tion from this plane is 0.07 Å. It should be noted that C(8) sits on the twofold axis so that half of the glutaronitrile molecule is related to the other half by the twofold symmetry.

The tin is octahedrally coordinated, the nitrogen atoms being in the *cis* configuration. Examination of Figure 2 indicates that the octahedron is somewhat, although not greatly, distorted. Sn, N(5), N(5′), Cl(4), and Cl(4′) are nearly planar, the best least-squares plane being described by the equation $-0.3240X + 0.9461Y + 0.0000Z = 7.2514$; maximum deviations of any atoms from this plane are only about 0.01 Å. Also, Sn, Cl(2), Cl(3), Cl(4), and N(5) are close to being planar, the equation being $0.3362X + 0.4679Y + 0.8173Z = 5.2602$, with Sn being about 0.2 Å from this plane.

The Sn–Cl distance of 2.35 ± 0.01 Å agrees well with those in $SnCl_4(OSeCl_4)_2$, *i.e.*, 2.36 and 2.41 Å.[10] In $SnCl_4(OSeCl_4)_2$ the octahedron around tin is slightly more distorted than in $SnCl_4$(gn). In benzaldeminium stannichloride[11] the $SnCl_6^{2-}$ ion shows three distances, 2.42, 2.50, 2.54 Å, all of which are somewhat longer than those in $SnCl_4$(gn). The distance shown in $SnCl_4$ gas by electron diffraction is 2.31 ± 0.01 Å,[11] this of course being a tetrahedral molecule. No Sn–N distances are available for comparison.

Thus the conformation of the glutaronitrile as TT has been confirmed, and it has been shown that this complex is, in fact, a one-dimensional polymer. There is no immediately obvious explanation of the difference in spectral assignments for the glutaronitrile in the tin(IV) complex from those in the pure glutaronitrile.

Acknowledgment.—D. M. B. wishes to acknowledge a postdoctoral fellowship granted to him by Harvey Mudd College, Claremont, Calif., during which period the experimental data were collected. We acknowledge a grant from the Montana State University Computing Center without which it would not have been possible to perform the calculations, and we also wish to thank the University of Washington Computing Center for time on their IBM-7094 and Keith Watenpaugh for assistance in this computation.

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[10] Y. Hermodsson, *Acta Cryst.*, **13**, 656 (1960).

[11] "Tables of Interatomic Distances and Configuration in Molecules and Ions," Supplement Special Publication No. 18, The Chemical Society, London, 1965, p M22S.

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Ligand Preferences of Transition Metals in Complexes as Determined from Nuclear Magnetic Resonance Contact Shifts

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The Fermi contact term causes a large change in the nuclear magnetic resonance chemical shift of a nucleus in a ligand bonded to a paramagnetic transition metal atom as compared to the same ligand in the free state. When there is rapid exchange of ligand between the free state and the metal complex(es), the variation in the position (depending on the ratio of free to coordinated ligand) of the resonance is large so that for ligand mixtures a reasonably precise measurement may be obtained of the fraction for each kind of ligand which is coordinated. From data of this type, the competitive equilibria for coordination of nickel by pyridine *vs.* α-, β-, or γ-picoline, picoline oxide, triphenylphosphine, or triphenylphosphine oxide were investigated. An equilibrium constant for treating these data is derived and applied to the appropriate systems.

The literature[1] dealing with labile replacement of one ligand by another on transition metals has been essentially limited to spectral studies involving mixtures of molecules which exhibit appreciably different electronic transitions. Thus these studies, based on electronic spectra as well as on a few other techniques such as nuclear magnetic resonance (nmr), are generally limited to pairs of ligands involving coordination through two different elements. By the technique described herein, it is possible to make reasonably precise measurements on systems in which the rapidly exchanging, competing ligands are very similar.

For diamagnetic systems, it is generally found that the nmr chemical shift of a magnetically active nucleus which is part of a ligand is not very different in the complex as compared to the free state, except when the nucleus is directly bonded to the acceptor atom. When the acceptor is a paramagnetic atom,[2] delocalization of the unpaired electron(s) into the ligand orbitals leads to a large difference in shift between the coordinated and free ligand, with delocalization into the ligand σ orbitals causing downfield shifts as large as several hundred parts per million and delocalization into the π orbitals usually giving severalfold smaller shifts which alternate in sign in a conjugated system. This led us to consider the applicability to paramagnetic systems of a quantitative treatment of the shifts of the

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[1] *E.g.*, A. E. Harvey and D. L. Manning, *J. Amer. Chem. Soc.*, **72**, 4488 (1950).

[2] D. R. Eaton and W. D. Phillips, *Advan. Mag. Resonance*, **1**, 103 (1965).

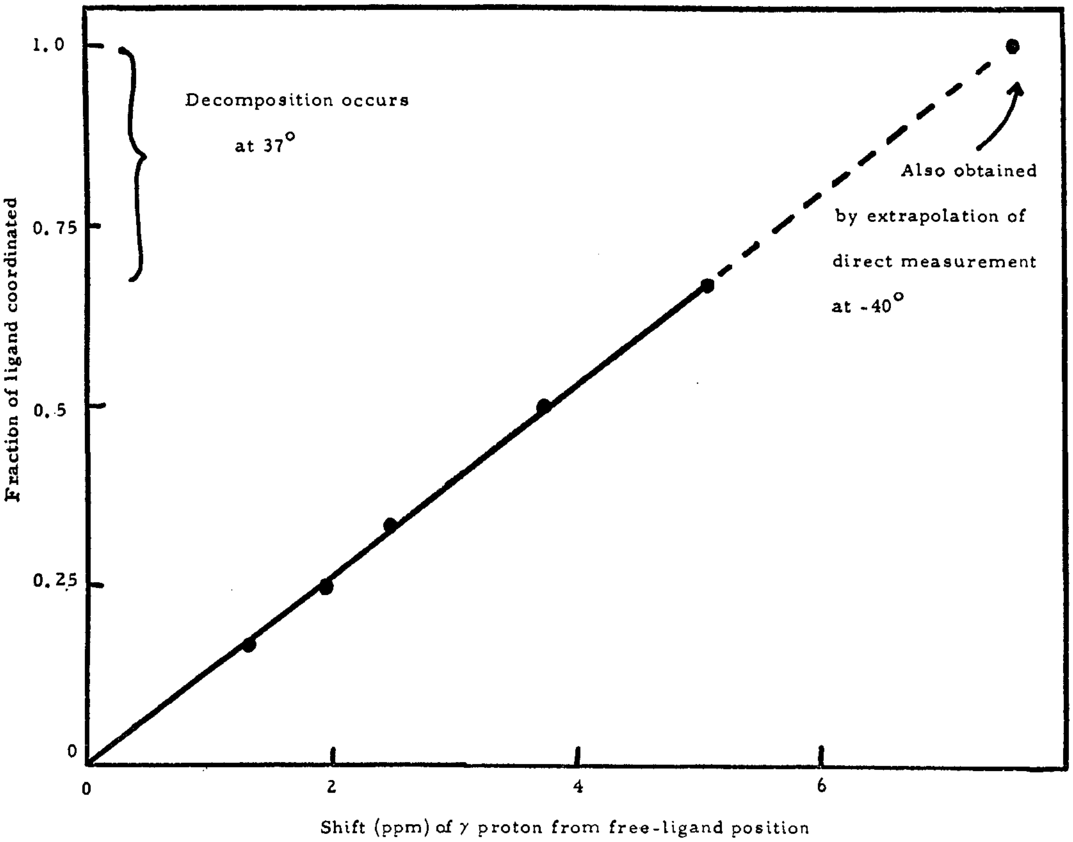

Figure 1.—A plot showing the relationship between the proportions of the components as directly weighed and the nmr shift of the γ proton in the system $Ni(py)_4Cl_2$ plus excess pyridine at 37°.

fully coalesced ligand resonances resulting from rapid exchange between the free and coordinated forms of the ligand. The systems chosen as examples for study include six-coordinate nickel on which four equatorial ligand sites are available for exchange. Emphasis was placed on pyridine and its monomethyl substitution products, since the ratio of the free to coordinated forms of each ligand in such mixtures based on electronically similar ligands could not be obtained by any other method known to us.

Experimental Section

The nickel–pyridine complex, $Ni(NC_5H_5)_4Cl_2$, and the corresponding monomethyl-substituted pyridine (picoline) complexes were prepared according to the method of Gill, *et al.*[3] Proton nmr spectra were recorded with Varian A-56/60 and HA-100 spectrometers equipped with a variable-temperature probe. Tetramethylsilane was employed as the internal reference, with positive shifts being upfield.

The studies were all carried out in deuteriochloroform with an excess of no less than 4 mol of total free ligands per mol of total complexed ligands, since lesser amounts of free ligand resulted in precipitate formation—presumably of polymeric species such as $[Ni(py)_2Cl_2]_\infty$. Likewise, the ligand/nickel mol ratio was always kept below 40–65 because of insolubility of the complexes in the concentrated free ligand. The solutions, which were always held at 0.05 *M* with respect to nickel, were prepared according to the following routine. First, the desired proportions of free ligands were weighed into a 1-ml volumetric flask followed by a weighed quantity of the chosen nickel complex, and the mixture was then made to volume with the $CDCl_3$ before shaking to dissolve the complex.

Results and Interpretation

An X-ray structural determination[4] of $Ni(py)_4Cl_2$ has shown that the two chlorine atoms are *trans* to each other. Electronic spectral data reported for this complex in chloroform solution[5] as compared to the solid state[5,6] show that the *trans*-chloro structure based on hexacoordinated nickel is retained in solution. The situation is quite different for the α-picoline, triphenylphosphine, and triphenylphosphine oxide ligands for which the nickel complex in the presence of excess free ligand has the formula $Ni(ligand)_2Cl_2$ with a tetrahedral configuration being assigned from the electronic spectrum[7] or from X-ray diffraction[8] in the case of the phosphine complex.

Nmr Spectra.—At room temperature, mixtures of any one of the pyridine or picoline complexes with varying amounts of the same ligand in excess show the same number of nmr resonances (exclusive of spin–spin splitting) as the free ligand by itself. It is found that the position of these resonances varies linearly with the proportion of coordinated to free ligand so that an extrapolation can be made to the shift corrresponding to the pure complex, as illustrated by Figure 1. The

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[3] N. S. Gill, R. S. Nyholm, G. A. Barkley, T. I. Christie, and P. J. Pauling, *J. Inorg. Nucl. Chem.*, **18**, 88 (1961).

[4] M. A. Porai-Koshits, A. S. Antsishkina, L. M. Dickareva, and F. K. Jukhnov, *Acta Cryst.*, **10**, 788 (1957).

[5] D. A. Rowley and R. S. Drago, *Inorg. Chem.*, **6**, 1092 (1967).

[6] D. M. L. Goodgame, M. Goodgame, M. A. Hitchman, and M. J. Weeks, *J. Chem. Soc., A*, 1769 (1966).

[7] L. M. Vallarino, W. E. Hill, and J. V. Quagliano, *Inorg. Chem.*, **4**, 1598 (1965).

[8] G. Garton, D. E. Henn, H. M. Powell, and L. M. Venanzi, *J. Chem. Soc.*, 3625 (1963).

extrapolated shifts are listed in Table I along with the shifts of the respective free ligands. As expected,[9] the resonances of the hydrogens directly bonded to ring carbon atoms were much broader for the positions close to the metal, while, at the same time, the extrapolated shifts for the pure complexes were farther from the respective free-ligand shifts. The best compromise between the advantage of a large shift difference and the disadvantage of concomitant line broadness appeared to be the use of the γ hydrogen.

TABLE I

NMR CHEMICAL SHIFTS IN PPM

	Pyridine	β-Picoline	γ-Picoline
Coordinated Ligand at +37° (Isothermal Extrapolated Value)			
CH_3	...	−8.40 ± 0.2	+6.56 ± 0.1
α-H	−99 ± 4	−102 ± 4	−99 ± 4
β-H	−40.0 ± 1.0	−41.1 ± 1.0	−38.2 ± 1.0
β-H	−15.25 ± 0.1	−14.15 ± 0.1	...
Free Ligand at −40° (in Solution with Complex)			
CH_3	...	−2.38	−2.42
α-H	−8.78	(−8.54)[a]	−8.64
β-H	−7.37	(−7.13)	−7.30
γ-H	−7.67	(−7.45)	...
Coordinated Ligand at −40° (in Solution Containing Excess Free Ligand)			
CH_3	...	−10.58 ± 0.2	+9.62 ± 0.1
α-H	−133 ± 3	−136 ± 3	−132 ± 4
β-H	−51.1 ± 1.0	−53.2 ± 1.0	−49.1 ± 1.0
γ-H	−17.69 ± 0.1	−16.50 ± 0.1	...

[a] Values in parentheses taken from J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High-Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Ltd., London, 1966, p 795.

At a temperature of −40° where the ligand exchange is slowed sufficiently so as to give fully separated and reasonably narrow lines for the free and complexed forms of pyridine and β- or γ-picoline, the values shown in Table I for the chemical shifts of the complexes were obtained. On the assumption that the shifts of a ligand in a complex (based only on this ligand) upon extrapolation to infinite temperature (where the paramagnetism has disappeared, leaving only a residual diamagnetism) are the same as that of the free ligand, the Curie law in its applicable form $(\delta_{\text{complex}} - \delta_{\text{free}}) \propto 1/T$ may be used to calculate the shift of the coordinated ligand at 37°. It was found that the value of the various shifts at 37° (reported in Table I) obtained on the basis of isothermal extrapolation of the shifts of the rapidly exchanging mixtures to zero free ligand agreed within experimental error with the value obtained from Curie-law extrapolation to 37° of the shifts directly measured at −40°.

When more than one ligand is employed, the shift of the resonances corresponding to each ligand can be linearly related to the proportion of its free and complexed forms by the same relationship applying to each ligand studied alone. This approximation is applicable since the resonance positions at a given temperature for a specific ligand in the various mixed species (if present) or in the pure complex will necessarily be very close to each other as compared to the over-all shift from the free ligand.

Results from Mixed Systems.—Although the technique described herein can be employed on combinations of any number of different ligands with a paramagnetic transition metal atom, only data on pairs of different ligands are reported herein. These data are shown in Table II in which the percentage of the total amount of ligand present in coordinated form is presented. For mixtures of pyridine with β- or γ-picoline, data for several different mole ratios of the ligands are given, since varying the ratio gave meaningful changes in the percentage of each total ligand in coordinated form. However, in the case of the other pairs of ligands studied, the preference for coordination of one of the ligands is extremely great so that a large excess of the other ligand was needed in order to have any of the less preferred ligand appear in complexed form. Thus, although several different mole ratios of the ligands were employed, data are reported only for the large excess. In the case of pyridine *vs.* triphenylphosphine, no detectable amount of the latter was found to be in a complex under any experimental condition.

With respect to the complexes formed, the analytical method described in this paper gives the proportion of the bonds between a given ligand and the transition metal to the total number of bonds between all of the ligands and the metal. This value is shown in the last column of Table II from which it can be seen that pyridine, γ-picoline, and β-picoline have approximately the same affinity for hexacoordinate nickel and this affinity is many times greater than those of α-picoline, γ-picoline oxide, triphenylphosphine, and triphenylphosphine oxide.

Equilibrium Constants.—Since at a temperature of −40° where the resonances for the complex(es) stand alone, the nmr patterns for the systems based on pyridine plus γ- or β-picoline are apparently identical with those of simple mixtures of the pure $Ni(py)_4Cl_2$ and $Ni(pic)_4Cl_2$ complexes, we shall first test the assumption that only the following reaction occurs

$$Ni(py)_4Cl_2 + 4\ pic \rightleftarrows Ni(pic)_4Cl_2 + 4py \qquad (1)$$

The equilibrium constant calculated on this assumption for eq 1 is found to vary widely when calculated from the data of Table II. Thus, for experiments 1–4, the values for this equilibrium constant are 0.28, 0.39, 3.0, and 22, respectively. For experiments 5–7, they are 0.13, 1.0, and 8.0, respectively.

The next reasonable approach is to assume equal weighting of the Ni–py and Ni–pic bonds to give a random distribution of all of the various $Ni(py)_{4-i}(pic)_iCl_2$ species, with $0 \geq i \geq 4$. On this assumption,

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[9] I. Solomon, *Phys. Rev.*, **99**, 559 (1955). This paper shows that the electron–nuclear dipolar broadening is inversely dependent on the sixth power of the distance separating the nucleus and the electron.

TABLE II

DATA ON MIXED-LIGAND SYSTEMS AT 37°

Expt no.	Ligands		Over-all mole ratio, A:B:Ni	Percentage coordinated		Bond ratio, (Ni–A)/[(Ni–A) + (Ni–B)]
	A	B		A	B	
1	py	γ-pic	6:12:1	16.1[a]	25.3[c]	0.24,[a] 0.24[c]
2			4:8:1	25.1	38.0	0.25, 0.24
3			6:6:1	27.4	39.5	0.41, 0.41
4			12:6:1	18.7	30.0	0.56, 0.55
5	py	β-pic	6:12:1	22.3[a]	21.6,[b] 22.2[c]	0.33,[a] 0.35,[b] 0.33[c]
6			6:6:1	33.2	33.5, 32.4	0.50, 0.50, 0.51
7			12:6:1	22.1	22.3, 22.1	0.66, 0.67, 0.67
8	py	α-pic	6:60:1	56.1[a]	(1.1)[d]	0.84[a]
9	py	γ-pic oxide	6:40:1	36.6	(4.5)	0.55
10	py	$(C_6H_5)_3P$	6:40:1	66.7	(0.0)	1.00
11	py	$(C_6H_5)_3PO$	6:40:1	61.3	(0.5)	0.92

[a] Determined from shift difference of γ proton for ligand A. [b] Determined from shift difference of γ proton for ligand B. [c] Determined from shift difference of methyl proton. [d] Calculated from the bond ratio which is based on the pyridine shift difference.

the "random" equilibrium constant for eq 1 may be given[10] in terms of the Ni–py and Ni–pic bonds

$$K' = \frac{\dfrac{[\text{Ni–pic}]^4}{4([\text{Ni–py}] + [\text{Ni–pic}])^3}[\text{py}_{\text{free}}]^4}{\dfrac{[\text{Ni–py}]^4}{4([\text{Ni–py}] + [\text{Ni–pic}])^3}[\text{pic}_{\text{free}}]^4} \qquad (2)$$

It should be noted that K' of eq 2 reduces to the equilibrium constant for eq 1, when no other complexes but those given in eq 1 are assumed to be present, if (a) the [Ni–py] in the denominator of the numerator is set equal to zero on the basis that these ligands would then not be available for formation of the $Ni(pic)_4Cl_2$ molecule and (b) the same thing is done to the [Ni–pic] term in the denominator of the denominator.

By canceling the terms $4([\text{Ni–py}] + [\text{Ni–pic}])^3$ in eq 2, another equilibrium constant, K, may be obtained, which is equal to $\sqrt[4]{K'}$

$$K = [\text{Ni–pic}][\text{py}_{\text{free}}]/[\text{Ni–py}][\text{pic}_{\text{free}}] \qquad (3)$$

Equation 3 can be shown to apply generally to the equilibrium

$$Ni(py)_i(pic)_{4-i}Cl_2 + pic \rightleftarrows Ni(py)_{i-1}(pic)_{5-i}Cl_2 + py \qquad (4)$$

Obviously if the same equilibrium constant is found for eq 4 regardless of the value of i, it will also hold for any mixture of molecules (all values of i in the range $1 \leq i \leq 4$).

Substituting the values from Table II into an equilibrium constant of the form of eq 3 gives good constancy for the first two sets of data. In the case of the pyridine *vs.* γ-picoline system, the calculated equilibrium constants for experiments 1–4 are 1.78, 1.75, 1.72, and 1.81, respectively; and, for the pyridine *vs.* β-picoline system (experiments 5–7), the calculated constants are 1.00, 1.00, and 1.04.

If in the complex there is equal weighting of the Ni–py and Ni–pic bonds, the bond ratio of Table II should equal $^1/_2$ when the amount of total pyridine equals the amount of total picoline. Further, on this basis, the equilibrium constant of eq 3 should be exactly constant only when it exhibits its random value of unity. For the systems based on pyridine *vs.* β- or γ-picoline, the equilibrium constant of eq 3 is sufficiently near the random value so as to be sensibly constant. In terms of stochastic graph theory,[11] the reorganization heat order, ρ, is zero with respect to the nmr chemical shift data; and, for the two systems described in experiments 1–7 of Table II, $\rho = 1$ with respect to the thermodynamic properties.

If the data for experiments 8 through 11 of Table II are plugged into eq 3, with pic being replaced by the appropriate ligand, the resulting values of K are small, being 0.008, 0.081, <0.001, and 0.003, respectively. Since these values deviate greatly from unity, the K values are not expected to be constant. In other words, there are not sufficient experimental data available to define these systems in terms of equilibrium constants, except to say that the equilibria of the form of eq 3 must exhibit reaction enthalpies around several kilocalories per mole. If all five of the compounds $Ni(py)_{4-i}(L)_iCl_2$, where L is the other ligand, could be distinguished, there would be seven compounds in all (these five plus the two free ligands). The concentrations of these could then be solved in terms of a set of seven simultaneous equations consisting of (a) four independent equilibrium constants which may be of the form of eq 3 with $i = 0, 1, 2,$ and 3; (b) the two over-all composition parameters needed to establish the ratio of the two ligands; (c) the ratio of the ligands to the nuclei; and (d) a normalization equation to account for the fact that the equilibrium is independent of the total volume of the system.

Discussion

The nearly random values for the exchange of pyridine, γ-picoline, and β-picoline with each other on the four available sites of the hexacoordinate nickel result from the fact that the electron-pair-donating nitrogen and its two neighboring carbon atoms in these three ligands are essentially electronically equivalent. This is borne out by the near equivalence of the nickel d–d

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(10) For a random distribution of QT_iZ_{4-i} molecules, the amount of the QZ_4 species in terms of the Q–Z and Q–T bonds is obtained by multiplying the probabilities of supplying the four Q–Z bonds. The probability of the first Q–Z bond is simply [Q–Z], and, for the second through the fourth, it is for each [Q–Z]/([Q–Z] + [Q–T]). Multiplying these four probabilities and dividing by 4 to account for the fact that the QZ_4 molecule has fourfold symmetry, we obtain $[Q–Z]^4/4([Q–Z] + [Q–T])$.

(11) D. W. Matula, L. C. D. Groenweghe, and J. R. Van Wazer, *J. Chem. Phys.*, **41**, 3105 (1964).

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]

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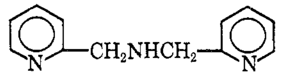
The synthesis of the tridentate ligand bis(2-pyridylmethyl)amine by reaction of 2-chloromethylpyridine and excess 2-aminomethylpyridine is described, and the proton dissociation constants are reported. The coordination tendencies have been studied potentiometrically (at 25° and $\mu = 0.10$ in KNO_3) 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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[2] National Science Foundation, Washington, D. C.

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[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).