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Combination of Dioxygen with *N*,*N*-Bis(2-aminoethyl)glycinatocobalt(II) and with Diethylenetriamine-*N*-acetatocobalt(II)[1]

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The two isomers *N*,*N*-bis(2-aminoethyl)glycine (SDTMA) and diethylenetriamine-*N*-acetic acid (UDTMA) were synthesized and isolated as crystalline hydrobromide salts. They were found to react with Co(II) in the absence of dioxygen to give a chelate CoL^+ which when exposed to molecular oxygen forms a stable dimeric oxygen adduct of the formula $CoLO_2OHCoL^+$. These complexes did not further react with oxygen nor rearrange to give an inert cobalt(III) product. Purging a low pH solution of the complex with nitrogen resulted in complete reversal of complex formation giving CoL^+ and O_2. The complex is also reversible to acid. Stability constants of the complexes formed by Cu(II), Ni(II), Co(II), and Zn(II) with SDTMA and UDTMA were determined potentiometrically. Equilibrium constants for protonated complex formation (MHL^{2+}) were determined. Kinetics of the formation and decomposition of the oxygen adducts were studied, and the rate constants were determined. The equilibrium constants $K_{O_2} = [Co_2L_2O_2OH^+][H^+]/[Co^{2+}]^2[L^-]^2P_{O_2}$ determined under air and oxygen were found to be $10^{23.72}$ M^{-2} atm^{-1} for SDTMA and $10^{23.54}$ M^{-2} atm^{-1} for UDTMA. Structures for the oxygenated complex and other metal chelate complexes are considered, and comparisons are made with previously studied systems.

Introduction

A number of cobalt(II)–μ-dioxygen complexes[2–9] have been characterized and have been found to differ markedly in their oxygenation properties. The data on solution stoichiometry of these oxygen complexes and other evidence indicate that 1 mol of dioxygen bridges two cobalt atoms as a μ-peroxo bridge and in addition a μ-hydroxo bridge forms where a vacant coordination site is available on each cobalt atom of the binuclear pair. The oxygen complexes of ethylenediamine,[3,7] diethylenetriamine,[3,7] and triethylenetetramine[3–5,8] (all designated as L) have μ-hydroxo bridges and may be represented by the formulas $CoL_2O_2(OH)CoL_2^{3+}$ for the first and $CoLO_2(OH)CoL^{3+}$ for the latter two. The μ-hydroxo bridge is absent when the polyamine ligand is tetraethylenepentamine, and the complex $CoLO_2CoL$ is formed. All of the above polyamine–cobalt(II) dioxygen complexes undergo irreversible conversions to cobalt(III) complexes.

Of the above μ-dioxygen complexes, the most readily reversible one is that of diethylenetriamine.[7] On the other hand the oxygen complex of diethylenetriamine rapidly and irreversibly decomposes to the corresponding cobalt(III) complex. Although previous work had already addressed itself to many questions, there remained several fundamental problems unsolved in the area of cobalt μ-dioxygen carriers: (1) the specific ligand features which determine the stability of the cobalt–dioxygen system, (2) the factors governing reversibility and irreversibility, (3) the modifications in the ligand structure which are required to either retard or stop the irreversible reaction, (4) the number and combination of donor groups which are optimum for oxygen-carrier formation and reversibility, (5) the stereochemistry of the ligand and of its binding to the metal ion.

In the interest of providing at least a partial answer to these interrelated questions, this paper describes new multidentate ligands whose Co(II) chelates react reversibly with oxygen in aqueous solution. *N*,*N*-Bis(2-aminoethyl)glycine (SDTMA) and diethylenetriamine-*N*-acetic acid (UDTMA) have the diethylenetriamine backbone and an auxiliary acetate donor, and their cobalt(II) complexes do not undergo at a measurable rate any side reaction to cobalt(III) complexes. Because of the high affinity of the cobalt(II) complex of these ligands for oxygen, and the unusual property of complete reversibility without side reactions, these cobalt(II)–SDTMA and –UDTMA systems provide an ideal subject for definitive (mechanistic) studies.

Experimental Section

Synthesis. Preparation of SDTMA·3HBr·2H$_2$O. The procedure of Collman[10] was followed for the preparation of SDTMA from diethylenetriamine, phthalic anhydride, and ethyl bromoacetate. Although Schneider and Collman[10] worked with the hydrolysate solutions without isolating the SDTMA, it was found that the diethylenetriamine monoacetic acid could be isolated as the crystalline trihydrobromide monohydrate. It was characterized by NMR, ir, and elemental analysis.

Anal. Calcd for $C_6H_{20}N_3O_3Br_3$: C, 17.08; H, 4.29; N, 9.96; Br, 56.80. Found: C, 17.28; H, 4.38; N, 9.97; Br, 56.57.

Preparation of UDTMA·3HBr·H$_2$O. A solution of bromomalonic acid (36.5 g, 0.2 mol) in 50 ml of water was neutralized with 10% NaOH solution and mixed with diethylenetriamine (20.6 g, 0.20 mol). The reaction mixture was maintained at 60° and pH 10 for 2.5 hr. Upon acidification with concentrated hydrochloric acid a colorless precipitate was obtained, which was centrifuged and washed. The wet intermediate was boiled in concentrated hydrobromic acid until carbon dioxide evolution ceased. On concentrating and cooling the solution, lustrous colorless crystals were obtained; yield 60 g (70%).

Anal. Calcd for $C_6H_{20}Br_3N_3O_3$: C, 17.08; H, 4.29; N, 9.96; Br, 56.80. Found: C, 17.21; H, 4.29; N, 9.85; Br, 57.09.

Reagents. Standard base was prepared from "Dilute It" KOH concentrate by dilution under CO_2-free conditions, and the 0.10 *M* solution was standardized against potassium acid phthalate. Stock solutions of zinc(II) nitrate, cobalt(II) nitrate, copper(II) nitrate, and nickel(II) nitrate were standardized with EDTA by methods outlined by Schwarzenbach.[11] Dioxygen and dinitrogen gases were of the prepurified variety. Anaerobic titrations were achieved by scrubbing dinitrogen with basic pyrogallol solutions. Air was scrubbed free of carbon dioxide with solutions of strong alkali.

Instrumentation. A Beckman Research Model pH meter was fitted with blue-glass and calomel electrodes and standardized through potentiometric titration of a standard acid solution with KOH under experimental conditions (25 ± 0.05° and ionic strength of 0.10 maintained with a supporting electrolyte, KNO_3). The pH meter was calibrated to read hydrogen ion concentration directly. Electronic spectra were recorded with a Cary Model 14 spectrophotometer with matching 1.00 cm and 1.00 mm quartz cells. Kinetic measurements were performed at 25° with a Durrum Model D-150 Temperature Jump-Stopped Flow System.

Procedure. All solution work was performed at a ligand and/or metal ion concentration of about 0.0020 *M*. The ligand was titrated with standard KOH and the protonation constants were calculated. The anaerobic formation curves for systems having a 1:1 ratio of metal ion to ligand were next determined and the appropriate stability constants were computed. The metal–ligand curves were then remeasured under CO_2-free air and under pure dioxygen. After confirmation of the reaction stoichiometry from the potentiometric data, evaluation of the formation constant corresponding to the species $MLO_2(OH)ML^+$ was finally made.

For the UDTMA system only, titrations were performed by bringing a solution of the ligand, or ligand and metal, to a high pH by addition of a known aliquot of base, then back titrating with acid. Such a procedure was found necessary to completely avoid an undesirable partial lactamization of the ligand which occurs at low pH.

The cobalt(II)–dioxygen complexes were allowed to stand in solution at pH 10.5 for several weeks. No diminution of the absorption intensity was observed. Upon acidification, the brown color of the dioxygen

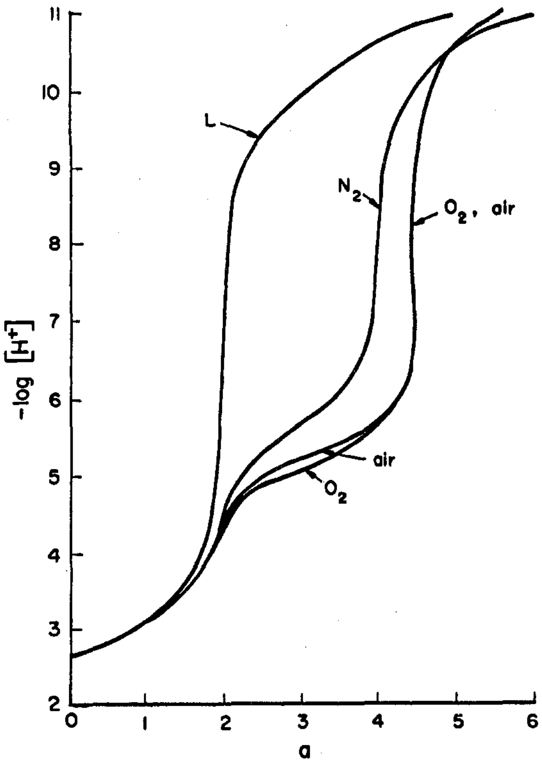


Figure 1. Potentiometric equilibrium curves for SDTMA (L) and a 1:1 molar ratio of SDTMA to Co(II) under nitrogen (N_2), oxygen (O_2), and air atmospheres (air) at 25°; ionic strength 0.10 (KNO_3); *a* = moles of base/mole of ligand.

complex faded to the pink color of Co(II) and gaseous dioxygen was evolved. Raising the pH and bubbling dioxygen through the solution resulted in re-formation of the complex with identical uv spectrum with respect to wavelength and intensity.

The cobalt(II)–dioxygen complexes were also discharged by passing dinitrogen through the solution in the pH range 2.0–4.5, with a concomitant rise in pH. The process was then reversed by bubbling dioxygen through the solution at the higher pH, whereupon a concomitant drop in pH to the previous equilibrium value occurred. This cyclic process was repeated several times without any changes in the pH values and absorption intensities.

At a lower pH of about 4.5, at which the decomposition reaction might be expected to be more rapid, there was still no observable decrease in intensity in either case over a month long period.

Results

Metal Ion–Ligand–Dioxygen Interactions. Figures 1 and 2 are graphical illustrations of the formation equilibria of the DTMA–cobalt(II)–dioxygen systems as a function of pH. In Figures 1 and 2, the top curve (ligand alone) shows a low pH two-proton buffer region, followed by a basic two-proton buffer region. When cobalt(II) is added in a 1:1 molar ratio, proton-releasing complex formation is seen to occur under nitrogen, commencing at about pH 3.5, with an ultimate release of four protons from each complex molecule formed. The curves labeled air and dioxygen represent 0.21 and 1.00 atm of dioxygen. With 1.00 atm of dioxygen, the formation of the dioxygen complex is more complete than is the case at 0.21 atm, at a given value of *a* (moles of base per mole of ligand present). The stoichiometry indicated by the sharp vertical rise of the potentiometric equilibrium curve at *a* = 4.5 showed that a binuclear hydroxo-bridged dioxygen complex had formed.

Metal–Ligand Interactions in the Absence of Dioxygen. In Figures 3 and 4 potentiometric equilibrium curves are illustrated for 1:1 molar ratios of ligand to Cu(II), Zn(II), and Ni(II). The shapes of the curves are oxygen insensitive and therefore these metal ions probably do not complex oxygen. The relative positions of the potentiometric equilibrium curves indicate that the ligand–metal interaction is strongest for copper(II), intermediate for Ni(II), and weakest for Zn(II). Beyond *a* = 4, the potentiometric data indicate that the copper(II)- and zinc(II)–SDTMA and -UDTMA chelates form hydroxo species, whereas the nickel(II)–SDTMA and nickel(II)–UDTMA complexes do not.

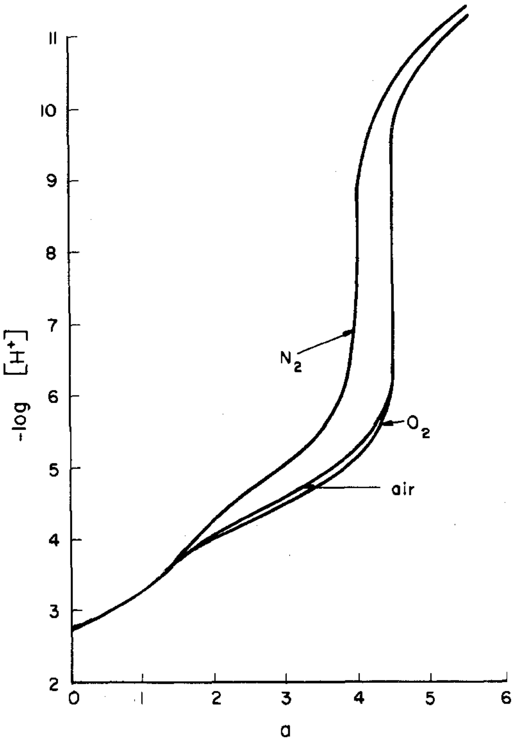


Figure 2. Potentiometric equilibrium curves for a 1:1 molar ratio of UDTMA to Co(II) under nitrogen (N_2), oxygen (O_2), and air atmospheres (air) at 25°; ionic strength 0.10 (KNO_3); *a* = moles of base/mole of ligand.

Table I. Metal-SDTMA Stability Constants[a]

	Cu^{2+}	Ni^{2+}	Zn^{2+}	Co^{2+}
$\log K_{ML}$	18.07 (1)	14.37 (1)	13.13 (1)	12.11 (2)
$\log K_{MHL}$	2.90 (5)	4.65 (5)	4.20 (5)	5.20 (5)
$\log K_{MOHL}$	9.22 (2)		9.89 (1)	10.24 (2)
$\log K_{O_2}'$				2.39 ± 0.02
$\log K_{O_2}$				23.71 ± 0.04

[a] $\mu = 0.100$ (KNO_3); $t = 25°$.

Table II. Metal-UDTMA Stability Constants[a]

	Cu^{2+}	Ni^{2+}	Zn^{2+}	Co^{2+}
$\log K_{ML}$	17.29	14.40	12.94	12.04
$\log K_{MHL}$	3.82	4.00	4.40	5.90
$\log K_{MOHL}$	9.32		9.70	10.40
$\log K_{O_2}'$				2.35 ± 0.02
$\log K_{O_2}$				23.54 ± 0.04

[a] $\mu = 0.100$ (KNO_3); t = 25°.

Equilibrium Constants. The SDTMA ligand proton association constants calculated from the potentiometric data in Figure 1 are (log values) 10.81 ± 0.01, 9.59 ± 0.01, 3.24 ± 0.05, and 1.7 ± 0.1 ($\mu = 0.100$ *M* (KNO_3), at 25°).

In Tables I and II are listed the metal–ligand stability constants calculated from the data measured for the following equilibria:

$$L^- + M^{2+} \rightleftharpoons ML^+ \qquad K_{ML} \tag{1}$$

$$ML^+ + H^+ \rightleftharpoons MHL^{2+} \qquad K_{MHL} \tag{2}$$

$$MLOH + H^+ \rightleftharpoons ML^+ \qquad K_{MOHL} \tag{3}$$

$$2ML^+ + O_2 + H_2O \rightleftharpoons M_2L_2O_2OH + H^+ \tag{4}$$

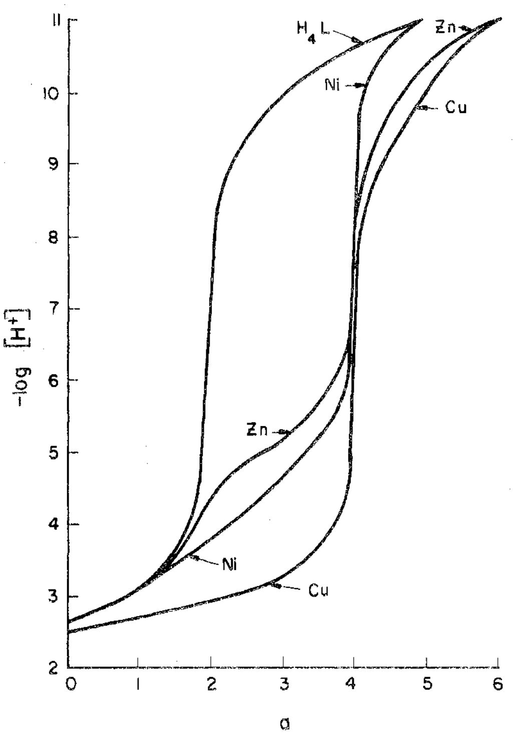


Figure 3. Potentiometric equilibrium curves for SDTMA (L) and a 1:1 molar ratio of SDTMA to zinc(II) (Zn), nickel(II) (Ni), and copper(II) (Cu); ionic strength 0.10 (KNO_3); at 25°; a = moles of base/mole of ligand.

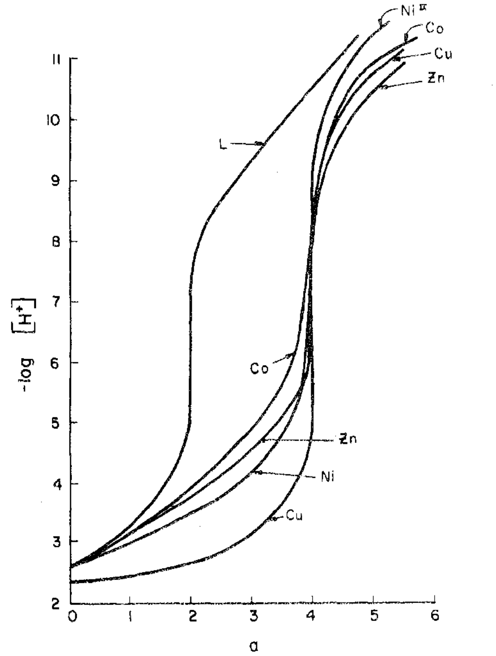


Figure 4. Potentiometric equilibrium curves for UDTMA (L) and a 1:1 molar ratio of UDTMA to zinc(II) (Zn), nickel(II) (Ni), cobalt(II) (Co), and copper(II) (Cu) at 25°; ionic strength 0.10 (KNO_3); a = moles of base/mole of ligand.

The thermodynamic equilibrium constants corresponding to the formation of the oxygen complex, defined by eq 5 and 6, are tabulated in Table I. In the presence of air, the constant

$$2Co^{2+} + 2L^- + O_2 \rightleftharpoons Co_2L_2O_2OH^+ + H^+ \qquad (5)$$

$$K_{O_2} = [Co_2L_2O_2OH^+][H^+]/[Co^{2+}]^2[L^-]^2P_{O_2\,(atm)}$$

calculated was in excellent agreement with the value calculated using pure dioxygen.

Table III. Ligand Protonation Constants

	Log K_1^H	Log K_2^H	Log K_3^H	Log K_4^H
SDTMA	10.81	9.59	3.24	1.70
UDTMA	9.92	8.70	4.32	1.30
SEDDA[a,d]	9.59	6.53	(1.7)	(1.3)
DIEN[b,d]	9.94	9.13	4.34	
TREN[c,d]	10.29	9.59	8.56	2.6

[a] Ethylenediamine-*N,N*-diacetic acid. [b] Diethylenetriamine. [c] Triaminotriethylamine. [d] Stability constants for *a*, *b*, and *c* from ref 16.

Rate Constants. The rate constants of the forward and reverse reactions corresponding to the formation and disappearance of the 351 nm peak are given below.

k_1, M^{-1} sec^{-1}	3.0×10^3	1.4×10^4
k_{-2}, sec^{-1}	0.6	0.3

The rate constants k_1 and k_{-2} are defined according to the following scheme similar to that proposed by Wilkins[4,5] for dioxygen complexes without hydroxo bridges:

$$CoL^+ + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CoLO_2^+$$

$$CoL^+ + CoLO_2^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Co_2L_2O_2OH^+ + H^+$$

Discussion

The Ligands. The symmetric and unsymmetric isomeric DTMA's were chosen for this study since they possess four coordinating groups, low charge, and are two of several isomers and analogs of compounds which should provide answers to the problem areas described in the Introduction. In order to provide answers to the remaining questions, other polyamines and polyamino acids are also under study in these laboratories as ligands for cobalt(II)–dioxygen carriers.[12] Some of these include: (1) the tetramine analog of DTMA, *N,N,N*-tris(2-aminoethyl)amine; (2) the tetradentate diacetic acid analog of DTMA, and its isomers; and (3) *N*-(2-hydroxyethyl)ethylenediamine. The DTMA isomers are new ligands in the sense that they have not been isolated previously in solid form. Collman[10] had prepared them in solution and isolated metal complexes but in this laboratory the actual hydrobromide salts were prepared and used in exact stoichiometric amounts for experimental investigations.

Protonation Constants and Metal Ion Equilibria. The protonation constants may be compared with those of several model compounds (Table III). The first protonation constant of SDTMA is quite high relative to DIEN and may reflect both the higher electron density on the tertiary nitrogen of SDTMA relative to the secondary nitrogen of DIEN and the inductive effect of the deprotonated negative acetate substituent. For UDTMA, the value of K_1^H is virtually identical with that of DIEN, indicating isostructural monoprotonated species. The observed similarity implies that in this case the inductive effects of the terminal acetate group upon the basicity of the central nitrogen are probably small.

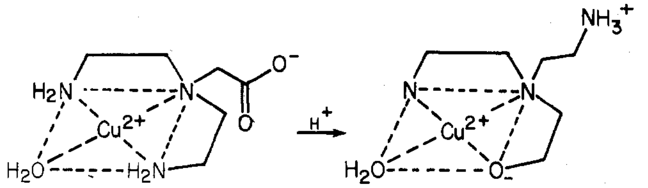
The second protonation constants for all species (log K_2^H) fall within a relatively narrow range, reflecting the minimized effect of the acetate group in the isomeric DTMA's due to a greater physical separation.

For SDTMA, log K_3^H is quite a bit lower than that of either UDTMA or DIEN, implying that the structure of H_2L^+ and/or H_3L^{2+} may have unique properties not possible in the corresponding forms of the other ligands. The low pK value of the acetic acid substituent, log K_4, for SDTMA and UDTMA is to be expected on the basis of the high positive charge on the ligand.

It was found that the metal complex formation curves measured under nitrogen, shown in Figures 1–3, could be quantitatively expressed in terms of eq 1 and 2. Thus the stoichiometry of the reactions indicated the formation of complexes having the formulas ML^+ and MHL^{2+} in acid solution. Equation 3 was found to hold in basic solution for Cu(II), Zn(II), and Co(II) under nitrogen with MOHL representing a hydrolyzed species involving the loss of one proton per complex from a coordinated water molecule.

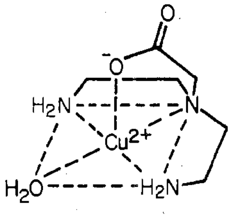
The values of Cu(II) complex formation (for SDTMA K_{ML} = 18.07; for UDTMA K_{ML} = 17.29) are in line with the relative basicities of the ligands as measured by their pK's.

On coordination, the entropy change for SDTMA, a more ordered ligand in solution, should be less negative than that of UDTMA, a more extended and disordered ligand. One might therefore expect a higher value of K_{ML} for copper(II)–SDTMA complex (and for other metal complexes) relative to UDTMA, due to this entropic effect. Alternately, ligands isostructural to DTMA (e.g., TREN and Me_6TREN) are known[13,14] to readily adapt to five coordination. Thus possible structures for the complexes of SDTMA are illustrated by **1**–**3**, and for UDTMA by **4** and **5**. The protonated chelate structures are suggested on the basis of the fact that the amino group should be a better proton acceptor than the carboxylate group. The low value of the protonation constant is considered due to the concomitant rearrangement required for transformation of **1** → **2**.



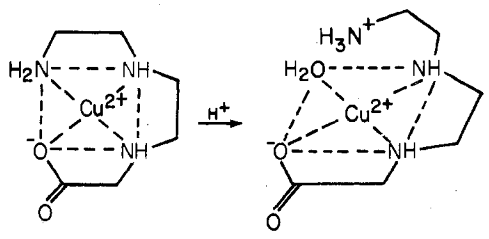
1 **2**

CuL⁺ CuHL²⁺



3

distorted square pyramid

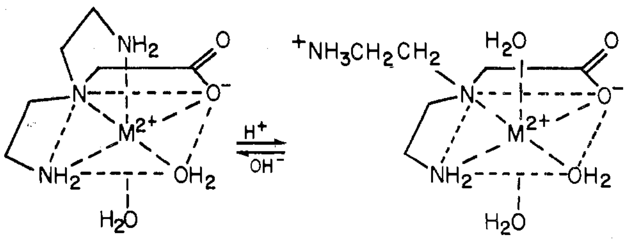


4 **5**

It is interesting to compare the relative reaction tendencies between metal ions with DIEN and the DTMA isomers. Log K_{ML} data are available only for Cu^{2+}, Ni^{2+}, and Zn^{2+} with DIEN and are respectively 16.0, 10.7, and 8.9.[16] These are 2.1, 3.7, and 4.2 log units lower than the corresponding constants for SDTMA, and 1.3, 3.7, and 4.0 log units lower than for UDTMA. The smaller differences shown for Cu(II) reflect the preference of copper for nitrogen donation, so that a coordinated carboxylate contributes less than a nitrogen donor to complex stability. Comparison with the tetradentate ligand SEDDA in which all four groups would presumably be coordinated in a square planar arrangement shows log K_{ML} = 15.9.[16]

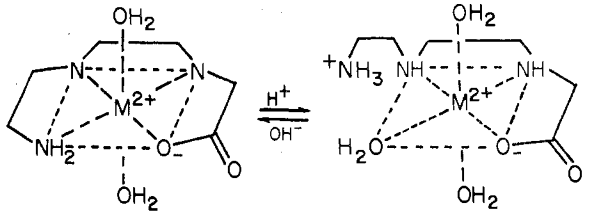
Four coordination in this case involving two oxygen donors does not result in any large enhancement of stability over DIEN. The larger differences in log K_{ML} for the remaining metal ions probably reflect the added stability resulting from an additional chelate ring. An additional indication of solution structure may be deduced from ease of hydrolysis of the Cu(II) complexes. For DIEN log K_{MOHL} is 9.03 and is only slightly higher for SDTMA (9.22) and UDTMA (9.32). Thus as expected, very little increase in stability is observed with the additional acetate because in both cases the hydrolysis reaction involves the dissociation of a proton from a coordinated water molecule.

Based on the relative values of the chelate protonation constants (K_{MHL}) listed in Tables I and II, the proposed structures for the chelates of cobalt(II), nickel(II), and zinc(II) are consistent with formulas **6**, **7**, **8**, and **9**. It is not implied that any three coordinated donor groups must be in the same plane.



6 **7**

ML⁺ MHL²⁺

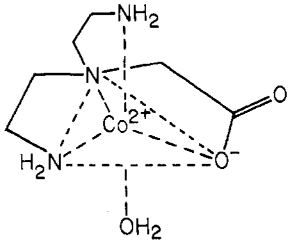


8 **9**

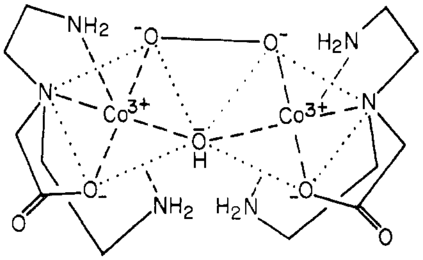
The fact that the affinity of the proton for the Ni(II), Co(II), and Zn(II) chelates (as measured by log K_{MHL}) is much greater than for the Cu(II) chelate reflects the weaker binding of the amino nitrogens by Ni(II), Co(II), and Zn(II) in complexes of the type represented by **6**, which are presumed to form type **7** on protonation. The Cu(II) chelate may be considered to have the planar or pyramidal forms **1** and **3**. In both cases the stronger bonding of the Cu(II) to the nitrogens would result in the proton combining with the weakly or noncoordinated carboxylate group. Such a complex would be tautomeric with **2**, with the relative amounts of amino-protonated and carboxylate-protonated species unknown on the basis of the data currently available.

The fact that the Cu(II)–UTDMA complex has a higher proton affinity than does the Cu(II)–SDTMA isomer is a reflection of the stronger binding to the nitrogens in **3** relative to **4**, and the fact that the carboxylate in **1** or **3** has lower proton affinity than does the terminal amino nitrogen in **4**.

In the hydrolysis indicated in Table I for the zinc(II) and cobalt(II) complexes, proton dissociation could occur at the two aquo sites. In the pH range actually studied (pH <11), these metal chelates form only one coordinated hydroxo group. In the case of the nickel(II) complex, $NiHL^+$–hydroxo complex formation did not occur in the pH range studied. Considering the aforementioned possibility of five coordination, structures for SDTMA–metal complexes might be formulated as in **10** or, alternately, as square pyramidal complexes.



10



11

Oxygenation Equilibria. Under dioxygen (or air) the cobalt(II)-DTMA complex, CoHL, reacts in the ratio of 2 mol of the complex to 1 mol of dioxygen and 1 mol of hydroxide, in accordance with eq 4 and 5. The probable rearrangement of coordinate bonds for this complex in solution is indicated by **11**. While a cis arrangement of peroxo and hydroxo bridges is necessary, **5** should not be interpreted as ruling out one axial bridge (e.g., peroxo) cis to the equatorial bridge. This structure is in some respects analogous to those proposed for the cobalt(III)-polyamine dioxygen complexes.[3,5,7,8] The unusual and surprising degree of stability with respect to oxidation or irreversible rearrangement to cobalt(III) complexes and its consequent complete reversibility on lowering the pH or lowering the concentration of oxygen is a new and important observation. The stoichiometry of the complex indicated by **11** is supported by the formation constant, calculated under pure oxygen and under air. Agreement of the constants obtained at two levels of dioxygen concentration (and at varying ligand, cobalt(II), and hydroxide ion concentrations) demonstrated the correctness of the number of molecular groupings involved.

Taking the solubility of dioxygen into account and correcting for metal chelate stability, the formation constants K_{O_2} may be recast into a more convenient format K_{O_2}', described by eq 6, where log K_{O_2}' = 2.39 and 2.35 for SDTMA and UDTMA,

$$2CoL^+ + O_2(aq) \rightleftharpoons Co_2L_2O_2OH^+ + H^+ \qquad (6)$$

$$K_{O_2}' = [Co_2L_2O_2OH^+][H^+]/[CoL^+]^2[O_2]$$

respectively. The similarity in formation constants for UDTMA and SDTMA may reflect their similar donor groups and, by inference, a similar electronic environment at the cobalt center. By contrast the value for triethylenetetramine (TRIEN)[8] is 8.0, that for diethylenetriamine (DIEN) is 1.7 log units,[7] and that for bis(ethylenediamine) is 7.0 log units.[7] For TREN (triaminotriethylamine) the corresponding value is 4.40.[12] It may be true that these literature values may be slightly inaccurate because of the formation of an unspecified amount of irreversible oxidation product. Nevertheless, whatever factors control the value of the stability constants (K_{O_2}') may also contribute to the inertness of $Co_2L_2O_2OH^{n+}$ toward further oxidation. The constants for SDTMA and UDTMA, 2.39 and 2.35, respectively, lie orders of magnitude below that of TRIEN, 8.0, or of DIEN, 7.0, while that value found for TREN, 4.40, is closer. This similarity in formation constants may or may not be related to the fact that the μ-dioxygen complexes involved are nearly unique in being very stable and completely reversible.

Since μ-dioxygen complexes of both TREN and SDTMA contain ligands that have comparable steric requirements, there seems to be a possibility that the unusual stabilities of the oxygen complexes are due to steric effects. UDTMA, however, has less rigid stereochemical requirements than its symmetric isomer yet also exhibits ready reversibility and no observable irreversible oxidation to cobalt(III) products.

Kinetics of Oxygenation. The stopped flow measurements of the appearance of the 350 nm peak show excellent pseudo-first-order dependence on CoL^+. Assuming the same mechanism as previously reported,[4,5] rate constants were calculated, and are given below. These values fall within the fairly narrow range previously reported. Interestingly, steric differences may be more closely reflected in the kinetic data than in the equilibrium data. For SDTMA, the value of k_1 ($3.0 \times 10^3\ M^{-1}\ sec^{-1}$) is quite close to that determined for TREN[7] ($k_1 = 2.8 \times 10^3\ M^{-1}\ sec^{-1}$), its isostructural N isomer, while the value for the linear isomer, UDTMA, is larger ($k_1 = 1.4 \times 10^4\ M^{-1}\ sec^{-1}$) and comparable to that measured for its nitrogen analog, TRIEN ($k_1 = 2.0 \times 10^4\ M^{-1}\ sec^{-1}$).

If the possibility of five coordination in the case of SDTMA were assumed, a slower rate might be expected, but then the expected reaction would be formally an oxidative addition (for the final dibridged product must be octahedral) and one might expect a larger rate difference than that observed. The usual explanation for the similar rates observed in dioxygen complex formation is that a similar mechanism operates in all cases involving replacement of coordinated water by O_2 (presumably in an octahedral intermediate) dominated by H_2O exchange.

The fact that the kinetic parameters obtained fall within the range previously observed suggests that this mechanism is also followed here, but does not entirely rule out the possibility of a nonoctahedral intermediate, since dioxygen is known to add to a tetrahedral cobalt(II) species with a rate constant quite similar to that of the octahedral species.[15]

Detailed mechanistic studies are in progress on this and similar systems in order to clarify the pathways of reactions leading to the formation of μ-dioxygen complexes, as well as the steric and constitutional requirements for producing stable μ-dioxygen complexes that are effective in the oxidation of reducing substrates.

Registry No. SDTMA, 55682-20-7; SDTMA·3HBr, 55682-21-8; UDTMA, 55682-22-9; UDTMA·3HBr, 55682-23-0; Cu, 7440-50-8; Ni, 7440-02-0; Zn, 7440-66-6; Co, 7440-48-4; $Co_2(SDTMA)_2O_2OH^+$, 55701-24-1; $Co_2(UDTMA)_2O_2OH^+$, 55701-25-2; bromomalonic acid, 600-31-7; diethylenetriamine, 111-40-0.

References and Notes

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