Chelating Tendencies of Pyridyl-Containing Polyamines and Oxygenation of the Cobaltous Complexes[1]

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The synthesis of the new pyridyl-containing, pentadentate ligands 1,9-bis(2-pyridyl)-2,5,8-triazanonane (pydien), 1,11-bis(2-pyridyl)-2,6,10-triazaundecane (pydpt), and 2,6-bis(5-(1,4-diazahexyl))pyridine (epyden) is described. Acid dissociation constants, the stability constants of the Co(II), Ni(II), Cu(II), and Zn(II) chelates, and the oxygenation constants (K_{O_2} = $[MLO_2ML]/[ML]^2[O_2]$) of the cobaltous chelates have been determined. The cobalt(II) chelates are shown to be exceptionally effective at coordinating molecular oxygen at low pH. Electronic spectra of the cobalt(II) and nickel(II) chelates indicate that the ligands form high-spin octahedral complexes in aqueous solution.

Introduction

The interaction of molecular oxygen with cobaltous chelates has received much attention recently, and several reviews of the field are now available.[2,3] Most of the previous work involving aqueous solutions used aliphatic polyamines, amino acids, or peptides as ligands. It is characteristic of such systems that formation of the oxygen complex in appreciable amounts occurs only at pH 5 and above. This is generally due to strong competition by hydrogen ion for the basic coordinating sites on the ligand which prevents formation of the cobaltous chelates at lower pH. Recently Huchital and Martell[4,5] investigated mixed-ligand cobaltous complexes of terpyridine and either 1,10-phenanthroline or 2,2'-bipyridine. These complexes have the unusual ability to react with molecular oxygen at very low pH, with oxygenation virtually complete at pH 3. Subsequent studies on the bis(bipyridyl) and bis-(phenanthroline)cobalt complexes by Bogucki et al.[6] showed that these complexes form only about 6% of the dioxygen complex below pH 4.5. However, in these complexes only four coordination sites are chelated, and the presence of an aquated site in the oxygen complex permits an olation reaction, forming a μ-peroxo-μ-hydroxo-dibridged complex. It appears that the second bridge is necessary for the formation of stable oxygen complexes in these systems.[6] Since this olation reaction does not occur until the pH is raised to 7 and higher, these complexes do not mimic the low pH affinity for oxygen exhibited by the terpyridine mixed-ligand chelates.

This study deals with the new multidentate ligands 1,9-bis(2-pyridyl)-2,5,8-triazanonane (pydien), **1**, 1,11-bis(2-pyridyl)-2,6,10-triazaundecane (pydpt), **2**, and 2,6-bis(5-(1,4-diazahexyl))pyridine (epyden), **3**. The interaction of
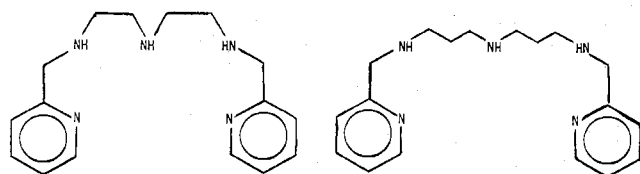
1 pydien   **2** pydpt
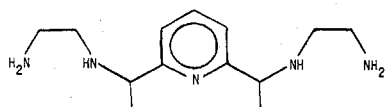
3 epyden

these ligands with a series of first-row transition metals has been investigated, and the equilibrium constants for the interaction of the cobaltous chelates with molecular oxygen have

been determined. The use of pentadentate ligands permits the study of oxygenation reactions without the complication of hydroxo bridging. There have been previous reports on the coordinating tendencies of other multidentate pyridyl ligands.[7,8] However, this is the first investigation of the new pentadentate ligands listed above and the only report on the oxygenation of cobaltous chelates of any multidentate pyridyl-containing polyamine in aqueous solution.[11]

Experimental Section

Reagents. 1,9-Bis(2-pyridyl)-2,5,8-triazanonane Trihydrochloride. Pyridine-2-carboxaldehyde (4.3 g, 0.01 mol) and diethylenetriamine (2.1 g, 0.02 mol) were dissolved in 70 mL of absolute alcohol and heated on a water bath for 10 min. The solution was then hydrogenated at room temperature over 1.5 g of 5% palladium on charcoal at slightly higher than 1 atm of hydrogen. After reaction of the calculated amount of hydrogen, the catalyst was filtered and the filtrate saturated with dry hydrogen chloride until no additional colorless precipitate formed. The precipitate was filtered on cooling, washed with absolute alcohol, and dried over KOH under vacuum. The crude trihydrochloride was recrystallized three times from 95% ethanol and dried at 100 °C under vacuum; mp 213–216 dec. Anal. Calcd for $C_{16}H_{23}N_5\cdot3HCl$: C, 48.67; H, 6.65; N, 17.74; Cl, 26.94. Found: C, 48.19; H, 6.56; N, 17.53; Cl, 27.15.

1,11-Bis(2-pyridyl)-2,6,10-triazaundecane Trihydrochloride. Pyridine-2-carboxaldehyde (6.5 g, 0.06 mol) and 1,5,9-triazanonane (3.9 g, 0.03 mol) were dissolved in 100 mL of absolute alcohol and heated in a water bath for 10 min. The solution was hydrogenated and the ligand isolated and purified as described above for pydien; mp 245 dec. Anal. Calcd for $C_{18}H_{27}N_5\cdot3HCl$: C, 51.12; H, 7.17; N, 16.56; Cl, 25.15. Found: C, 51.31; H, 6.88; N, 16.59; Cl, 25.11.

2,6-Bis(5-(1,4-diazahexyl))pyridine Tetrahydrochloride Monohydrate. 2,6-Diacetylpyridine (9 g, 0.055 mol) and N-acetylethylenediamine (12 g, 0.12 mol) were dissolved in 70 mL of dry benzene, and the solution was refluxed for 3 h in a flask equipped with a Deen starch trap. After about 2 mL of water had been collected, the solvent was distilled off under reduced pressure, and the residue was recrystallized from a 1:1 mixture of ethanol and acetone. The yield of pure Schiff base (mp 197 °C) was 70–80%. The Schiff base (5.0 g) was dissolved in 200 mL of absolute alcohol and hydrogenated over 0.50 g of 10% palladium on charcoal at slightly greater than 1 atm of hydrogen. After the reaction of a calculated amount of hydrogen, the catalyst was filtered off and the solvent was evaporated from the filtrate to yield a pale yellow oil. Without further purification, this oil was boiled overnight with 28 g of 20% hydrochloric acid, followed by the removal of solvent under reduced pressure. Addition of methanol to the resulting oily residue and evaporation of the solvent under reduced pressure were repeated to remove any excess hydrochloric acid. On treating with hot absolute alcohol, the residue solidified as a colorless hydrochloride salt, which was recrystallized three times from 95% ethanol and dried at 100 °C under vacuum; mp 152–153 dec. Anal. Calcd for $C_{13}H_{25}N_5\cdot4HCl\cdot H_2O$: C, 37.60; H, 7.54; N, 16.87; Cl, 34.15. Found: C, 37.82; H, 7.40; N, 17.01; Cl, 33.36.

Stock solutions of metal salts were prepared from reagent grade nitrates and standardized by titration with EDTA.
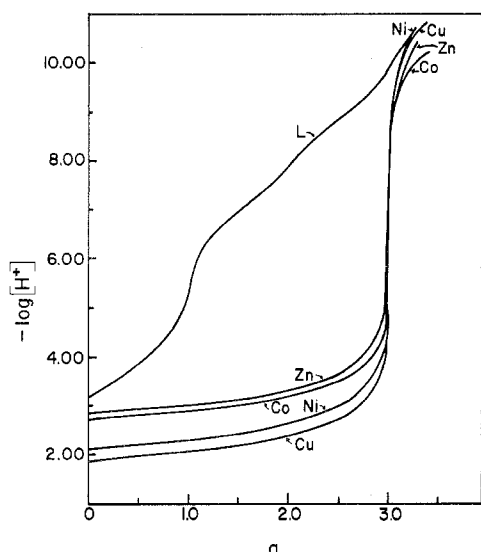
Figure 1. Potentiometric equilibrium curves for 1:1 ratios of pydien with Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. $T_L = T_M = 2.5 \times 10^{-3}$ M; $T = 25$ °C; $\mu = 0.100$ M (KNO_3).

Table I. Ligand Protonation Constants for pydien, pydpt, epyden, and tetren[a, b]

Ligand	$\log K_H^1$	$\log K_H^2$	$\log K_H^3$	$\log K_H^4$	$\log K_H^5$
pydien	8.88 (2)	7.04 (2)	3.82 (2)	1.44 (1)	
pydtp	9.92 (1)	7.63 (1)	6.76 (1)	1.79 (1)	
epyden	9.75 (1)	9.05 (1)	6.32 (1)	5.47 (1)	
tetren[c]	9.85 (3)	9.27 (3)	8.19 (3)	5.08 (2)	3.43 (5)

[a] All values determined at 25 °C and $\mu = 0.100$ M (KNO_3).
[b] Numbers in parentheses represent average deviations in least significant digits. [c] tetren = 1,4,7,10,13-pentaazatridecane.

Equilibrium Measurements. Potentiometric measurements were carried out 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 to read $-\log [H^+]$ rather than activity. Solutions were adjusted to 0.10 M ionic strength by the addition of KNO_3 and maintained at 25.0 ± 0.05 °C. All titrations were carried out using carbonate-free KOH under an atmosphere of prepurified nitrogen which was passed through two alkaline pyrogallol scrubbers and bubbled through a 0.10 M KNO_3 solution.

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. The required amount of KNO_3 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. One equivalent of cobaltous nitrate was pipetted into the cell and the percent O_2 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.

Visible spectra were recorded on a Cary 14 spectrophotometer using matched 1.000-cm cells. The spectra of the cobalt(II) complexes were measured using an anaerobic quartz cell. NMR spectra were recorded using a Varian T-60 NMR spectrometer.

Results

pydien. The potentiometric equilibrium curve for free pydien, **1**, is shown in Figure 1. Ligand protonation constants were calculated using a slightly modified version of an iterative computer program previously described.[9] The values of log K_H^n, defined as $K_H^n = [H_nL]/[H][H_{n-1}L]$, are given in Table I. The ligand was isolated as a trihydrochloride, but it is not intuitively obvious which three of the five basic groups are protonated. The higher intrinsic basicity of the aliphatic amino groups obviously favors protonation of the diethylenetriamine bridge. However, electrostatic repulsion favors the widest possible separation of charges, i.e., protonation of the pyridyl

Table II. NMR Chemical Shifts of pydien as a Function of the Degree of Protonation

	$\delta^{a,b}$		
	Ethyl-ene	Methyl-ene	Pyridyl
pydien	2.68 s	3.84 s	7.33 m, 7.80 m, 8.26 m
pydien·3HCl	3.90 s	4.50 s	7.66 m, 8.23 m, 8.76 m
pydien·5HCl	3.93 s	4.80 s	8.20 m, 8.83 m

[a] δ values in ppm downfield relative to 3-(trimethylsilyl)propanesulfonic acid. [b] s = singlet, m = multiplet.
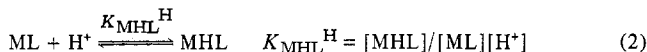
Table III. Stability and Chelate Protonation Constants for Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} Complexes of pydien, pydpt, epyden, and tetren[a, b]

Ligand	Equil Const	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
pydien	$\log K_{ML}$	14.73 (1)	19.2 (2)	20.85 (11)	13.71 (1)
	$\log K_{MHL}^H$	2.28 (1)			1.83 (1)
pydpt	$\log K_{ML}$	11.47 (1)	15.38 (2)	18.85 (1)	11.18 (1)
	$\log K_{MHL}^H$	4.42 (1)	3.35 (1)	2.46 (2)	4.03 (1)
epyden	$\log K_{ML}$	13.99 (1)	17.78 (1)	21.22 (2)	15.73 (1)
	$\log K_{MHL}^H$	4.35 (2)	3.50 (2)	4.95 (5)	2.74 (2)
tetren	$\log K_{ML}$	13.66 (1)	17.4[c]	22.8[c]	15.1[c]
	$\log K_{MHL}^H$	5.40 (5)	4.1[c]	5.2[c]	

[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 10.

groups and the central amino group. The NMR spectral parameters of pydien as the free base, trihydrochloride, and pentahydrochloride are listed in Table II. The significant shift in the methylenic protons of the diethylenetriamine moiety upon addition of the first 3 equiv of acid indicates protonation of the aliphatic amino groups. Although there is also a slight shift in the ring proton signal, the splitting pattern remains largely the same. However, in strongly acidic solution this splitting pattern is significantly altered, indicating protonation of the pyridyl nitrogens by the fourth and fifth equivalents of hydrogen ion. Thus it seems that the order of protonation of the basic groups of this ligand with decreasing pH is N5, N2 and N8, N2, N5 and N8, pyridyl N, pyridyl N.

The metal–ligand potentiometric equilibrium curves are shown in Figure 1. These curves generally represent the overlapping equilibria defined by eq 1 and 2.

$$M + L \overset{K_{ML}}{\rightleftharpoons} ML \qquad K_{ML} = [ML]/[M][L] \qquad (1)$$

$$ML + H^+ \overset{K_{MHL}^H}{\rightleftharpoons} MHL \qquad K_{MHL}^H = [MHL]/[ML][H^+] \qquad (2)$$

The formation constant K_{ML} can be easily calculated if the value of K_{MHL}^H is known. The constants listed in Table I were determined using a computer program written by Dr. R. J. Motekaitis which varies the value of K_{MHL}^H such as to minimize the differences between the observed and calculated pH values at every point in the potentiometric curve which is within ±2.0 pH units of the value of log K_{MHL}^H. The average deviation between calculated and observed pH values over the entire potentiometric curve was ±0.006 pH unit in most cases.

The interaction of pydien with copper and nickel ions is so strong that the complexes are virtually 100% formed prior to the addition of base and the calculation of log K_{ML} by the above method is impossible. For these two systems the formation constants were determined by spectrophotometric competition using EDTA as the competing ligand. The procedure has been previously described.[9] Since this method determines only the ratio of the formation constants of the unknown and standard ligand, it was necessary to use literature

Table IV. Equilibrium Constants for the Oxygenation of Cobaltous Chelates of pydien, pydpt, epyden, and tetren in Aqueous Solution[a]

Ligand	$\log K_{O_2}$ [b]	$\log K'_{O_2}$ [c]
pydien	11.4 (1)	40.8 (1)
pydpt	7.7 (2)	30.6 (2)
epyden	14.7 (1)	42.6 (1)
tetren	15.83 (6)	43.15 (6)

[a] All values determined at 25 °C and $\mu = 0.100$ M (KNO_3). [b] K_{O_2} defined by eq 7. [c] K'_{O_2} defined by eq 8.
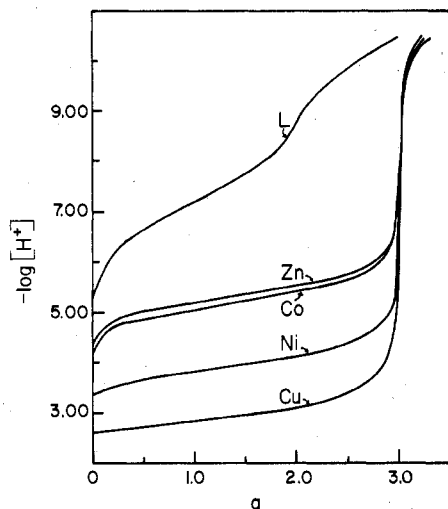
Figure 2. Potentiometric equilibrium curves for 1:1 ratios of pydpt with Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. $T_L = T_M = 2.5 \times 10^{-3}$ M; $T = 25$ °C; $\mu = 0.100$ M (KNO_3).

values of the EDTA complexes[10] to determine the absolute values of K_{ML} of the pydien complexes, which are listed in Table III.

The calculation of the oxygenation equilibrium constant is complicated somewhat by the overlap of the oxygenation and metal chelate formation equilibria. The oxygenation constant was determined by the simultaneous solution of eq 3-6. T_L

$$T_L = A_1[L] + X_1[ML] + 2[M_2L_2O_2] \tag{3}$$

$$T_M = Y_1[M] + X_1[ML] + 2[M_2L_2O_2] \tag{4}$$

$$O = [ML] - K_{ML}[M][L] \tag{5}$$

$$[M_2L_2O_2] = 2.75 \times 10^{-4}(1 - \alpha) \tag{6}$$

and T_M represent the analytical concentrations of ligand and metal, 2.75×10^{-4} is the molar concentration of oxygen in air-saturated 0.10 M KNO_3 solution at 25 °C,[11] α represents the fractional air saturation of the solution, and A_1 and X_1 are the normal protonation functions for the free ligand and the cobalt chelate. The oxygenation equilibrium may be written in two forms:

$$K_{O_2} = [M_2L_2O_2]/[ML]^2[O_2] \tag{7}$$

$$K'_{O_2} = [M_2L_2O_2]/[M]^2[L]^2[O_2] \tag{8}$$

Values of $\log K_{O_2}$ and $\log K'_{O_2}$ are listed in Table IV.

pydpt. The potentiometric equilibrium curves for free pydpt and the metal–ligand systems are shown in Figure 2. It is assumed that the protonation sites are analogous to those in pydien, since the electrostatic repulsion between the positive charges is reduced by the presence of an additional methylene group in each of the alkyl bridges of the dipropylenetriamine group. Equilibrium constants for the pydpt systems are listed in Tables I, III, and IV. In the oxygen-uptake experiments the initial rapid decrease in free-oxygen concentration due to
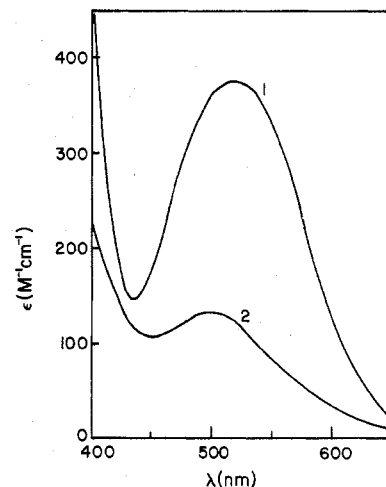
Figure 3. Room-temperature spectra of aqueous solutions of the product of the irreversible oxidation of the pydien–Co^{2+}–O_2 complex produced by either air oxidation (curve 2) or Cl_2 oxidation in HCl solution (curve 1).
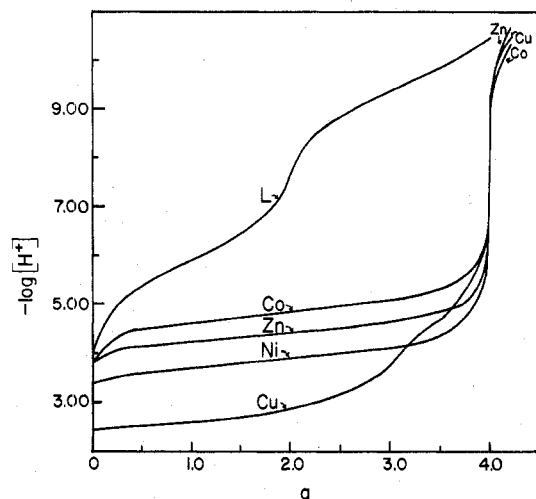
Figure 4. Potentiometric equilibrium curves of epyden with Co^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+}. $T_L = T_M = 2.5 \times 10^{-3}$; $T = 25$ °C; $\mu = 0.100$ M (KNO_3).

oxygen complex formation is followed by a slower continuous decrease in free oxygen. This would presumably indicate irreversible oxidation of the dioxygen complex to cobalt(III) chelates. Similar results have been observed in other systems.[12,13] This continuous change in oxygen concentration introduces some uncertainty into the value of the oxygenation constant for this system, as indicated by the larger value of the standard deviations in $\log K_{O_2}$ and $\log K'_{O_2}$. Solutions of the pydpt–cobalt–dioxygen complex also undergo a slow color change from dark green to reddish brown. However, as shown in Figure 3, the spectra of solutions obtained by slow aerial oxidation of the dioxygen complex are slightly different from those obtained by rapid chlorine oxidation in acidic solution. The precise number and nature of all the species present in this system have not yet been conclusively established.

epyden. The potentiometric equilibrium curves for the epyden systems are shown in Figure 4. Equilibrium constants were determined as described above and are listed in Tables I, III, and IV. In contrast to the pydien and pydpt systems, the dioxygen complex of epyden was stable to irreversible oxidation over the time period of the oxygen-upake experiments.

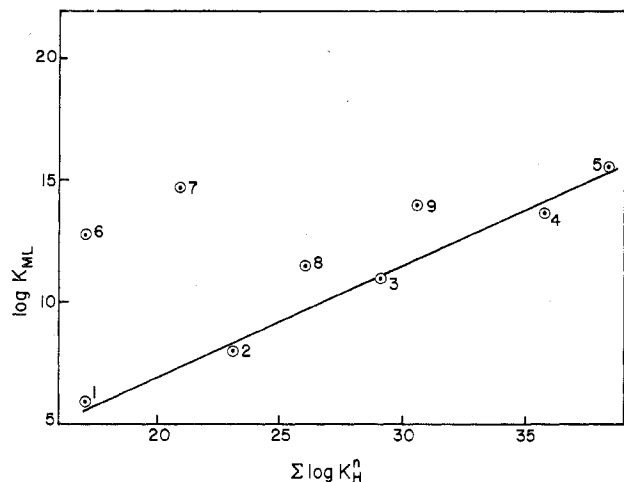The ligand protonation constants, cobalt(II) stability constants, and the oxygenation constant of tetren were also

Figure 5. 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), N,N'-bis(2-methylpyridyl)-1,2-diaminoethane (6), pydien (7), pydpt (8), and epyden (9).

Figure 6. Plot of log K_{ML} vs. $\sum$log $K_H{}^n$ for the complexes of Ni^{2+} with the ligands en (1), dien (2), trien (3), tetren (4), penten (5), N,N'-bis(2-methylpyridyl)-1,2-diaminoethane (6), pydien (7), pydpt (8), and epyden (9).

determined and are listed in Tables I, III, and IV. This ligand is of particular interest since it has the same number of donor groups and geometry as the pyridyl ligands but contains only aliphatic amino groups. Visible spectra were also recorded for cobalt(II) and nickel(II) complexes of some of these pentadentate ligands.

Discussion

Since the NMR data show that the initial protonation of pydien involves the three central amino groups, the three highest ligand protonation constants are comparable with those of dien (log $K_H{}^n$ = 9.84, 9.02, 4.23). However, the inductive effect of the two pyridyl groups of pydien lowers these constants by a considerable amount (log $K_H{}^n$ = 8.88, 7.04, 3.82). This effect was also observed in a previous study on other pyridyl-containing ligands.[7] The protonation constants of pydpt show the increase expected on going from two-carbon to three-carbon bridging groups.

The chelate protonation constants ($K_{MHL}{}^H$) of the pydpt complexes are higher than one would predict for the protonation of an uncoordinated pyridyl group. This is best illustrated by comparing the $K_{MHL}{}^H$ values of the cobalt complexes. The pydpt complex has a value intermediate between those of the epyden and tetren complexes and much higher than that of the pydien complex. Since the epyden and tetren values reflect protonation of a more basic aliphatic amino group, a comparable value for the pydpt complex may indicate a protonated chelate of the type shown by **4**, where

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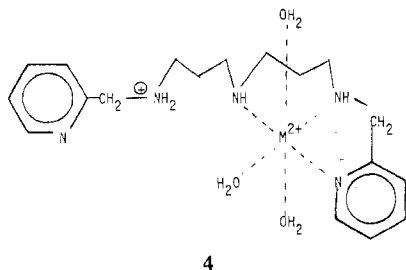
two potentially coordinating groups are dangling in solution. Such a structure would also explain why the chelate protonation constants are so much higher than the log value of 1.79 observed for the first protonation constant of a pyridyl group in the free ligand.

As pointed out in an earlier report on other pyridyl-containing ligands,[7] the stability constants of these types of complexes tend to be higher than one would predict on the
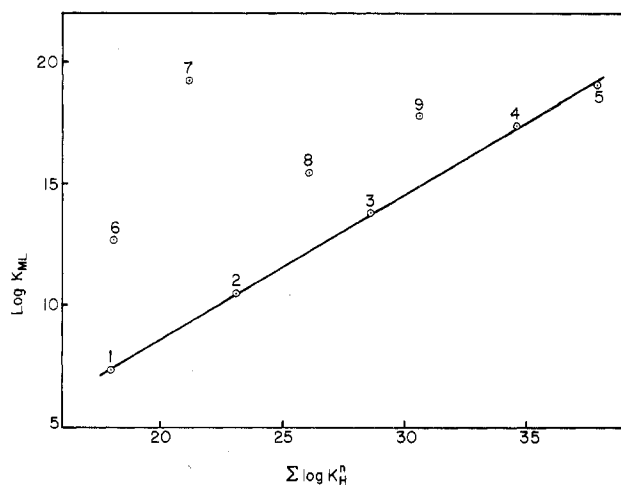

Figure 7. Plot of log K_{ML} vs. $\sum$log $K_H{}^n$ for the complexes of Zn^{2+} with the ligands en (1), dien (2), trien (3), tetren (4), penten (5), N,N'-bis(2-methylpyridyl)-1,2-diaminoethane (6), pydien (7), pydpt (8), and epyden (9).
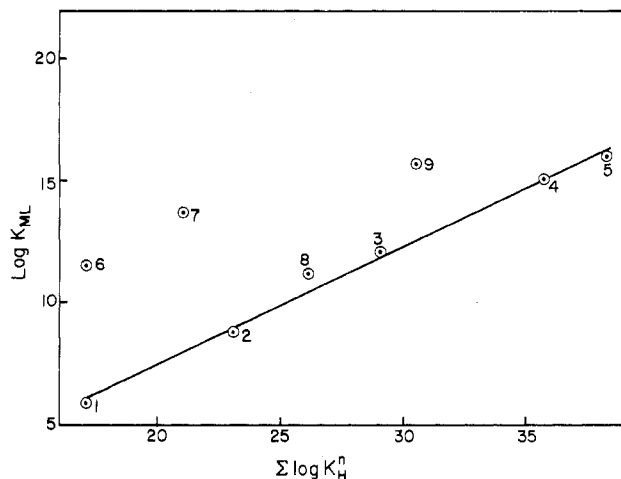
basis of the weak σ-donating ability of the pyridyl group, assuming that the ligand protonation constants reflect such ability. In the plots of $\sum$log $K_H{}^n$ vs. log K_{ML} for Co(II) and Ni(II), shown in Figures 5 and 6, respectively, a line is drawn through the points corresponding to the series of linear, aliphatic polyamine ligands en, dien, trien, tetren, and penten.[14] The four points corresponding to the pyridyl-containing ligands all lie above the line formed by the aliphatic ligands, indicating a higher affinity for metal ions relative to their affinity for protons. This enhanced stability is probably due to π bonding between the pyridyl π or π^* orbitals and the appropriate metal d orbitals. Since such an interaction is impossible between the ligands and protons, there is less effective competition from hydrogen ions for the basic coordinating groups of the ligands. This not only increases the value of K_{ML} but also permits the formation of such complexes at much lower pH than those at which complexes of normal, aliphatic polyamines are formed.

A plot of log K_{ML} vs. $\sum$log $K_H{}^n$ for the zinc complexes is shown in Figure 7. It is interesting that the points corresponding to pyridyl-containing ligands are almost as far above the line as are those of the nickel and cobalt complexes. Because of the d^{10} electronic configuration of the zinc(II) ion, one would expect the metal d orbitals to be too low in energy to overlap strongly with ligand orbitals. Therefore, it seems

Table V. Equilibrium Constants[a] for Complexes of Ethylenediamine (en), 2-Aminomethylpyridine (amp), and Mercaptoethylamine (mea)

	log K_{ML}		
	mea	amp	en
Co^{2+}	7.68	5.49	5.6
Ni^{2+}	10.05	7.18	7.32
Zn^{2+}	9.90	5.29	5.66
Cd^{2+}	10.97	4.67	5.41
Pb^{2+}	11.10		7.00

[a] Data from ref 10.

Table VI. $\Delta S°$ Values[a] of Complexation of Ethylenediamine (en), 2-Aminomethylpyridine (amp), 1,10-Phenanthroline (phen), and Bipyridine (bpy) with a Series of First-Row Transition-Metal Ions, Zinc, and Cadmium

	$\Delta S°$, eu			
	en	amp	bpy	phen
Mn^{2+}	3		0	7
Co^{2+}	4	0	-1	2
Ni^{2+}	4	-1	0	2
Cu^{2+}	6	10		
Zn^{2+}	4	3	0	4
Cd^{2+}	6	2	2	5

[a] Values from ref 10.

unlikely that the enhanced stability of the zinc complexes is due to strong π bonding.

It was initially suspected that a strong interaction of "soft" pyridyl groups with Zn^{2+} might be the result of the higher polarizability of the zinc ion. However, the stability constants for en, 2-aminomethylpyridine (amp), and mercaptoethylamine (mea), listed in Table V, do not support such an explanation. The constants of mea are exceptionally large for the ions Zn^{2+}, Cd^{2+}, and Pb^{2+}, indicative of the strong interaction expected between soft metals and soft ligands. However, unlike the mea constants, the amp values do not show any increase compared to the en complexes. In addition, the zinc constants of simple bidentate ligands such as bipyridine and 2-(4-imidazole)-pyridine are not exceptionally large.[8,15,16] This and the dissimilarity between the values for the mea and amp complexes suggest that there is not an extraordinarily strong bonding interaction between zinc(II) and the pyridyl nitrogen.

A second explantion considered for the high zinc constants is an entropy effect due to the diminished rotational freedom of a pyridyl group compared to a 2-aminoethyl group. Chelation involves a loss of rotational freedom for the ligating groups, which makes a negative contribution to the $\Delta S°$ of chelate formation. When the structure of the ligand results in an intrinsic barrier to free rotation, this negative entropy contribution is diminished, which results in a more positive value of $\Delta S°$. The simplest systems on which to test such an explanation is the series of bidentate ligands en, amp, bpy, and phen. If the decrease in rotational freedom of a pyridyl group is a major factor, one would expect the $\Delta S°$ values to decrease in the order phen > bpy > amp > en. However, as shown in Table VI, this is not the case and the $\Delta S°$ values of both amp and bpy are all lower than those of en. Thus it does not appear that there is sufficient rotational restriction to result in a large increase in $\Delta S°$ for complexation by pyridyl-containing ligands. There are insufficient calorimetric data currently available on complexation by multidentate ligands to determine what factors contribute to the enhanced stability of zinc complexes of polydentate pyridyl-containing ligands.

The ability to chelate metal ions in fairly acidic solutions has important consequences in relation to the oxygenation of the cobaltous chelates. Oxygen complexation occurs at lower pH than in the tetren system, and the pydien complex is exceptional in that oxygenation is complete at pH 2.5 in

air-saturated solutions. Only the mixed-ligand complexes of terpyridine studied by Huchital and Martell[4,5] are known to react with molecular oxygen at such low pH. This is not the result of an exceptionally strong interaction between the cobaltous chelates and molecular oxygen, since none of the pyridyl-containing complexes has an oxygenation constant as great as that of the tetren complex. Instead, it is the lower proton competition and consequent unusually high degree of chelate formation at low pH which result in appreciable equilibrium concentrations of the dioxygen complexes. Because of the high values of log K_{O_2}, the concentration of the polyamine complex does not have to be more than a few percent of the total cobalt concentration in order to observe oxygenation. It has been shown that for a series of dibridged oxygen complexes of amino acids and polyamines, the value of log K_{O_2} is linearly related to the sum of the ligand protonation constants.[17] Unfortunately, there are not yet enough data available to construct a similar graph for monobridged oxygen complexes. Thus it is difficult to establish what would be "normal" values of log K_{O_2} for the pyridyl-containing complexes in the absence of π-bonding effects. Although there does not appear to be an exceptional increase in the oxygen affinity of the cobaltous complexes of these types of ligands, it is impossible with the data presently available to evaluate the subtle effects that π bonding between the cobalt and the ligand may have on the oxygenation reaction.

Coordination by all five donor groups of these pentadentate ligands is clearly indicated by the magnitudes of the chelate protonation and formation constants. The values of log K_{ML} are too large to be due to coordination of only four donor groups. Therefore, only five- or six-coordinate configurations (with H_2O occupying the sixth coordination site) are reasonable for these complexes. The electronic spectra of the cobalt(II) complexes all have three bands, one at roughly 9000 cm^{-1} and two overlapping bands at $\sim 19\,000$ cm^{-1}, with molar absorptivities in the 5–20 M^{-1} cm^{-1} range. Both the band positions and low molar absorptivities are characteristic of high-spin octahedral cobalt(II) complexes. The spectra of the nickel(II) pydien and pydpt complexes were also recorded. Three bands are expected for octahedral, high-spin nickel complexes, but the highest energy band appears only as a shoulder on a more intense pydpt ligand band at $\sim 33\,300$ cm^{-1} and is totally obscured by ligand bands in the Ni(pydien) spectrum. In each case two other bands at $\sim 18\,000$ and $11\,000$ cm^{-1} with $\epsilon \sim 10$–20 M^{-1} cm^{-1} are observed. These energies and intensities are consistent with high-spin, octahedral nickel(II) complexes.

References and Notes

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Synthesis, Properties, and Structure of Iodosulfinate Salts

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A series of iodosulfinate salts, [X](ISO$_2$) where X is a large organo cation, have been synthesized and characterized by vapor pressure tensimetric and spectroscopic methods. The compounds have SO$_2$ dissociation pressures of 0.5–17 Torr at ambient temperature and dissociation enthalpies of 5–19 kcal/mol. An x-ray diffraction study of [PPh$_3$Bz](ISO$_2$) reveals a pyramidal ISO$_2$ anion with an I–S distance of 3.251 (3) Å and I–S–O angles of 102.1 (5) and 105.7 (4)°. Crystallographic data: space group P2$_1$/c, Z = 4, a = 10.92 (1) Å, b = 17.643 (9) Å, c = 15.49 (2) Å, β = 125.88 (7)°, R = 0.054 for 2079 diffractometric reflections with I $\geq$ 2σ(I).

Introduction

The halosulfinate anions, XSO$_2^-$, which form by the Lewis acid–base interaction of SO$_2$ and halide ions, are well-known moieties which contain reversibly bound sulfur dioxide.[1] In recent years, these anions have received some spectroscopic and thermodynamic study, particularly in solution.[2–8] Unfortunately, the variety of experimental conditions used in these studies makes quantitative evaluation of the actual complex strengths difficult. For example, it appears that the stability order of XSO$_2^-$ in solution is often I < Br < Cl < F, but the order may be altered by solvent changes.[6–8] The FSO$_2$ anion is the most stable halosulfinate in the solid state.[9,10] An approximate force constant treatment gave the S–X bond strength order as F > Cl < Br < I, consistent with observed shifts in electronic spectra of XSO$_2^-$ species.[8] An additional complication in earlier studies is the tendency for salts containing simple cations (such as alkali and alkaline earth metal ions) to be hygroscopic and to form highly solvated entities, e.g., KI·4SO$_2$.[7]

Although force constant calculations have been carried out on the FSO$_2^-$ and ISO$_2^-$ anions using assumed structural parameters, a structure determination has never been carried out for a simple halosulfinate ion.[8,10] The only directly relevant structures are for Pt(PPh$_3$)$_2$(CH$_3$)I·SO$_2$[11] and Cu$_2$-(PPh$_2$Me)$_4$I$_2$·SO$_2$[12] which contain SO$_2$ groups attached very weakly (I–S = 3.39–3.41 Å) to coordinated iodides.

During our study of substrates which bind SO$_2$ reversibly[12,13] and as part of a more comprehensive study of SO$_2$ coordination chemistry in general,[14–16] we discovered that large organo cations (such as [PPh$_3$Bz]$^+$ and [K(18-crown-6)]$^+$) afford easily handled, crystalline, 1:1 ISO$_2^-$ complexes. We decided to use the series to define more carefully certain physical properties of the ISO$_2^-$ anion. We report herein the syntheses and physical properties of a series of ISO$_2^-$ salts and an x-ray structure determination of a typical member of the series, [PPh$_3$Bz](ISO$_2$).

Experimental Section

Materials, Equipment, and Experimental Methods. Reagent grade solvents and chemicals were used without further purification. The sulfur dioxide used was 99.98% pure (Matheson). Phosphonium and arsonium salts were purchased from Strem Chemical and Pressure Chemical Co. and the crown ethers were purchased from Aldrich Chemical Co. Elemental analyses were performed by Galbraith Laboratories, Inc. Infrared and Raman spectra were recorded on Perkin-Elmer 521 and Cary 82 spectrometers, respectively.

Measurements of SO$_2$ Dissociation Pressures and Stoichiometries. To determine relative stabilities and stoichiometries of the various SO$_2$ adducts, the solid complex was placed in a glass tube which was then attached via an O-ring joint to a grease-free tensimeter or to a small evacuable manifold connected to a Validyne Engineering Corp. AP10 absolute pressure transducer (0–100 Torr). After careful pumping of the system at –63 °C, the dissociation pressure of the sample was monitored as a function of temperature and time. Similarly, SO$_2$:I ratios were determined by complete decomplexation of SO$_2$ at 70–120 °C and measurement of the SO$_2$ evolved using a calibrated portion of the vacuum system.

Preparation of the Iodosulfinate Compounds. The general procedure involved bubbling SO$_2$ through a warm solution of the appropriate iodide salt in acetonitrile solution, followed by addition of diethyl ether. Since the preparations differed only in detail, we present only representative preparations for salts containing phosphonium and crown ether complexed metal cations. The selenocyanate– and thiocyanate–SO$_2$ compounds were prepared similarly. Characterization data for the complexes are presented in Tables I and II.

[PPh$_3$Bz](ISO$_2$). Sulfur dioxide was bubbled through a warm solution of triphenylbenzylphosphonium iodide (1.00 g, 2.08 mmol) in 5 mL of warm acetonitrile, giving a bright orange-yellow solution. Diethyl ether (20 mL) saturated with sulfur dioxide was added dropwise and the resulting mixture was allowed to stand for 2 h at 0 °C. The bright yellow crystals which formed were collected on a frit, washed twice with 5-mL portions of SO$_2$-saturated diethyl ether, and dried under a stream of SO$_2$. Yield 1.05 g (93%).

[Rb(18-crown-6)](ISO$_2$). Rubidium iodide (2.12 g, 10 mmol) and 18-crown-6 (2.64 g, 10 mmol) were dissolved in 200 mL of warm acetonitrile. Sulfur dioxide was bubbled through the solution for several minutes and the volume of the resulting orange solution was reduced to 20 mL using a hot plate. Upon addition of 10 mL of SO$_2$-saturated diethyl ether, an orange crystalline product precipitated. The product was collected on a frit, washed twice with 10-mL portions of SO$_2$-saturated diethyl ether, and dried under a stream of SO$_2$. Yield 2.8 g (51%).

Collection and Reduction of the Crystallographic Data, Structure Solution, and Refinement for [PPh$_3$Bz](ISO$_2$). Unless otherwise noted, crystallographic procedures were as described in earlier publications from this laboratory.[15,17] Details of the data collection are given in Table III. A crystal was selected from the preparative batch described above and encased in a thin veneer of epoxy cement to inhibit loss