transitions[6] of the unmixed complexes. Since the measured basicities[12] of pyridine and β-picoline are closer to each other than those of pyridine and γ-picoline, the electronic factors in these amines which control the ligand preference of the nickel seem to be the same as those dictating the proton affinity. However, basicity cannot account for the great differences between these ligands and α-picoline. Instead, the strong affinity of the nickel for pyridine as compared to α-picoline must be ascribed to the difference in the nickel coordination number, with the fourfold nickel coordination of the α-picoline being attributable to steric hindrance.

From the extrapolated shift of the complexed ligand, the electron–nuclear hyperfine interaction constant may be determined.[13] We find the following hyperfine interaction constants (cps) for the pyridine complex: $a_N = 1.2 \times 10^6$ for the α-H, 4.3×10^5 for the β-H, and 9.8×10^4 for the γ-H; for the γ-picoline: $a_N = 1.2 \times 10^6$ for the α-H, 4.0×10^5 for the β-H, and 1.2×10^5 for the γ-CH_3. Since these interaction constants are related to the ligand–metal orbital overlap, the closeness of their values for the two amines reflects the electronic similarity of these ligands.

Acknowledgment.—We wish to thank Dr. L. C. D. Groenweghe for many helpful discussions.

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[12] H. C. Brown and X. R. Mihm, *J. Amer. Chem. Soc.*, **77**, 1723 (1955). For pyridine; pK_a = 5.17; α-picoline, 5.97; β-picoline, 5.68; and γ-picoline, 6.02.

[13] J. P. Jesson, *J. Chem. Phys.*, **47**, 582 (1967). Since the magnetic anisotropy of hexacoordinate nickel compounds as determined by esr (B. R. McGarvey, "Transition-Metal Chemistry," Vol. III, R. L. Carlin, Ed., Marel Dekker, New York, N. Y., 1966, p 89) is found to be less than 5%, we shall assume that $|g_{\parallel} - g_{\perp}| = 0.05$. Therefore, eq 5 of the Jesson reference applies to these molecules.

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New Multidentate α-Pyridyl Ligand. Coordination of Bis(2-pyridylmethyl)amine with Transition Metal Ions[1]

By J. KIRK ROMARY,[2] J. D. BARGER, and JIM E. BUNDS

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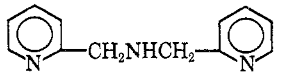
The synthesis of the tridentate ligand bis(2-pyridylmethyl)amine by reaction of 2-chloromethylpyridine and excess 2-aminomethylpyridine is described, and the proton dissociation constants are reported. The coordination tendencies have been studied potentiometrically (at 25° and μ = 0.10 in KNO_3) with Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Mn(II), and Ag(I). Chelation was observed and the corresponding stepwise formation constants and Gibbs free energies are reported. These results are compared with the coordination tendencies of the analogous aliphatic amine, diethylenetriamine. Geometrical considerations for bis(2-pyridylmethyl)amine coordination are discussed. The proton dissociation constants of bis(3-pyridylmethyl)amine are also reported.

Introduction

Coordination compound formation between transition metal ions and completely aliphatic polyamines has been widely studied.[3] More recently, the literature describes the interesting results of some investigations of chelation by ligands containing the α-pyridyl group in combination with an aliphatic amine group.[4,5] There is, however, a paucity of coordination data for completely heterocyclic polyamines (with the notable exception of 2,2′-bipyridine) as has been previously pointed out.[4]

In order to extend the investigation of chelation effects to systems possessing a higher degree of heterocyclic character, the synthesis and coordination study of bis(2-pyridylmethyl)amine (or dipicolyamine; 2-DPA) was undertaken. This particular ligand structure provides for the possible formation of two identical five-member chelate rings.



bis(2-pyridylmethyl)amine (2-DPA)

Experimental Section

Bis(2-pyridylmethyl)amine (2-DPA).—Chloromethylpyridine hydrochloride (25 g, 0.15 mol) was dissolved in 50 ml of water and neutralized slowly (and with cooling) with 15 ml of saturated aqueous K_2CO_3. The chloromethylpyridine-free base, which separates from the aqueous layer as a straw yellow oil, was added immediately (to minimize decomposition) to 82.5 g (0.75 mol) of 2-aminomethylpyridine. During addition, the reaction mixture was vigorously stirred and kept at 5°. The mixture was then allowed to warm to room temperature with continued stirring. Reaction began at about 15° as evidenced by a gradual color change from light yellow to reddish brown. The product mixture was acidified with tartaric acid, extracted with ether, and neutralized with 30% aqueous KOH. Excess KOH pellets caused separation of the aqueous and organic layers. The organic layer was further dried with anhydrous $MgSO_4$ and distilled at reduced pressure. The product distilled at 148–149° (1.05 mm). The yield was 73%.

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[1] The authors gratefully acknowledge the support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant 2185-B) and by the National Science Foundation (Grants GE-6492 and GY-274).

[2] National Science Foundation, Washington, D. C.

[3] L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, Burlington House, London, 1964.

[4] R. G. LaCoste and A. E. Martell, *Inorg. Chem.*, **3**, 881 (1964).

[5] D. E. Goldberg and W. C. Fernelius, *J. Phys. Chem.*, **63**, 1246 (1959).

The nmr spectrum (obtained with the Varian A-60A spectrometer using carbon tetrachloride as the solvent and tetramethylsilane as the internal reference) consists of a band from τ 1.6 to 3.2 due to aromatic hydrogen, a sharp peak at τ 6.15 due to methylene hydrogen, and a peak at τ 7.42 due to amine hydrogen. The area ratios for the three resonance regions are 8:4:1, respectively, in agreement with theory. The infrared spectrum (obtained with a Perkin-Elmer 521 spectrophotometer) shows sharp absorption at 3300, 3050, 2850, 1575, 1450, and 800 cm^{-1}.

Anal. Calcd for $C_{12}H_{13}N_3$: C, 73.33; H, 6.57; N, 21.10; mol wt, 199.2. Found: C, 72.35; H, 6.67; N, 21.24; mol wt, 202.

The compound forms a trihydrochloride out of ethanol saturated with dry HCl which melts at 199–200°.

Anal. Calcd for $C_{12}H_{13}N_3 \cdot 3HCl$: C, 46.70; H, 5.23; N, 13.61; Cl, 34.46. Found: C, 46.71; H, 5.26; N, 13.60; Cl, 34.46.

Potentiometric Determination of Dissociation and Formation Constants.—All measurements were made with a Metrohm Hereassau 388 Research pH meter with Beckman calomel and E-2 glass electrodes. Standard buffer solutions at pH 4.01 and 7.00 were used to standardize the potentiometric apparatus. All solutions were 0.10 *M* in KNO_3, the temperature was 25°, and a nitrogen atmosphere was maintained. The titrant was standard CO_2-free KOH. Systems of varying concentrations and varying ligand to metal ion ratios were investigated in order to detect any concentration effects.

Calculations.—The proton dissociation constants and the chelate stability constants were obtained by rigorous treatment of the potentiometric data using the method of Bjerrum.[6]

All calculations leading to the results reported here have been performed by use of a set of eight previously described digital computer programs.[7] These programs, based upon the (proton) dissociation function and the (complex) formation function of Bjerrum,[6] provide for formation curve calculations, simultaneous equations solutions, successive approximations solutions, and theoretical formation curve generation. In those cases of insufficiently large spreading factors, the reported stepwise constants were obtained by use of the iteration program. The reliability of these final constants was in each case verified by generation of a theoretical formation curve which was compared for agreement with the experimental formation curve (*e.g.*, Figure 2).

Results and Discussion[8]

The proton dissociation constants of 2-DPA, bis(3-pyridylmethyl)amine (3-DPA), and diethylenetriamine (dien) are listed in Table I. The experimental and theoretical proton dissociation curves for 2-DPA and 3-DPA are included in Figure 2. It is noteworthy that pK_1 and pK_2 are significantly larger for 3-DPA than for 2-DPA, as a result of the greater distance of separation between the pyridine and side-chain nitrogens, while pK_3 differs only slightly. A comparison of 2-DPA with 2-aminomethylpyridine also shows that substitution of the 2-pyridylmethyl group on the terminal nitrogen results in reduced basicity of both the side-chain and hetero nitrogens. Similar observations have been reported for N-(pyridylmethyl)-1,2-diaminoethanes.[9]

TABLE I

PROTON DISSOCIATION CONSTANTS FOR 2-DPA, 3-DPA, AND dien AT 25° IN 0.10 *M* KNO_3

	pK_1	pK_2	pK_3
2-DPA	1.12	2.60	7.30
3-DPA	2.95	3.90	7.15
dien	4.34	9.13	9.94

Potentiometric titrations of bis(2-pyridylmethyl)amine in the presence and in the absence of metal ions are shown in Figure 1. The ligand curve with inflections at 2 and 3 mol of base per mol of ligand indicates the simultaneous removal of the pyridinium protons followed, in an apparently stepwise fashion, by the amine proton. The titration curves in the presence of metal ions are for solutions containing equimolar concentrations of ligand and metal. The curves for cobalt and zinc ions (not shown) lie between, and are of the same shape as, those for Ni(II) and Cd(II) with a single inflection at *a* = 3. In the case of Mn(II), precipitation occurred just short of the final end point. The titration curve for Ag(I) closely followed the latter curve except that precipitation was not observed. Thus, tridentate formation is indicated for the 1:1 complexes with all of the metal ions except Mn(II) and Ag(I) where monodentate formation is indicated.

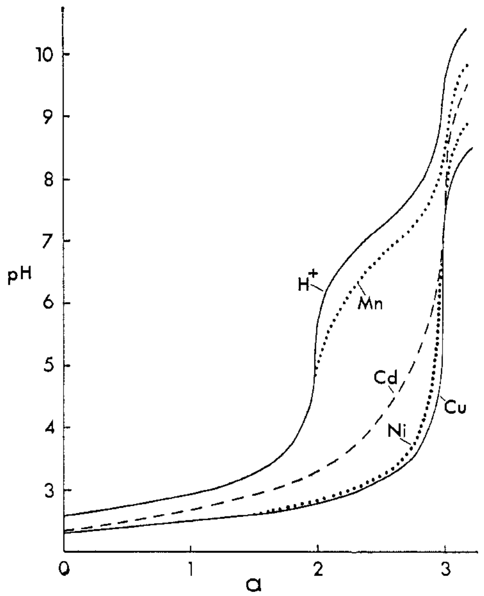

Figure 1.—Potentiometric titration of 0.002 *M* bis(2-pyridylmethyl)amine alone (protonated) and in the presence of equimolar concentrations of Cu(II), Ni(II), Cd(II), and Mn(II) ions at 25° and μ = 0.10 in KNO_3. Abscissa shows moles of base added per mole of amine.

Representative experimental and theoretical formation curves are shown in Figure 2. The ligand curve for 2-DPA more clearly illustrates the stepwise nature of the removal of the amine proton in contrast to the pyridinium protons. Coordination of 2-DPA with Cu(II) is likewise observed to occur in a stepwise fashion while with Co(II) there is significant overlapping of the first and second coordination steps. The case of Zn(II) (not shown) is intermediate between that

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[6] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1957.

[7] J. K. Romary, A. C. Andrews, and D. L. Donnelly, *J. Inorg. Nucl. Chem.*, **29**, 1805 (1967).

[8] Original data have been deposited as Document No. 9882 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and remitting $2.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[9] E. Hoyer, *Chem. Ber.*, **93**, 2475 (1960).

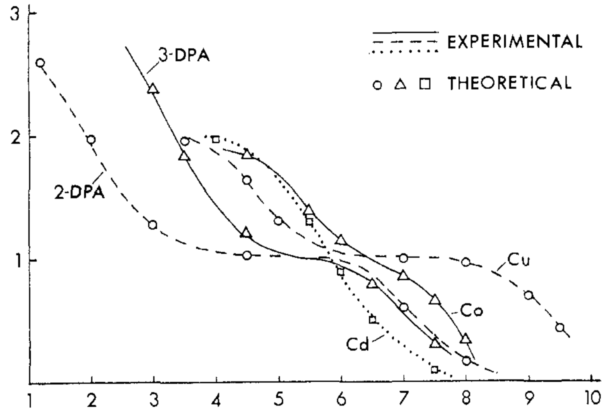


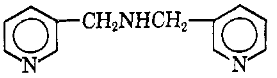
Figure 2.—Experimental and theoretical formation curves at 25° and 0.10 M KNO_3 for bis(2-pyridylmethyl)amine coordination with Cu(II), Co(II), and Cd(II) ions (X = ligand) and proton dissociation curves for bis(2-pyridylmethyl)amine and bis(3-pyridylmethyl)amine (X = hydrogen ion).

of Cu(II) and Co(II). For the remaining metal ions, formation occurs in the manner characterized by Cd(II). The theoretical curves shown are those generated by the formation (stability) constants reported in Table II. A limited investigation of coordination by 3-DPA was also conducted.

Table II

Formation Constants and Gibbs Free Energies for Transition Metal Ion Chelation by 2-DPA and dien at 25° in 0.10 M KNO_3

		Log K_n			$-\Delta G_n°$, kcal/mol	
	Order n	2-DPA	dien[4]	dien − 2-DPA	2-DPA	dien
Cu(II)	1	9.31	15.9	6.6	12.7	21.7
	2	4.54			6.20	
Ni(II)	1	8.70	10.7	2.0	11.9	14.6
	2	7.90			10.8	
Co(II)	1	7.74	8.1	0.4	10.6	11.1
	2	5.31			7.25	
Zn(II)	1	7.57	8.9	1.3	10.3	12.1
	2	4.36			5.95	
Cd(II)	1	6.44	8.4	2.0	8.78	11.5
	2	5.30			7.24	
Mn(II)	1	4.16			5.68	
	2	2.91			3.98	
Ag(I)	1	5.5			7.5	
		3.1			4.2	



bis(3-pyridylmethyl)amine (3-DPA)

These results have not been included owing to the fact that, although a tendency to coordinate was evident, the formation curves were poorly formed and nondefinitive. This coordination tendency, however, was quite weak as would be expected in view of the unfavorable ligand structure.

The 1:1 chelates of 2-DPA are observed in all cases to be considerably less stable than those for the analogous aliphatic ligand, dien. This, however, is not surprising in view of the fact that the basicity of dien is much greater than that of 2-DPA. Furthermore, 2-DPA has greater steric limitations imposed by the fact that the pyridine nitrogens and the adjacent carbons must maintain their mutually fixed positions in the rings. Although such comparisons between related heterocyclic and aliphatic ligands have obvious limitations, they frequently lead to additional interesting results.

While dien demonstrates greater affinity than 2-DPA for all of the metal ions studied, this is substantially offset at low pH where the relative pK values lead to a much more favorable competition for metal ions by 2-DPA. For example, it was observed that with Cu(II) significant coordination was involved at a pH as low as 2 as evidenced by the calculated values of $\bar{n}$ and the formation of deep blue-violet solutions. Work previously reported by Martell[4,10] cites similar cases of favorable complex equilibria at low pH. The Gibbs free energies for the coordination reactions and the log K_1 differences between 2-DPA and dien are also given in Table II. Differences in log K_2 are not given since only in the case of Cu(II) has a second-order complex with dien been previously reported.[11] In the latter case, Fernelius reported a value of 4.68 (30°) which is of the same order of magnitude as that reported here for log K_2 of 2-DPA and Cu(II).

In the case of Cu(II) coordination by 2-DPA, in marked contrast to that with the remaining metal ions, there is an enormous decrease in the strength of binding of the second ligand. A number of explanations could be advanced. In the analogous case with dien mentioned above, Fernelius supports the explanation that only a single coordinate bond forms between the second dien ligand and Cu(II) with the retention of a coordination number of 4. Also, assuming a maximum coordination number of 4, one could propose that one of the nitrogen–metal bonds with the original ligand is first broken. Following this, the second ligand coordinates through two nitrogen atoms leaving both then acting as bidentate. A third explanation is the possibility of coordination of all nitrogens of both ligands leading to a distorted octahedron. Such an attainment of a coordination number of 6 by Cu(II) has been previously discussed.[12] In the latter case, it would be necessary for a chelate ring of the first coordinated ligand to be broken and recoordinated with octahedral geometry before the addition of the second ligand.

In an attempt to answer this question in the case of 2-DPA and Cu(II), additional titrations were made in which the ligand concentration was double that of Cu(II). The results are shown in Figure 3. Curves A and B compare, respectively, the titration of a solution of the ligand itself with the titration of a solution containing a 2:1 ratio of 2-DPA to Cu(II). The shift of curve B away from curve A corresponds to the overall formation of the 2:1 complex whereas the corresponding comparison in Figure 1 corresponds to the

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[10] S. Westerback, K. S. Rajan, and A. E. Martell, *J. Am. Chem. Soc.*, **87**, 2567 (1965).

[11] G. H. McIntyre, B. P. Block, and W. C. Fernelius, *ibid.*, **81**, 529 (1959).

[12] L. E. Sutton, *J. Inorg. Nucl. Chem.*, **8**, 23 (1958).

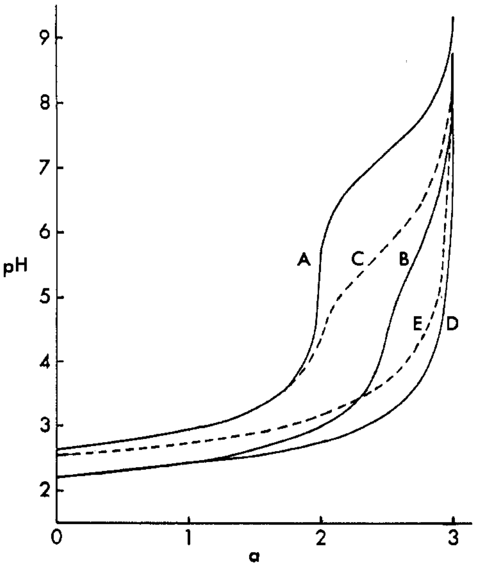

Figure 3.—Potentiometric titration of the bis(2-pyridylmethyl)amine ligand under the conditions: A, 0.002 *M* ligand; B, 0.004 *M* ligand and 0.002 *M* Cu(II); C, data of curve B replotted to show monodentate coordination of second ligand; D, 0.004 *M* ligand and 0.002 *M* Ni(II); E, data of curve D replotted to show tridentate coordination of second ligand.

formation of the 1:1 complex only. To place emphasis upon the coordination of the *second* ligand alone, the dotted curve C is shown. Curve C was obtained by replotting the data of curve B after correction of the a values to eliminate the effect of the first ligand. (That it, the pH at $a = 1.5$ on curve B corresponds, stoichiometrically, to the beginning of the titration of the second ligand and is thus transposed to a value of $a = 0$ on curve C. Likewise, the pH at $a = 2$ is transposed to $a = 1$, etc. This procedure leads to the most meaningful results in those cases where the coordination of the first ligand is substantially complete prior to the beginning of the coordination of the second ligand.) From curve C it is observed that the titration of the *second* ligand, in the presence of the already formed 1:1 complex, follows the titration of the ligand itself until the two pyridine protons have been almost completely removed thus indicating little, if any, coordination. During the neutralization of the third (amine) proton, coordination is occurring as evidenced by the departure of curve C from curve A. These results indicate that for the second ligand there is negligible coordination until the amine nitrogen becomes involved in a monodentate fashion. This agrees with the explanation based upon enthalpies given by Fernelius for dien and Cu(II). Similar 2:1 titrations for 2-DPA and the other metal ions indicated that only for Ni(II) and Cd(II) does the second ligand appear to coordinate in a tridentate manner. Curves D and E are similarly obtained in the case of Ni(II).

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The Mechanistic Role of Dibenzyl Sulfide as an Entering and Leaving Group in Neutral Gold(III) Systems

BY L. CATTALINI, G. MARANGONI, AND M. MARTELLI

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The kinetics of displacement of amines (am) from a series of complexes of the type $AuCl_3(am)$ by dibenzyl sulfide and of the reverse reactions have been measured in acetone at 25° and compared with the data relative to other reactions of the same substrates. The discrimination between complexes containing amines of different basicity is related to the relative influence of the bond-making and bond-breaking aspects of the substitution process. The steric effects observed with pyridine derivatives having methyl group(s) *ortho* to the nitrogen are discussed in terms of steric perturbations in the transition state.

Introduction

The range of reagents which have been used in the study of the kinetics of displacement of ligands from planar gold(III) complexes[1] is limited because the rates and nature of the reaction of Au(III) substrates are extremely sensitive to the nature of the nucleophile. In many cases the reactions are too fast to measure by conventional techniques and in many others reduction occurs in preference to substitution.

In order to extend the range of nucleophiles examined and also to obtain systematic information about the reactivity of thioethers toward planar d^8 substrates we have examined the kinetic behavior of dibenzyl sulfide.

A preliminary study indicated that the tetrachloroaurate(III) anion reacts rapidly with dibenzyl sulfide and other thioethers in methanol at 25° and is reduced.[2] However, in acetone at 25° it is possible to study the forward and reverse steps of reactions of the type

$$AuCl_3(am) + Bz_2S \rightleftarrows AuCl_3(Bz_2S) + am$$

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(1) L. Cattalini, A. Orio, and M. L. Tobe, *J. Am. Chem. Soc.*, **89**, 3130 (1967), and references therein.

(2) V. Ricevuto, unpublished results.