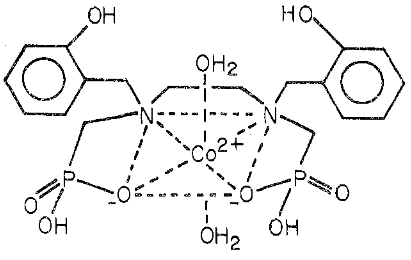
least one) are coordinated in octahedral complexes. The large mutual charge repulsions of the binegative phosphonate groups discussed above would make it doubtful that complexes having all six fully dissociated donor groups coordinated to a divalent metal ion would form completely when divalent ions are involved (more highly charged metal ions, however, would be expected to combine more completely with two or more phosphonate groups in a multidentate ligand).



IV, metal chelate of HBEDPO, $ML^{4-}$ (HBEDPO = $H_6L$)

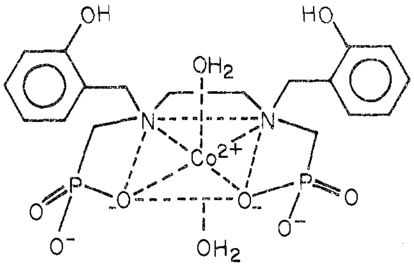
In the case of the Co(II) complex it is interesting to note that $K_{1c}$ is smaller than $K_{1d}$, while $K_{1b}$ is much larger, as expected. These relative values of the equilibrium constants indicate a relatively low stability of the species $CoH_3L^-$ with respect to $CoH_2L^{2-}$ and $CoH_4L$ and a very small maximum concentration of the species $CoH_3L^-$. Implied in the unusual relative values of these successive chelate protonation constants is that a structural change takes place after the second deprotonation step. Thus when a proton is removed from $CoH_4L$, rearrangement of the geometry of the complex occurs, giving rise to the relatively less stable complex $CoH_3L^-$ which then very readily loses another proton forming $CoH_2L^{2-}$. Since $K_{1c}$ and $K_{1d}$ are of the order of magnitude of $K_{H5}$, it seems that the corresponding reactions involve the protonation of phosphonate groups. The magnitude of $K_{1b}$ indicates the protonation of a coordinated phenolic group.

The deprotonation scheme (formulas V–VIII) is consistent with the results presented. If the initial neutral species formed is $CoH_4L$ (V) (octahedral) which possesses two monoprotonated metal-coordinated phosphonate ($-PO_3H^-$) groups, then the first deprotonation reaction of V involves the dissociation of a proton from the $-PO_3H^-$ group to give VI. This complex is considerably less stable than the deprotonated complex VII with both phosphonate groups dissociated. While it is not possible with the data presently available to determine the reason(s) for the relative instability of VI, this behavior may be related to the change from octahedral to distorted tetrahedral cobalt(II) in going from VI to VII (shown as octahedral). The next two deprotonations involve the successive removal of the phenolate proton. This process may require a full change in geometry toward tetrahedral cobalt in the formation of the fully deprotonated complex $CoL^{4-}$ indicated by VIII.

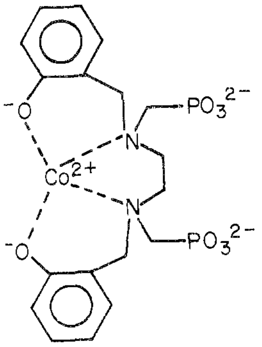


V, $CoH_4L$

$\xrightleftharpoons{K_{1d}}$ $CoH_3L$ $\xrightleftharpoons{}$
VI $K_{1c}$



VII



VIII

Structure VIII is supported by the deep violet color of the complex at $a$ = 6, by favorable charge distribution considerations, and by a comparison with similar bis(salicylidine)ethylenediamine complexes.

With calcium(II) and magnesium(II), it is seen that the order of overall stability is reversed from the situation found with HBED. This is possibly a combination of a steric effect and a coulombic effect, the larger calcium ion being more able to accommodate the bulky phosphonate groups, allowing for stronger interaction between ligand and metal.

**Registry No.** HBEDPI, 53431-86-0; HBEDPO, 53431-87-1; EDDPI, 34160-37-7; *o*-acetoxybenzyl bromide, 704-65-4; Cu, 7440-50-8; Ni, 7440-02-0; Co, 7440-48-4; Zn, 7440-66-6; Ca, 7440-70-2; Mg, 7439-95-4.

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Contribution from the Institut für Anorganische Chemie der Universität,
D 8700 Würzburg, Germany

# Tris(trimethylphosphine)cobalt(I) Halides. Preparation and Properties

H. F. KLEIN* and H. H. KARSCH

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Syntheses and properties of stable cobalt(I) halides of the formula $CoXL_3$ ($L = (CH_3)_3P$; X = Cl, Br, I) are reported. In solution these compounds add carbon monoxide under normal pressure to form pentacoordinate complexes of the composition $CoX(CO)L_3$ which, in a subsequent step, are converted into dicarbonyl compounds $CoX(CO)_2L_2$. By addition of a phosphine ligand ionic species $[Co(CO)L_4]^+X^-$ are formed. In the absence of CO the first tetrahedral cobalt(I) cation is isolated in the form $[CoL_4]^+[B(C_6H_5)_4]^-$. An even higher coordination number is accessible in the presence of dimethylphosphine in the form of $[CoL_4L']^+X^-$ ($L = (CH_3)_3P$; $L' = (CH_3)_2PH$; X = Cl, Br). This pentacoordinate species is not formed with trimethylphosphine alone. Infrared, nmr, and magnetic measurements suggest probable structures of these complexes in solution.

Recently we described a tetrahedral chlorotris(trimethylphosphine)cobalt(I) which appears to be indispensable in the preparation of methyltetrakis(trimethylphosphine)cobalt(I).[1] For this type of complex a detailed investigation was desirable not only because its composition matches that of the well-known hydrogenation catalyst chlorotris(triphenylphosphine)rhodium(I) but also since only very few examples of four-coordinate $d^8$ complexes of cobalt have been reported.[2,3] In contrast to Sacco's Co(I) halides with triphenylphosphine ligands,[3] $CoClL_3$ ($L = (CH_3)_3P$) is stable in the solid state and in solution. Thus a chemistry of tetrahedral Co(I) complexes with simple unidentate ligands has become accessible.[4,5]

**Table I.** Properties of Co(I) Complexes ($L = (CH_3)_3P$)

| Compd | Color | Dec pt, °C | Solubility[a] | Magnetism,[b] $\mu_{eff}$, $\mu_B$ |
|---|---|---|---|---|
| $CoClL_3$ | Blue | >90 | P 1 | $3.1_0$ |
| $CoBrL_3$ | Blue | >140 | P 1 | $3.1_8$ |
| $CoIL_3$ | Violet-blue | >114 | P 2 | $3.3_5$ |
| $CoO_2CCH_3L_3$ | Dark blue | >135[g] | P 3 | ~3.0[e] |
| $[CoL_4]^+[B(C_6H_5)_4]^-$ | Green | >188 | A-E 3 | $3.3_9$[f] |
| $CoCl(CO)L_3$ | Wine red | >94 | P 2 | Diamag |
| $CoBr(CO)L_3$ | Red | >65 | P 1 | Diamag |
| $CoI(CO)L_3$ | Brown-red | >170 | E 1 | Diamag |
| $[Co(CO)L_4]^+Cl^-$ | Yellow | >110 | C[c] 3 | Diamag |
| $[Co(CO)L_4]^+Br^-$ | Orange | >115 | C[c] 3 | Diamag |
| $[Co(CO)L_4]^+I^-$ | Orange | >115 | C[c] 3 | Diamag |
| $CoCl(CO)_2L_2$ | Yellow | >125 | E 1 | Diamag |
| $CoBr(CO)_2L_2$ | Yellow | >175 | E 1 | Diamag |
| $CoI(CO)_2L_2$ | Light brown | >215 | E 1 | Diamag |
| $[CoL_4L']^+Cl^-$ [d] | Orange | >60 | C[c] 3 | Diamag |
| $[CoL_4L']^+Br^-$ [d] | Orange | >65 | C[c] 3 | Diamag |

[a] A = acetone, C = methylene chloride, E = ether, P = pentane; 1 = 0–10 mg, 2 = 10–500 mg, 3 = 1 g in 10 ml of solvent. [b] In benzene solution (see Experimental Section). [c] Decomposition above 10°. [d] $L' = (CH_3)_2PH$. [e] Some decomposition in solution. [f] In $CH_2Cl_2$ solution containing 10% cyclohexane. [g] Sealed capillary.

## Results

**Preparation and Characterization of Compounds.** In the presence of trimethylphosphine, anhydrous $CoCl_2$ is reduced by metals in THF solution to give tetrakis(trimethylphosphine)cobalt(0).[1,6] In this reduction $CoCl[P(CH_3)_3]_3$ could be isolated as an intermediate. We subsequently found that a comproportionation reaction between Co(0) and Co(II) according to eq 1 provides a simple high-yield synthesis of this

$$CoCl_2 + CoL_4 + 2L \rightarrow 2CoClL_3 \tag{1}$$

$$CoX_2L_2 + CoL_4 \rightarrow 2CoXL_3 \tag{2}$$

$$CoL_4 + {}^3/_2I_2 \rightarrow CoIL_3 + (CH_3)_3PI_2 \tag{3}$$

$$L = (CH_3)_3P; X = Cl, Br, I$$

complex. Instead of anhydrous Co(II) salts Jensen's bis(trimethylphosphine)cobalt(II) halides[7] are conveniently employed especially for the bromo and iodo complexes according to eq 2. The oxidation of the Co(0) complex by iodine was found to proceed according to eq 3 with loss of a phosphine ligand. A more general method is based on the cleavage of the CoC bond of methyltetrakis(trimethylphosphine)cobalt(I)[1] by protic acids (eq 4) or, in a smooth reaction, by their ammonia salts (eq 5). The tris(trimethylphosphine)cobalt(I) halides are thermally stable. They are only slightly dissolved in pentane or ether but are quite soluble in benzene, THF, or methanol. Under normal conditions no decomposition products are observed, provided that the material is kept under an inert gas. The deep blue color of the crystals corresponds to the

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* To whom correspondence should be addressed at the Anorganisch-Chemisches Laboratorium der Technischen Universität München, 8000 Munich, Germany.