

Contribution from the Department of Chemistry,  
Texas A&M University, College Station, Texas 77843**New Multidentate Ligands. XVII. Chelating Tendencies  
of *N*-(*o*-Hydroxybenzyl)iminodiacetic Acid (H<sub>3</sub>L)**

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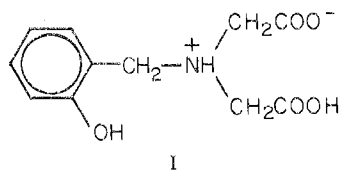
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*N*-(*o*-Hydroxybenzyl)iminodiacetic acid (H<sub>3</sub>L, HBIDA) has been synthesized by a new procedure and its aqueous coordination chemistry involving interactions with Fe(III), Cu(II), Ni(II), Zn(II), and Co(II) is described. At 25° and 0.10 *M* ionic strength, the logarithms of the protonation constants of the ligand are 11.71, 8.07, and 2.34. The logarithms of the normal formation constants  $[ML^{n-3}]/[M^{n+}][L^{3-}]$  were found to be 22.4, 16.11, 13.83, 12.99, and 12.87 with the above metals, respectively. The presence of  $MHL^{n-2}$  species was detected for all metals studied except for Fe<sup>3+</sup>, in which case all deprotonation reactions occurred simultaneously with complexation at low pH. Co(II) and Zn(II) ions react with excess ligand to form  $M(HL)_2^{2-}$ , but it was shown that no 1:2 complexes form with Cu(II), Ni(II), and Fe(III). In addition, both spectrophotometric and potentiometric results indicated that Fe<sup>III</sup>-HBIDA chelates are all mononuclear throughout the pH range, although  $FeL(OH)^-$  and  $FeL(OH)_2^{2-}$  do form in two well-defined steps. The appropriate formation constants for all of the hydrolytic 1:1 species and of the 2:1 complexes have also been calculated and probable ligand-bonding sites of the complexes are proposed.

**Introduction**

The high stability of ferric complexes of hydroxybenzylamines has been established in studies of *N,N'*-bis(*o*-hydroxybenzyl)ethylenediamine-*N,N'*-diacetic acid (HBED),<sup>1</sup> ethylene-*N,N'*-bis(*o*-hydroxyphenyl)glycine (EHPG),<sup>2,3</sup> and *N,N'*-bis(*o*-hydroxybenzyl)ethylenediamine-*N,N'*-bis(methylenephosphonic acid) (HBEDPO).<sup>4</sup> This unusually high stability has been shown to be due to the high affinity of the phenolate group for the iron and to the favorable arrangement of their donor groups toward chelate formation. This study deals with the tetradentate ligand *N*-(*o*-hydroxybenzyl)iminodiacetic acid (HBIDA), I, which has only a single phenolate group, as compared to the previous investigation of sexadentate ligands containing two such groups.

**Experimental Section**

***N*-(*o*-Hydroxybenzyl)iminodiacetic Acid (H<sub>3</sub>L).** A solution of 9.76 g (0.050 mol) of the disodium salt of iminodiacetic acid in 20 ml of water was treated with 60 ml of 95% ethanol and the resulting well-stirred suspension was alternately treated in small portions with 11.4 g (0.050 mol) of *o*-acetoxybenzyl bromide and a solution of 2.0 g (0.050 mol) of NaOH in 7.0 ml of water. After about 8 min, the temperature of the oil bath was raised to 70° for 4 hr, 2.0 g (0.050 mol) of solid NaOH was added, and the reaction mixture was heated at 70° for another hour. The solution was stripped off to dryness under vacuum, some water was added, the solution was made acidic to pH ~2 with 12 *M* HCl, and the colorless solid thus formed was recrystallized several times from water. Overall yield of purified *N*-(*o*-hydroxybenzyl)iminodiacetic acid was 2.30 g (19.2%). The nmr spectrum (D<sub>2</sub>O; 5% NaOD; shifts relative to 3-(trimethylsilyl)propanesulfonate) showed three peaks: 3.12 (singlet), 3.57 (singlet), 6.83 ppm (multiplet), in the ratio of 2:1:2. Molecular weight by titration: found, 242; calcd, 239.

**Reagents and Procedure.** Stock solutions of the metal salts were prepared from reagent grade chlorides and nitrates and standardized by direct titration with EDTA using the appropriate indicator.<sup>5</sup> Solutions of both 1:1 and 2:1 ligand:metal ratios were titrated with 0.10 *M* carbonate-free KOH, and the free hydrogen ion concentration was measured with a Beckman Research pH meter, Model 1019. During each titration the solutions were kept under a nitrogen atmosphere and maintained at 25.00 ± 0.05°. The ionic strength was maintained at either 0.100 *M* (KNO<sub>3</sub>) or 1.00 *M* (KCl).

The visible and ultraviolet absorption spectra of the ligand and the metal complexes were determined in 1.00-cm matched quartz cells using a Cary Model 14 recording spectrophotometer. In this paper

**Table I.** Proton Association Constants of  
*N*-(*o*-Hydroxybenzyl)iminodiacetic Acid<sup>a</sup>

	$\mu = 0.1 M$ (KNO <sub>3</sub> )	$\mu = 1.0 M$ (KCl)
$\log K^H$ , <sup>b</sup>	11.71	
$\log K^{H_1}$	8.07	8.05
$\log K^{H_2}$	2.34	2.36

<sup>a</sup> All values for 25.00 ± 0.05°. <sup>b</sup>  $K^H_n = [H_n L^{n-3}]/[H^+][H_{n-1} L^{n-4}]$

the extinction coefficient  $\epsilon$  is given in units of  $M^{-1} \text{ cm}^{-1}$ .

**Results**

In the titration of the ligand in the absence of any metal ions (Figure 2, top curve), the buffer regions corresponding to the two most acidic proton association constants were found to occur in a pH range low enough so that the two lower  $\log K^H$  values were calculated directly from the potentiometric data. This has been done using an iterative computer program which computes a new pH curve from interval midpoint  $pK_a$ 's, adjusts the values of the  $pK_a$ 's according to the deviation of the new curves from the experimental values, recomputes a new curve, etc., until convergence criteria are met.

The third proton association constant corresponding to the loss of the phenolic hydrogen was found to be too high to be determined from the potentiometric data and therefore was calculated from the pH dependence of the ultraviolet spectra of the ligand shown in Figure 1. From the spectra taken under conditions of total protonation and total deprotonation of the phenolic group, the extinction coefficients of the  $L^{3-}$  and  $HL^{2-}$  species have been determined to be  $\epsilon_{292} 4028$  and  $\epsilon_{276} 2165$  for  $L^{3-}$  and  $\epsilon_{292} 403$  and  $\epsilon_{276} 3021$  for  $HL^{2-}$ . The ultraviolet spectra of several ligand solutions with pH's ranging from 11 to 13 have been determined. The concentrations of  $L^{3-}$  and  $HL^{2-}$  were calculated from eq 1 and 2 ( $A$  is total absorbance

$$A_{292} = [L^{3-}]\epsilon_{292}L^{3-} + [HL^{2-}]\epsilon_{292}HL^{2-} \quad (1)$$

$$A_{276} = [L^{3-}]\epsilon_{276}L^{3-} + [HL^{2-}]\epsilon_{276}HL^{2-} \quad (2)$$

of the solution). The hydrogen ion concentration was calculated from the analytical concentrations of acid and base used to prepare each solution. In all cases the ligand concentration was very small compared to the hydroxide ion concentration and therefore the protons released from the ligand were neglected. The proton association constant values obtained in this study are shown in Table I.

The potentiometric titration curves for the 1:1 metal-ligand systems shown in Figure 2 clearly indicate the formation of a protonated chelate with the addition of 2 mol of base/mol of ligand, followed by the loss of the third proton after the

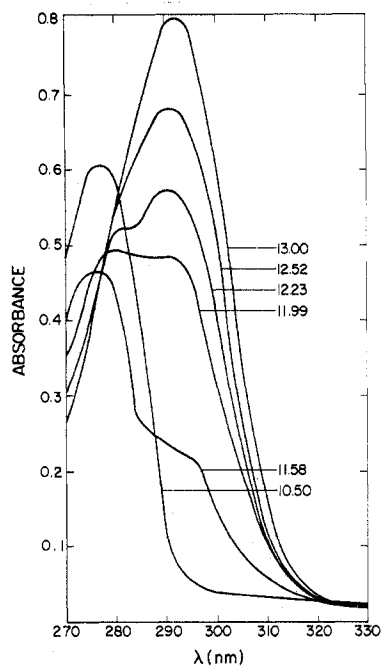


Figure 1. Ultraviolet absorption spectrum of HBIDA as a function of  $-\log [H^+]$ .  $T_L = 1.99 \times 10^{-4} M$ ;  $\mu \approx 0.10$  (NaOH + NaCl);  $25^\circ$ .

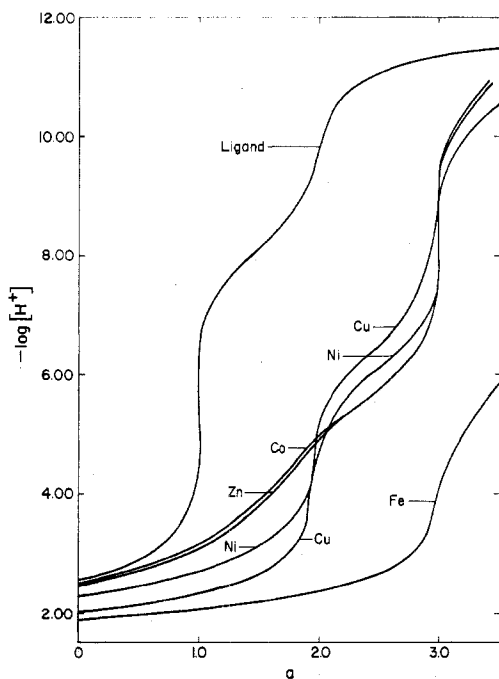
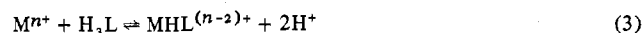


Figure 2. Potentiometric equilibrium curves for 1:1 ratios of HBIDA and  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Zn^{2+}$ , and  $Fe^{3+}$ . Top curve represents HBIDA in the absence of metal ions.  $T_L = T_M = 5.20 \times 10^{-3} M$ ;  $\mu = 0.100 M$  ( $KNO_3$ );  $25.0^\circ$ .

addition of another 1 equiv of base. This occurs in all cases except with iron(III), in which case all three of the ligand protons are lost simultaneously. The equilibria studied for the 1:1 systems are represented by eq 3 and 4. The equilibrium constants are however written as formation constants in eq 5-7.



$$K_{MHL}^H = \frac{[MHL]}{[ML][H]} \quad (5)$$

$$K_{MHL}^M = \frac{[MHL]}{[M][HL]} \quad (6)$$

$$K_{ML} = \frac{[ML]}{[M][L]} \quad (7)$$

Table II. Equilibrium Constants as Defined by Eq 5-7<sup>a</sup>

Cation	$\log K_{MHL}^H$	$\log K_{MHL}^M$	$\log K_{ML}$
$Co^{2+}$	5.81	6.97	12.87
$Zn^{2+}$	5.79	7.07	12.99
$Ni^{2+}$	6.12	8.24	13.83
$Cu^{2+}$	6.51	10.91	16.11
$Fe^{3+}$			22.4 <sup>b</sup>

<sup>a</sup> Values obtained at  $\mu = 0.1 M$  ( $KNO_3$ ),  $25^\circ$ . <sup>b</sup> Determined by a ligand competition method discussed in text.

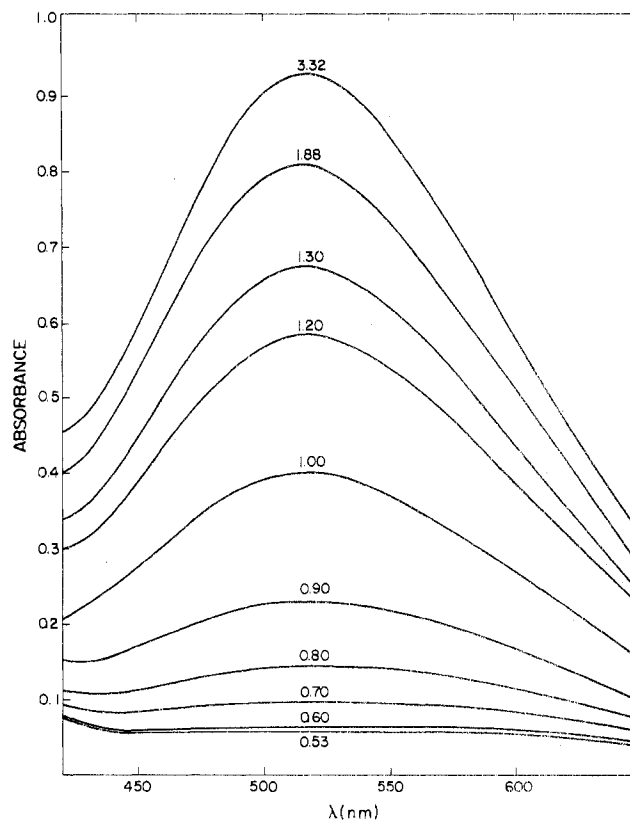
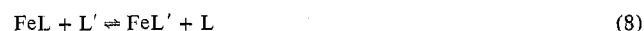


Figure 3. Visible absorption spectrum of  $Fe^{III}$ -HBIDA as a function of  $-\log [H^+]$ .  $T_L = T_{Fe} = 8.20 \times 10^{-4} M$ ;  $25.0^\circ$ .

The chelate proton association constants  $K_{MHL}^H$  have been calculated in the same manner as described for the ligand association constants. The overall normal stability constants  $K_{ML}$  were calculated from the ligand and metal mass balance equations and the charge balance equation using  $K_{MHL}^H$  obtained before. The simultaneous solution of these three equations gives the concentrations of M, L, and ML for each point in the titrations. These values and the measured hydrogen ion concentration were then used to calculate the equilibrium constants whose values are listed in Table II.

As can be judged from the titration curve of the iron-ligand system (Figure 2, bottom curve), the equilibrium is displaced almost completely toward the chelate, giving a curve similar to a strong acid titration. The formation of the ferric chelate is so nearly complete, even at low pH, that the stability constant cannot be accurately calculated from the potentiometric data. For this reason the value of  $K_{ML}$  for the ferric chelate has been determined spectrophotometrically.

The determination of  $K_{ML}$  is based on the exchange equilibrium



where L' is (hydroxyethyl)ethylenediaminetriacetic acid (HEDTA). The absorbance of the iron complex as a function of pH is shown in Figure 3. The extinction coefficient of the iron complex at the 518-nm absorbance maximum is calculated

Table III.<sup>a</sup> Determination of  $K_{ML}$  for  $\text{Fe}^{\text{III}}(\text{HBIDA})$ 

$10^3$ [L <sub>t</sub> ] <sub>0</sub> M	$10^3$ [L' <sub>t</sub> ] <sub>0</sub> M	$10^3$ [M <sub>t</sub> ] <sub>0</sub> M	$-\log$ [H <sup>+</sup> ]	$10^4$ [FeL], M	$K_X$	$\log K_{ML}$
1.00	1.00	1.00	2.09	1.046	361	22.36
1.00	1.00	1.00	2.10	1.065	376	22.38
						Av 22.4 <sup>b</sup>

<sup>a</sup> The proton association constants used for HEDTA<sup>6</sup> are  $\log K^{\text{H}_1} = 9.81$ ,  $\log K^{\text{H}_2} = 5.37$ ,  $\log K^{\text{H}_3} = 2.6$ .<sup>6</sup>  $\log K_{ML}$  of the HEDTA-Fe complex is 19.8. <sup>b</sup> All values obtained at  $\mu = 0.1 M$  ( $\text{KNO}_3$ ), 25°.

to be  $1.10 \times 10^3$ . The method depends on the fact that the Fe-HEDTA complex does not have an appreciable absorption at the 518-nm absorption maximum of the HBIDA complex and that no mixed-ligand complexes form. Therefore in a solution containing both complexes the concentration of the HBIDA chelate was easily determined from the absorbance at 518 nm. The three mass balance equations (eq 9-11) were solved at pH ~2 in order to obtain the individual concentrations of each species for substitution into eq 12. The

$$[M_t]_0 = [\text{FeL}] + [\text{FeL}'] \quad (9)$$

$$[L_t]_0 = [\text{FeL}] + A_1[L] \quad (10)$$

$$[L'_t]_0 = [\text{FeL}'] + A_2[L'] \quad (11)$$

$$K_X = \frac{[\text{FeL}][L']}{[\text{FeL}'][L]} = \frac{K_{ML}}{K_{ML}'} \quad (12)$$

symbols  $A_1$  and  $A_2$  represent distribution functions containing the proton association constants of the respective ligands and the "o" subscripted symbols represent the analytical metal ion and ligand concentrations. Since these constants, the hydrogen ion concentration, the total amount of each reagent, and the concentration of FeL are known, all the other variables can be calculated and used to obtain the displacement constant  $K_X$ . Using the  $K_{ML}$  value obtained from the literature,  $K_{ML}$  can be calculated. Thermostated solutions of equimolar amounts of ferric chloride, HBIDA, and HEDTA were allowed to equilibrate overnight. In one case the HBIDA was added to a solution of the HEDTA complex, while in the other the HEDTA was added to a solution of the HBIDA complex. The results are shown in Table III.

It was also determined from the titration curve (Figure 2) of the Fe-HBIDA system that the chelate forms mono- and dihydroxy complexes with the addition of the fourth and fifth moles of base per mole of ligand. These complexes form in the pH range between 5.0 and 10.5, and the equilibrium constants are defined as

$$K^1_{\text{OH}} = [\text{FeL}]/[\text{FeL}(\text{OH})^-][\text{H}^+] \quad (13)$$

$$K^2_{\text{OH}} = [\text{Fe}(\text{OH})\text{L}^-]/[\text{Fe}(\text{OH})_2\text{L}^{2-}][\text{H}^+] \quad (14)$$

These have been calculated by the iteration method used to determine the ligand-proton association constants, and the values obtained are  $\log K^1_{\text{OH}} = 5.71$  and  $\log K^2_{\text{OH}} = 9.1$ , for  $\mu = 1.00 M$  (KCl), 25°.

Another likely reaction which was considered in the iron system was that of ololation. These equilibria are given in eq 15 and 16 followed by their appropriate definitions of the



$$K^1_{\text{OH}} = [\text{FeL}]/[\text{Fe}(\text{OH})\text{L}^-][\text{H}^+]$$



$$K_D = [(\text{Fe}(\text{OH})\text{L}^2)_2][\text{H}^+]^2/[\text{FeL}]^2$$

equilibrium constants. These constants have been evaluated by the method of Gustafson and Martell.<sup>7</sup> From eq 15 and

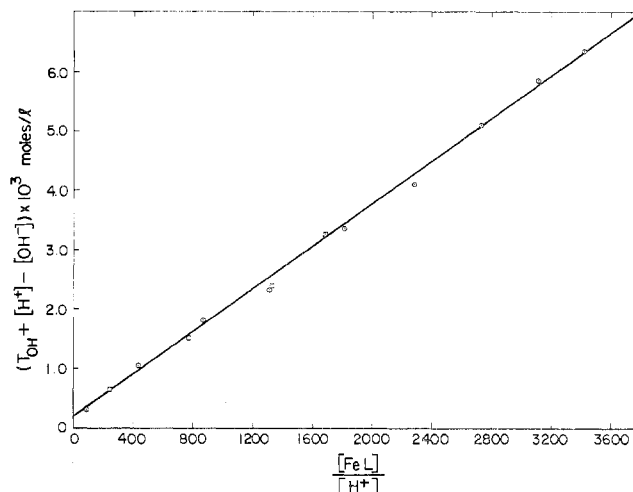


Figure 4. Plot of eq 18 for  $\text{Fe}^{\text{III}}(\text{HBIDA})$  at two concentrations: circles,  $T_L = T_{\text{Fe}} = 1.00 \times 10^{-2} M$ ; squares,  $T_L = T_{\text{Fe}^{3+}} = 4.92 \times 10^{-3} M$ . Slope is  $1/K^1_{\text{OH}} = 10^{-5.74}$ ; intercept  $\approx 0$ , confirming  $K_D \approx 0$  (see text).

16 and the normal mass balance equations, we obtained the relation

$$\frac{[\text{H}^+](T_{\text{OH}} + [\text{H}^+] - [\text{OH}^-])}{[\text{FeL}]} = \frac{1}{K^1_{\text{OH}}} + 2K_D \frac{[\text{FeL}]}{[\text{H}^+]} \quad (17)$$

where  $T_{\text{OH}}$  is the total concentration of base added in excess of the amount required for the complete formation of the normal FeL chelate. The concentration of FeL is calculated as  $[\text{FeL}] = T_M - T_{\text{OH}} - [\text{H}^+] + [\text{OH}^-]$ . A plot of  $[\text{H}^+](T_{\text{OH}} + [\text{H}^+] - [\text{OH}^-])/[\text{FeL}]$  vs.  $2[\text{FeL}]/[\text{H}^+]$  should give values of  $1/K^1_{\text{OH}}$  as intercept and  $K_D$  as slope. The large spread in the first few data points and the manner in which the data appeared to approach a horizontal line ( $K_D = 0$ ) as more base was added indicated that very little if any ololation occurs. The absence of polynuclear complexes was also indicated by the fact that the value of  $K^1_{\text{OH}}$  as calculated originally remained constant with changing concentrations of metal and ligand. The value of  $K^1_{\text{OH}}$  obtained from the y intercept of the horizontal graph discussed above is  $10^{5.75}$ , well within experimental error of the computer-calculated values.

With  $K_D = 0$ , (17) was rearranged to (18) and  $(T_{\text{OH}} + [\text{H}^+]$

$$T_{\text{OH}} + [\text{H}^+] - [\text{OH}^-] = \frac{1}{K^1_{\text{OH}}} \frac{[\text{FeL}]}{[\text{H}^+]} \quad (18)$$

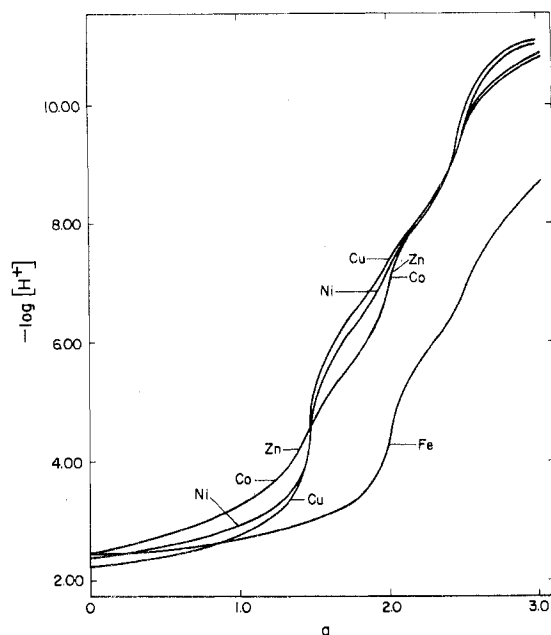
$- [\text{OH}^-]$  was plotted against  $[\text{FeL}]/[\text{H}^+]$ . This plot (Figure 4) was found to be linear with an intercept near zero and the slope value for  $\log K^1_{\text{OH}} = 5.75$  also, thus confirming the above results.

Titration curves have also been done with solutions containing 2:1 ratios of ligand to metal, and the curves obtained are shown in Figure 5. The stability constants of the 2:1 complexes have been calculated using the mass and charge balance equations and the previously determined stability constants of the 1:1 complexes. The stability constants of the 2:1 complexes are expressed as

$$K_2 = \frac{[\text{M}(\text{HL}^2)_2]}{[\text{M}^{2+}][\text{HL}^2]^2} \quad (19)$$

The values obtained are  $\log K_2 = 11.54$  for  $\text{Co}^{2+}$  and  $\log K_2 = 11.53$  for  $\text{Zn}^{2+}$ . The calculations indicate no 2:1 complexes of HBIDA with  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , or  $\text{Fe}^{3+}$ .

The iron 2:1 system was also investigated spectrophotometrically. Since the extinction coefficient of the 1:1 complex is known, for any solution  $A_0$ , defined here as the absorbance one would observe if all the metal is present as the 1:1 complex,



**Figure 5.** Potentiometric equilibrium curves for 2:1 ratios of HBIDA and  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Fe}^{3+}$ .  $T_L = 5.20 \times 10^{-3} M$ ;  $T_M = 2.60 \times 10^{-3} M$ ;  $\mu = 0.100 M (\text{KNO}_3)$ ;  $25.0^\circ$ .

**Table IV.<sup>a</sup>** Dissociation Constants of Basic Nitrogen Atoms of Related Compounds ( $\mu = 0.1 M$ ;  $25^\circ$ )

Compd	$\text{p}K_a$
<i>N,N</i> -EDDA ( <i>N,N</i> -ethylenediaminediacetic acid)	10.87
NTA (nitrilotriacetic acid)	9.65
IDA (iminodiacetic acid)	9.34
HIDA ((hydroxyethyl)iminodiacetic acid)	8.66

can be calculated at the 518-nm absorbance maximum of the 1:1 complex. The presence of any 2:1 complex would be expected to cause the observed absorbance to deviate from  $A_0$ , unless by chance the 2:1 complex has an extinction coefficient identical with that of the 1:1 complex. It has been found that even with a 10-fold excess of ligand, the absorbance reaches  $A_0$  around pH 2 and remains constant as the pH increases further. Even at pH values above 10.5 the absorbance does not deviate, neither higher nor lower, from the calculated  $A_0$ . This seems to confirm the results from the earlier calculation indicating no formation of a 2:1 complex.

**Discussion**

One of the unusual properties of HBIDA is the low basicity of the nitrogen atom compared to iminodiacetic acid (IDA) and other similar IDA derivatives. Table IV, which lists the  $\text{p}K_a$  of the central nitrogen atom of each compound, clearly demonstrates this point.

This phenomenon is believed to be due to intramolecular hydrogen bonding between the deprotonated nitrogen and the phenolic hydrogen. Such bonding stabilizes the deprotonated form of the nitrogen and thus facilitates loss of the hydrogen ion, as shown by the lower  $\log K^{H_2}$ . The proposed intramolecular hydrogen bonding also offers a reasonable explanation for the large value of  $\log K^{H_1}$ .

Since intramolecular hydrogen bonding of this type is not possible in the protonated HBIDA chelates MHL, the actual basicity of the central nitrogen atom now becomes essentially identical with that in IDA. As a consequence, the stability constants  $\log K^{M_{MHL}}$  for HBIDA are expected to be at least as large as the corresponding  $\log K_{ML}$  in IDA, with any excess stability ascribable to the degree of coordination of the undeprotonated hydroxybenzyl group. Such an increase in stability can be seen in the chelates of (2-hydroxyethyl)iminodiacetic acid (HIDA), where coordination of the hydr-

**Table V.** Comparison of Stability Constants of MHL Complexes of HBIDA with the ML Complexes of IDA and HIDA

Cation	$\log K_{ML}^a$		$\log K_{MHL}^{M^b}$
	IDA	HIDA	
$\text{Co}^{2+}$	6.94	8.02	6.97
$\text{Zn}^{2+}$	7.24	8.45	7.07
$\text{Ni}^{2+}$	8.13	9.33	8.24
$\text{Cu}^{2+}$	10.57	11.72	10.91

<sup>a</sup> From ref 6. <sup>b</sup> This work.

**Table VI.** Comparison of Metal Ion Affinities of Ligand with Protonation Constants of Metal Chelates

Cation	$\Delta K$	$\log K_{MHL}^H$	$\log K_{ML}$
$\text{Zn}^{2+}$	5.92	5.79	12.99
$\text{Co}^{2+}$	5.90	5.81	12.87
$\text{Ni}^{2+}$	5.59	6.12	13.83
$\text{Cu}^{2+}$	5.20	6.51	16.11
$\text{Ca}^{2+}$ <sup>a</sup>	3.74	8.06	6.74
$\text{Sr}^{2+}$ <sup>a</sup>	2.74	9.06	4.99
$\text{Ba}^{2+}$ <sup>a</sup>	2.44	9.34	4.40

<sup>a</sup> Values for  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  obtained from ref 8.

oxyethyl group increases the stability of these chelates relative to the complexes of unsubstituted IDA. These values are shown in Table V.

Apparently, the gain in stability through the coordination of the protonated phenolic group is minimal, giving  $K_{MHL}^M$  values of HBIDA which are nearly equal to the corresponding  $K_{ML}$  of IDA.

A closer examination of the chelate deprotonation constants reveals an unusual trend. Presumably the more stable the fully deprotonated chelate ML, the more readily the MHL species will lose its proton. However, the  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  complexes show a reversal of this trend, in that although they have  $K_{ML}$  values significantly greater than those of  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$ , they have higher  $K_{MHL}^H$  values as well (Table VI). This is the result of the fact that the loss of the phenolic hydrogen and the subsequent coordination of this fourth donor group contributes less added stability to the copper and nickel complexes than it does to the chelates of cobalt and zinc. The value of  $K_{MHL}^H$ , which is a measure of the position of equilibrium between the initial protonated state and the final deprotonated state, is determined by the difference in stability of the two states. Table VI clearly demonstrates the correlation between  $\Delta K$  ( $\Delta K = \log K_{ML} - \log K_{MHL}^M$ ) and the observed value of  $K_{MHL}^H$ .

The anomalous behavior of the copper and nickel complexes may be due to differences in configuration of the ligand about these two metal ions. The structure of the ligand is such that in a regular octahedral configuration there will be three donor groups in an equatorial plane, while the fourth group will occupy an axial coordination site. A tetragonal distortion of these axial positions, lengthening and thus weakening these bonds, might be responsible for the relatively small increase in stability that accompanies coordination of the fourth group. It does not seem unreasonable to expect such behavior in the case of copper, which normally prefers a square-planar arrangement of donor groups. For the nickel complex a similar effect is suggested by the visible spectra. In general, the extinction coefficient of nickel complexes is characteristic of the configuration of the complex. Octahedral complexes of nickel have an  $\epsilon$  of 1-10, while square-planar complexes have an  $\epsilon$  of about 60, and the tetrahedral complexes have an  $\epsilon$  of around 100.<sup>9</sup> The value of  $\epsilon$  determined for the  $\text{Ni}^{2+}$ -HBIDA complex is 18 at 395 nm, which lies between the expected values of an octahedral and square-planar complex. This suggests the type of distortion of the octahedral configuration described above.

The same line of reasoning could also explain why there are

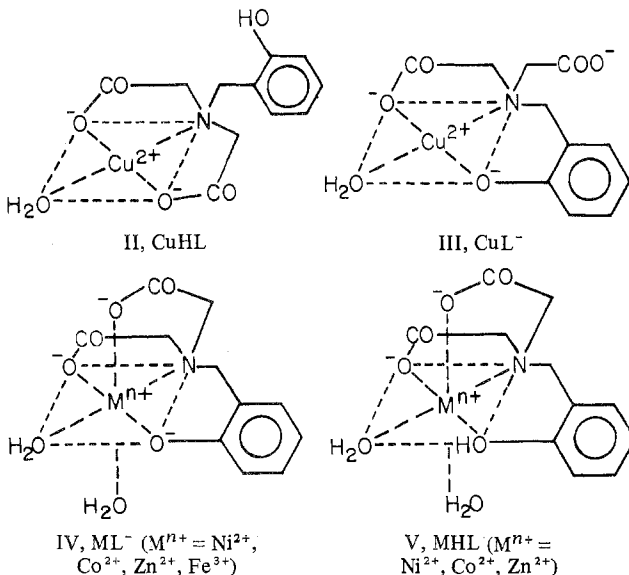
no 2:1 complexes with the copper(II) or nickel(II) cations. However, there is no obvious reason for the fact that no 2:1 complex forms with the  $\text{Fe}^{3+}$  ion. In the cases of cobalt(II) and zinc(II) the 2:1 complexes are of the formula  $\text{M}(\text{HL})_2$ . Such complex formation is aided by the initial formation of the MHL protonated chelate, which has three available coordination sites for a second ligand molecule. The high affinity of the phenolic group for the ferric ion results in the immediate formation of the tetracoordinated complex, ML, without the formation of an intermediate protonated chelate. The result is a neutral chelate with only two coordination sites available. The strong interaction between the metal ion and the phenolic group apparently satisfied the coordination requirements of the iron to an extent that this effect, in combination with the neutrality of the complex and the shortage of available positions for a second ligand molecule, is enough to prevent formation of a 2:1 complex.

Since HBED could be considered as being composed of two molecules of HBIDA minus two acetic acid groups, the calculation of  $\Delta = 2 \log K_1(\text{HBIDA}) - \log K_1(\text{HBED}) - 2 \log K_1(\text{acetate})$  should be of interest in comparing the relative stabilities of the complexes of the two ligands with the metal ions studied. Table VII lists the results of this calculation, and the values of  $\Delta G$  which were calculated from the relationship  $\Delta G = -RT \ln \Delta$ .

Although the significance of the results of this computation must be weighed with caution, it does nevertheless seem encouraging that the  $\Delta G$  values are in the vicinity of  $-8$  kcal/mol which is not an unreasonable value for the entropy contribution at  $298^\circ$  for one chelate ring. The fact that the value for Fe(III) is reversed probably involves additional considerations such as specific iron(III)-phenolate  $\pi$  interaction and unusually high degree of hydration of the Fe(III) ion.

### Structures of Complexes

Although no evidence has been provided in this work on the structures of the chelates formed, the comparisons in the

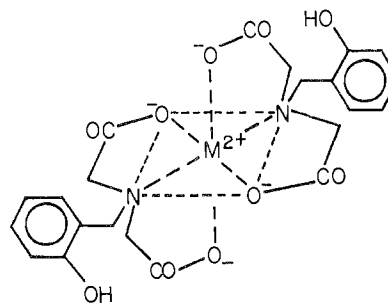


**Table VII.**<sup>a</sup> Comparison of Ligands Containing *o*-Hydroxybenzyl Donor Groups

Cation	$K_{\text{ML}}$			$\Delta$	$\Delta G$ , kcal/mol
	HBIDA, <sup>b</sup> $\text{L}^{3-}$	HBED, $\text{L}^{4-}$	Acetate, $\text{L}^-$		
$\text{Zn}^{2+}$	12.99	18.37	1.04	5.53	-7.5
$\text{Co}^{2+}$	12.87	19.89	0.81	2.93	-5.8
$\text{Ni}^{2+}$	13.83	19.31	0.83	6.69	-9.1
$\text{Cu}^{2+}$	16.11	21.38	1.86	7.12	-9.7
$\text{Fe}^{3+}$	22.4	39.68	3.38	-1.28	+2.2

<sup>a</sup> Reference 10. <sup>b</sup> This work.

foregoing discussion, the stoichiometry of the metal chelate formation, and the values of the various types of equilibrium constants determined make possible suggestion of the bonding sites and to some extent the structures of these complexes in solution. The most reasonable structures are given by formulas II-V. Since the  $\text{Fe}^{\text{III}}(\text{HBIDA})$  chelate forms  $\text{ML}(\text{OH})^-$  and  $\text{ML}(\text{OH})_2^{2-}$  in discrete steps, the structures of these two species must therefore correspond to V with successive deprotonation of the coordinated water molecules. The 1:2 chelate structures  $\text{M}(\text{HL})_2^{2-}$  for the metal ions which form such complexes are probably best represented by VI.



VI,  $\text{M}(\text{HL})_2$

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**Registry No.** HBIDA, 7372-13-6; CoHL, 54181-76-9; CoL<sup>-</sup>, 54193-00-9; ZnHL, 54275-83-1; ZnL<sup>-</sup>, 54191-92-3; NiHL, 54191-93-4; NiL<sup>-</sup>, 54274-48-5; CuHL, 54181-77-0; CuL<sup>-</sup>, 54181-78-1; FeL, 54230-20-5; FeL(OH)<sup>-</sup>, 54181-83-8; FeL(OH)<sub>2</sub><sup>2-</sup>, 54193-01-0; Co(HL<sup>2-</sup>)<sub>2</sub><sup>2-</sup>, 54181-81-6; Zn(HL<sup>2-</sup>)<sub>2</sub><sup>2-</sup>, 54181-82-7; iminodiacetic acid, disodium salt, 928-72-3; *o*-acetoxybenzyl bromide, 704-65-4.

### References and Notes

- (1) F. L'Eplattenier, I. Murase, and A. E. Martell, *J. Amer. Chem. Soc.*, **89**, 837 (1967).
- (2) G. Anderegg and F. L'Eplattenier, *Helv. Chim. Acta*, **47**, 1067 (1964).
- (3) K. H. Schroder, *Acta Chem. Scand.*, **18**, 596 (1964).
- (4) D. T. MacMillan, I. Murase, and A. E. Martell, to be submitted for publication.
- (5) G. Schwarzenbach and H. Flaschka, "Die Komplexometrische Titration," Verlag Enke, Stuttgart, 1965.
- (6) R. M. Smith and A. E. Martell, "Critical Stability Constants," Vol. I, Plenum Press, New York, N.Y., 1974.
- (7) R. L. Gustafson and A. E. Martell, *J. Phys. Chem.*, **67**, 576 (1963).
- (8) G. Schwarzenbach and G. Anderegg, *Helv. Chim. Acta*, **30**, 1785 (1952).
- (9) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N.Y., 1972, pp 895-897.