

New Multidentate Ligands. X. Chelating Tendencies of N,N'-Diglycylethylenediamine-N'',N'',N''',N''''-tetraacetic Acid and Ethylenediamine-N,N'-di(acetylglycine)-N,N'-diacetic Acid¹

R. J. Motekaitis and A. E. Martell²

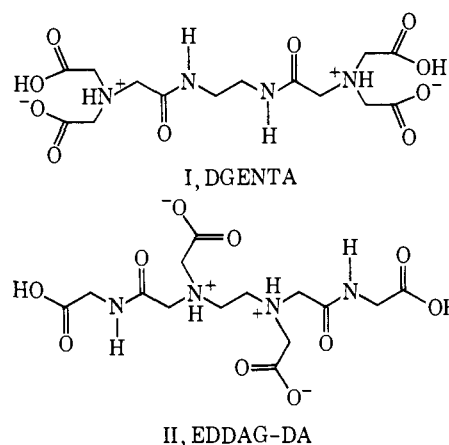
Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. Received January 14, 1970

Abstract: The synthesis and quantitative equilibrium studies of two new amide-group-containing multidentate ligands, N,N'-diglycylethylenediamine-N'',N'',N''',N''''-tetraacetic acid (DGENTA) and ethylenediamine-N,N'-di(acetylglycine)-N,N'-diacetic acid (EDDAG-DA), are described in detail. Their acid-base and metal-ligand reaction stoichiometries have been determined, and the equilibrium constants of the corresponding proton and metal ion association constants have been calculated from potentiometric data. The probable structures of the chelate compounds formed in aqueous solution were deduced by analysis of infrared spectra in D₂O, and stability constants are compared with those of analogous peptide chelates. The Fe(III) ion was found to displace two peptide protons at low pH from EDDAG-DA and Cu(II) displaced only one at moderate pH. The Cu(II)-DGENTA system involves metal ion promoted dissociation of both amide protons. The Co(II)-DGENTA chelate also shows similar behavior. These reactions provide the first examples of amide proton displacement by Fe(III) and Co(II) ions.

A full appreciation of the coordinating characteristics of the ambident amido group has been precluded up to now by the lack of a sufficient variety of ligands containing this donor group. Previous studies³⁻⁶ have largely utilized oligopeptides,⁴ such as di-, tri-, and tetraglycine.⁵ A recent study was made on N,N'-diglycylethylenediamine (DGEN).³ Up to the present time copper(II) and nickel(II) ions are the only metal ions that have been observed to displace amidic protons from these ligands. It has been shown by aqueous infrared studies⁵ that proton displacement from these ligands is associated with rearrangement of coordinate bonds from M-O to M-N⁻ bonding with the amide linkage. Other metal ions form only relatively very unstable complexes or chelates with oligopeptides, with DGEN, or other amide-containing ligands. These complexes hydrolyze when the pH is raised and the metal ion thus becomes unavailable for peptide bonding or for the rearrangement from metal-O bonding to metal-N bonding with the attendant release of the amido proton.

This paper describes two new isomeric multidentate ligands containing two nitrogen and four carboxylate oxygen coordinating groups in addition to the amidic linkages already present. These new ligands are N,N'-diglycylethylenediamine-N'',N'',N''',N''''-tetraacetic acid (DGENTA, I) and ethylenediamine-N,N'-di(acetylglycine)-N,N'-diacetic acid (EDDAG-DA, II).

The selection of these ligands for study was based on the idea that the auxiliary amino and carboxylate donor groups would coordinate the metal ion sufficiently in the intermediate pH range to prevent hydrolysis and decomposition of the complex until the pH is raised to a



high enough value to assist displacement of amide protons by the metal ion. When this occurs, the very much higher metal ion affinity of the negative amide nitrogens would greatly stabilize the metal complex and prevent its dissociation as the pH is raised to still higher values. Thus the new ligands would offer the promise of stabilizing ions other than those of Cu(II) and Ni(II) through binding by negative amide groups.

Experimental Section

Reagents. DGENTA. A 25-ml aqueous solution containing 2.47 g of diglycylethylenediamine dihydrochloride^{7a} and 5.56 g of bromoacetic acid was treated dropwise for 1 hr with 10 ml of 10 M NaOH and was allowed to stand overnight. The reaction mixture was poured onto ~140 ml of Dowex 50WX8 cation-exchange resin in the hydrogen form and was eluted with water. Aliquots of the eluate were tested until the calculated amount of strong acid was eluted. The product was concentrated from about 15 l. of eluate and was recrystallized from water: yield 1.5 g; mp 205-210° dec; nmr in D₂O-NaOD showed three peaks about 100 Hz upfield from HOD resonance in the ratio of 1:1:2.

Anal. Calcd for C₁₄H₂₂N₄O₁₀·0.5H₂O: C, 40.5; H, 5.6; N, 13.5. Found: C, 40.6; H, 5.9; N, 13.6.

EDDAG-DA. A 20-ml solution containing 0.400 g of ethylenediamine-N,N'-diacetic acid and 0.980 g of bromoacetyl glycine^{7b} was treated with 6 ml of 2.5 M NaOH in the same manner as described above for the synthesis of DGENTA. The reaction mixture

(1) This work was supported by the U. S. Atomic Energy Commission under Contract No. AT (4010) 3621 with the Texas A&M Research Foundation.

(2) To whom inquiries should be addressed.

(3) K. Sun Bai and A. E. Martell, *J. Amer. Chem. Soc.*, **91**, 4412 (1969).

(4) See ref 4-16 cited in ref 3.

(5) A. E. Martell in "Recent Topics in Coordination Chemistry," S. Misume and K. Ueno, Ed., Special Publication No. 84, Nankodo, Tokyo, Japan, 1968, pp 47-67.

(6) M. Kim and A. E. Martell, *J. Amer. Chem. Soc.*, **89**, 5138 (1967), and references cited therein.

(7) (a) T. L. Cottrell and J. E. Gill, *J. Chem. Soc.*, 129 (1947); (b) E. Abderhalden and E. Hasse, *Fermentsf.*, **12**, 313 (1930).

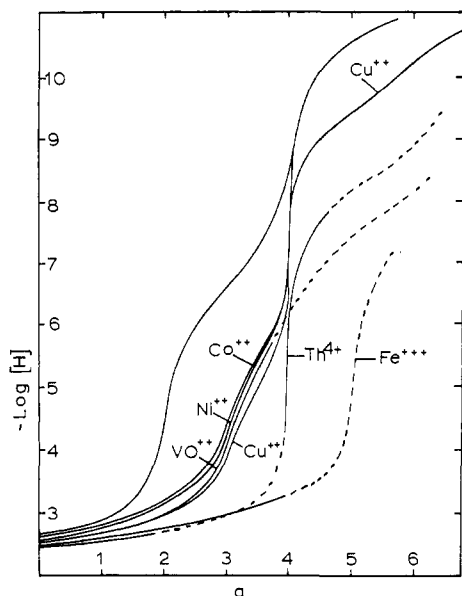


Figure 1. Potentiometric equilibrium curves for the 1:1 molar titration of metal ions to DGENTA; the unlabeled curve represents titration of the pure ligand; broken lines indicate precipitation; a = number of moles of 0.10 M sodium hydroxide added per mole of ligand; concentrations are 0.0010 M in ligand and metal salts; solution contains 0.100 M KNO_3 ; $t = 25^\circ$.

was then passed through ~ 30 ml of Dowex 50WX8 and eluted with 6 l. of H_2O . After recrystallization from water, the yield was 0.371 g; mp 213–217° dec; the nmr in D_2O -NaOD showed four sharp peaks in the ratio 1:1:1:1 about 50 Hz upfield from the HOD resonance.

Anal. Calcd for $C_{14}H_{22}N_4O_{10} \cdot 0.5H_2O$: C, 40.5; H, 5.6; N, 13.5. Found: C, 40.7; H, 5.5; N, 13.4.

Reagent grade metal nitrate salts were used and were standardized by methods of Schwarzenbach.⁸

Measurements. Appropriate aliquots of standard solutions of ligand or ligand and metal were diluted to 50.00 ml with water and titrated with 0.10 M standard CO_2 -free NaOH while $-\log [H^+]$ was measured by means of a Beckman research pH meter fitted with E-2 glass and calomel extension electrodes calibrated in the usual way.⁹ The test solutions were all originally 0.100 M in KNO_3 and 0.002–0.001 M in metal and/or ligand. The test solutions were protected from air by a stream of humidified prepurified nitrogen and were maintained at $25.0 \pm 0.05^\circ$ during measurements. Infrared spectra were measured on a Beckman IR12 with 0.015-mm cells containing 0.1 M solutions.

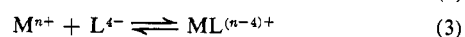
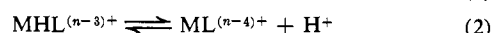
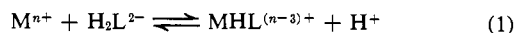
Results

DGENTA. The potentiometric titration curve of DGENTA (= H_4L) is shown in Figure 1. Two protons per ligand molecule dissociate between $a = 0$ and $a = 2$ (where a = moles of base added per mole of ligand present). At higher pH two more protons dissociate between $a = 2$ and $a = 4$. The four protonation constants obtained graphically for DGENTA at several concentrations are $\log K_1^H = 7.30$, $\log K_2^H = 6.18$, $\log K_3^H = 2.66$, and $\log K_4^H = 1.93$. A fifth protonation constant is estimated by successive approximations for acidic solutions to be $\log K_5^H \approx 1.2$. Note: $K_n^H = [H_nL^{(n-4)+}]/([H^+][H_{n-1}L^{(n-5)+}]$.

Low-pH DGENTA Complexes. The 1:1 DGENTA curves with Co(II), Ni(II), VO(IV), Cu(II), Fe(III), and Th(IV) are shown in Figure 1. The complex equilibria may be represented by

(8) G. Schwarzenbach, "Complexometric Titrations," Interscience Publishers, New York, N. Y., 1957.

(9) R. Courtney, R. Gustafson, S. Chaberek, Jr., and A. E. Martell, *J. Amer. Chem. Soc.*, **81**, 519 (1959).

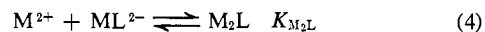


The equilibrium curves of all the divalent metal ions have a long buffer region from $a = 0$ to $a = 3$ and another at higher pH between $a = 3$ and $a = 4$. Iron(III) forms a red-brown precipitate at $a = 4$ which does not contain ligand and is therefore ferric hydroxide. Similarly, the Th(IV) ion forms a cloudy suspension which dissolves in the potential jump at $a = 4$; however, it soon thereafter reprecipitates inorganic thorium(IV).

Between $a = 0$ and $a = 3$ the stability constants for divalent ions were calculated from the expression for the equilibrium constant for eq 1, and mass balance and charge balance equations. Between $a = 3$ and $a = 4$, eq 1 was replaced by eq 2. For Fe(III) and Th(IV) eq 3 was used. For Co(II), Cu(II), Ni(II), and VO(IV) the formation constants corresponding to eq 3 were calculated from eq 1 and 2 utilizing the appropriate protonation constants of DGENTA. For Fe(III) and Th(IV) the stability constants corresponding to eq 3 were calculated directly. All these stability constants are listed in Table I.

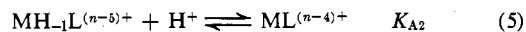
The potentiometric titration curves of 2:1 M-DGENTA systems are shown in Figure 2. Cu(II) formed the neutral precipitate Cu_2L at about $a = 2$ which redissolved only at about $a = 6$. At $3 \times 10^{-4} M$ concentration of ligand (curve not shown), the Cu(II) system remained in solution. The Ni(II) and Co(II) 2:1 M-DGENTA systems were soluble at the usual concentrations.

The parallel curves of Figure 2 between $a = 0$ and $a = 4$ depict the simple formation reaction



The formation constants K_{M_2L} were calculated utilizing eq 2, 3, and 4 together with the appropriate mass and charge balance equations and were found to be 8.29, 6.46, and 5.77 log units for Cu(II), Ni(II), and Co(II).

High-pH Metal Ion-DGENTA Interaction. In 1:1 systems there is no further reaction beyond $a = 4$ for Co(II) and Ni(II) with DGENTA. The VO(IV), Fe(III), and Th(IV) chelates of this ligand hydrolyze and form precipitates. However, as is evident from Figure 1, when the pH is raised to about 8.5 two protons are displayed by the Cu(II) ion. The reactions involved may be described by the equilibria



The two-band infrared spectrum of DGENTA at $a = 4$ becomes a rather complex spectrum when 1 mol of Cu(II) ion per mole of ligand present is added to the solution. However, once again it becomes a simple two-band spectrum when 2 additional mol of base is added. These spectral changes are summarized in Table II.

The 2:1 M-DGENTA solutions of Cu(II) and Co(II) undergo interesting changes as further base is added. Between $a = 4$ and $a = 6$ the initially light blue Cu(II) solution turns deep blue and the originally light pink 2Co(II)-DGENTA system reverts to a deep violet color. The latter time-stable complex is rapidly oxidized by atmospheric oxygen. These two complexes react with a

Table I. Equilibrium Constants^{a,b} for the Interaction of DGENTA with Metal Ions

Symbol	Equilibrium quotient	Log K					
		Cu ²⁺	Ni ²⁺	Co ²⁺	VO ²⁺	Fe ³⁺	Th ⁴⁺
K_1	$\frac{[ML^{(n-4)+}]}{[M^{n+}][L^{4-}]}$	10.16	9.52	8.54	10.3	14.7	14.0
K_{MHL^H}	$\frac{[MHL^{(n-3)+}]}{[ML^{(n-4)+}][H^+]}$	4.98	5.44	5.69	5.39		
K_{A2}	$\frac{[ML^{(n-4)+}]}{[MH_{-1}L^{(n-5)+}][H^+]}$	9.05					
K_{A1}	$\frac{[MH_{-1}L^{(n-5)+}]}{[MH_{-2}L^{(n-6)+}][H^+]}$	9.61					
K_{M_2L}	$\frac{[M_2L]}{[M^{2+}][ML^{2-}]}$	8.29	6.46	5.77			
K_{A1}	$\frac{[M_2H_{-1}L^-]}{[M_2H_{-2}L^{2-}][H^+]}$	7.38		9.60			
K_{A2}	$\frac{[M_2L]}{[M_2H_{-1}L^-][H^+]}$	7.58		9.36			
K_X	$\frac{[M_2H_{-2}L^{2-}]}{[M_2H_{-2}L(OH)^{3-}][H^+]}$	8.62		10.10			

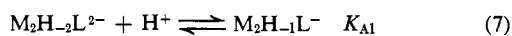
^a Medium consists of 0.10 M KNO₃; *t* = 25.00 ± 0.05°. ^b Log values of successive proton association constants of ligand are 7.30, 6.18, 2.66, and 1.93. ^c Ligand represented by H₄L.

Table II. Infrared Spectra of DGENTA and Its Copper(II) Chelates in D₂O Solution

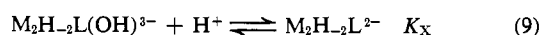
Molecular species present	Ir absorption frequency, cm ⁻¹	Assignment
L ⁴⁻	1583	-COO ⁻
	1632	-CONH-
CuL ²⁻	1585	-COO ⁻
	1605	-COO...Cu ²⁺
	1630	-CONH-
	1651	Cu ²⁺ ...N(<)CH ₂ CONH-
CuH ₋₂ L ⁴⁻	1590	-COO ⁻
	1630	-CON...Cu ²⁺

further equivalent of base. Since there are no further displaceable protons on the ligand the formula assigned to these complexes is M₂H₋₂L(OH)³⁻. Beyond *a* = 7 the titration curves indicate that all additional base exists in solution as free OH⁻ ion. Thus two Cu(II) and two Co(II) ions each release two amidic protons from one ligand anion at -log [H] ~ 7 and -log [H] ~ 9, respectively, followed by proton dissociation of coordinated water molecules without decomposition of the metal chelates formed.

Equilibrium constants for the two amide proton dissociations occurring from *a* = 4 to *a* = 6 were calculated from a linear slope-intercept equation derived from the respective equilibrium expressions (eq 7 and 8)



and appropriate mass balance and charge balance equations. The equilibrium constants corresponding to eq 9 for the formation of the M₂H₋₂L(OH)³⁻ species was calculated using the two constants corresponding to eq 7 and 8, in addition to the appropriate mass and charge conservation equations. The calculated values



of these constants are listed in Table I.

Beyond *a* = 4 the 2:1 Ni(II)-DGENTA system (Figure 2) underwent hydrolysis to some extent but no stoichiometric equilibrium expression could be determined with certainty.

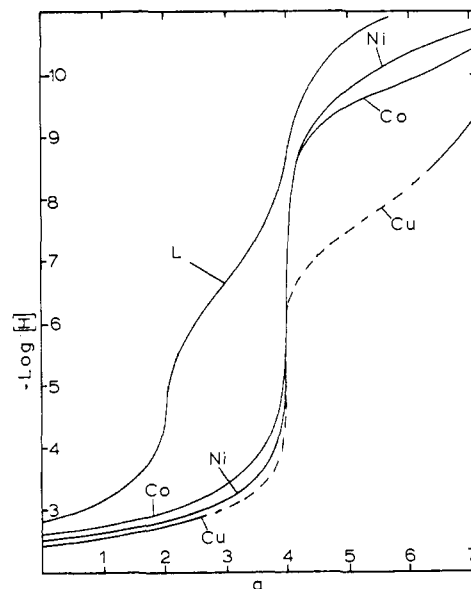


Figure 2. Potentiometric equilibrium curves for DGENTA (top) and for 2:1 molar ratios of metal ions to DGENTA; broken lines indicate precipitation; *a* = moles of 0.10 M sodium hydroxide added per mole of ligand; concentrations of metal ion and ligand are 0.0010 M; solution contains 0.100 M KNO₃; *t* = 25°.

EDDAG-DA. Computer-assisted algebraic methods were used to solve for the three protonation constants involved in the three low-pH overlapping dissociation equilibria of EDDAG-DA describing the potentiometric titration curve between *a* = 0 and *a* = 3. The buffer region between *a* = 3 and *a* = 4 involves the dissociation of only one proton and the corresponding equilib-

Table III. Equilibrium Constants for the Interaction of EDDAG-DA with Metal Ions

Symbol	Equilibrium quotient	Log K					
		Cu ²⁺	Ni ²⁺	Co ²⁺	VO ²⁺	Fe ³⁺	Th ⁴⁺
K_1	$\frac{[ML^{(n-4)+}]}{[M^{n+}][L^{4-}]}$	11.23	10.68	10.47	12.46		12.0 ^a
K_{MHL^H}	$\frac{[MHL^{(n-3)+}]}{[ML^{(n-4)+}][H^+]}$	3.88	3.86	3.83	3.64		
$K_{MH_2L^H}$	$\frac{[MH_2L^{(n-2)+}]}{[MHL^{(n-3)+}][H^+]}$	2.94	2.94	2.97	2.70		
K_{A_2}	$\frac{[ML^{(n-4)+}]}{[MH_{-1}L^{(n-5)+}][H^+]}$	6.89				2.95	
K_{A_1}	$\frac{[MH_{-1}L^{(n-5)+}]}{[MH_{-2}L^{(n-6)+}][H^+]}$					3.57	

^a For the calculation of this constant, two hydrolysis constants of Th(IV) were employed [K. A. Kraus and R. W. Holmberg, *J. Phys. Chem.*, **58**, 325 (1954)]: $-\log K (Th^{4+} \rightleftharpoons ThOH^{3+} + H^+) = 4.3$ and $-\log K (ThOH^{3+} \rightleftharpoons Th(OH)_2^{2+} + H^+) = 3.4$.

rium constant was calculated directly. The successive protonation constants K_n^H of the tetranegative ion of EDDAG-DA are $10^{7.37}$, $10^{4.38}$, $10^{3.51}$, and $10^{2.87}$, where $K_n^H = [H_nL^{(n-4)+}]/([H^+][H_{n-1}L^{(n-5)+}])$. The corresponding potentiometric titration curve is shown as the unlabeled curve in Figure 3.

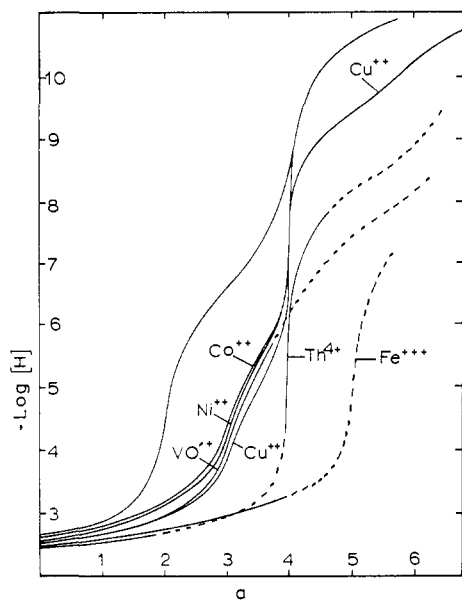
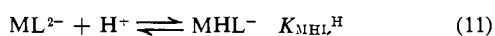
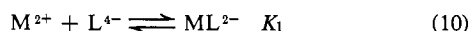


Figure 3. Potentiometric equilibrium curves for 1:1 molar ratios of metal ions to EDDAG-DA; unlabeled curve represents the titration of pure ligand; broken lines represent precipitation; a = moles of 0.10 M base added per mole of ligand; concentration is 0.0010 M in ligand and metal ion; solution contains 0.10 M KNO_3 ; $t = 25^\circ$.

Low-pH EDDAG-DA Complexes. The potentiometric titration curves of the EDDAG-DA complexes of VO(IV), Co(II), Ni(II), Cu(II), and Th(IV) ions are very similar, as is indicated in Figure 3. All have an inflection at $a = 4$, indicating complete formation of the normal complex $ML^{(n-4)+}$. For the EDDAG-DA systems containing dipositive metal ions, the complex equilibria in the region between $a = 0$ and $a = 4$ were explained in terms of eq 10–12. For the calculation of



the three equilibrium constants defined in (10)–(12), K_1 was expressed as a function of K_{MHL^H} and $K_{MH_2L^H}$ (eq 13) by utilizing charge and mass balance equations as well as expressions for the ligand protonation constants.

$$K_1 = f(K_{MHL^H}, K_{MH_2L^H}) \quad (13)$$

The constants K_{MHL^H} and $K_{MH_2L^H}$ were then iterated systematically until the calculated K_1 assumed the same value at each titration point with the criterion of convergence being the minimum of the sum of the squares of the deviation from the mean. These stability constants are listed in Table III.

Fe(III)-Amide Complexes. The potentiometric equilibrium of the 1:1 Fe(III)-EDDAG-DA system, shown in Figure 3, is strikingly different from those of the other metal complexes. The initial part of the curve shows a flat buffer region terminating at $a = 6$, and demonstrates the direct displacement of two amide protons as well as of the four normally dissociable (acidic) protons in a single step. The potentiometric data were found to be completely described by appropriate equilibrium constants corresponding to eq 5 and 6, with the assumption that the four acidic hydrogen ions are completely displaced at the beginning of the titration ($a = 0$). The equilibrium constants for the two successive amide proton association reactions for the completely deprotonated chelate, $FeH_{-2}L^{3-}$, are $10^{3.57}$ and $10^{2.95}$ at $25 \pm 0.05^\circ$ in 0.10 M KNO_3 solution.

The infrared absorption bands found for the 1:1 Fe(III)-EDDAG-DA system in D_2O are presented in Table IV.

Cu(II)-Amide Complexes. From Figure 3, it is evident that in the 1:1 Cu(II)-EDDAG-DA system only one amide proton is displaced from the ligand by the Cu(II) ion. The equilibrium involved is described by eq 5 and the corresponding equilibrium constant for the combination of one proton with the species $CuH_{-1}L^{3-}$ is $10^{6.89}$. The ir absorption spectra obtained for the 1:1 Cu(II)-EDDAG-DA system in D_2O are summarized in Table IV.

Other Metal Ions. It is possible that VO^{2+} and Th^{4+} also release at least one amidic proton from this ligand, since the potentiometric titration curves of the 1:1 VO^{2+} -EDDAG-DA and of the 1:1 Th^{4+} -EDDAG-DA systems in Figure 3 seem to parallel the curve of the corresponding 1:1 Cu^{2+} -EDDAG-DA system. It is, however, difficult to arrive at definite conclusions on

Table IV. Infrared Spectra of EDDAG-DA and Its Copper(II) and Iron(III) Chelates in D₂O Solution

Molecular species	Ir frequency, cm ⁻¹	Assignment
L ⁴⁻	1588	-COO ⁻
	1635	-CONH-
CuL ²⁻	1604	-COO ⁻ ...Cu ²⁺ O...Cu ²⁺
	1620	-CNH-
	1651	Cu ²⁺ ...NCH ₂ CONH- Cu ²⁺
CuH ₋₁ L ³⁻	1575	-N-CH ₂ COO ⁻
	1593	-COO ⁻
	1630 (broad)	-CON ⁻ ...Cu ²⁺ -CONH- Fe ³⁺
FeH ₋₂ L ³⁻	1582	-N-CH ₂ COO ⁻
	1620	-CON ⁻ ...Fe ³⁺

this point, since the hydrolysis of these metal ions sets in with formation of some insoluble material before the amide dissociation step is completed.

Discussion

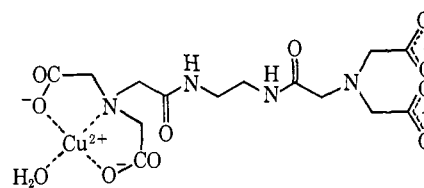
DGENTA. The values of the four proton association constants listed in Table I (footnote *b*) are consistent with the structure of this ligand. If the DGENTA molecule were considered to consist of two iminodiacetic (IDA) molecules joined by an inert eight-atom bridge, one would expect two rather acidic protons and two that are much less acidic. For iminodiacetic acid¹⁰ $\log K_1^H = 9.33$ and $\log K_2^H = 2.58$. The fact that the most basic group has a proton affinity 10² less than that of IDA (whereas the statistical factor would make it a factor of 2 greater) shows that the intrinsic basicity of the tertiary amino nitrogens of the DGENTA is much lower than that of IDA. This effect must be due to the electron-withdrawing influence of the amide carbonyl groups one carbon atom away.

If the basicities of the carboxylate groups of DGENTA and IDA were the same, the third proton association of the former would have a constant 10^{0.3} higher than the second proton association of the latter. The difference is only 10^{0.08}, showing that the basicity difference caused by the electron-withdrawing groups in DGENTA is transmitted in greatly diminished magnitude to the more remote carboxylate groups.

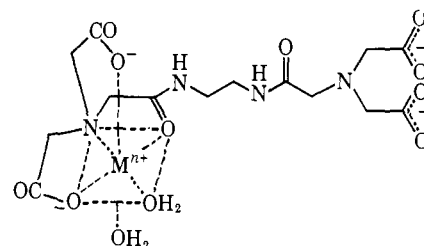
DGENTA Complexes at Low pH. The similarity of the 1:1 titration curves shown in Figure 1 for divalent ions indicates that Cu(II), Ni(II), Co(II), and VO(IV) behave similarly in 1:1 M-DGENTA systems. In each case the initial complex formed from $a = 0$ to $a = 3$ is most reasonably concluded to be a substituted IDA-type chelate. The formation constants¹¹ $\log K_1 (M^{n+} + L^{2-} \rightleftharpoons ML^{(n-2)+})$ for Cu(II), Ni(II), and Co(II)-IDA complexes are 10.63, 8.19, and 6.97. However, in the present study the formation constants for the corresponding 1:1 DGENTA chelates are 10.16, 9.52, and

8.54. The values for Ni(II) and Co(II) are seen to be about 1.5 log units higher for the DGENTA chelates as compared to IDA. The Cu(II) stability constants, on the other hand, are quite similar.

The explanation now advanced for these similarities and differences in metal chelate stabilities is based on the reasonable arrangement of the coordinate bonds in the chelates of predominantly four-coordinate Cu(II) and six-coordinate Ni(II) and Co(II), as indicated by III and IV.



III, Cu(II)-DGENTA chelate, CuL²⁻



IV, Ni(II)- and Co(II)-DGENTA chelates, ML²⁻

From III and IV it is seen that the neighboring amide group does not participate directly in the essentially planar bonding of the Cu(II), while the amide carbonyl oxygen is directly coordinated to the octahedral Co(II) and Ni(II). The increased stability of the latter chelates over those of IDA is thus due to the participation of an additional coordinating group of the ligand.

It is of interest to compare the DGENTA and IDA chelate stabilities in somewhat greater detail on the basis of formulas III and IV. If the intrinsic Cu(II) affinities of the two ligands were the same, the $\log K_1$ value of the DGENTA chelate would be 0.3 higher because of the statistical factor favoring its formation. Actually it is 0.47 log unit lower, giving a difference of about 0.77 log unit (lower for DGENTA), attributable to the lower basicity of DGENTA (L⁴⁻) compared to IDA (L²⁻).

Using this reasoning, one would predict constants for the terdentate Ni(II) and Co(II) chelates of DGENTA to be approximately 7.9 and 6.8 log units, rather than the observed values, 9.5 and 8.5. On this basis the increment of stability due to amide carbonyl oxygen coordination would be about 1.6 log *K* units, or about 2 kcal/mol.

Further evidence in favor of the coordinate bonding indicated in formulas III and IV is the formation of protonated chelates, MHL⁻, the acid dissociation constants of which are not strongly influenced by the coordinated metal ion. In the structures shown, it is obvious that the proton becomes attached to the basic nitrogen atom eight or nine atoms removed from the metal ion.

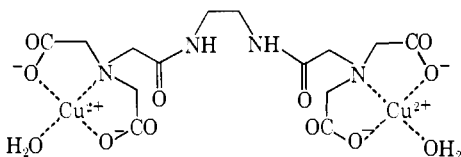
The data obtained for the DGENTA chelates of Th(IV) and Fe(III) are not of sufficient quality to deduce reliable information on the nature of the bonding involved, since precipitation occurs in the systems even at low pH. The stoichiometry of these precipitates has

(10) M. M. Taqui Khan and A. E. Martell, *J. Amer. Chem. Soc.*, **89**, 7104 (1967).

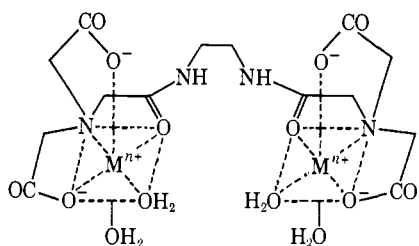
(11) G. Anderegg, *Helv. Chim. Acta*, **47**, 1801 (1964).

not been determined except that the final precipitate was shown to be free of ligand. The acidity of the solution and the absence of a separate buffer region between $a = 3$ and $a = 4$ seems to indicate that all donor groups in the ligand, including the terminal acetate groups, participate in coordinate bonding of Fe(III) and Th(IV).

The relative positions of the 2:1 M-DGENTA curves between $a = 0$ and $a = 4$ of Figure 2 show that the decreasing order of stability of the 2:1 chelates follows the usual order of Cu(II) > Ni(II) > Co(II). The respective stability constants K_{M_2L} are $10^{8.29}$, $10^{6.46}$, and $10^{5.77}$. When these are compared with values of K_1 (from 1:1 M-DGENTA studies these constants are $10^{10.16}$, $10^{9.52}$, and $10^{8.54}$), it becomes apparent that the differences are respectively $10^{1.87}$, $10^{3.07}$, and $10^{2.77}$. The fact that the values of K_1 and K_{M_2L} for Cu(II) are closer together than for Ni(II) and Co(II) helps to reinforce the existence of the postulated structures III and IV for the 1:1 chelates. There is less attenuation of the metalphilicity of the uncoordinated end of the DGENTA-M chelate molecule in a structure such as III than is present in one such as IV where the shorter distance between the coordinated end and the uncoordinated IDA moiety produces greater interaction. Thus reasonable structures in accord with the stabilities and equilibrium data for the 2:1 M-DGENTA chelates are represented by V and VI.



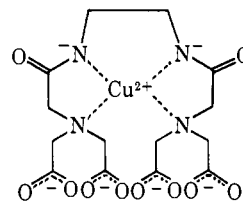
V, Cu(II)-DGENTA chelate, Cu_2L



VI, Ni(II)- and Co(II)-DGENTA chelates, M_2L

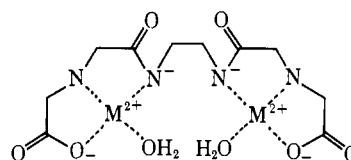
Metal Chelates of DGENTA at High pH. As seen from Figure 1 for the 1:1 M-DGENTA system in the high-pH region (above $a = 4$) only the Cu(II)-DGENTA chelate is of interest. The 1:1 chelates of VO^{2+} , Th^{4+} , and Fe^{3+} hydrolyze or precipitate and Co^{2+} and Ni^{2+} do not undergo further reaction. Copper(II) displaces two amide protons per mole of DGENTA, in a simple two-step acid dissociation reaction. It is not possible to compare the behavior of Cu-DGENTA with Cu-DGEN³ since in the latter case the reactions involving amide proton displacement are quite unusual in that dimerization occurs during the release of the first proton followed by depolymerization when the second proton is displaced. However, a comparison of equilibrium constants involving the amide proton may be made with triglycine which contains two peptide linkages. For Cu(II)-triglycine⁵ $\log K_{A_1} = 6.72$ and $\log K_{A_2} = 5.20$. From Table I, the amide proton constants for Cu-DGENTA are $\log K_{A_1} = 9.61$ and $\log K_{A_2} = 9.05$, or from 3 to 4 log units higher. The fact

that it is easier for the Cu(II) ion to displace amide protons from triglycine than from DGENTA is reasonable in view of the presence of the iminodiacetate groups, that compete with the amide groups for coordination of the metal ion. On the basis of reaction stoichiometry, interpretation of infrared spectra shown in Table III, and examination of models, a planar structure, VII, is proposed for the Cu-DGENTA chelate, $CuH_{-2}L^{4-}$.

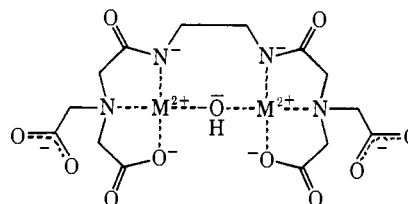


VII, Cu(II)-DGENTA chelate, $CuH_{-2}L^{4-}$, at high pH

Figure 2 reveals that the 2:1 DGENTA chelates of both Cu(II) and Co(II) are capable of reacting with base (from $a = 4$ to $a = 6$) to release amidic protons. With copper this result is not surprising, but with Co(II) it is to the best of our knowledge unprecedented. It is to be noted from Table I that the release of amidic protons is facilitated by about 2 log units in going from Cu(II)-DGENTA to $2Cu(II)$ -DGENTA (M_2L to M_2L). This 100-fold labilization in having an extra dipositively charged ion present in the ligand may indeed be the type of additional driving force that is necessary to accomplish the displacement of amidic protons in the 2:1 Co(II) case. The solution turns a beautiful deep violet color ($a = 4$ to $a = 6$), which is stable under nitrogen. Thus the oxidation state of cobalt must be 2 since exposure to oxygen rapidly oxidizes one or both of the Co(II) ions as attested by the disappearance of color and subsequent precipitate formation. Between $a = 6$ and $a = 7$, one more proton is titrated, with no subsequent changes upon further addition of base. The following structures (VIII and IX) are consistent with the above observations for the Cu(II) and Co(II) 2:1 M-DGENTA chelates.



VIII, Cu(II)- and Co(II)-DGENTA chelate, $M_2H_{-2}L^{2-}$, at high pH



IX, binuclear Cu(II)- and Co(II)-DGENTA chelates, $M_2H_{-2}L(OH)^{3-}$, at high pH

EDDAG-DA. The protonation constants of EDDAG-DA (II) can be best understood in terms of the component parts of this ligand. The ligand molecule possesses both an EDDA (ethylenediamine diacetate) group and what appears to be two N-substituted N-protonated glycyglycines. The protonation con-

stants of EDDA¹² are $\log K_1^H = 9.46$, $\log K_2^H = 6.42$ and those of glycylglycine¹³ are $\log K_1^H = 8.10$ and $\log K_2^H = 3.15$. Thus the four protonation constants of EDDAG-DA ($\log K = 7.37, 4.38, 3.51, 2.87$) can be thought of as arising from an EDDA molecule, with considerable lowering of proton affinities of the amino groups by the adjacent electron-withdrawing amide carbonyl groups. The carboxylate groups can be seen to have proton affinities similar to that of glycylglycine, adjusted for the statistical factor involving the number of donor groups present. A more detailed rationalization of proton association constants similar to that given above for DGENTA is also possible.

Metal Chelates of EDDAG-DA. EDDAG-DA (II) possesses two widely separated amidic groups and a centrally located strongly coordinating EDDA moiety. With this arrangement of donor groups available, one would expect that the EDDA structure would strongly coordinate the approximately square-planar four-coordinate Cu(II) ion at relatively low pH. Further, the lowered basicity of the amino groups would tend to favor an EDDA-type structure in acid solution to a much greater extent than would take place with EDDA itself. Thus the chelate first formed as the pH of a 1:1 solution of Cu(II) and EDDAG-DA is gradually increased is represented by X.

In terms of equilibrium constants, the proton affinities of both basic nitrogen atoms of EDDAG-DA are a factor of 10^2 less than those of EDDA. This lowering of intrinsic basicity of the tertiary amino nitrogens parallels the case seen in DGENTA, and similarly must be due to the electron-withdrawing influence of the amide carbonyl groups one carbon atom away.

The considerable lowering of the values of $\log K$ with the preservation of the Irving-Williams order, when comparing EDDAG-DA with EDDA (Table V) can be

Table V. Chelate Stability Constants

M	Log K_1	
	EDDAG-DA	EDDA ^a
Cu ²⁺	11.23	16.2
Ni ²⁺	10.68	13.5
Co ²⁺	10.47	11.2
VO ²⁺	12.46	

^a Reference 11; EDDA = N,N'-ethylenediaminediacetic acid.

rationalized by the following analysis. There is a basic reduction of coordination potential upon going from EDDA to EDDAG-DA caused by lowering of the basicity of the tertiary nitrogen atoms as pointed out above. Because of its preference for four-coordination (in a planar conformation), the comparison of the two ligands for Cu(II) can be restricted to the two amino nitrogens and two carboxylate groups. Thus the lowering of stability constant by 10^5 is fully ascribed to the electronic effect of the amidic carbonyls separated from each nitrogen atom by one carbon atom. To a first approximation the Ni(II) and Co(II) 1:1 chelate formation constants should also then be lowered by 10^5 ; however, a second consideration enters here. Since nickel(II) and cobalt(II) possess coordination numbers

(12) S. Chaberek and A. E. Martell, *J. Amer. Chem. Soc.*, **74**, 6228 (1952).

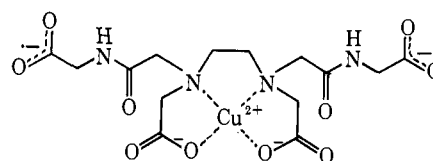
(13) L. C. Thompson, *J. Inorg. Nucl. Chem.*, **24**, 1083 (1962);

of six, there is some gain in stability by coordination of the flanking amido carbonyl oxygens to form two additional chelate rings. A simple calculation (assuming that the influence of the carbonyl groups is proportional to the magnitudes of the interactions with EDDA) shows that this gain amounts to about $10.7 - (13.5 - 4.0) = 1.2$ log units for Ni²⁺ and about $10.5 - (11.2 - 3.5) = 2.8$ log units for Co²⁺.

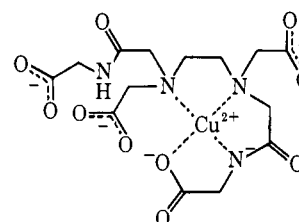
The displacement of an amide proton at higher pH results in the formation of a chelate compound with the arrangement of coordinate bonds similar to that indicated in XI. The fact that only one negative amide nitrogen bond is formed may be rationalized to some extent on the basis of the coulombic repulsion that would result from two such coordinated negative groups in adjacent (*cis*) positions, and the steric and coulombic repulsions of the acetate groups substituted on the amide nitrogen. The arrangement of groups in this hypothetical high-energy complex is indicated by XII.

The bonding in X and XI, the low-pH and high-pH forms of the 1:1 Cu(II)-EDDAG-DA chelate, are consistent with the infrared spectra of D₂O solutions of these complexes, summarized in Table IV.

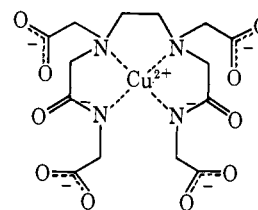
From the potentiometric data in Figure 3 it can be definitely concluded that the interaction of the Fe(III)



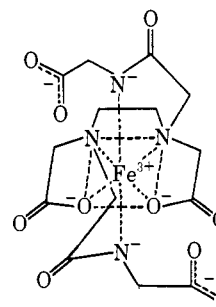
X, low pH Cu(II)-EDDAG-DA chelate, CuL²⁻



XI, high pH Cu(II)-EDDAG-DA chelate, CuH₁L³⁻



XII, hypothetical high pH Cu(II)-EDDAG-DA chelate, CuH₂L⁴⁻



XIII, a possible arrangement of coordinate bonds in the high-pH Fe(III)-EDDAG-DA chelate, FeH₂L³⁻

ion with EDDGA-DA results in the formation of a very stable chelate, $\text{FeH}_{-2}\text{L}^{3-}$, in which two amide protons have been displaced by the metal ion. This conclusion is further supported by calculation of two successive dissociation constants of the normal chelate, FeL^- , from the potentiometric data, showing that the chelate with one negative amide donor group also exists in solution as an intermediate. The structure suggested for the chelate compound $\text{FeH}_{-2}\text{L}^{3-}$ is indicated by XIII. It is suggested that the negative amide nitrogen donors are arranged in a *trans* position to minimize steric and coulombic repulsions.

The chelate compound represented by XIII is unique in that it is the first stable amide complex in which the

Fe(III) ion displaces amide protons. Thus it is seen that suitably designed ligands may be useful in demonstrating previously unknown properties of ligand donor groups. This may be especially true of heavy metal ions and highly charged metal ions that hydrolyze readily at relatively low pH. The presence in the ligand of auxiliary donor groups may serve to stabilize the metal chelate in the low to moderate pH range, until the pH becomes high enough to assist the metal ion in displacing protons from the donor group being studied. Examples of strongly coordinating donor groups that may be studied in this way are peptide, hydrazide, and hydroxamide groups, as well as simple amides, imide linkages, and hydroxyalkyl groups.

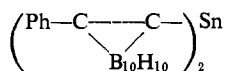
Antimony-121 Mössbauer Spectra of Some Organoantimony Compounds^{1,2}

G. G. Long,³ J. G. Stevens,⁴ R. J. Tullbane, and L. H. Bowen

Contribution from the Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27607, and the Physics Division, Argonne National Laboratory, Argonne, Illinois 60439. Received February 2, 1970

Abstract: The Mössbauer resonance of ^{121}Sb has been studied in a series of 21 organoantimony compounds at $\sim 80^\circ\text{K}$ and 12 of these at 4.2°K . Isomer shift and quadrupole splitting variations within the Ph_4SbX and Ph_3SbX_2 series (where X is a negative group such as F, Cl, ClO_4 , etc.) are generally consistent with the electronegativity variation of the X groups. Spectra are much more readily and more precisely determined at the lower temperature owing to the marked increase in the per cent effect. Infrared and electrical conductivity data are presented to support the conclusion from the Mössbauer studies that the Sb-X bonds of most of the Ph_4SbX compounds have considerable covalent character in the solid state. Of the compounds studied, $\text{Ph}_4\text{SbClO}_4$ is the only compound found to contain a Ph_4Sb^+ cation in the solid state. Differences in the Mössbauer parameters for the various series studied are discussed in terms of likely bond hybridizations and structures of the compounds.

In recent years a large amount of work has been reported on ^{119}Sn Mössbauer spectra of organotin compounds which has been of value in the study of structure, reactivity, and mechanism of transformation of these compounds.⁵ Although a large variety of organotin compounds is known, including compounds in two different oxidation states, the range of isomer shifts (IS) is very narrow and falls between -0.2 and -1.0 mm/sec with respect to gray tin for the vast majority of these compounds; the extremities of the range are -1.22 mm/sec for $[(p\text{-ClC}_6\text{H}_4)_2\text{SnO}]_n$ and $+0.85$ mm/sec for the divalent molecule⁶



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(2) Presented in part at the 4th IUPAC Conference on Organometallic Chemistry, Bristol, July 27–Aug 1, 1969.

(3) To whom correspondence may be addressed at North Carolina State University.

(4) Summer Research Participant at Argonne National Laboratory.

(5) V. I. Goldanskii, V. V. Khrapov, O. Yu. Okhlobystin, and V. Ya. Rochev in "Chemical Applications of Mössbauer Spectroscopy," V. I. Goldanskii and R. H. Herber, Ed., Academic Press, New York, N. Y., 1968, p 338.

(6) See ref 5, pp 336–376.

^{121}Sb isomer shifts are spread over a much greater range⁷ than ^{119}Sn isomer shifts,⁸ and thus the opportunity may exist to readily observe differences in the Mössbauer spectra of organoantimony compounds owing to relatively subtle changes in geometric environment, bonding, and substituents. The success of such experiments is not guaranteed, however, because the natural line width⁷ of ^{121}Sb is considerably larger than that for ^{119}Sn , the quadrupole splitting of ^{121}Sb is more complex than that for ^{119}Sn , and the per cent effect in organoantimony compounds at liquid nitrogen temperature was found to be rather low (2–6%) in the only ^{121}Sb Mössbauer study of these compounds to date.⁹

We have determined the ^{121}Sb Mössbauer spectra for a number of organoantimony compounds in the initiation of a systematic study of the spectra of these substances. The natural line width and the complexity of the quadrupole splitting pattern cannot be avoided, but a decrease in temperature markedly increases the per cent effect, and thus results are reported for some of the

(7) S. L. Ruby in "Mössbauer Effect Methodology," Vol. 3, I. J. Gruverman, Ed., Plenum Press, New York, N. Y., 1967, pp 203–215.

(8) M. C. Hayes in ref 5, pp 314–335.

(9) S. E. Gukasyan and V. S. Shpinel, *Phys. Status Solidi*, **29**, 49 (1968).