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Metal Chelates of Ether- and Thioether-Containing Pentadentate Ligands and Oxygenation of the Cobaltous Complexes

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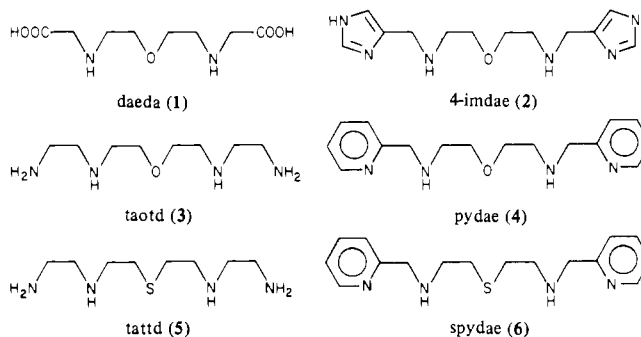
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The syntheses of six ether and thioether pentadentate ligands, 1,9-dicarboxy-2,8-diaza-5-oxanonane (daeda), 1,9-bis(4-imidazolyl)-2,8-diaza-5-oxanonane (4-imdae), 1,4,10,13-tetraaza-7-oxatridecane (taotd), 1,9-bis(2-pyridyl)-2,8-diaza-5-oxanonane (pydae), 1,4,10,13-tetraaza-7-thiatridecane (tattd), and 1,9-bis(2-pyridyl)-2,8-diaza-5-thianonane (spydae), are described. Acid dissociation constants and metal chelate formation constants for Co(II), Ni(II), Cu(II), and Zn(II) as well as formation constants for dioxygen adducts of the cobaltous chelates of taotd, tattd, and spydae are reported. The thioether cobaltous complexes form more stable dioxygen adducts than their oxygen analogues but less stable complexes than the cobaltous complexes of the analogous amino nitrogen ligands. Work now in progress on these new dioxygen complexes involves a study of their redox rearrangement to inert cobalt(III) complexes and of their potential reactivities in the oxidation of organic substrates.

Introduction

The interaction of dioxygen with cobaltous complexes has been the subject of several recent reviews.[2–4] Although emphasis has been placed on their similarity to biological oxygen carriers, more recent work[5,6] has centered about the use of metal dioxygen complexes as catalysts for the insertion of oxygen into organic substrates. Dioxygen complexed to a metal ion seems to become "activated" and is more reactive toward the substrate than free, uncoordinated dioxygen.

Much of the previous work on cobaltous dioxygen complexes has involved aqueous solutions with aliphatic polyamines, amino acids, or peptides as ligands. In two recent papers,[7,8] the chelating tendencies of some pentadentate ligands containing imidazolyl and pyridyl donor groups were described, along with the oxygenation of their cobaltous complexes. A characteristic of these pentadentate ligands is that upon oxygenation of the cobalt complexes, a coordinatively saturated μ-peroxo dimer is formed with no available binding sites for the formation of a μ-hydroxo dibridged species. The ability to form this dibridged complex seems to "lock-in" the dioxygen bridge and shift the equilibrium in favor of dioxygen complex formation.[9]

The study reported here deals with new multidentate ligands that are analogues of previously studied pentadentate polyamine ligands with the central amino group replaced by an ether oxygen or sulfur. The ligands of this type that have been synthesized are 1,9-dicarboxy-2,8-diaza-5-oxanonane (daeda) (1), 1,9-bis(4-imidazolyl)-2,8-diaza-5-oxanonane (4-imdae) (2), 1,4,10,13-tetraaza-7-oxatridecane (taotd) (3), 1,9-bis(2-pyridyl)-2,8-diaza-5-oxanonane (pydae) (4), 1,4,10,13-tetraaza-7-thiatridecane (tattd) (5), and 1,9-bis(2-pyridyl)-2,8-diaza-5-thianonane (spydae) (6). The stabilities of the metal chelates formed by these ligands with first-row transition-metal ions have been investigated potentiometrically. The equilibrium constants for the reactions of the cobalt(II) complexes of 1–6 formed with molecular oxygen have been determined.

(1) Abstracted in part from a dissertation to be submitted by Stephen A. Bedell to the faculty of Texas A&M University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.
(2) McLendon, G.; Martell, A. E. *Coord. Chem. Rev.* **1976**, *19*, 1.
(3) Basolo, F.; Hoffman, B. M.; Ibers, J. A. *Acc. Chem. Res.* **1975**, *8*, 384.
(4) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139.
(5) Nishinaga, A. "Biochemical and Medical Aspects of Active Oxygen"; Hayaishi, O., Asada, K., Eds.; University Park Press: Baltimore, MD, 1977; p 13.
(6) Lyons, J. E. "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ugo, R., Eds.; Plenum Press: New York, 1977; p 1.
(7) Harris, W. R.; Murase, I.; Timmons, J. H.; Martell, A. E. *Inorg. Chem.* **1978**, *17*, 889.
(8) Timmons, J. H.; Harris, W. R.; Murase, I.; Martell, A. E. *Inorg. Chem.* **1978**, *17*, 2192.
(9) Bogucki, R. F.; McLendon, G.; Martell, A. E. *J. Am. Chem. Soc.* **1976**, *98*, 3202.

daeda (1)　　　　4-imdae (2)

taotd (3)　　　　pydae (4)

tattd (5)　　　　spydae (6)

Experimental Section

Syntheses. 1,9-Bis(4-imidazolyl)-2,8-diaza-5-oxanonane Tetrahydrochloride. A mixture of imidazole-4-carboxaldehyde (10 g, 0.1 mol) and 2,2'-diaminodiethyl ether (5 g, 0.05 mol) in 150 mL of ethanol was hydrogenated with a 10% palladium–charcoal catalyst at a pressure of 1.9 atm at room temperature. After the calculated amount of hydrogen was taken up, the catalyst was filtered off and the filtrate saturated with dry hydrogen chloride. The resulting precipitate was filtered and recrystallized from 95% ethanol. The pure sample was dried over P_2O_5 under vacuum at room temperature; mp 240–242 °C dec; yield 61%. Anal. Calcd for $C_{12}H_{20}N_6O\cdot4HCl$: C, 35.15; H, 5.91; N, 20.49. Found: C, 35.15; H, 5.86; N, 20.55.

1,9-Dicarboxy-2,8-diaza-5-oxanonane Dihydrobromide. A mixture of 2,2'-diaminodiethyl ether (6.3 g, 0.06 mol) and bromomalonic acid (24 g, 0.13 mol) (which had been dissolved in 20 mL of water and neutralized with 20% aqueous sodium hydroxide at a temperature of less than 10 °C) was heated at 50–70 °C for 50 min while 0.13 mol of 20% aqueous sodium hydroxide was added dropwise to maintain a constant pH as indicated by the blue color of thymolphthalein. After additional heating at 80 °C for 1 h, the solution was cooled to below 10 °C and acidified to pH 1.0 with concentrated hydrochloric acid. Upon addition of ethanol and after refrigeration for 12 h, the colorless crystals obtained were filtered and dried over calcium chloride. The crystals were then dissolved in 75 g of 15% hydrobromic acid, and the solution was heated in a water bath. Generation of carbon dioxide ceased within 40 min, and the solution was evaporated to near dryness. The residue was dissolved in hot methanol and filtered. Upon addition of ethanol and after subsequent refrigeration, the crystals obtained were filtered and dried over P_2O_5 under vacuum at room temperature; mp 216–218 °C dec. The overall yield based on diaminodiethyl ether was over 70%. Calcd for $C_8H_{16}N_2O_5\cdot2HBr$: C, 25.15; H, 4.76; N, 7.33. Found: C, 25.31; H, 4.87; N, 7.46.

1,4,10,13-Tetraaza-7-oxatridecane Tetrahydrobromide. A mixture of N-acetyl-N'-(benzenesulfonyl)ethylenediamine (48.4 g, 0.2 mol), 2,2'-dibromodiethyl ether (23.2 g, 0.1 mol), and potassium hydroxide (11.2 g, 0.2 mol) in 250 mL of absolute ethanol was refluxed for 24 h. The potassium bromide produced was filtered off, and the solvent was distilled from the filtrate under reduced pressure. The oily residue was refluxed with 350 mL of concentrated hydrochloric acid for 70 h with occasional addition of hydrochloric acid (total 150 mL), and the solution was concentrated with a rotary evaporator. The residue was boiled with a large amount of ethanol to yield a crystalline solid

(45 g), which was the dihydrochloride bis(benzenesulfonate) of the tetramine. The tetrahydrobromide was obtained by passing an aqueous solution of this product through an anion-exchange resin followed by evaporation of the eluate. The yield based on 2,2'-dibromodiethyl ether was 70%. A pure sample was obtained through repeated recrystallizations from dilute ethanol, and the material was dried over P_2O_5 under vacuum at room temperature. It did not show a sharp melting point, softening from 100–125 °C and not decomposing up to 250 °C. Anal. Calcd for $C_8H_{22}N_4O\cdot4HBr$: C, 18.69; H, 5.11; N, 10.90. Found: C, 18.38; H, 5.01; N, 11.19.

1,9-Bis(2-pyridyl)-2,8-diaza-5-oxanonane Tetrahydrobromide. A mixture of pyridine-2-carboxaldehyde (11 g, 0.1 mol) and 2.2'-diaminoethyl ether was hydrogenated with a 10% palladium–charcoal catalyst at 1.9 atm pressure at room temperature. The catalyst was filtered off, and concentrated hydrobromic acid (37 g) was added to the filtrate. After the solution was concentrated with a rotary evaporator, the remaining yellow oil was dissolved in a minimum amount of hot methanol. After addition of ethanol and 12 h of refrigeration, a crystalline solid was obtained in a yield of over 80%. The product was recrystallized from a methanol–ethanol mixture and dried over P_2O_5 under vacuum at room temperature; mp 192–193 °C dec. Anal. Calcd for $C_{16}H_{22}N_4O\cdot4HBr$: C, 31.50; H, 4.30; N, 9.19. Found: C, 31.52; H, 4.37; N, 9.25.

1,4,10,13-Tetraaza-7-thiatridecane Bis(benzenesulfonate) Dihydrochloride. A mixture of potassium hydroxide (13.5 g, 0.20 mol), 2,2'-dichlorodiethyl sulfide (16 g, 0.10 mol), and *N*-acetyl-*N'*-(benzenesulfonyl)ethylenediamine (48 g, 0.20 mol) in 250 mL of absolute ethanol was refluxed in an oil bath at 90 °C for 12 h. The potassium chloride that formed was filtered off at room temperature, and the filtrate was evaporated to dryness under reduced pressure. The viscous residue (~60 g) was refluxed with 250 mL of concentrated hydrochloric acid for 120 h, during which time eight portions of 50 mL of concentrated hydrochloric acid (total 400 mL) were added at intervals. The resulting dark brown solution was filtered, and the filtrate was evaporated to dryness under reduced pressure. The residue was washed with a large amount of ethanol to give a gray crystalline powder; yield 43 g (72%).

The pure sample was obtained as colorless crystals, mp 199–200 °C dec, by repeated recrystallization from 90–95% ethanol and was dried at 100 °C under vacuum over P_2O_5. Anal. Calcd for C_{20}-$H_{36}N_4O_6S_3Cl_2$ ($C_8H_{22}N_4S\cdot2C_6H_5SO_3H\cdot2HCl$): C, 40.32; H, 6.10; N, 9.41. Found: C, 40.07; H, 6.11; N, 9.37.

1,9-Bis(2-pyridyl)-2,8-diaza-5-thianonane Tetrakis(benzenesulfonate) Monohydrate. Pyridine-2-carboxaldehyde (4.2 g, 0.40 mol) was dissolved in 40 mL of absolute ethanol, and bis(2-aminoethyl) sulfide (2.4 g, 0.20 mol) was added to the solution. The mixture was heated on a water bath for 30 min; to this was added sodium borohydride (2.0 g, 0.50 mol), and heating was continued for 2 h. The pale yellow solution that resulted was cooled to room temperature, and the pH of the solution was brought to ~1 by dropwise addition of dilute hydrochloric acid. The dark red-brown solution was treated with active carbon to give a pale brown solution. It was evaporated to dryness under reduced pressure, the residue was dissolved in methanol, and the insoluble sodium chloride that formed was filtered off. Benzenesulfonic acid (14 g, 0.08 mol) was added to the filtrate, and the solution was kept in a refrigerator at −15 °C for 12 h. The crystalline solid was collected by filtration and washed with ethanol and with acetone. Dissolution in hot ethanol and refrigeration at −15 °C were repeated, and the crystals that formed were dried over P_2O_5 under vacuum at room temperature; yield ~70%, mp 164–166 °C. Anal. Calcd for $C_{16}H_{22}N_4S\cdot4C_6H_5SO_3H\cdot H_2O$: C, 50.40; H, 5.09; N, 5.88. Found: C, 50.89; H, 5.07; N, 5.98.

Reagents and Materials. The potassium hydroxide solution employed in the potentiometric studies was prepared from J. T. Baker "Dilut-It" potassium hydroxide concentrate under CO_2-free conditions and standardized against potassium hydrogen phthalate. Metal ion stock solutions were prepared from the nitrate salts and standardized by titration with ethylenedinitrilotetraacetic acid (EDTA).[10]

Equilibrium Measurements. In all potentiometric measurements, hydrogen ion concentrations were determined with a Beckman Research Model pH meter equipped with glass and calomel electrodes calibrated with standard HCl and NaOH to read $-\log[H^+]$ rather than activity. Solutions were adjusted to 0.10 M ionic strength by

Table I. Protonation Constants of Pentadentate Ligands[a,b]

ligand[c]	log K_H^1	log K_H^2	log K_H^3	log K_H^4	log K_H^5
daeda	9.61 (2)	8.65 (1)	2.60 (1)	1.9 (1)	
4-imdae	9.16 (2)	8.17 (1)	4.66 (2)	3.88 (1)	
pydae	8.32 (2)	7.28 (1)	1.9 (1)	1.4 (1)	
spydae	7.98 (1)	6.96 (1)	1.9 (1)	0.9 (1)	
taotd	9.81 (1)	9.24 (1)	6.89 (1)	5.98 (1)	
tattd	9.78 (1)	9.10 (1)	6.51 (1)	5.64 (1)	
4-imdien[d]	9.22 (3)	8.18 (2)	4.91 (3)	3.90 (2)	2.92 (3)
pydien[e]	8.88 (2)	7.04 (2)	3.82 (2)	1.44 (1)	
tetren[e]	9.85 (3)	9.27 (3)	8.19 (3)	5.08 (2)	3.43 (5)

[a] All values determined at 25 °C and $\mu = 0.10$ M (KNO_3). [b] Numbers in parentheses represent average deviations in least significant digit. [c] Definitions of ligand abbreviations given in text. [d] Values from ref 8. [e] Values from ref 7.

the addition of KNO_3 and maintained at 25.00 ± 0.05 °C with constant-temperature water circulated through a sealed, jacketed cell. An inlet tube in the cell kept the solution under an atmosphere of nitrogen, prepurified by passing it through two alkaline pyrogallol scrubbers and through a 0.10 M KNO_3 solution. For the equilibrium measurements under an oxygen atmosphere, pure oxygen was passed through an ascarite column to remove traces of CO_2 and then through a 0.10 M KNO_3 solution. The acid forms of the ligands were reacted with standard carbonate-free potassium hydroxide solution, and the hydrogen ion concentrations were recorded after addition of each increment of base. Metal chelate formation equilibria were measured with 1:1 molar ratios of the ligands with Cu^{2+}, Ni^{2+}, Zn^{2+}, and Co^{2+} at a concentration of 2.50×10^{-3} M.

Visible Spectra. Electronic spectra were recorded on a Cary Model 14 spectrophotometer.

Results

Ligand Protonation Constants. For any general protonation equilibrium (eq 1), the constants, defined by $K_H^n = [H_nL]/$

$$H^+ + H_{n-1}L \xrightleftharpoons{K_H^n} H_nL \qquad (1)$$

$[H^+][H_{n-1}L]$, may be determined from the hydrogen ion concentrations of an aqueous solution of a ligand for each increment of added base. A computer program developed by Dr. R. J. Motekaitis[11] was used to calculate the protonation constants for the ligands. Values of log K_H^n for the ligands involved in this study are given in Table I. Also listed for comparison are the protonation constants for the closely related ligands tetraethylenepentamine (tetren), 1,9-bis(4-imidoxolyl)-2,5,8-triazanonane (4-imdien), and 1,9-bis(2-pyridyl)-2,5,8-triazanonane (pydien).

Metal Chelate Formation Constants. A representative set of ligand and metal–ligand potentiometric equilibrium curves is shown in Figure 1. The equilibrium involved in formation of the metal ligand complexes is represented in eq 2. In some

$$M + L \xrightleftharpoons{K_{ML}} ML \qquad K_{ML} = [ML]/([M][L]) \qquad (2)$$
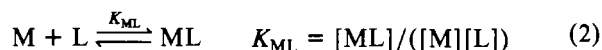
cases the formation constant of a stable protonated chelate species can be calculated by considering the equilibrium defined in eq 3.

$$ML + H^+ \xrightleftharpoons{K_{MHL}^H} MHL$$
$$K_{MHL}^H = [MHL]/([ML][H^+]) \qquad (3)$$
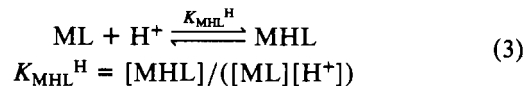
If the value of K_{MHL}^H is known, then K_{ML} can be calculated with mass balance equations involving total metal, total ligand, and total hydrogen ion concentrations. These equations have been described in detail in a previous paper.[8] In practice, a computer program calculates K_{ML} on the basis of an initial

(10) Welcher, F. J. "The Analytical Uses of Ethylenediaminetetraacetic Acid"; Van Nostrand: Princeton, NJ, 1958.

(11) Motekaitis, R. J.; Martell, A. E. *Can. J. Chem.*, in press.
(12) (a) Martell, A. E.; Smith, R. M. "Critical Stability Constants"; Plenum Press: New York, 1974; Vol. 1. (b) Martell, A. E.; Smith, R. M. "Critical Stability Constants"; Plenum Press: New York, 1975; Vol. 2.

Table II. Formation and Protonation Constants of Chelates of Pentadentate Ligands with Various Metal Ions[a,b]

ligand[c]	equil const	Co²⁺	Ni²⁺	Cu²⁺	Zn²⁺
dadae	$\log K_{ML}$	9.46 (3)	11.83 (2)	14.54 (1)	10.15 (2)
	$\log K_{MHL}{}^{H}$				
4-imdae	$\log K_{ML}$	9.64 (3)	12.38 (2)	15.94 (1)	9.52 (3)
	$\log K_{MHL}{}^{H}$		2.80 (2)	3.84 (1)	
pydae	$\log K_{ML}$	9.84 (4)	13.28 (2)	15.38 (2)	9.52 (6)
	$\log K_{MHL}{}^{H}$	3.80 (4)	2.48 (3)		
spydae	$\log K_{ML}$	11.75 (1)	14.88 (1)[d]	18.1 (1)[e]	10.64 (1)
	$\log K_{MHL}{}^{H}$	2.92 (1)			2.88 (1)
taotd	$\log K_{ML}$	9.47 (2)	12.47 (2)	17.96 (2)	10.97 (3)
	$\log K_{MHL}{}^{H}$	6.20 (3)	5.21 (4)	3.83 (5)	5.57 (5)
tattd	$\log K_{ML}$	11.46 (1)	15.45 (1)	19.67 (1)	11.24 (3)
	$\log K_{MHL}{}^{H}$	4.29 (5)		2.34 (5)	
4-imdien[f]	$\log K_{ML}$	13.84 (1)	17.35 (1)	20.41 (2)	13.303 (4)
	$\log K_{MHL}{}^{H}$	3.3 (1)	2.01 (1)	3.35 (1)	2.69 (3)
pydien[g]	$\log K_{ML}$	14.73 (1)	19.2 (2)	20.85 (1)	13.71 (1)
	$\log K_{MHL}{}^{H}$	2.28 (1)			1.83 (1)
tetren	$\log K_{ML}$	13.66 (1)[g]	17.4[h]	22.8[h]	15.1[h]
	$\log K_{MHL}{}^{H}$	5.40 (5)[g]	4.1[h]	5.2[h]	

[a] All values determined at 25 °C and $\mu = 0.10$ M (KNO₃). [b] Numbers in parenthese represent average deviation in least significant digit. [c] Definitions of ligand abbreviations given in text. [d] Determined by potentiometric competition with tattd. [e] Determined by spectrophotometric competition with EDTA. [f] Values from ref 8. [g] Values from ref 7. [h] Values from ref 12b.
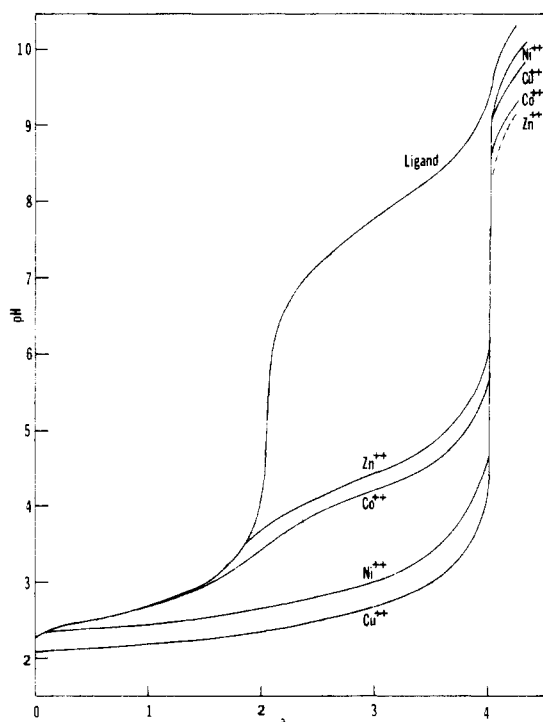

Figure 1. Potentiometric equilibrium curves for 1:1 molar ratios of pydae with Zn²⁺, Co²⁺, Ni²⁺, Cu²⁺. $T_L = T_M = 2.5 \times 10^{-3}$ M; $t = 25$ °C; $\mu = 0.10$ M (KNO₃); a is the number of moles of base added per mole of metal ion or ligand present.

estimate of the magnitude of $K_{MHL}{}^{H}$. The value of $K_{MHL}{}^{H}$ is varied until the calculated value of K_{ML} is constant throughout all the data points.

The chelation of copper and nickel ions by spydae is so strong that virtually 100% of the ligand is complexed after mixing the ligand salt and the metal ion. The formation constant for spydae and copper was determined by spectrophotometric competition with EDTA as the competing ligand. This method has been described previously.[13] Since the nickel–EDTA and Ni–spydae formation constants differ by several orders of magnitude and because both complexes have low molar absorptivities, a potentiometric competition was employed.[14]

Table III. Equilibrium Constants for the Oxygenation of the Cobaltous Chelates of Pentadentate Ligands[a]

ligand[b]	$\log K_{O_2}{}^{c}$	$\log K_{O_2}{}'{}^{d}$
spydae	5.02 (2)	28.53 (2)
taotd	2.20 (3)	21.14 (3)
tattd	8.40 (1)	31.32 (1)
tetren[e]	15.83	43.15
pydien[e]	11.4	40.8

[a] All values determined at 25 °C and $\mu = 0.10$ M (KNO₃). [b] Definitions of ligand abbreviations given in text. [c] K_{O_2} defined by eq 4. [d] K_{O_2}' defined by eq 5. [e] Values from ref 7.

The formation constants for all the ligands with Cu(II), Co(II), Ni(II), and Zn(II) are listed in Table II. Values for tetren, pydien, and 4-imdien are also given for comparison. In several cases the protonated metal chelate MHL was not formed in sufficient concentration to be determined potentiometrically, as indicated by the corresponding blank position in Table II.

Oxygen Complex Formation Constants. Interaction of some of the cobaltous chelates with molecular oxygen resulted in the formation of μ-peroxo-cobalt dioxygen adducts. These complexes exhibited the brown color characteristic of the μ-peroxo complexes. The visible spectra showed peaks in the high-energy region (taotd, $\lambda = 358$ nm; tattd, $\lambda = 327$ nm; spydae, $\lambda = 350$ nm) that are generally assigned to a ligand to metal charge-transfer band. This transition serves as a fingerprint for identifying peroxo bridge formation.[2] Potentiometric equilibrium curves for tattd with Co²⁺ under both nitrogen and oxygen atmospheres are shown in Figure 2. From the potentiometric equilibrium curves measured under oxygen, the stability constants of the dioxygen complexes difined by eq 4–6 can be calculated. Values of $\log K_{O_2}$ and

$$K_{O_2} = \frac{[M_2L_2O_2]}{[ML]^2[O_2]} \qquad (4)$$

$$K_{O_2}'' = \frac{[M_2L_2O_2]}{[M]^2[L]^2[O_2]} \qquad (5)$$

$$\log K_{O_2}' = 2 \log K_{ML} + \log K_{O_2} \qquad (6)$$

$\log K_{O_2}'$ are listed in Table III. For ligands not listed, oxygen

(13) Harris, W. R.; Motekaitis, R. J.; Martell, A. E. *Inorg. Chem.* **1975**, *14*, 974.

(14) Schwarzenbach, G.; Anderegg, G.; Schneider, W.; Senn, H. *Helv. Chim. Acta* **1955**, *38*, 1147.
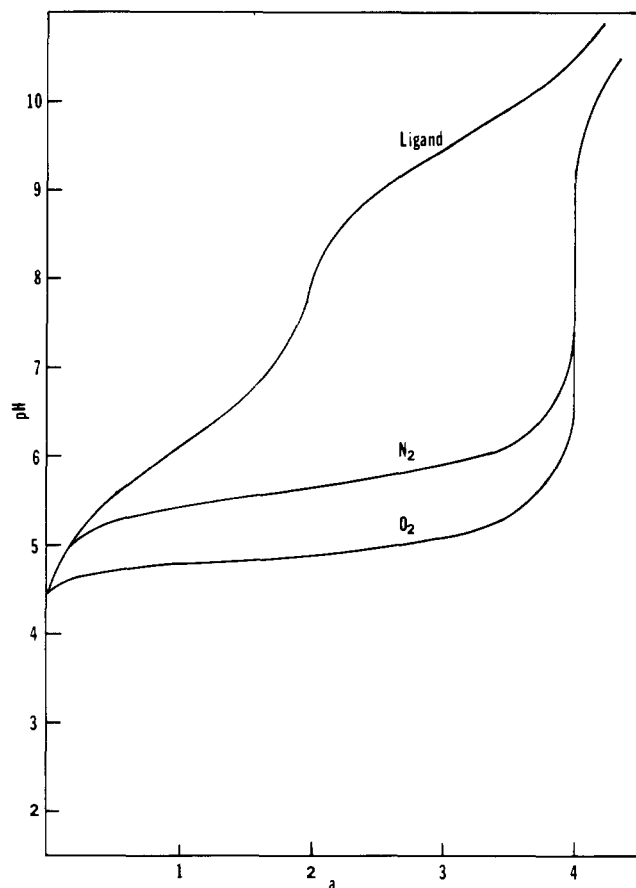
Figure 2. Potentiometric equilibrium curves for tattd and for a 1:1 molar ratio of the ligand to Co(II) under nitrogen and oxygen. T_L = T_M = 2.5 × 10⁻³ M; t = 25 °C; μ = 0.10 M (KNO₃); a is the number of moles of base added per mole of metal ion or ligand present.

complex formation did not occur to a sufficient extent to be detected potentiometrically.

When base was added to a solution of cobaltous ion and spydae under oxygen, the pH first decreased and then began to increase. The increase in pH became faster at larger "a" values. The initial decrease can be attributed to slow equilibrium in the formation of the dioxygen complex followed by an irreversible oxidation to an inert cobalt(III) complex, the rate of which is dependent on the concentration of the dioxygen complex. The latter reaction is assumed to be responsible for the increase in pH. Further studies will be aimed at identification of ligand oxidation products. Since this decomposition interfered with normal potentiometric titration measurements, a batch method was employed. Upon addition of cobalt to premixed solutions of spydae and KOH under oxygen, the pH was measured as a function of time. Extrapolation of the linear pH increase to time zero gave the pH value used in solving the oxygenation equilibrium constants.

Since the half-lives of the redox reactions for cobaltous ion with taotd and tattd under dioxygen were found to be 2 days or more and the potentiometric experiments required only 2 h, the irreversible oxidation did not appear to affect the pH measurements.

Discussion

Ligand Protonation Constants. Table I shows the protonation constants of the completely aliphatic polyamines taotd and tattd compared with the parent pentamine, tetren. The first two protonation constants involve the terminal amino groups and are seen to be similar for these three ligands, since the differences in the inductive effects of the central heteroatom are not expected to influence the terminal basic nitrogens six atoms away. It is seen from the data in Table I that the

values of log K_H^3 for taotd and tattd are much lower than that of tetren, since in the latter case, the third protonation occurs at the central nitrogen, which is shielded from the positive charge of the terminal amines to a greater degree than the third protonation sites on the other ligands, which cannot occur at the central oxygen and sulfur ether groups. Thus the protonation sites on these ligands are the nitrogen atoms only two carbons away from one of the positive terminal ammonium groups.

Comparison of acidities of spydae and pydae with the parent pydien shows greater differences in the protonation constants than those of the aliphatic amine series described above. In this case, because of the lower intrinsic basicities of the pyridine nitrogens, the first protonations of the neutral base probably occur on the secondary nitrogens at the 4 and 10 positions. The values of log K_H^1 and log K_H^2 for these ligands are indeed influenced by the oxygen and sulfur atoms. In the case of diethylenetriamine, protonation constants K_H^1 and K_H^2 of 9.84 and 9.02[12b] are nearly 2 log units higher than those of the corresponding thioether and ether ligands. While some of this effect may be due to the electronegativities of the adjacent heterocyclic rings, the major factor lowering basicity must be due to the electron-withdrawing effects of the central sulfur and oxygen ether atoms, relative to a central NH group.

It is also of interest to compare the relative effects of the central oxygen and sulfur atoms on the basicities of the adjacent (two carbons away) basic amino groups. The sulfur ether is seen to result in a reduction of log K_H by 0.3 unit more than the oxygen ether, for both the first and second protonation reactions. Since this result is contradictory to the relative electronegativities of the sulfur and oxygen atoms, a search of the literature was made to determine if this kind of reversal had been observed for other compounds. Indeed, an early study by Schwarzenbach and co-workers[14] on N-substituted iminodiacetic acids has indicated a similar trend in the effects of sulfur and oxygen ether groups on the protonation of basic nitrogen atoms. Their results also showed that the influence of a sulfur ether group two carbon atoms away in reducing the basicity of the basic amino group was considerably greater than that of an oxygen ether group.

The protonation values for the aliphatic nitrogens in 4-imdae are slightly lower than the first two values for 4-imdien, indicating the stronger electron-withdrawing effect of the oxygen ether function relative to a secondary amino group. The higher protonation constants for 4-imdae relative to pydae are a reflection of the greater electronegativity of the pyridine ring relative to that of imidazole.

The first two protonation reactions of daeda must involve the basic nitrogen atoms. Comparison of the log K_H values with those of diethylenetriaminediacetic acid[15] (dtda, log K_H^n = 9.55, 8.60, 4.45, 2.60, <1) shows that the first two protonation constants are almost identical. Any effect of the heteroatom is apparently hidden by the inductive effect of the carboxylate anions and by the more effective hydrogen bonding by the carboxylates to the protonated secondary amine compared to the relative influences of the central ether oxygen and amino groups.

Stability Constants. The metal chelate formation constants for all ligands in this study follow the expected relative ligand field effects of the transition-metal ions involved (i.e., the Irving–Williams series). Replacement of a central amino group with either an oxygen or sulfur results in weaker metal–ligand bonding and hence lower K_{ML} values. Previous reports have shown a general correlation between the intrinsic basicity of polyamine ligands and log K_{ML}. However, it is generally recognized that ether sulfur coordinates more

(15) Caraco, R.; Braun-Steinle, D.; Fallab, S. *Coord. Chem. Rev.* **1975**, *16*, 147.

strongly than ether oxygen to divalent transition metals, an effect that is not reflected by the relative basicities of the ligands. The values of log K_{ML} shown in Table II for the series pydien, pydae, and spydae and the series tetren, taotd, and tattd follow the stability trend N > S > O. That these metals prefer binding to the "softer" thioether may also be explained by the larger size of the sulfur atom, allowing it to more closely approach the metal ion with less contraction of the ligand backbone.

Dioxygen Complexes. All of these ligands have been expected to form less stable dioxygen complexes than their nitrogen analogues. Other pentadentate ligands have been shown to follow a general correlation between log K_{O_2} and the sum of the ligand protonation constants for ligands with similar structures.[16] Replacement of the central amine by an oxygen or sulfur indeed reduced the overall ligand basicity and consequently also log K_{O_2}. Comparison of the log K_{O_2} values of tetren (log K_{O_2} = 15.83[7]) with those of taotd and tattd and of pydien (log K_{O_2} = 11.4)[7] with spydae shows this to be the case. It is noteworthy that pydae, 4-imdae, and daeda did not form oxygen complexes at all.

The two thioether ligands, tattd and spydae, form more stable dioxygen complexes than their oxygen analogues, taotd and pydae, even though the latter have higher total basicities. An earlier study,[17] correlating log K_{O_2} with the sum of the logarithms of the ligand protonation constants, explained greater oxygen complex stability by increased σ bonding, as measured by the basicities of the ligands. Each metal center is visualized as donating an electron into the π^* orbital of the electrophilic dioxygen, resulting in the now widely accepted formalism of two cobalt(III) centers bridged by peroxo dioxygen. Such concepts cannot explain the apparent anomaly between the ether and thioether ligands. Factors contributing to the stability of the cobaltic complex should stabilize the dioxygen complex. A ligand containing oxygen would normally be favored by cobalt(III) over the sulfur analogue based on the simple hard–soft acid–base concept of coordinate bonding.

Steric effects are probably very much involved in influencing chelate ring formation in view of the considerable differences in the C–O–C and C–S–C bond angles, which are about 111° for oxygen and about 105° for sulfur. Therefore it is possible that for the multidentate ligands involved in this study, a more important consideration is the ability of sulfur to coordinate the cobalt ion and produce less conformational strain. This is the same argument that was invoked in explaining the increased stability of the cobaltous chelates. As the metal center attains cobalt(III) character, its radius will decrease, and under these circumstances it is possible that the sulfur atom may more easily move in to coordinate the metal ion and thus accommodate more easily than oxygen ether donors to the changing bonding geometry that occurs on electron transfer.

That dadae does not form a dioxygen adduct in measurable concentrations illustrates the importance of a μ-hydroxo bridge in stabilizing the μ-peroxo bridge. The cobaltous complex of ethylenediamine-N,N'-diacetic acid (SEDDA) forms a dibridged oxygen complex.[17] On the other hand, dadae, being pentacoordinate, cannot accommodate the μ-hydroxo bridge. Fallab[15] reported the formation of a stable dioxygen adduct by the cobaltous chelate of diethylenetriaminediacetic acid (dtda), a pentadentate ligand analogous to dadae with a central amino group in place of the ether oxygen of dadae. The increased basicity of dtda compared to dadae is probably the most important factor contributing to the difference in stabilities of the dioxygen complexes of these ligands.

(16) Harris, W. R.; Timmons, J. H.; Martell, A. E. *J. Coord. Chem.* **1979**, *8*, 251.

(17) McLendon, G.; Martell, A. E. *J. Chem. Soc., Chem. Commun.* **1975**, 223.