analysis shows, however, that all modes except those attributed to C–H motion include motion of all atoms of the ring.

Acknowledgment. This work was supported by a grant (MH-07825) from the National Institutes of Health. The authors wish to thank Dr. C. Van Hall, The Dow Chemical Company, for his help with the reflectance spectrum, Professor Robert C. Taylor and Mr. Harlen Clark, University of Michigan, for their assistance in obtaining the Raman spectra, and Mr. Hans Sachse for his assistance in the vibrational analysis.

Contact-Shift Studies, Delocalization Mechanisms, and Extended Hückel Calculations of Nickel(II)–Alkylamine Complexes[1a]

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Abstract: The proton nmr contact shifts of $[Ni(RNH_2)_6]^{2+}$ (R = CH_3, C_2H_5, n-C_3H_7) have been investigated in an attempt to extend our knowledge of unpaired spin delocalization mechanisms. The amino and alkyl protons are assigned in the nmr spectra of these complexes, and the contact shifts and hyperfine coupling constants are reported. A large upfield shift for the amino protons and a downfield shift for the alkyl protons were observed in all of the complexes studied. The nmr data indicate an attenuation in the magnitude of the contact shift as one proceeds down the chain from the nitrogen. This is in agreement with prediction for a σ delocalization mechanism. Molecular orbital calculations, using extended Hückel theory, were carried out on the ligands. The calculated electron spin density ratios, evaluated by using a Ψ^2 program for calculating electron density at a given nucleus, are compared with the experimental ratios. Justification for using only the ligand in these calculations is discussed and a method of averaging the rotational configurations of the amine is given.

The general theory and interpretation of nmr contact shifts have been extensively discussed in a previous publication from this laboratory[2] and in a recent review article.[3] One of the major problems in this area involves interpretation of the mechanism of spin delocalization onto the ligands. In most of the systems studied previously, the ligands are complex, and it often becomes difficult to sort out σ and π contributions to the delocalization mechanisms. This difficulty was demonstrated in a recent report[4] on the contact shifts of $[Ni(C_6H_5CH_2NH_2)_6]^{2+}$. Consequently, we chose relatively simple ligands to evaluate delocalization of unpaired spin density in a σ molecular orbital. If we can obtain a quantitative understanding of these simple systems, the more complex systems can then be attacked with greater confidence.

There have been several studies in which σ delocalization mechanisms have been reported to be the dominant mechanism. Happe and Ward[5] reported proton nmr contact shifts indicating a σ delocalization in nickel(II)–pyridine type complexes. Very recently, Eaton, *et al.*,[6] have investigated electron delocalization in σ systems in a series of substituted nickel(II) aminotroponiminates. Fessenden and Schuler have also investigated the esr spectra of some alkyl radicals.[7] These latter two studies are fundamentally different, however, from our study, since in the latter studies unpaired electron spin essentially in the π system is delocalized into the σ system *via* a hyperconjugative or some indirect $\pi \rightarrow \sigma$ mechanism.

The alkylamine–nickel(II) complexes, $[Ni(RNH_2)_6]^{2+}$ (where R = CH_3, C_2H_5, n-C_3H_7), offered us an opportunity to examine a σ delocalization mechanism in a complex where the metal–ligand bonding is essentially σ and the free ligand contains no π orbitals.

The recent success in calculating epr hyperfine coupling constants with an extended Hückel treatment, for some hydrocarbon σ radicals[8] and some σ radicals containing nitrogen and oxygen atoms,[9] prompted us to attempt to apply these calculations to nmr contact shifts. The nickel(II)–alkylamine complexes were thought to represent a relatively simple system for this initial attempt.

Experimental Section

Apparatus. a. Nmr Spectra. The nmr spectra were obtained on a Varian Model DP-60 spectrometer. All nmr spectra were measured relative to TMS as an internal standard.

b. Visible and Near-Infrared Spectra. All near-infrared and visible spectra were determined using a Cary recording spectrophotometer, Model 14RI.

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[1] (a) Presented in part before the Division of Inorganic Chemistry, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967. (b) Abstracted in part from the Ph.D. thesis of R. Fitzgerald, University of Illinois, 1968; National Institutes of Health Predoctoral Fellow, 1966–1968.

[2] B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, **87**, 2372 (1965).

[3] D. R. Eaton and W. D. Phillips in "Advances in Nuclear Magnetic Resonance," Vol. I, J. S. Waugh, Ed., Academic Press Inc., New York, N. Y., 1965, pp 103–148.

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[9] R. S. Drago and R. E. Cramer, to be published.

Table I. Nmr Results

Complex	Solvent	Group	δ, cps[a]	Δν, cps[b]	A, G[c]	g[d]
$[Ni(CH_3NH_2)_6]^{2+}$	CH_3NO_2	NH_2	+5895	+6010	−0.510	2.29
		CH_3	−4795	−4610	+0.391	...
$[Ni(C_2H_5NH_2)_6]^{2+}$	CH_3NO_2	NH_2	+5351	+5424	−0.464	2.31
		CH_2	−2418	−2218	+0.189	...
		CH_3	−730	−629	+0.0537	...
$[Ni(n\text{-}C_3H_7NH_2)_6]^{2+}$	CH_2Cl_2	NH_2	+8158	+8250	−0.699	2.45
		$CH_{2\alpha}$	−2259	−2067	+0.173	...
		$CH_{2\beta}$	−527	−406	+0.0344	...
		CH_3	−106	−15	+0.00127	...

[a] The chemical shifts are relative to TMS as an internal standard and at a temperature of 28°. [b] The contact shift, Δν, is relative to the free ligand at 28°: ref 15; H. Hirata, K. Fueki, and T. Sakai, *Bull. Chem. Soc. Japan*, **35**, 1545 (1962); J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961); E. Uhlig and K. Steiger, *Z. Anorg. Allgem. Chem.*, **336**, 42 (1965). [c] *A* (in gauss) calculated from Δν at 28° using eq 1 and the appropriate g_{av}. [d] *g* calculated from μ = 3.23 for $[Ni(CH_3NH_2)_6]I_2$ and μ = 3.26 for $[Ni(C_2H_5NH_2)_6]I_2$: C. Giesner-Prettre, *Ann. Phys.*, **9**, 557 (1964).

c. Magnetic Susceptibility Measurements. The solution moment was determined by nmr at 37° using a method first reported by Evans.[10] The measured suceptibility was corrected for diamagnetism by the use of Pascal's constants.[11]

Reagents and Solutions. Hydrated nickel(II) perchlorate (G. Fredrick Smith), anhydrous reagent grade diethyl ether, anhydrous methylamine (Matheson), and anhydrous ethylamine (Eastman Organics) were used without further purification. Eastman Organics *n*-propylamine was distilled from BaO, a constant-boiling middle fraction being selected for use.

Fisher reagent grade nitromethane was dried over Linde 3A molecular sieves for at least 24 hr. Eastman Organics methylene chloride was dried over Linde 4A molecular sieves for at least 48 hr. Baker absolute methanol was dried over Linde 4A molecular sieves for at least 24 hr.

Preparation of the Complexes. The procedures used to synthesize the complexes were essentially those previously reported from this laboratory.[12] In all instances the elemental analyses of the complexes were in excellent agreement with theoretical values.

Treatment of the Nmr Data. These complexes were studied in solution at 28°. The contact shifts, Δν, were measured relative to the free ligand. The relationship between the contact shift and the nuclear spin–electron spin coupling constant is then given by the Bloembergen equation[13]

$$\frac{\Delta\nu}{\nu} = \frac{-A_n g_{av}{}^2 \beta^2 S(S+1)}{g_N \beta_N 3kT} \tag{1}$$

where $g_N = 5.58$, $\beta_N = 5.05 \times 10^{-24}$ erg/G, $g_{av} = \mu_{eff}/\sqrt{S(S+1)}$, $\beta = 9.27 \times 10^{-21}$ erg/G, S is the sum of the electron spins, A_n is the nuclear spin–electron spin coupling constant (in gauss), Δν is the contact shift relative to the free ligand, and ν is the probe frequency (both in cps); the other symbols have their usual significance.

Calculations. The extended Hückel theory calculations were carried out on the ligand essentially by the method previously described.[14] Prior modifications, previously described,[8] were incorporated with the following exception. We used charge corrected Burns exponents,[15] except for a value of 1.2 for hydrogen, which was not charge corrected.

The unpaired spin density at different protons was evaluated by using a Ψ^2 program previously described.[8] We used the highest filled, *i.e.*, lone pair, molecular orbital of the ligand for these calculations and assumed (*vide infra*) that at least for the alkyl groups the ratios of the hydrogen coefficients in the mo were not changed by coordination.

Results

1. Nmr Data. All of the complexed peaks appeared as broad singlets. The results of the nmr studies are contained in Table I.

2. Evidence for the Octahedral Species. Previous workers[12] have shown that $[Ni(CH_3NH_2)_6]^{2+}$ and $[Ni(C_2H_5NH_2)_6]^{2+}$ exist as the octahedral species in solutions of CH_3NO_2. Our spectral data shown in Table II indicate that $[Ni(n\text{-}C_3H_7NH_2)_6]^{2+}$ exists as the octahedral species in CH_2Cl_2 as well as *n*-propylamine.

Table II. Spectral Data for $[Ni(n\text{-}C_3H_7NH_2)_6]^{2+}$

Solvent	ν_{max}, cm^{-1}	Band assignment
n-Propylamine	9,756	$^3A_{2g} \longrightarrow {}^3T_{2g}$
	16,502	$\longrightarrow {}^3T_{1g}(F)$
	26,846	$\longrightarrow {}^3T_{1g}(P)$
n-Propylamine[a]	9,920	$^3A_{2g} \longrightarrow {}^3T_{2g}$
	16,447	$\longrightarrow {}^3T_{1g}(F)$
	27,174	$\longrightarrow {}^3T_{1g}(P)$
CH_2Cl_2[a]	9,823	$^3A_{2g} \longrightarrow {}^3T_{2g}$
	16,502	$\longrightarrow {}^3T_{1g}(F)$
	26,809	$\longrightarrow {}^3T_{1g}(P)$
CH_2Cl_2 + excess *n*-$PrNH_2$	9,856	$^3A_{2g} \longrightarrow {}^3T_{2g}$
	16,529	$\longrightarrow {}^3T_{1g}(F)$
	26,846	$\longrightarrow {}^3T_{1g}(P)$

[a] Data taken from ref 12.

Further evidence for the octahedral nature of $[Ni(n\text{-}C_3H_7NH_2)_6]^{2+}$, in CH_2Cl_2, is provided by the magnetic susceptibility data in Table III, which is in the range of octahedral nickel(II) complexes.[11]

Table III. Magnetic Susceptibility Data for $[Ni(n\text{-}C_3H_7NH_2)_6](ClO_4)_2$[a]

	$\chi_m \times 10^6$	χ_d[b]	χ_m (cor) $\times 10^6$	μ_{eff}, BM
$[Ni(n\text{-}C_3H_7NH_2)_6](ClO_4)_2$	4421	−376	4797	3.46 ± 0.05

[a] The moment was determined at 37°. [b] Diamagnetic.

3. Results of the Calculations. Results of the Ψ^2 calculations for H_{1s} in CH_3NH_2 are given in Table IV. Since all three methyl hydrogens are not equivalent in a given rotamer, an arithmetic mean of electron densities for H_3, H_4, and H_5 was used to calculate $\Psi^2{}_{av}$. The

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(10) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(11) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, pp 400–454.

(12) R. S. Drago, D. W. Meek, R. Longhi, and M. D. Joesten, *Inorg. Chem.*, 2, 1056 (1963).

(13) N. Bloembergen, *J. Chem. Phys.*, 27, 595 (1957).

(14) P. C. Van der Voorn and R. S. Drago, *J. Am. Chem. Soc.*, 88, 3255 (1966).

(15) G. Burns, *J. Chem. Phys.*, 41, 1521 (1964).

Table IV. Ψ^2 Calculations for Rotamers in CH_3NH_2

Group	Ψ^2_{av} ($\times 10^2$) for H_{1s}	Rotamer angle, deg
$CH_{3(av)}$	1.362	0
	1.361	15
	1.360	20
	1.360	60

angle given under rotamer refers to the degree of rotation about the N–C bond axis, assuming a staggered configuration to be 0°.

In the case of ethylamine we are concerned with rotation about both the C–C and C–N bonds. The results of the Ψ^2 calculations on the C,C rotational conformers of $C_2H_5NH_2$ are given in Table V. $\Psi^2(CH_{3(av)})$ and $\Psi^2(CH_{2(av)})$ are calculated again as arithmetic means. The first angle given under rotamers refers to the degree of rotation about the N–C bond, while the second angle refers to the degree of rotation about the C–C bond, again assuming a completely staggered (*i.e.*, NH_2 and CH_2 staggered as well as CH_2 and CH_3) configuration as 0°,0°.

Table V. Ψ^2 Calculations for C–C Rotamers of $C_2H_5NH_2$

Group	$\Psi^2_{av} \times 10^3$ for H_{1s}	Rotamers
$CH_{2(av)}$ $CH_{3(av)}$	2.656 2.421	0°,0°
$CH_{2(av)}$ $CH_{3(av)}$	2.390 1.992	0°,5°
$CH_{2(av)}$ $CH_{3(av)}$	2.409 1.991	0°,10°
$CH_{2(av)}$ $CH_{3(av)}$	2.543 2.054	0°,15°
$CH_{2(av)}$ $CH_{3(av)}$	2.580 2.050	0°,20°
$CH_{2(av)}$ $CH_{3(av)}$	3.285 1.997	15°,0°
$CH_{2(av)}$ $CH_{3(av)}$	3.346 1.988	15°,5°
$CH_{2(av)}$ $CH_{3(av)}$	3.396 1.998	15°,10°
$CH_{2(av)}$ $CH_{3(av)}$	3.466 1.944	15°,15°
$CH_{2(av)}$ $CH_{3(av)}$	3.536 1.976	15°,20°

The results of the Ψ^2 calculations on the N, C rotational conformers of $C_2H_5NH_2$ are given in Table VI. $\Psi^2(CH_{2(av)})$ is an arithmetic mean of electron densities for the two methylene protons, while $\Psi^2(CH_{3(av)})$ is an arithmetic mean of electron densities for methyl protons. The angle under rotamers has the same meaning as in Table V.

Discussion

1. Interpretation of the Contact Shifts. The contact shifts, $\Delta\nu$ (cps), for the protons of all the complexes studied are listed in Table I. The contact shifts are relative to the free ligand. The electron spin–nuclear spin coupling constants, A (gauss), were calculated according to eq 1 and are also listed in Table I. The assignments of the protons was made on the basis of the line widths and peak areas. The amino peak is severely broadened and can only be seen in the pure complex under optimum instrument operating conditions.

Table VI. Ψ^2 Calculations for the N–C Rotamers of $C_2H_5NH_2$

Group	$\Psi^2_{av} \times 10^3$ for H_{1s}	Rotamers
$CH_{2(av)}$ $CH_{3(av)}$	2.656 2.421	0°,0°
$CH_{2(av)}$ $CH_{3(av)}$	14.90 0.962	65°,0°
$CH_{2(av)}$ $CH_{3(av)}$	16.30 0.813	70°,0°
$CH_{2(av)}$ $CH_{3(av)}$	17.56 0.674	75°,0°

The relationship between the contact shift, $\Delta\nu$, and the hyperfine coupling constant A (gauss) was given in eq 1. The coupling constants are related to the spin densities by

$$A = K_\sigma \rho \qquad (2)$$

where K_σ is a proportionality constant which may be derived from other fundamental constants and ρ represents the spin density. K_σ for Slater orbitals is

$$K_\sigma = \frac{8\pi}{3\hbar\gamma_e} g\beta g_N \beta_N \frac{1}{(a^0)^3} = 1596^{16}$$

These symbols have been defined in eq 1 except for a^0 which is the Bohr radius for hydrogen; $a^0 = 0.529$ Å. Thus, using the ratio of hyperfine coupling constants, we may obtain experimental ratios of spin densities to compare with our calculated results.

Since octahedral nickel(II) complexes are of cubic symmetry and possess a $^3A_{2g}$ ground state, the g tensor should be isotropic and there should be no significant pseudo-contact interaction.[17] The observed shifts are contact shifts which are related to the spin density on the proton.

Since there are two unpaired electrons in the metal e_g orbitals, which are aligned with the magnetic field, a σ-type metal–ligand interaction places positive spin density (spin aligned with the field) in the σ antibonding orbital which is mainly metal e_g. Thus, positive spin density is placed on all atoms, making a substantial contribution to the σ^* antibonding orbital giving rise to a downfield shift at these atoms. The spin densities on the protons for $[Ni(CH_3NH_2)_2]^{2+}$ and $[Ni(C_2H_5NH_2)_6]^{2+}$, as indicated by the nmr data, are shown in Figures 1 and 2. The attenuation and nonalternation of the signs of the coupling constants for the alkyl protons indicate that a σ delocalization mechanism is operative in the alkyl chain.[3,5] It is interesting to note that considering the difference in structure the attenuation of the contact shift in $[Ni(n\text{-}C_3H_7NH_2)_6]^{2+}$ is fairly similar to that reported[5] for the bis(acetylacetonato)-bis(pyridine) nickel(II) complex: $(-10.00:-1.96:$

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(16) R. S. Drago and H. Peterson, Jr., *J. Am. Chem. Soc.*, **89**, 5774 (1967).

(17) H. H. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

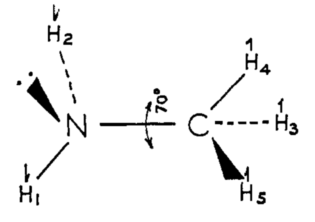


Figure 1. Geometry and spin densities of methylamine.

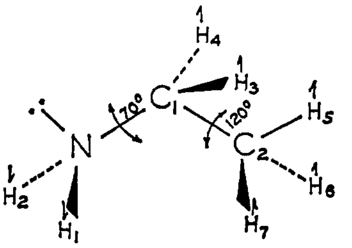
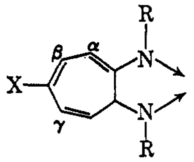


Figure 2. Geometry and spin densities of ethylamine.

−0.07 *vs.* −10.00:−2.94:−0.77, where − indicates a downfield shift and the α proton is assigned a valve of −10). On the basis of the structural similarity of the alkyl groups in our amines and the substituted aminotroponiminates one might expect very close agreement in the contact shift ratios. However, this is not the case as the observed ratios are −10.0:−1.40:−1.06 to +0.01) for an *n*-butyl group, attached at the R position (see structure below) of an aminotroponiminate ligand coordinated to nickel(II).



Fesseden and Schuler[7] found ratios of 10.00:12.01 and 10.00:15.02:0.17) for the α, β, and γ epr hyperfine coupling constants in the ethyl and *n*-propyl radicals, respectively. Both the alkyl radicals and the aminotroponiminates are fundamentally different from the alkylamines. In the former two studies, the unpaired electron is in a p_z (π-type) orbital and must reach the σ system by some type of hyperconjugative or "indirect" mechanism, while in the alkylamine complexes the unpaired spin is delocalized directly into the σ system.

The large upfield shift of the amino protons in these amine complexes has recently been noted by several investigators[4,18] for other nickel(II) complexes with ammonia and amines. Wayland[19] has discussed this apparently anomalous behavior in terms of competition between opposing mechanisms, namely, a direct delocalization mechanism, as discussed earlier, which places positive spin on the protons and a spin-polarization effect that causes negative spin density to reside on the protons. Apparently spin-polarization is dominant in the amino protons of the six-coordinate nickel(II) complexes with ammonia and amines.

2. Interpretation of the Extended Hückel Calculations. We shall attempt to calculate the ratio of the spin densities at various protons in the ligand rather than their magnitudes. The reason for this is twofold: (1) the basis set for the entire complex is very large making the full calculation expensive; (2) at this state of development of our calculations we are not confident about applying it to systems where there are large formal charges on the atoms in the molecule. Our approach will involve taking the ratios of the coefficients of the alkyl protons in the highest filled mo of the amine (largely nitrogen lone pair) and comparing these to the measured ratios of the contact shifts. We did not carry out calculations for the ligand free radical, for we feel that in view of the small amount of covalency in the metal–ligand bond the neutral ligand is a better approximation of the complexed ligand than the free radical would be. This approach also requires the assumption that complexation of the nitrogen will not distort the ratio of the alkyl protons in the highest filled mo; *i.e.*, the ligand mo mixed into the antibonding (essentially metal) e_g^* mo will have the same ratio of alkyl hydrogen coefficients as the highest filled orbital in the uncomplexed amine.

One of the first questions to be answered is: does rotation affect the form of the lone pair mo? If it does we shall have to worry about averaging the rotational configurations. For the case of methylamine, the spin density is invariant to the rotation of the methyl group as illustrated by the data in Table IV. In the case of ethylamine, rotational configurations may arise from rotation about either the N–C bond or the C–C bond. First consider rotation about the C–C bond with the C–N bond fixed. As may be seen from the data in Table V, the value of the spin density on the CH_3 and CH_2 group changes most significantly when the methyl group is rotated and the methylene and amino protons are staggered (*i.e.*, 0°,0° to 0°,20°). The effect is not as pronounced when the C–N bond is rotated 15° and methyl rotation studied. The following procedure was applied to give an approximate average value for these spin densities. Assuming the methyl group is free to rotate, and using the experimental value for the barrier to rotation in ethane[20] (2.9 kcal/mole) and a variable potential function[19] (eq 3, which was

$$U(\phi) = 0.5U_0(1 - \cos n\phi) \tag{3}$$

used to calculate the barrier at 5° intervals between the staggered and eclipsed forms), one can derive eq 4.

Here $U(\phi)$ is the potential at a given angle, U_0 is the maximum potential, n is the symmetry rotation axis, and ϕ is the angle of rotation. We then calculated the probability of each configuration, neglecting fractions less than 0.05, using the standard Boltzmann distribution expression.[21] The following formula for averaging the methyl configurations resulted.

$$\begin{aligned} CH_{3(av)} = {} & 0.17(0°) + 0.31(5°) + \\ & 0.25(10°) + 0.17(15°) + 0.10(20°) \end{aligned} \tag{4}$$

The nonzero conformers were double weighted since the molecule is free to rotate clockwise or counterclockwise and the staggered–staggered (or normal) geometry is the middle point of the rotation. We realize this is a classical treatment of a quantum mechanical problem,

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[18] B. B. Wayland and W. L. Rice, *J. Chem. Phys.*, **43**, 3150 (1966).

[19] B. B. Wayland and W. L. Rice, *Inorg. Chem.*, **6**, 2270 (1967).

[20] D. R. Lide, Jr., *J. Chem. Phys.*, **29**, 1426 (1958).

[21] N. Davidson, "Statistical Mechanics," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 91, 195.

and the averaging procedure is approximate. However, we are only interested in approximate values (10%). This procedure is more rigorous than taking an arithmetic average or using the 0°,0° results and considerably simpler than a detailed quantum mechanical approach. At 15° from the staggered CH_2–NH_2 configuration, and at all angles tried except 0°, the difference between the staggered methyl group and the value obtained by the above weighting procedure is less than 4%. Therefore, this weighting procedure is utilized only in determining the average shift for the configurations with staggered (0°) CH_2 and NH_2 protons.

Next let us consider rotation about the N–C bond. As can be seen from the data in Table VI, significant variations occur in the values of the spin density at the CH_3 and CH_2 protons when this bond is rotated.

The CH_3/CH_2 ratios of spin densities ranged from 0.911 (0°,0°) to 0.014 (100°,0°). Therefore, we built a Courtauld atomic model of $[Ni(C_2H_5NH_2)_6]^{2+}$ in an attempt to estimate which rotamers would be preferred in the complex. From this model we decided that only three configurations would be stable: a 0°,0° and configurations corresponding to rotation about the N–C bond, from 0°,0° to ±70° (with an error of ±5°). No intermolecular barrier to rotation appears to be imposed on the CH_3 groups in the model. The 0°,0° configuration is less sterically hindered and should be a more probable configuration. We found that, when the probability of the 0° rotameter is two and one-half times as great as the ±70° rotamers, a good fit is obtained for the ratio of the methyl and methylene coupling constants in the ethylamine complex. Admittedly, an additional check is needed on this procedure for we are in a position to vary the ratio of the rotamers and drastically affect the ratio of the coupling constants to fit that observed. Such a check is provided by the methylamine complex.

Since Δ is almost identical[12] for the $[Ni(CH_3NH_2)_6]^{2+}$ and $[Ni(C_2H_5NH_2)_6]^{2+}$ complexes, and since the amines are structurally similar, one may expect the spin delocalization mechanism to be almost identical in the two complexes. Thus, one may test the reasonableness of the assumptions for ethylamine by calculating the ratio $CH_2(C_2H_5NH_2)/CH_3(CH_3NH_2)$ from coefficients of the highest filled mo in CH_3NH_2. If we are forcing a fit in ethylamine by our averaging procedure, this calculated ratio will be in poor agreement with experimental. The excellent agreement in the ratios reported in Table VII lends credibility to our previous estimates.

Table VII. Final Ratios of Spin Densities

Group (ligand)	Ratio (calcd)	Ratio (exptl)
$CH_3(C_2H_5NH_2)/CH_2(C_2H_5NH_2)$	0.268	0.284
$CH_2(C_2H_5NH_2)/CH_3(CH_3NH_2)$	0.471	0.475

We were able to calculate the experimentally observed attenuation in the spin densities of our σ system. Consequently, in more complex systems where the ligand can undergo both σ and π bonding with the metal, calculations of the type described here may be of help in sorting out the relative importance of these various mechanisms.

Acknowledgment. The authors acknowledge with thanks the financial support of this research by the National Science Foundation through Grant GP-5498. One of us (R. J. F.) is also indebted to Dr. Donald H. Dugre for his aid and helpful discussions throughout the course of the theoretical part of this problem.

The Kinetics of the Reaction of Cobalt(III) and Iron(III) Hematoporphyrin with Cyanide and Thiocyanate. Evidence for a Dissociative Mechanism

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Abstract: The kinetics of reaction between cobalt(III) and iron(III) hematoporphyrin with the anions thiocyanate and cyanide were followed with a stopped-flow system. The kinetic data fit a reaction mechanism scheme that involves a dissociative mechanism with a five-coordinate intermediate. The cobalt(III) hematoporphyrin is very labile with respect to substitution reactions compared to the usual inert behavior of Co(III) complexes.

The reaction of metalloporphyrins with the ligands cyanide and thiocyanate has been investigated in order to determine the mechanism of this substitution reaction and also to obtain data in order to understand the unusual lability of the Co(III) ion toward substitution reactions when it is coordinated to porphyrins[2] or porphyrin-like compounds.[3]

The over-all reaction[4] that takes place can be represented by

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[1] Alfred P. Sloan Fellow.

(2) P. Hambright, Ph.D. Thesis, University of Chicago, 1966, p 164.

(3) W. C. Randall and R. A. Alberty, *Biochemistry*, **6**, 1520 (1967); **5**, 3189 (1966).

(4) Abbreviations used in this study: HP = hematoporphyrin IX, $M^{III}HP$ = metal(III) hematoporphyrin IX complex, AC ≡ aquocobalamin. The over-all charge on the metalloporphyrin molecule is not shown; the porphyrin side chains have a 2− charge due to two ionized carboxyl groups.