be observed. Comparison with *cis*- and *trans*-$Co(en)_2Cl_2^+$ is profitable. The lowest energy chloride to cobalt(III) charge-transfer transition in *cis*-$Co(en)_2Cl_2^+$ occurs[18] at about 256 nm, blue-shifted as expected from the analogous band in the trans isomer[19] (305 nm). A further blue shift of approximately one-tenth of an optical electronegativity unit[7,20] occurs with the superoxide complex (Figure 2). This reflects some small contribution of cobalt(II) character to the ground state of the superoxide complex.

Intense ligand absorption in the 300–400-nm region has made it difficult to identify $O_2^- \rightarrow Co(III)$ CT bands in the spectra of 1:1 cobalt(II)–dioxygen complexes containing π-conjugated nitrogen donors. Nevertheless, there is a shoulder near 320 nm in the spectrum of low-temperature-oxygenated vitamin B_{12}[21] and an extra peak in the Soret region of the MCD spectrum of oxygenated (dimethylmesoporphyrin IX ato)(pyridine)cobalt(II).[22] To equate these bands as charge transfer from bound superoxide would be premature; however, the possibility certainly warrants further study.

Acknowledgment. We are grateful to N. Dennis Chasteen of the University of New Hampshire for supplying Q-band EPR spectra as well as helpful discussion. Research at Texas A&M University was supported by Grant No. A-259 from the Robert A. Welch Foundation. G. McLendon (1974–1976) and S. R. Pickens (1976–1977) acknowledge Texas A&M University Health Fellowships. Research at the California Institute of Technology was supported by the National Science Foundation (Grant CHR 72-04989). This is Contribution No. 5630 from the Arthur Amos Noyes Laboratory.

Registry No. $[Co(s\text{-}Me_2en)_2Cl_2]$, 42590-61-4; $[Co(s\text{-}Me_2en)_2Br_2]$, 42590-63-6; $[Co(s\text{-}Me_2en)_2I_2]$, 42590-65-8; $[Co(s\text{-}Me_2en)_2(NO_3)_2]$, 42534-16-7; $[Co(s\text{-}Me_2en)_2(CH_3CN)(O_2)](NO_3)_2$, 66119-81-1; $[Co(s\text{-}Me_2en)_2(CH_3CN)(O_2)]Br_2$, 66119-79-7; $[Co(s\text{-}Me_2en)_2(MeOH)(O_2)](NO_3)_2$, 66119-78-6; $[Co(s\text{-}Me_2en)_2Cl(O_2)]Cl$, 66119-76-4; $[Co(s\text{-}Me_2en)_2(CH_3CN)(O_2)]I_2$, 66119-75-3.

References and Notes

(1) (a) Texas A&M University. (b) University of Rochester. (c) York University. (d) California Institute of Technology.
(2) (a) G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, **19**, 1 (1976); (b) J. M. Pratt, "Inorganic Chemistry of Vitamin B_{12}", Academic Press, London, 1972.
(3) D. A. White, A. J. Soldar, and M. Baizer, *Inorg. Chem.*, **11**, 2160 (1972).
(4) F. Basolo, J. A. Ibers, and B. M. Hoffman, *Acc. Chem. Res.*, **8**, 384 (1975).
(5) G. P. Khare, E. Lee Ruff, and A. B. P. Lever, *Can. J. Chem.*, **54**, 3424 (1976).
(6) A. B. P. Lever and E. Mantovani, *Can. J. Chem.*, **51**, 1567 (1973).
(7) A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968.
(8) R. G. Wilkins, *Adv. Chem. Ser.*, **No. 100**, 111 (1971).
(9) D. V. Stynes, H. C. Stynes, J. A. Ibers, and B. R. James, *J. Am. Chem. Soc.*, **95**, 1142 (1973).
(10) Q. H. Gibson, *Prog. Biophys. Biophys. Chem.*, **9**, 1 (1959).
(11) R. W. Noble, Q. H. Gibson, M. Brunori, E. Antonini, and J. Wyma, *J. Biol. Chem.*, **244**, 3905 (1973).
(12) G. McLendon and A. E. Martell, *J. Chem. Soc., Chem. Commun.*, 223 (1975).
(13) M. J. Carter, D. P. Rillema, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 392 (1974).
(14) A. B. P. Lever and E. Lee Ruff, to be submitted for publication.
(15) V. Miskowski, J. Robbins, I. Treitel, and H. B. Gray, *Inorg. Chem.*, **14**, 2318 (1975).
(16) A. B. P. Lever and H. B. Gray, *Acc. Chem. Res.*, in press.
(17) R. Marsh, M. Goldberg, A. B. P. Lever, and I. M. Walker, to be submitted for publication.
(18) J. Bolard and A. Garnier, *J. Chem. Phys.*, **66**, 1919 (1969).
(19) G. Chottard, *Chem. Phys. Lett.*, **23**, 443 (1973).
(20) C. K. Jorgensen, *Solid State Phys.*, **13**, 376 (1962).
(21) E. W. Abel, J. M. Pratt, R. Whelan, and P. J. Wilkinson, *J. Am. Chem. Soc.*, **96**, 7119 (1974).
(22) T. Nozawa, M. Hatano, H. Yamamoto, and T. Kwan, *Bioinorg. Chem.*, **5**, 267 (1976).

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

Stabilities of Metal Chelates of Imidazolyl-Containing Pentadentate Polyamines and Their Dioxygen Complexes[1a]

JAMES H. TIMMONS,[1b] WESLEY R. HARRIS, ICHIRO MURASE, and ARTHUR E. MARTELL*

Received December 9, 1977

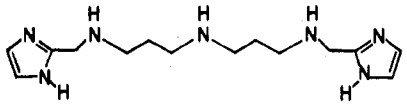
The synthesis of the new imidazolyl containing polyamines 1,9-bis(4-imidazolyl)-2,5,8-triazanonane (4-IMDIEN), 1,11-bis(4-imidazolyl)-2,6,10-triazaundecane (4-IMDPT), and 1,11-bis(2-imidazolyl)-2,6,10-triazaundecane (2-IMDPT) is described. Ligand protonation constants, the stability constants of the Co(II), Ni(II), Cu(II), and Zn(II) chelates, and the oxygenation constants ($K_{O_2} = [ML_2O_2]/[ML]^2[O_2]$) of the cobaltous chelates have been determined. The cobaltous chelates form stable oxygen complexes below pH 4, 5.5, and 5, respectively. Equilibrium data are compared with those of aliphatic polyamines and with those of the analogous pyridyl-containing ligands previously described. The imidazolyl ligands are found to be slightly more effective than their pyridyl analogues at coordinating molecular oxygen and are also more stable to irreversible oxidation to Co(III)-containing species. These results are discussed in terms of differences between pyridyl and imidazolyl donors. Differences in the equilibria of the isomeric IMDPT's are also discussed.

Introduction

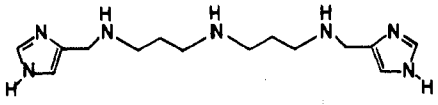
The reactions of metal chelate compounds, especially cobaltous chelates, with dioxygen have received considerable attention over the past few years, and recent reviews of the field are available.[2] In a recent paper,[3] the chelating tendencies of some pentadentate ligands with pyridyl donor groups and the oxygenation equilibria of the cobaltous complexes of these ligands were discussed. The present paper continues the investigation of pentadentate ligands having potential π-bonding donor groups with a discussion of the imidazolyl-containing ligands 1,9-bis(4-imidazolyl)-2,5,8-triazanonane (4-IMDIEN), 1,11-bis(4-imidazolyl)-2,6,10-triazaundecane (4-IMDPT), and 1,11-bis(2-imidazolyl)-2,6,10-triazaundecane (2-IMDPT), shown schematically (formulas I–III).

The imidazole group is of special interest due to the presence of histidine at the active site of the biological oxygen carriers hemoglobin and myoglobin. Thus, imidazole-containing ligands were used in model studies of biological oxygen carriers,[4,5] and the reactions of dioxygen with cobalt complexes of histidine and peptides containing histidine have been extensively studied.[2a,6] Gruenwedel[7] has already described a tetradentate ligand having two imidazolyl groups (BIMEDA), for which he determined the protonation constants and stability constants with several transition-metal cations. The oxygenation equilibrium for the cobaltous complex of this ligand, however, is complicated by

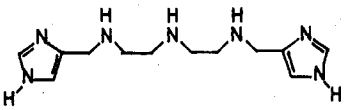
0020-1669/78/1317-2192$01.00/0



I 2-IMDPT



II 4-IMDPT



III 4-IMDIEN

a subsequent olation reaction which results in a μ-peroxo-μ-hydroxo-dibridged species.[8] This olation reaction is generally observed when less than five coordination sites of cobalt are chelated so that an aquated site is available after μ-peroxo bridge formation.[9,10] In such complexes the μ-hydroxo bridge seems to "lock in" the dioxygen bridge and shift the equilibrium in favor of dioxygen complex formation.[10] In the present study, this complication is avoided through the use of pentadentate ligands.

The present study is the first investigation of chelation by pentadentate imidazolyl-containing ligands. In addition, the structural similarity of these ligands to the pyridyl-containing ligands previously studied[3] allows a direct comparison of the effectiveness of these two groups. Cobaltous complexes containing these ligands have the interesting ability to complex dioxygen below pH 5. With aliphatic polyamines, amino acids, or peptides as ligands, competition by hydrogen ion for the basic coordination sites of the ligand normally prevent significant oxygenation below this pH.

Experimental Section

Synthesis. Preparation of 1,9-Bis(4-imidazolyl)-2,5,8-triazanonane Pentahydrochloride (4-IMDIEN·5HCl). Imidazole-4-carboxaldehyde (1.9 g, 0.020 mol) and diethylenetriamine (1.3 g, 0.010 mol) were dissolved in 50 mL of absolute alcohol, and the solution was heated on a water bath for 10 min. The mixture was then hydrogenated at room temperature over 0.80 g of 5% palladium on charcoal at slightly higher than 1 atm pressure. After the calculated amount of hydrogen was taken up, the catalyst was filtered, and the filtrate was saturated with dry hydrogen chloride until precipitation ceased. The white precipitate was filtered on cooling, washed with absolute alcohol, and dried over potassium hydroxide under vacuum. The crude hydrochloride of 4-IMDIEN was recrystallized three times from 95% methanol and dried at 100 °C under vacuum; mp 231–232 °C dec. Anal. Calcd for $C_{12}H_{21}N_7 \cdot 5HCl$: C, 32.33; H, 5.89; N, 22.00; Cl, 39.77. Found: C, 31.68; H, 5.88; N, 21.31; Cl, 39.76

Preparation of 1,11-Bis(4-imidazolyl)-2,6,10-triazaundecane Tetrahydrochloride (4-IMDPT·4HCl). Imidazole-4-carboxaldehyde (4.6 g, 0.048 mol) and 3,3′-diaminodipropylamine (3.0 g, 0.023 mol) were dissolved in 100 mL of absolute alcohol, and the solution was heated on a water bath for 10 min. The mixture was hydrogenated in the manner described for 4-IMDIEN. After treatment with dry hydrogen chloride, the crude hydrochloride of 4-IMDPT was dissolved in hot 80% methanol and precipiated by adding a large amount of absolute alcohol. The precipitate was recrystallized three times from 85% methanol and dried at 100 °C under vacuum; mp 248–250 °C dec. Anal. Calcd for $C_{14}H_{25}N_7 \cdot 4HCl$: C, 38.46; H, 6.69; N, 22.42; Cl, 32.43. Found: C, 38.23; H, 6.76; N, 22.53; Cl, 31.66

Preparation of 1,11-Bis(2-imidazolyl)-2,6,10-triazaundecane Trihydrochloride (2-IMDPT·3HCl). Imidazole-2-carboxaldehyde (3.8 g, 0.040 mol) and 3,3′-diaminodipropylamine (2.6 g, 0.020 mol) were dissolved in 200 mL of absolute ethanol, and the solution was heated on a water bath for 10 min. On cooling of the mixture the resulting compound was hydrogenated over 0.4 g of 10% palladium on charcoal at slightly higher than 1 atm pressure. The catalyst was filtered and the filtrate saturated with dry hydrogen chloride until no further precipitation occurred. The precipitate was filtered and dried over potassium hydroxide under vacuum. Thereafter, it was recrystallized three times from 75% ethanol to yield the pure hydrochloride of 2-IMDPT, which was dried under vacuum at 100 °C; mp 275 °C dec. Anal. Calcd for $C_{14}H_{25}N_7 \cdot 3HCl$: C, 41.95; H, 7.06; N, 24.47; Cl, 26.53. Found: C, 41.87; H, 7.16; N, 24.28; Cl, 26.53.

Table I. Ligand Protonation Constants for 4-IMDIEN, 4-IMDPT, and 2-IMDPT[a,b]

ligand	$\log K_H^1$	$\log K_H^2$	$\log K_H^3$	$\log K_H^4$	$\log K_H^5$
4-IMDIEN	9.22 (3)	8.18 (2)	4.91 (3)	3.90 (2)	2.92 (3)
4-IMDPT	10.12 (2)	8.62 (2)	7.36 (1)	4.51 (1)	3.82 (1)
2-IMDPT	9.76 (2)	7.22 (1)	6.51 (1)	3.92 (1)	3.29 (1)

[a] All values at 25 °C and $\mu = 0.100$ M (KNO_3). [b] Numbers in parentheses represent average deviation in least significant digit.

Reagents and Materials. Imidazole-4-carboxaldehyde was prepared according to the method of Pyman.[11] Imidazole-2-carboxaldehyde[12] was prepared by the oxidation of 2-hydroxymethylimidazole.[13,14] Standard base solution was prepared from "Dilute It" potassium hydroxide analytical concentrate by dilution under CO_2-free conditions and standardized against primary standard grade potassium hydrogen phthalate using phenolphthalein as indicator. A Gran's plot[15] showed that the base solution was indeed free of CO_2. Stock solutions of the metal ions were prepared from reagent grade nitrate salts and standardized by titration with EDTA using standard methods.[16]

Equilibrium Measurements. The ligand hydrochloride salts were titrated potentiometrically with standard potassium hydroxide solution and the $-\log [H^+]$ (pH) values were recorded after addition of each increment of base. Other titrations were performed on 1:1 molar ratios of the ligands with Cu^{2+}, Ni^{2+}, and Zn^{2+}. In all cases, the ligand was present at 2.50×10^{-3} M concentration. The potentiometric measurements were performed in a sealed, jacketed, glass cell equipped with glass and calomel electrodes using a Beckman Research Model pH meter standardized with dilute hydrochloric acid and sodium hydroxide solutions to read $-\log [H^+]$ rather than activity. Solutions were adjusted to 0.10 M ionic strength by addition of KNO_3 and maintained at 25.0 ± 0.05 °C. Titrations were carried out under an atmosphere of prepruified nitrogen which was passed through two alkaline pyrogallol scrubbers and bubbled through a 0.10 M KNO_3 solution. Those titrations by which oxygenation equilibria were measured were carried out under prepurified oxygen which was first passed through Ascarite to remove CO_2 and then bubbled through 0.10 M KNO_3. Standard acid was added to the titration vessel in order to obtain acid dissociation constants for those ligands which did not precipitate as pentahydrochlorides. The titrations were discontinued after somewhat over 5 a values, at a pH of 10–10.5.

Oxygenation equilibria were studied both by potentiometry and by oxygen uptake. Oxygen uptake measurements were made with a Yellow Springs Instruments biological oxygen meter. Ligand solutions were adjusted to the appropriate pH by the addition of either KOH or HCl. Several pH values were selected in order to obtain oxygen uptake varying from about 20% to about 90%. An amount of stock KNO_3 solution was added such that the final solution was 0.10 M in KNO_3, and this solution was saturated by a stream of Ascarite-scrubbed air. After the cell was closed, 1 equiv of cobaltous nitrate was pipetted into the cell and the percent oxygen saturation of the final solution was recorded. The pH of this solution was then measured using a Corning Model 12 research pH meter equipped with a combination semimicro electrode standardized as described above.

Results

Ligand Protonation Constants. The logarithms of the ligand protonation constants for the ligands studied are given in Table I. These constants, defined by $K_H^n = [H_nL]/[H^+][H_{n-1}L]$ for the general protonation equilibrium given (eq 1), were

$$H^+ + H_{n-1}L \overset{K_H^n}{\rightleftharpoons} H_nL \quad (1)$$

determined by measuring the pH of an aqueous solution of the ligand hydrochloride as a function of the moles of base added per mole of ligand. A slightly modified version of an iterative computer program previously described[17] was used to calculate the protonation constants from these data. In essence, the program assigns values of K_H^n for each deprotonation step from the pH at half-integral "a" values, where

the "*a*" value is the number of moles of KOH which have been added per mole of ligand in the solution. A new titration curve is then calculated on the basis of these assumed constants, and average deviations of the calculated titration curve from the actual curve are determined. These average deviations are used to select more accurate values for the protonation constants by a Newton–Raphson procedure, and iteration is continued until the average deviation of the calculated pH curve from the actual curve is minimized.

The order of protonation of the nitrogen donor groups of the ligand were determined by comparing the protonation constants with those of model compounds, since the order of placement of protons on the ligand cannot be unambiguously determined from first principles. If the first three protons are placed on the central nitrogen and the two imidazole nitrogens, as favored by electrostatic repulsion between the positively charged hydrogen ions, the third protonation constant would be expected to be close to that observed for substituted imidazoles such as 2-methylimidazole or 4-methylimidazole. If instead, the three aliphatic nitrogens were protonated, a possibility favored by the higher intrinsic basicity of these groups, the third protonation constant would be expected to be closer to the third protonation constant of diethylenetriamine or dipropylenetriamine in the case of 4-IMDIEN and 2- or 4-IMDPT, respectively. For 4-IMDIEN, the protonation constants indicate that the aliphatic nitrogens are protonated first, so that the order of protonation with decreasing pH is probably as follows: N_5; N_2 and N_8; N_2, N_5, and N_8; imidazolyl N; imidazolyl N.

The possibility that N_5 is protonated after one or both imidazoles cannot be eliminated since the log K_H^n's for these three groups are closely spaced. However, protonation of very similar pyridyl-containing ligands has been shown to occur first at the aliphatic nitrogens.[3] It should be noted that, although protonation of N_5 first is statistically favored, the first proton may occupy any of the three aliphatic nitrogens at a particular moment. The order of protonation cannot be determined unambiguously from first principles for the ligands 4-IMDPT or 2-IMDPT, but since these ligands have an additional methylene group between the aliphatic nitrogens, electrostatic repulsions between protonated nitrogen atoms would be reduced relative to 4-IMDIEN, and the order of protonation would be expected to be the same. The third protonation constant for 2-IMDPT is surprisingly low, as it is lower than the constants for either 2-methylimidazole or the third protonation constant of dipropylenetriamine.

Stabilities of Metal Chelates. A sample of the metal–ligand potentiometric equilibrium curves obtained is shown in Figure 1 for Ni(II), Cu(II), Zn(II), and Co(II). These curves are representative of the overlapping equilibria represented in eq 2 and 3. Where the value of K_{MHL}^{H} is known, the calculation

$$M + L \overset{K_{ML}}{\rightleftharpoons} ML \qquad K_{ML} = [ML]/[M][L] \tag{2}$$

$$ML + H \overset{K_{MHL}^{H}}{\rightleftharpoons} MHL \qquad K_{MHL}^{H} = [MHL]/[ML][H^+] \tag{3}$$

of K_{ML} is straightforward. The calculation involves simultaneous solution of four equations, those expressing total metal (T_M), total ligand (T_L), and total hydrogen ion concentrations (eq 4–6) and the defining equation for K_{ML} as given in eq 2.

$$T_L = A_1[L] + X_1[ML] \tag{4}$$

$$T_M = Y_1[M] + X_1[ML] \tag{5}$$

$$B = \frac{N_B V_B}{V_T} + [H^+] - [OH^-] = A_2[L] + X_2[ML] + Y_2[M] \tag{6}$$

The coefficients in these equations are the normal functions

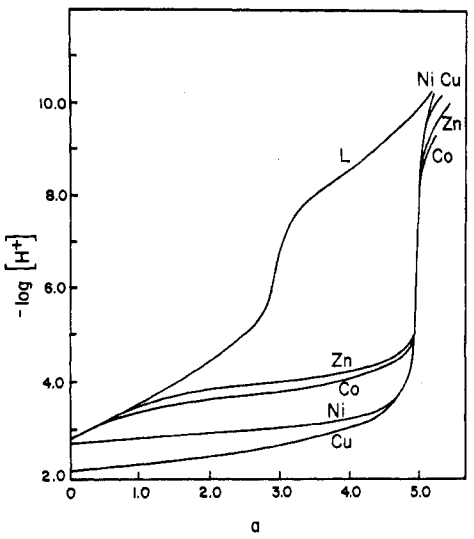


Figure 1. Potentiometric equilibrium curves for 1:1 ratios of 4-IMDIEN with Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. $T_L = T_M = 2.5 \times 10^{-3}$ M; $t = 25 \pm 0.05$ °C; $\mu = 0.100$ M (KNO_3). *a* is the number of equivalents of base added.

of ligand and chelate protonation and metal hydrolysis constants shown below in eq 7 through 12 (K_{MOH} = $[MOH^{(n-1)+}][H^+]/[M^{n+}]$). A previously described[3] computer program written by Dr. R. J. Motekaitis selects a value of log K_{MHL}^{H}, calculates a value of log K_{ML} on the basis of this constant, and then calculates a new potentiometric equilibrium curve using log K_{ML} and log K_{MHL}^{H} so determined. The value of log K_{MHL}^{H} is then varied to minimize the deviation of the calculated curve from the actual curve at experimentally determined points which are within ±2.0 pH units of the value of log K_{MHL}^{H} and which do not lie close to an inflection region of the potentiometric equilibrium curve.

$$A_1 = 1 + K_H^1[H^+] + K_H^1K_H^2[H^+]^2 + \ldots + K_H^1K_H^2K_H^3K_H^4K_H^5[H^+]^5 \tag{7}$$

$$A_2 = 5 + 4K_H^1[H^+] + 3K_H^1K_H^2[H^+]^2 + \ldots + K_H^1K_H^2K_H^3K_H^4K_H^5[H^+]^4 \tag{8}$$

$$X_1 = 1 + K_{MHL}^{H}[H^+] \tag{9}$$

$$X_2 = 5 + 4K_{MHL}^{H}[H^+] \tag{10}$$

$$Y_1 = 1 + K_{MOH}/[H^+] \tag{11}$$

$$Y_2 = K_{MOH}/[H^+] \tag{12}$$

Table II gives the logarithms of the chelate stability constants (K_{ML}) and the chelate protonation constants (K_{MHL}^{H}) for all metal–ligand combinations studied. In addition, values of 1,9-bis(2-pyridyl)-2,5,8-triazanonane (PYDIEN)[3] and *N*,*N*′-bis(4-methylimidazolyl)ethylenediamine (BIMEDA)[7] are given for comparison. For complexes where no value of log K_{MHL}^{H} is given, protonated chelates were not detected potentiometrically.

Oxygenation Equilibria. The oxygenation equilibria were studied by potentiometric and oxygen uptake methods for the cobaltous complexes of 2- and 4-IMDPT. Only oxygen uptake measurements were obtained for the cobaltous complex of 4-IMDIEN due to the long periods of time necessary for equilibration of this system. Values obtained by oxygen uptake are less accurate than those obtained potentiometrically due to limitations in the sensitivity of polarographic oxygen meters. However, agreement between the two methods was quite good where both methods were employed.

Figures 1 and 2 show the potentiometric equilibrium curves for the cobaltous complexes under an oxygen atmosphere. The

Table II. Stability and Protonation Constants for Co^{2+}, Zn^{2+}, Ni^{2+}, and Cu^{2+} Complexes of 4-IMDIEN, 4-IMDPT, 2-IMDPT, and Related Pyridyl-Containing Ligands[a,b]

ligand	equilibrium constant	Co^{2+}	Zn^{2+}	Ni^{2+}	Cu^{2+}
4-IMDIEN	$\log K_{ML}$	13.84 (1)	13.303 (4)	17.35 (1)	20.41 (2)
	$\log K_{MHL}{}^{H}$	3.3 (1)	2.69 (3)	2.005 (5)	3.35 (1)
4-IMDPT	$\log K_{ML}$	11.36 (1)	11.83 (1)	14.93 (1)	18.97 (1)
	$\log K_{MHL}{}^{H}$	3.99 (1)	4.52 (2)	3.23 (1)	3.62 (1)
2-IMDPT	$\log K_{ML}$	11.55 (3)	11.902 (3)	15.01 (1)	18.46 (2)
	$\log K_{MHL}$		3.0 (2)	2.59 (2)	2.93 (3)
PYDIEN	$\log K_{ML}$	14.73 (1)[c]	13.71 (1)[c]	19.2 (2)[c]	20.85 (11)[c]
	$\log K_{MHL}{}^{H}$	2.28 (1)[c]	1.83 (1)[c]		
PYDPT	$\log K_{ML}$	11.47 (1)[c]	11.18 (1)[c]	15.38 (2)[c]	18.85 (1)[c]
	$\log K_{MHL}{}^{H}$	4.42 (1)[c]	4.03 (1)[c]	3.35 (1)[c]	2.46 (2)[c]
BIMEDA	$\log K_{ML}$	11.43[d]	10.39[d]	14.02[d]	16.5[d]

[a] All values determined at 25 °C and $\mu = 0.100$ M (KNO_3). [b] Numbers in parentheses represent average deviation in least significant digit. [c] Values from ref 3. [d] Values from ref 7.

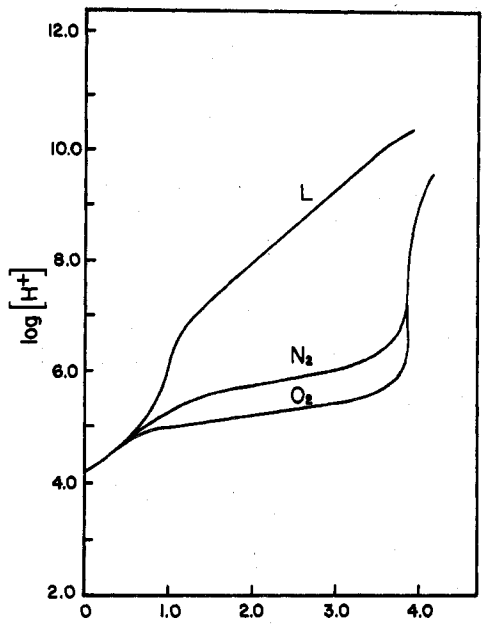


Figure 2. Potentiometric equilibrium curves for 4-IMDPT and for a 1:1 ratio of the ligand with Co^{2+} under N_2 and O_2. $T_L = T_M = 2.5 \times 10^{-3}$ M; $t = 25 \pm 0.05$ °C; $\mu = 0.100$ M (KNO_3). a is the number of equivalents of base added.

solutions employed exhibited the characteristic brown color of cobaltous oxygen complexes which results from a ligand to metal charge-transfer band beginning at the edge of the visible region and extending into the ultraviolet. Values beyond the final break in these titrations could not be accurately determined due to extremely slow equilibration at high pH. The cause of this slow equilibration has not been determined. The oxygenation equilibrium constants (K_{O_2}) were determined from these data by methods similar to those employed to determine protonation and stability constants, using a general purpose program which will be described in a future publication.

Determination of the oxygenation equilibrium constant from the oxygen uptake data requires the exact solution of four simultaneous equations, (13)–(16). The symbols employed

$$T_L = A_1[L] + X_1[ML] + 2[M_2L_2O_2] \quad (13)$$

$$T_M = Y_1[M] + X_1[ML] + 2[M_2L_2O_2] \quad (14)$$

$$0 = [ML] - K_{ML}[M][L] \quad (15)$$

$$[M_2L_2O_2] = 2.75 \times 10^{-4}(1 - \alpha) \quad (16)$$

have been previously defined, except that α is the fractional air saturation of the solution after formation of the oxygen complex. The quantity 2.75×10^{-4} is the molar concentration of oxygen in air-saturated 0.10 M KNO_3 solution at 25 °C.[19]

Table III. Equilibrium Constants for the Oxygenation of Cobaltous Chelates of 4-IMDIEN, 4-IMDPT, 2-IMDPT, PYDIEN, PYDPT, and tetren in Aqueous Solution[a]

ligand	$\log K_{O_2}$[b]		$\log K_{O_2}'$[c]	
	polarographic	potentiometric	polarographic	potentiometric
4-IMDIEN	12.6 (1)		40.3 (1)	
4-IMDPT	9.4 (1)	9.49 (3)	32.2 (1)	32.21 (3)
2-IMDPT	8.3 (1)	8.63 (1)	31.4 (1)	31.73 (1)
PYDIEN	11.4 (1)[d]		40.8 (1)[d]	
PYDPT	7.7 (2)[d]		30.6 (2)[d]	
tetren	15.83 (6)[d]		43.15 (6)[d]	

[a] All values determined at 25 °C and $\mu = 0.100$ M (KNO_3). [b] K_{O_2} defined by eq 17. [c] K_{O_2}' defined by eq 18. [d] Values from ref 3.

The values of $\log K_{O_2}$, where K_{O_2} is defined as in eq 17, are tabulated in Table III for the cobaltous chelates studied. In addition logarithms of the overall formation equilibrium constants for the oxygen complex ($\log K_{O_2}'$), where K_{O_2}' is defined as in eq 18, are given in the table. These two constants are related by eq 19.

$$K_{O_2} = \frac{[M_2L_2O_2]}{[ML]^2[O_2]} \quad (17)$$

$$K_{O_2}' = \frac{[M_2L_2O_2]}{[M]^2[L]^2[O_2]} \quad (18)$$

$$\log K_{O_2}' = 2 \log K_{ML} + \log K_{O_2} \quad (19)$$

Discussion

As previously noted, the three highest values of $\log K_H^n$ represent protonation of aliphatic amine groups while the two lowest values represent protonation of imidazolyl groups. The same order of protonation was found in the PYDIEN and 1,11-bis(2-pyridyl)-2,6,10-triazaundecane (PYDPT) systems.[3] An inductive effect of the imidazolyl groups lowers the first three protonation constants of 4-IMDIEN and 2- and 4-IMDPT below those of DIEN ($\log K_H^n = 9.84, 9.02, 4.23$) and dipropylenetriamine ($\log K_H^n = 10.65, 9.57, 7.72$), respectively.[18] The imidazolyl protonation constants are lower than the value for 4-methylimidazole ($\log K_H = 9.57$ at 0.16 M ionic strength)[18] due to electrostatic repulsion from the protonated aliphatic nitrogen groups. They are also lower than those of histamine ($\log K_H^n = 9.83, 6.07$) and isohistamine ($\log K_H^n = 9.27, 6.04$),[20] in which the protonated nitrogen is one carbon further removed; however, they are in the range expected from comparison with 4-aminomethylimidazole ($\log K_H^n = 9.24, 4.62$) and the tetradentate ligand BIMEDA[7] ($\log K_H^n = 9.05, 6.56, 4.26, 3.21$) which has two aliphatic and two imidazolyl nitrogens. The ligands show the expected increase in protonation constant on going from two-carbon to three-

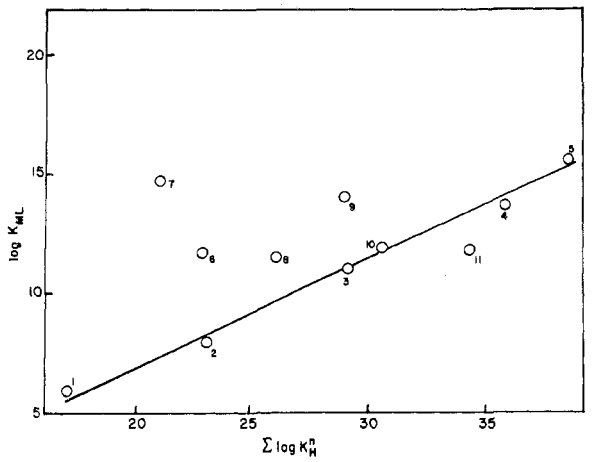
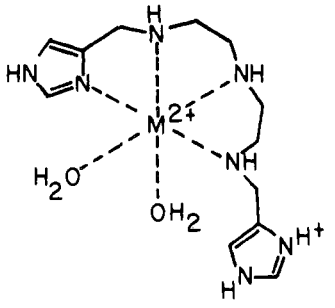


Figure 3. Plot of log K_{ML} vs. $\sum \log K_H^n$ for the complexes of Co^{2+} with the ligands en (1), dien (2), trien (3), tetren (4), penten (5), BIMEDA (*N*,*N*′-bis(4-imidazolylmethyl)ethylenediamine) (6), PYDIEN (7), PYDPT (8), 4-IMDIEN (9), 4-IMDPT (10), and 2-IMDPT (11).

carbon bridging groups. The chelate protonation constant (K_{MHL}^H) for all three complexes are consistent with complexes of the type shown by formula IV with one imidazolyl group



IV Protonated form of divalent metal chelate of 4-IMDIEN

protonated. There is no evidence for protonation of one of the more basic aliphatic amine groups as observed for PYDPT.

Previous reports indicate that pyridyl-containing ligands form transition-metal complexes which are more stable than would be expected on the basis of their weakly basic character, as measured by proton affinity. As indicated by the graph of the stability constant vs. $\sum \log K_H^n$ for chelates of various ligands with cobaltous ion (Figure 3), imidazolyl-containing ligands also have this enhanced stability but to a lesser degree. 4-IMDIEN lies significantly above the line formed by the aliphatic amines, showing that the complex is more stable than would be predicted from the total basicity of the ligand. 2- and 4-IMDPT, which should lie significantly below the line due to the reduced stability of the six-membered chelate rings, required by the extra bridging methylene groups in these ligands, lie very close to the line and somewhat below the line, respectively. The values for imidazolyl-containing ligands are not as high with respect to this "normal" line as are the values for pyridyl-containing ligands, demonstrating that the imidazolyl group is less effective than the pyridyl group at producing this additional stability; however, due to the higher basicity of imidazolyl compared to pyridyl donors, the two types of ligand give comparable chelate stability constants.

In the previous paper of this series,[3] possible reasons for the increased stability of transition-metal complexes of pyridyl-containing ligands were discussed; the analysis should apply equally to the imidazolyl-containing ligands. It seems unlikely that the effect is due to π bonding, since enhanced stability is observed for complexes of zinc(II), a d^{10} ion, which would not be expected to participate in π bonding. Another possible explanation is the entropic difference between chelation by an aliphatic amine and chelation by nitrogen bound in a heterocyclic ring. The aliphatic amine must sacrifice rotational freedom about the C–N bond in order to chelate a metal ion. Heterocyclic nitrogen has no rotational freedom about the C–N bonds, since both carbon and nitrogen are bound in the rather rigid geometry of the ring; therefore, no rotational freedom is lost on chelation of a metal ion, and chelation by heterocyclic nitrogen is thus favored on entropy considerations. Data for other complexes, however, indicate that the rotational restriction is insufficient to lead to a large increase in $\Delta S°$. Calorimetric studies are being performed in this laboratory to clarify this point.

It is also interesting to compare chelate stability constants for the isomers 2-IMDPT and 4-IMDPT. With the single exception of the cupric complexes, these constants are higher for the 2-isomer than for the 4-isomer. On the basis of protonation constants, complexes of 4-IMDPT would be expected to be more stable. Differences in entropy probably account for the discrepancy, as previously noted for histamine and isohistamine.[20] Since the imino hydrogen of the imidazole ring is quite labile, the two imidazolyl nitrogens of 2-IMDPT are sterically equivalent and formation of complexes with this ligand is favored statistically.

The cobaltous chelates of the imidazolyl-containing ligands are fairly exceptional in that oxygenation occurs at low pH; the oxygen complex of cobaltous 4-IMDIEN, for example, is completely formed at pH 4. This characteristic is shared only by the terpyridyl complexes studied by Huchital and Martell,[21,22] the dipyridyl and *o*-phenanthroline complexes of Bogucki et al.,[10] and the pyridyl-containing ligand complexes of Harris et al.[3] These complexes take up oxygen readily at low pH because the formation of the complexes is complete at low pH rather than because there is exceptionally strong bonding with molecular oxygen. Thus, the cobaltous complex of tetraethylenepentamine does not react with molecular oxygen until much higher pH values even though the oxygenation constant is higher for this complex than for any of the imidazolyl-containing ligands. The ligands employed in the present study give cobaltous complexes with somewhat higher oxygen affinities than the analogous pyridyl-containing ligands. This result is easily understood in terms of the greater basicity of imidazolyl nitrogen as compared to pyridyl nitrogen. Unfortunately, the contribution of π-bonding effects to the stability of these ligands cannot be accurately determined since few studies have been performed using pentacoordinate ligands which do not have potential π-bonding groups. Studies presently underway in this laboratory are aimed at synthesizing such ligands and determining their oxygenation constants.

Registry No. 4-IMDIEN·5HCl, 66750-73-0; 4-IMDPT·4HCl, 66750-74-1; 2-IMDPT·3HCl, 66750-75-2; imidazole-4-carboxaldehyde, 3034-50-2; imidazole-2-carboxaldehyde, 10111-08-7; diethylenetriamine, 111-40-0; 3,3′-diaminodipropylamine, 56-18-8; Co, 7440-48-4; Zn, 7440-66-6; Ni, 7440-02-0; Cu, 7440-50-8; O_2, 7782-44-7; 4-IMDIEN, 66750-76-3; 4-IMDPT, 66750-77-4; 2-IMDPT, 66750-78-5.

References and Notes

(1) (a) This work was supported by a research grant, A-259, from the Robert A. Welch Foundation. (b) Abstracted in part from a dissertation to be submitted by James H. Timmons to the faculty of Texas A&M University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.
(2) (a) G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, **19**, 1 (1976). (b) F. Basolo, B. M. Hoffman, and J. A. Ibers, *Acc. Chem. Res.*, **8**, 384 (1975).
(3) W. R. Harris, I. Murase, J. H. Timmons, and A. E. Martell, *Inorg. Chem.*, **17**, 889 (1978).
(4) C. K. Chang and T. C. Traylor, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 1166 (1975).

(5) J. P. Collman, R. R. Gagne, C. A. Reed, W. T. Robinson, and G. A. Rodley, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 1326 (1974).
(6) K. Watters and R. G. Wilkins, *Inorg. Chem.*, **13**, 752 (1974), and references therein.
(7) D. W. Gruenwedel, *Inorg. Chem.*, **7**, 495 (1968).
(8) A. Zuberbuhler, T. Kaden, and F. Koechlin, *Helv. Chim. Acta*, **54**, 1502 (1971).
(9) L. G. Stadther, R. Prados, and R. B. Martin, *Inorg. Chem.*, **12**, 1814 (1973).
(10) R. F. Bogucki, G. McLendon, and A. E. Martell, *J. Am. Chem. Soc.*, **98**, 3202 (1976).
(11) F. L. Pyman, *J. Chem. Soc.*, 190 (1916).
(12) H. Schubert and W. D. Rudorf, *Angew. Chem.*, **78**, 715 (1966).
(13) R. G. Jones, *J. Am. Chem. Soc.*, **71**, 383 (1949).
(14) P. E. Iverson and H. Lund, *Acta Chem. Scand.*, **20**, 2649 (1966).
(15) F. J. C. Rossotti and H. Rossotti, *J. Chem. Educ.*, **42**, 375 (1965).
(16) F. J. Welcher, "The Analytical Uses of Ethylenediaminetetraacetic Acid", Van Nostrand, Princeton, N.J., 1958.
(17) W. R. Harris, R. J. Motekaitis, and A. E. Martell, *Inorg. Chem.*, **14**, 974 (1975).
(18) R. M. Smith and A. E. Martell, "Critical Stability Constants: Amine", Vol. 2, Plenum Press, New York, N.Y., 1975.
(19) A. G. Loomis, "International Critical Tables of Numerical Data, Physics, Chemistry and Technology", Vol. III, E. W. Washburn et al., Ed., McGraw-Hill, New York, N.Y., 1928, p 257.
(20) W. J. Eilbeck, F. Holmes, and T. W. Thomas, *J. Chem. Soc. A*, 113 (1969).
(21) D. H. Huchital and A. E. Martell, *J. Chem. Soc., Chem. Commun.*, 868 (1973).
(22) D. H. Huchital and A. E. Martell, *Inorg. Chem.*, **13**, 2966 (1974).
(23) G. McLendon and A. E. Martell, *J. Chem. Soc., Chem. Commun.*, 223 (1975).

Contribution from the Department of Chemistry, University of Canterbury, Christchurch, New Zealand

Anionopentaaminecobalt(III) Complexes with Polyamine Ligands. 11. Synthesis, Characterization, and Reaction Kinetics of Some *cis*-Chlorobis(1,3-diaminopropane)(alkylamine)cobalt(III) Complexes

BARBARA M. OULAGHAN and DONALD A. HOUSE*

Received November 11, 1977

The *cis*-$CoCl(tmd)_2(A)^{2+}$ cation (A = NH_3, $MeNH_2$, $EtNH_2$, *n*-$PrNH_2$, *n*-$BuNH_2$, *i*-$BuNH_2$, and $BzNH_2$) is produced when *trans*-$[CoCl_2(tmd)_2](ClO_4)$, dissolved in dimethylacetamide (DMA), is reacted with aqueous, alcoholic, or DMA solutions of the amine. Tetrachlorozincate(II) and perchlorate salts have been isolated and characterized by analysis and ^{13}C NMR spectra. The cis configuration has been established by resolution of the complexes with A = $MeNH_2$ and $BzNH_2$. Rates of both acid and base hydrolysis are about 100 times faster than their bis(ethylenediamine) analogues due to a decrease of about 10 kJ mol^{-1} in the activation energies. The activation parameters for both reactions show the same trends with variation in A. Second-order rate constants for the Hg^{2+}-assisted aquation and Fe^{2+} reduction of this series of complexes have also been measured.

Introduction

Considerable reaction rate data have been accumulated for *cis*-$CoCl(en)_2(A)^{2+}$ complexes, where A is an aliphatic primary or aromatic heterocyclic tertiary amine.[1,2] However, the influence of the diamine on the kinetic parameters has not been investigated to any great extent.[1] In this paper, we describe the synthesis of some *cis*-$CoCl(tmd)_2(A)^{2+}$ (A = aliphatic primary amine) complexes.[3] We are thus able to study the influence of the six-membered chelate rings on the rates of acid and base hydrolysis for these chloropentaaminecobalt(III) systems. In addition, these complexes allow a comparison of the visible absorption and chiroptical parameters with their bis(ethylenediamine) analogues.

Experimental Section

The commercially available amines were used without further purification. Ammonia was used as an aqueous solution (ρ = 0.880), methylamine as a 40% aqueous solution, ethylamine as a 33% alcoholic solution, and the other amines as pure liquids. All other chemicals were AR or the best Reagent Grade available.

Caution! Although we have experienced no difficulties with the perchlorate salts of the complexes mentioned herein, these complexes should be treated as potentially explosive and handled with care.

***trans*-Dichlorobis(1,3-diaminopropane)cobalt(III) Perchlorate,[4] *trans*-$[CoCl_2(tmd)_2]ClO_4$.** A solution of 1,3-diaminopropane (62 g) in water (200 mL) was quickly added (over 1–2 min) to a solution of $CoCl_2 \cdot 6H_2O$ (100 g) in water (200 mL) which was stirred with a good stream of oxygen gas. A green precipitate formed but this slowly dissolved as the reaction proceeded and a dark brown solution was obtained after 1 h of oxygenation. Hydrochloric acid (150 mL, 12 M) and perchloric acid (50 mL, 72%) were separately added, and the solution was warmed on a steam bath for 10 min. Green crystals of the desired product deposited from the hot solution which was rapidly cooled to room temperature in ice before filtration. The product (60 g, 62%) was washed with 2-propanol and then ether and air-dried.

In certain cases, the mother liquor slowly deposited a mixture of green and red crystals, but the nature of this latter product has not yet been established.

***cis*-Chlorobis(1,3-diaminopropane)(amine)cobalt(III) Salts, *cis*-$[CoCl(tmd)_2(amine)]ZnCl_4$.** *trans*-$[CoCl_2(tmd)_2]ClO_4$ (10 g) was stirred into 40 mL of DMA to give a green solution. Amine, 1.5 times the theoretical amount, was added as quickly as possible. (The green starting material seems to recrystallize from the initial green solution after about 5 min at room temperature.) The color changed to violet and this color change was accelerated by heating. (Heating should not be excessive as most of the amines are low boiling liquids.) After overnight stirring at room temperature (17–20 h) the solution was filtered from a small amount of unreacted starting material and HCl (5 mL, 12 M), $ZnCl_2$ (15 g), and 2-propanol (80 mL) were successively added. The purple-red $ZnCl_4^{2-}$ salt (often contaminated with green starting material) usually crystallized within 30 min and was collected by filtration (8–12 g). One recrystallization from the minimum volume of 60 °C 0.1 M HCl (50–100 mL), with HCl (10 mL, 12 M) and $ZnCl_2$ (15 g) added after filtration of small traces of undissolved solid, gave 4.5–5 g of pure *cis*-$[CoCl(tmd)_2(amine)]ZnCl_4$. Tetrachlorozincate(II) salts for amine = $MeNH_2$, $EtNH_2$, *n*-$PrNH_2$, *n*-$BuNH_2$, and *i*-$BuNH_2$ were anhydrous while those of amine = NH_3 and $BzNH_2$ crystallized as monohydrates.

With amine = *i*-$PrNH_2$, *sec*-$BuNH_2$, and 3,5-dimethylpyridine, the reaction did not appear to take place, while with amine = cyclohexylamine, a favorable color change took place, but only unreacted starting material was recovered in the workup.

***cis*-$[CoCl(tmd)_2(amine)](ClO_4)_2$.** The appropriate tetrachlorozincate(II) salt (2 g) was dissolved in 20–40 mL of warm 0.1 M HCl. $HClO_4$ (5 mL, 72%) and $NaClO_4 \cdot H_2O$ (3 g) were added, and the solution was allowed to cool slowly to room temperature and then in ice. About 1–1.3 g (60–70%) of the diperchlorate salts was collected by filtration and washed with 2-propanol and then ether and air-dried.

0020-1669/78/1317-2197$01.00/0