Inorg. Chem. **1982**, *21*, 1525–1529

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

Calorimetric Investigation of the Complexation of Metal Ions by Pentadentate Ligands Having Pyridyl and Imidazolyl Donor Groups and the Oxygenation of the Cobaltous Complexes[1]

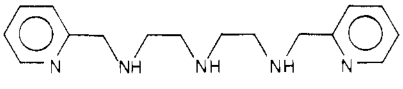
JAMES H. TIMMONS, ARTHUR E. MARTELL,* WESLEY R. HARRIS, and ICHIRO MURASE

Received February 25, 1981

Values of ΔG_{298}, ΔH_{298}, and ΔS_{298} are reported for the reactions of Cu^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+} ions with the pentadentate ligands 1,9-bis(2-pyridyl)-2,5,8-triazanonane (PYDIEN), 1,11-bis(2-pyridyl)-2,6,10-triazaundecane (PYDPT), 2,6-bis(5-(1,4-diazahexyl))pyridine (EPYDEN), 1,9-bis(4-imidazolyl)-2,5,8-triazanonane (4-IMDIEN), and 1,11-bis(4-imidazolyl)-2,6,10-triazaundecane (4-IMDPT). In general, the reactions exhibit significantly higher entropy changes than are observed for the reactions of metal ions with polyamines of similar basicity. The less favorable entropies of the polyamine ligand reactions are attributed to the greater loss of rotational freedom about the C–N bonds of the aliphatic bases on metal ion coordination; such rotational freedom does not exist for the aromatic nitrogen donor groups of pyridyl and imidazolyl ligands. The values of ΔH_{298} for the reactions of pyridyl donor ligands with Co^{2+}, Cu^{2+}, and Ni^{2+} are higher than one would predict on the basis of the weak σ-donating properties of the pyridyl nitrogens. The increases are partially attributed to π-bonding interactions between the pyridyl groups and the metal ions. The source of similar enthalpy increases for the reaction of pyridyl-containing ligands with Zn^{2+}, however, is uncertain. An assessment of the affect of chelate ring size on the values of ΔH and ΔS is also presented. Predictably, both enthalpies and entropies are more favorable for reactions that result in the formation of only five-membered chelate rings than for reactions in which both five- and six-membered chelate rings are formed. Values of ΔG_{298}, ΔH_{298}, and ΔS_{298} for the oxygenation of the cobaltous complexes of PYDIEN, PYDPT, 4-IMDIEN, 4-IMDPT, and EPYDEN are also reported. The previously reported correlation between the sum of the ligand pK's and the equilibrium constants (K_{O_2}) for oxygenation of the cobaltous complexes is shown to result from a combination of entropy and enthalpy terms. Both enthalpies and entropies of oxygenation of complexes having six-membered chelate rings are shown to be less negative (by 12–14 kcal/mol and 25–30 eu, respectively) than the values for analogous complexes having only five-membered chelate rings. Possible explanations for this behavior are discussed.

Introduction

The stability constants for complexes formed by the reaction of metal ions with ligands containing pyridyl donors tend to be higher than one would predict on the basis of the weak σ-donating ability of the pyridyl group,[2a] if it is assumed that the ligand protonation constants reflect this ability. The enhanced stabilities of these complexes are normally attributed to π bonding between the pyridyl π or π^* orbitals and appropriate metal d orbitals. As reported previously,[2b] the pyridyl-containing 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) form Cu^{2+}, Ni^{2+}, and Co^{2+} complexes with enhanced stabilities (compared with those of simple polyamines), as one would expect due to π bonding (Figure 1). The surprising result of the study was that Zn^{2+} complex stabilities are similarly enhanced for these ligands. Since Zn^{2+} has a d^{10} electronic configuration, the d orbitals are not likely to have high enough energies to strongly overlap with ligand orbitals. Thus, the concept of π bonding between Zn^{2+} and pyridyl groups cannot be seriously entertained. In a further study,[3] complexes of the metal ions Cu^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+} with the imidazolyl-containing ligands 1,9-bis(4-imidazolyl)-2,5,8-triazanonane (4-IMDIEN) and 1,11-bis(4-imidazolyl)-2,6,10-triazaundecane (4-IMDPT) were shown to have stabilities higher than those predicted on the basis of only the σ-donor strength of the imidazolyl groups (Figure 1). π-Bonding interactions between imidazolyl groups and divalent metal ions are expected to be rather weak, with all these metal ions, indicating that there may be other factors associated with the more rigid ring structures of these ligands.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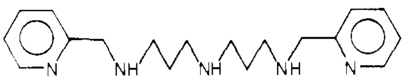
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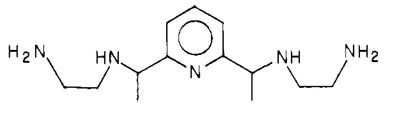
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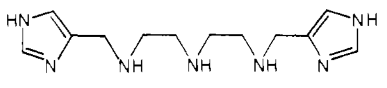
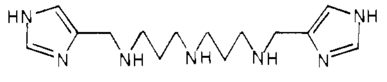

4-IMDIEN


4-IMDPT

Cobaltous complexes of the above pentadentate ligands react with dioxygen (O_2) to form μ-peroxo-bridged species. A correlation between the σ-donor strength of the ligand (as indicated by the sum of the ligand pK's ($\sum$pK_a's)) and the equilibrium constant (K_{O_2}) for oxygenation of the complex has been demonstrated.[4] π-Donor strength is apparently of little importance in determining the stability of binuclear (peroxo-bridged) dioxygen complexes since complexes of PYDIEN, 4-IMDIEN, and tetraethylenepentamine (tetren) all correlate equally well. However, the presence of six-membered chelate rings in the cobaltous complexes of PYDPT, 4-IMDPT, and 1,11-bis(2-imidazolyl)-2,6,10-triazaundecane (2-IMDPT) causes considerable reduction in K_{O_2} relative to that of dioxygen complexes having ligands of equivalent σ-donor strength. Structural studies of the cobaltous dioxygen com-

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(1) Abstracted in part from a dissertation 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) Lacoste, R. G.; Martell, A. E. *Inorg. Chem.* **1964**, *3*, 881. (b) Harris, W. R.; Murase, I.; Timmons, J. H.; Martell, A. E. *Inorg. Chem.* **1978**, *17*, 889.

(3) Timmons, J. H.; Harris, W. R.; Murase, I.; Martell, A. E. *Inorg. Chem.* **1978**, *17*, 2192.

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

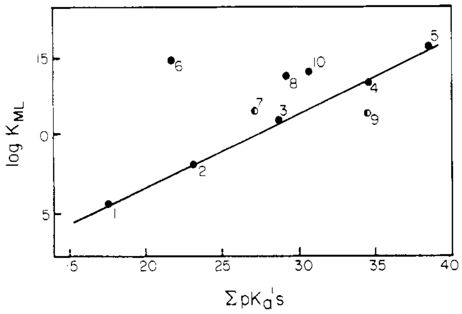

Figure 1. Graph of the Co(II) complex stability constant against the sum of the ligand pK_a's for linear polyamines and for pyridyl and imidazolyl amines. The graph indicates the additional stability which results from the presence of pyridyl or imidazolyl donors: 1 = en; 2 = dien; 3 = trien; 4 = tetren; 5 = penten; 6 = PYDIEN; 7 = PYDPT; 8 = 4-IMDIEN; 9 = 4-IMDPT; 10 = EPYDEN. Abbreviations are explained in ref 9. Values for linear polyamines are from ref 8. Half-filled circles indicate complexes containing six-membered chelate rings.

plexes of PYDIEN[5] and PYDPT[5,6] have been carried out in order to provide possible explanations for this phenomenon.

The present report describes a calorimetric study of the formation of Cu^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+} complexes of PYDIEN, PYDPT, 4-IMDIEN, 4-IMDPT, and EPYDEN and of the oxygenation of the cobaltous complexes of these ligands. The study was undertaken to investigate the extent of π bonding and the magnitudes of the entropic terms in the complexation reactions, to provide possible explanations for the stabilities of the Zn^{2+} complexes, and to investigate the nature of the effect of chelate ring size on the oxygenation of the cobaltous complexes.

Experimental Section

Materials. Solutions of Cu(II), Ni(II), Co(II), and Zn(II) were prepared from the corresponding nitrate salts and standardized by conventional methods.[7] Carbonate-free potassium hydroxide solution (Dilute-It) was purchased from J. T. Baker Chemical Co. The base was transfered to a serum bottle and sealed with a septum stopper. Thereafter, a calibrated micropipet fitted with a needle was used to transfer aliquots of the base solution as needed. Tetraethylenepentamine (tetren) was obtained as the hydrochloride salt and recrystallized twice prior to use.

Preparation of the Ligands. The ligands EPYDEN, PYDIEN, PYDPT, 4-IMDIEN, and 4-IMDPT were prepared by the methods described previously,[2b,3] which involve the formation of Schiff bases and subsequent hydrogenation with a palladium catalyst. EPYDEN formation required the condensation of 2 mol of ethylenediamine with 1 mol of 2,6-diacetylpyridine; the remaining ligands were prepared from diethylenetriamine or dipropylenetriamine and either 2-pyridinecarboxaldehyde of 4-imidazolecarboxaldehyde. The ligands were obtained and recrystallized as hydrochloride salts. Purity of these products was checked by potentiometric titration as well as by elemental analysis.

The ligands were employed as free bases in aqueous solution. The ligand solutions were prepared by adding the appropriate amounts of potassium hydroxide to solutions of the hydrochloride salts in a volumetric flask and adding potassium hydroxide for each equivalent of hydrochloride in the salt. The solutions were then diluted with carbonate-free distilled water, stoppered tightly, and mixed thoroughly to insure homogeneity.

Heats of Formation of Metal–Ligand Complexes. Cu^{2+}, Ni^{2+}, and Zn^{2+} Complexes. The heats of complex formation were determined calorimetrically with an LKB Produckter 8700-1 precision calorimetry system. An aliquot of the ligand solution containing approximately 0.10 mmol was sealed in a thin-walled glass ampule. An equivalent amount of metal solution was added to a glass cell containing a thermistor and a heating coil having a precisely known resistance. Potassium nitrate solution was added to give a total ionic strength of 0.10 M. Carbonate-free distilled water was then added so that the combined volume of liquid in the cell and in the ampule was 100 mL. The ampule was immersed in the metal ion solution, and the contents of the cell were stirred until equilibration with the calorimeter bath resulted in a solution temperature of 25 ± 0.05 °C (~12 h). The ampule was then shattered against a spindle. The change in solution temperature due to the subsequent complexation reaction was recorded as a change in the thermistor resistance.

After the reaction, the solution was allowed to return to 25.00 ± 0.05 °C. A calibration current of known amperage and duration was applied to the heating coil, and the change in thermistor resistance was recorded. The duration and amperage of the current were adjusted in order to reproduce the experimental heating curve as closely as possible.

The heat produced by the heating coil (Q_{calb}) was calculated from the known values of the heater resistance (R_h), the calibration current (I), and the duration of the calibration current (t), according to eq 1. The calorimeter constant (ϵ) was calculated from the heat of

$$Q_{\text{calb}} = \frac{R_h I^2 t}{4.1840} \tag{1}$$

calibration (Q_{calb}) and the change in thermistor resistance (ΔR) (eq 2). It was then possible to determine the heat of reaction (Q_{exptl})

$$\epsilon = Q_{\text{calb}}/(\Delta R/R) \tag{2}$$

from the calorimeter constant and the change in thermistor resistance due to complexation (eq 3). Division of the experimental heat by

$$Q_{\text{exptl}} = (\Delta R_{\text{exptl}}/R)\epsilon \tag{3}$$

the number of moles of metal–ligand complex formed gave an experimental ΔH. The experimental enthalpy was corrected for the heat of dilution of the ligand solution and the heat of breaking of the sample ampule. These heats were determined by breaking an ampule of the ligand solution into a 0.10 M KOH solution containing no transition-metal ions. The use of 0.10 M KOH instead of 0.10 M KNO_3 was necessary in order to avoid protonation of the basic amino nitrogens. The method employed also insured that the hydrochloride salts were completely neutralized, since neutralization of HCl by base would have resulted in a large enthalpy change. The corrections obtained were quite small in all cases, never exceeding ±0.2 kcal/mol. The heats of dilution of the metal ion solutions were also considered, but these proved to be negligible.

Previous studies[2b,3] demonstrated that all of the complexes investigated in this study are formed completely at pH values well below 7.0. Since the addition of the basic ligand solution to an essentially neutral metal salt solution results in a solution pH greater than 7.0, complete formation was assured in all cases. Use of pH buffers or measurement of the pH after each reaction was unnecessary, since no metal chelate hydrolysis occurs for these complexes[2b,3] in the pH range employed.

Cobalt(II) Complexes. In order to obtain values for ΔH for the formation of cobaltous complexes, it was necessary to employ a cell from which oxygen was completely excluded. A special cell was constructed, which allowed argon to be bubbled through the solution at a positive pressure to prevent back-diffusion of gas into the cell. During the course of 1 h prior to immersion of the can (containing the cell) in the calorimeter bath, argon was bubbled vigorously through the solution. The argon pressure was then reduced to achieve a slow steady flow, and the can was immersed for temperature equilibration. The gas was preequilibrated in an external bath and subsequently equilibrated in the calorimeter bath prior to being passed into the experimental solution. The remaining experimental details were handled as previously described.

Dioxygen Complexes. Heats of dioxygen complex formation were determined by a modification of the procedure described above for enthalpies of Co(II) complex formation, in which dioxygen replaced argon. The resulting enthalpy change consisted of the enthalpy for complex formation plus the enthalpy for oxygenation of the complex. The enthalpy for oxygenation was then determined from eq 4, with

$$Q_{\text{cor}} = \Delta H_{\text{ML}}(\text{mmol of ligand}) + \Delta H_{O_2}((\text{mmol of ligand})/2) \tag{4}$$

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(5) Timmons, J. H.; Niswander, R. H.; Clearfield, A.; Martell, A. E. *Inorg. Chem.* **1979**, *18*, 2977.

(6) Timmons, J. H.; Clearfield, A.; Martell, A. E.; Niswander, R. H. *Inorg. Chem.* **1979**, *18*, 1042.

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

Table I. Thermodynamic Constants for Complexation of Cu^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+} by the Ligands 4-IMDIEN, 4-IMDPT, PYDIEN, PYDPT, tetren, and EPYDEN[a,b]

ligand	metal ion	ΔG_{298}, kcal/mol	ΔH_{298}, kcal/mol	$T(\Delta S_{298})$, kcal/mol	ΔS_{298}, eu
4-IMDIEN	Cu^{2+}	−27.84 (3)	−21.3 (1)	6.5 (1)	22
	Ni^{2+}	−23.66 (2)	−18.0 (1)	5.7 (1)	19
	Co^{2+}	−18.88 (2)	−13.2 (2)	5.7 (2)	19
	Zn^{2+}	−18.14 (1)	−10.2 (1)	8.0 (1)	27
4-IMDPT	Cu^{2+}	−25.88 (2)	−20.2 (1)	5.7 (1)	19
	Ni^{2+}	−20.36 (2)	−16.4 (1)	4.0 (1)	13
	Co^{2+}	−15.50 (2)	−9.2 (2)	6.3 (2)	21
	Zn^{2+}	−16.14 (2)	−9.9 (1)	6.2 (1)	21
PYDIEN	Cu^{2+}	−28.4 (2)	−22.3 (2)	6.1 (3)	21
	Ni^{2+}	−26.2 (3)	−20.2 (1)	6.0 (3)	20
	Co^{2+}	−20.09 (2)	−15.4 (2)	4.7 (2)	16
	Zn^{2+}	−18.70 (2)	−13.0 (1)	5.7 (1)	19
PYDPT	Cu^{2+}	−25.71 (2)	−21.2 (2)	4.5 (2)	15
	Ni^{2+}	−20.98 (3)	−18.1 (2)	2.9 (2)	10
	Co^{2-}	−15.65 (2)	−13.1 (2)	2.5 (2)	9
	Zn^{2+}	−15.25 (2)	−9.7 (1)	5.6 (1)	19
tetren	Cu^{2+}	−31.09	−25	5.96	20
	Ni^{2+}	−23.72	−18.9	4.77	16
	Co^{2+}	−18.13	−13.9	4.17	14
	Zn^{2+}	−20.59	−13.9	6.56	22
EPYDEN	Cu^{2+}	−28.94 (3)	−21.6 (1)	7.4 (1)	25
	Ni^{2+}	−24.25 (2)	−16.5 (1)	7.8 (1)	26
	Co^{2+}	−19.08 (2)	−12.1 (2)	7.0 (2)	24
	Zn^{2+}	−21.46 (2)	−13.9 (2)	7.6 (2)	25

[a] All values obtained at 25 °C and $\mu = 0.10$ M (KNO_3).
[b] Numbers in parentheses represent average deviation in the least significant figure. Those for ΔG_{298} were obtained from the reported deviations in log K_{ML}.[2b,3] Those for $T(\Delta S_{298})$ reflect the limiting error in the ΔG_{298} and ΔH_{298} values from which the values of $T(\Delta S_{298})$ were calculated. The absolute errors in ΔH_{298} are estimated to be ±0.3 kcal/mol, and the absolute errors in ΔS_{298} are estimated as ±1 eu.

use of the previously determined enthalpy for cobaltous complex formation. The amount of dioxygen in solution was always greater than that required to completely oxygenate the complex. The rate of flow of dioxygen into the cell was sufficiently slow that a negligible amount of heat was generated by dissolution of dioxygen in water over the time scale of the experiment. All of the oxygen complexes studied were fully formed at pH values well below 7.0,[2b,3] so that complete oxygenation of the complexes was assured.

Calculation of ΔG and ΔS. Equation 5 was used to calculate values

$$\Delta G = -RT \ln K_{ML} = -1.364 \log K_{ML} \qquad (5)$$

of ΔG_{298} from stability constants for chelate formation (K_{ML}) reported previously.[2b,3] Values of ΔS_{298} were obtained by substituting the values of ΔG_{298} and the calorimetrically determined values of ΔH_{298} into eq 6.

$$\Delta S = (\Delta H - \Delta G)/T = 3.36(-1.364 \log K + \Delta H) \qquad (6)$$

Results

Chelate Formation Reactions. Enthalpies of complex formation for each ligand/metal ion combination are given in Table I. Enthalpies for complex formation are plotted against ligand basicity (expressed as $\sum \log K_H{}^n$) in Figure 2. Comparable values[8] for a series of aliphatic polyamine ligands are also plotted. In each plot, a straight line can be drawn through the points corresponding to aliphatic polyamine ligands; this line should indicate the enthalpies to be expected for ligands with normal geometries that participate in only σ-bonding interactions with the metal ion. The values for the pyridyl amines tend to lie above this line, indicating a bonding contribution other than σ-bonding (values for complexes containing six-membered chelate rings are of course lower than those for complexes containing only five-membered chelate rings).

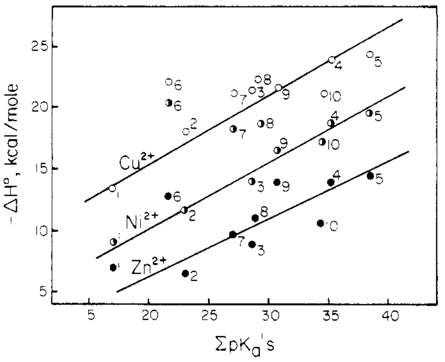

Figure 2. Plot of enthalpies for complex formation against the sum of the ligand pK_a's for linear polyamines and the ligands of this study (open circles = Cu(II), half-open circles = Ni(II), filled circles = Zn(II)). Data for polyamines are from ref 8.

Table II. Thermodynamic Constants for Oxygenation of Cobaltous Complexes of 4-IMDIEN, 4-IMDPT, PYDIEN, PYDPT, and EPYDEN

ligand	ΔG_{298}, kcal/mol	ΔH_{298}, kcal/mol	$T(\Delta S_{298})$, kcal/mol	ΔS_{298}, eu
4-IMDIEN	−17.2 (2)	−33.0 (3)	−15.8 (3)	−53
4-IMDPT	−12.8 (2)	−20.1 (3)	−7.3 (3)	−24
PYDIEN	−15.5 (2)	−32.6 (5)	−17.1 (5)	−57
PYDPT	−10.5 (3)	−19.7 (3)	−9.2 (4)	−31
EPYDEN	−20.1 (2)	−34.2 (3)	−14.1 (3)	−47

Values for ΔG_{298}, calculated from the values of log K_{ML} given in ref 2b and 3, and values of ΔS_{298} and $T(\Delta S_{298})$ are also listed in Table I. Values in parentheses represent average deviations for successive measurements and are not intended to indicate absolute errors. Deviations in ΔG_{298} are based on deviations in the reported values of log K_{ML}.

Dioxygen Complex Formation. Table II contains values of ΔG_{298}, ΔH_{298}, ΔS_{298}, and $T(\Delta S_{298})$ for the formation of dioxygen complexes from preformed cobaltous complexes. ΔH is less favorable for the complexes containing six-membered chelate rings than for those containing only five-membered chelate rings. ΔS, however, is more favorable for the six-membered ring complexes. Both ΔH and ΔS appear to be linearly correlated with $\sum pK_a$'s of the ligand, but this cannot be stated with any degree of certainty given the small number of complexes for which data are available.

Discussion

Metal-Ligand Complex Formation. In a previously published paper,[2b] possible reasons for the increased stability of transition-metal complexes of pyridyl-containing ligands were discussed: the analysis given should apply equally to the imidazolyl-containing ligands. That the elevated values of log K_{ML} are not limited to the ligands of this study is apparent from plots of log K_{ML} against $\sum pK_a$ for Ni(II) chelates of a variety of pyridyl amines and of a number of imidazolyl amines (Figure 3). π-Bonding effects alone do not appear to offer sufficient explanation for the observations in Figures 1 and 3, since enhanced stability is also observed for complexes of zinc(II) (Figure 4), a d^{10} ion, which would not be expected to participate in π bonding. Other possible explanations are

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(8) Smith, R. M., Martell, A. E., Eds. "Critical Stability Constants"; Plenum Press: New York, 1975; Vol. 2; Supplement No. 1, Vol. 5, in press.

(9) Abbreviations: en = ethylenediamine, dien = diethylenetriamine, trien = triethylenetetramine, penten = pentaethylenehexamine.

(10) Abbreviations: amp = 2-(aminomethyl)pyridine, mamp = 2-[(methylamino)methyl]pyridine, pyam = iminobis(methylene-2-pyridine), tpa = nitrilotris(methylene-2-pyridine), $(pyam)_2py$ = pyridine-2,6-bis((methylenimino)methylene-2-pyridine), pyen = ethylenebis(aminomethylene-2-pyridine), tpen = ethylenedinitrilotetrakis(methylene-2-pyridine).

(11) Im = imidazole, imam = 4-(aminomethyl)imidazole, bimeda = 1,6-bis(4-imidazolyl)-2,5-diazahexane.

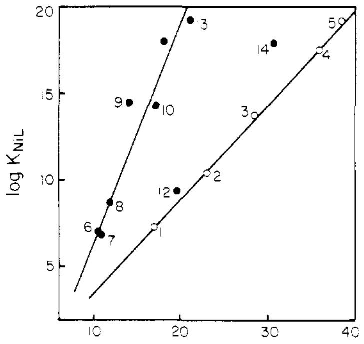

Figure 3. Linear correlation of Ni(II) chelate stability constants with the sum of the ligand pK_a's for amines and pyridyl amines: 1 = en; 2 = dien; 3 = trien; 4 = tetren; 5 = penten; 6 = amp; 7 = mamp; 8 = pyam; 9 = tpa; 10 = pyen; 11 = tpen; 12 = *N*-(pyridylmethyl)ethylenediamine; 13 = PYDIEN; 14 = EPYDEN. Note that as the ratio of aliphatic amines to pyridyl groups increases past 1.0, the points move toward the amine line. Abbreviations are explained in ref 9 and 10.

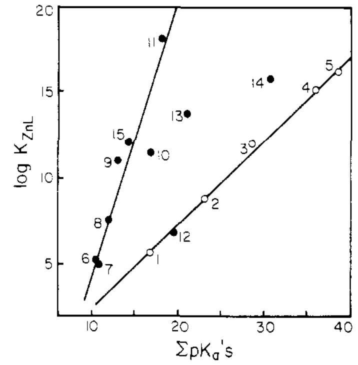

Figure 4. Linear correlation of Zn(II) chelate stability constants with the sum of the ligand pK_a's for amines and pyridyl amines: 1 = en; 2 = dien; 3 = trien; 4 = tetren; 5 = penten; 6 = amp; 7 = mamp; 8 = pyam; 9 = tpa; 10 = pyen; 11 = tpen; 12 = *N*-(pyridylmethyl)ethylenediamine; 13 = PYDIEN; 14 = EPYDEN; 15 = $(pyam)_2py$. Note that as the ratio of aliphatic amines to pyridyl groups increases past 1.0, the points move toward the amine line. Abbreviations are explained in ref 9 and 10.

the entropic and enthalpic differences between chelation by an aliphatic amine and chelation by nitrogen bound in a more rigid heterocyclic ring. The aliphatic amine must sacrifice rotational freedom about the C–N bonds in order to chelate a metal ion. Heterocyclic nitrogen donors have no rotational freedom about the C–N bonds, since both the nitrogen and adjacent carbon atoms are found in the rigid geometry of the aromatic rings; therefore, no rotational freedom is lost on chelation of an aromatic nitrogen with a metal ion, and chelation by heterocyclic nitrogen is thus favored on entropy considerations. The heterocyclic donor groups may also affect the ring strain that results from chelate ring formation. Calorimetric studies of complexation by these ligands were performed in part to provide a better understanding of these phenomena.

The data shown in Figure 2 clearly demonstrate that there is an enthalpic component in the enhanced stability of the complexes of pyridyl ligands, especially the nickel(II) complexes. A portion of this favorable enthalpy probably results from metal–ligand π bonding. This is consistent with the exceptional enhancement of ΔH for the nickel(II)–PYDIEN complex (~9.5 kcal/mol) relative to those of the more weakly π-bonding copper(II) and zinc(II) ions (~6 kcal/mol).

Since Zn^{2+} cannot π bond to pyridine at all, the enhancement of ΔH for the zinc complexes must reflect some factor other than π bonding. The formation of chelate rings involves a considerable amount of strain, which usually manifests itself in bond angle distortion and torsional strain.[12-15] Total strain energies have been calculated[13,14] for Co^{3+}(trien)(prolinate$^-$) and Co^{3+}(pypn)(oxalate^{2-}) (trien = triethylenetetramine; pypn = *N*,*N'*-bis(2-pyridylmethyl)-1,2-propanediamine). The complex of the purely aliphatic amine has a strain energy that is ~13 kcal/mol higher than that of the pyridyl-containing complex. The contribution of the prolinate groups was unspecified, but that of the oxalate group was only 3 kcal/mol. Thus it seems that the large difference in total strain energies must also reflect a lower ring strain for the pyridyl-containing complex, and this lower ring strain may contribute to the larger ΔH values for the zinc complexes of pyridyl-containing ligands.

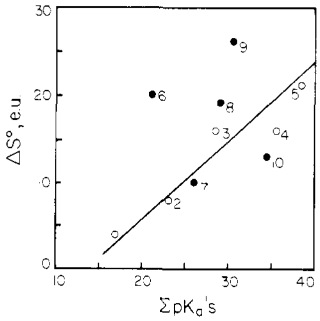

Figure 5. Plot of entropies of nickel(II) chelate formation against the sums of the ligand protonation constants for linear polyamines and the ligands of this study: 1 = en; 2 = dien; 3 = trien; 4 = tetren; 5 = penten; 6 = PYDIEN; 7 = PYDPT; 8 = 4-IMDIEN; 9 = EPYDEN; 10 = 4-IMDPT. Abbreviations are explained in ref 9. Data for polyamines are from ref 8.

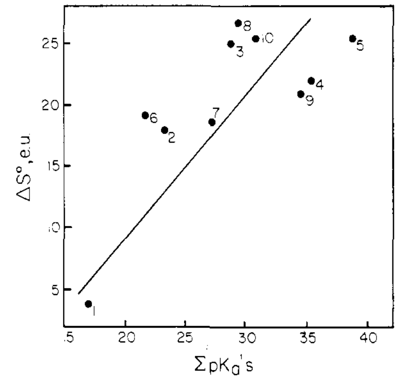

Figure 6. Plot of ΔS_{298} for zinc(II) complex formation against the sum of the ligand pK_a's for linear polyamines and the ligands of this study.

This effect could hold for imidazolyl complexes as well. However, the ΔH values of 4-IMDIEN lie near the lines in Figure 2 established by the aliphatic amines. Only Ni(II) is slightly above the line, which may indicate some weak π bonding. The large log K_{ML} value for the Zn(II)–IMDIEN complex is primarily due to an exceptionally large ΔS value for this complex. Thus ring strain does not appear to be an exceptional factor in imidazolyl complexes.

The plot of $\Delta S°$ vs. $\sum pK_a$ for nickel complexes shown in Figure 5 clearly indicates an entropic contribution to the enhanced stability of the pyridyl complexes. These data would support the "rotational freedom" argument discussed above. However, for both Cu(II) and Zn(II) the correlation between $\Delta S°$ and $\sum pK_a$ is much weaker. The scatter is especially

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notable for Zn(II) as shown in Figure 6, presumably due to the mixing of data for tetrahedral and octahedral zinc complexes. Thus it is not easy to predict $\Delta S°$ values with which one can compare the experimental values for pyridyl and imidazolyl ligands.

However, some useful comparisons are still possible. The linear, pentadentate polyamine tetren has a higher basicity than any of the pyridyl or imidazolyl ligands used in this study. With the only assumption that any plot of $\Delta S°$ vs. $\sum pK_a$ will have a positive slope, then the $\Delta S°$ values of tetren would certainly represent an upper limit for a "predicted" value of $\Delta S°$ for the pyridyl and imidazolyl ligands. However, the data in Table I clearly show that the $\Delta S°$ values of the heterocyclic ligands frequently exceed the corresponding values of the tetren complexes, in some cases by substantial amounts. In particular, the $\Delta S°$ values of EPYDEN with copper, nickel, and cobalt are 5–10 eu greater than the tetren values. Thus there is clearly some degree of entropic stablization of the heterocyclic complexes.

Oxygenation of Cobaltous Complexes. It was noted previously that PYDPT forms a cobaltous complex with an oxygen affinity 4 orders of magnitude lower than that of the cobaltous complex of PYDIEN. The present study shows that both cobalt dioxygen complexes of 2- and 4-IMDPT are 3–4 orders of magnitude less stable than the oxygen complex of 4-IMDIEN. It is apparent that the decrease in stability is due to the presence of larger chelate rings in the complexes formed from ligands based on dipropylenetriamine (DPT), since the complexes are essentially equivalent in all other respects. The original explanation assumed that the larger chelate rings caused a decrease in electron donation from the metal ion to dioxygen. This would occur if the donor atoms were sufficiently diplaced from their optimal angles for bonding that the electron donation from these atoms to the metal ion was reduced. The similarity in the observed angles in crystal structures of $[Co(PYDIEN)]_2O_2^{4+}$ and $[Co(PYDPT)]_2O_2^{4+}$ salts[5,6] makes this explanation appear untenable. The orbital overlap varies as a function of $\sin^2 \theta$, so that a large difference in N–Co–N angles would be required to reduce the electron donation significantly.

Steric factors that might hinder oxygenation should have been observed in the oxygen to equatorial nitrogen distances. These distances are constant in the PYDPT complex,[6] the maximum variation being only 0.05 Å. Two distances in the PYDPT complex (N3–O1 and N8–O2) are shorter than the corresponding distances in the PYDIEN complex[5] by 0.04 and 0.06 Å, respectively. Other distances in the PYDPT complex (N5–O1 and N10–O2) are longer than the corresponding distance in the PYDIEN complex by 0.05 and 0.09 Å, respectively. The average oxygen to equatorial nitrogen distance is approximately the same in each case. One could argue that these distances would be somewhat shorter in the PYDPT complex if the Co–O distance were reduced to the value of 1.876 (4) Å observed in the PYDIEN complex. With or without this argument, however, the structural data do not demonstrate that the Co–O distance is lengthened by steric factors.

The present calorimetric studies of the oxygenation of cobaltous PYDIEN and PYDPT and of the cobaltous complexes of similar ligands were undertaken to provide further information about the thermodynamics of oxygenation in solution and the factors influencing the metal–dioxygen affinities in complexes of this type. The interesting calorimetric result is that entropic factors oppose the enthalpic factors that are responsible for the reduced stability of the PYDPT, 4-IMDPT, and 2-IMDPT complexes. The entropy difference between PYDIEN and PYDPT complexes and between 4-IMDIEN and 4-IMDPT complexes amounts to ~8 kcal/(mol deg).

On consideration of all the factors involved, a new interpretation based on steric effects generated by the more highly folded six-membered chelate rings is now offered. Inspection of the coordinate bond distances in the dioxygen complexes containing PYDPT[6] and PYDEN[5] as ligands shows that the coordinate bond distances between cobalt and the aliphatic nitrogens are roughly the same for these two ligands. On the other hand, the dioxygen complex containing the ligand PYDPT, which forms two six-membered chelate rings, has significantly longer bond distances between the aromatic nitrogens and the cobalt. Thus it appears that the metal complexes strive to maintain the strengths of coordinate bonding to the aliphatic amino groups but that steric effects resulting from folding of the six-membered rings inhibit the approach of the aromatic nitrogens to the metal ion to the distance necessary for maintaining optimal coordinate bond strength. These steric effects are absent or very much lower in the dioxygen complexes having only five-membered chelate rings, resulting in much stronger coordination of the aromatic nitrogen donors. The weaker Co(III)–N coordinate bonds in the complexes with six-membered chelate rings result in less charge transfer from cobalt to dioxygen, corresponding to weaker dioxygen bonding. The interrelationship between these effects is seen in the corresponding bond angles and distances:[5,6] the cobalt chelates containing the more folded and more constrained six-membered rings have longer Co–N bonds, longer Co–O bonds, and shorter O–O bonds.

The reciprocal relationship between ΔH and ΔS in structurally related coordination compounds, which has been recognized in many series of complexes, is clearly evident from the data in Table II. Thus the weaker bonding increment in the ΔH of oxygenation (which involves both metal–oxygen bond formation and an increment in metal–nitrogen coordinate bonding) is associated with the lesser loss of entropy, which partially compensates for the loss in enthalpy. Thus the change in ΔG is not as large as the change in ΔH, which provides the driving force for the reaction. This effect is now generally recognized and expected, since large increases in bond energy tend to build rigidity into the molecular framework involved, resulting in unfavorable decreases in entropy.

Acknowledgment. This work was supported by a research grant, No. A-259, from the Robert A. Welch Foundation.

Registry No. Cu, 7440-50-8; Ni, 7440-02-0; Co, 7440-48-4; Zn, 7440-66-6; PYDPT, 58214-73-6; PYDIEN, 64739-67-9; EPYDEN, 64739-66-8; 4-IMDIEN, 66750-76-3; 4-IMDPT, 66750-77-4.