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Dichlorobis[N-methyl-α-(2-pyridyl)nitrone]nickel(II). Synthesis and Proton Magnetic Resonance Spectra[1a]

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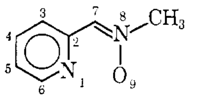
The synthesis, properties, and pmr spectra are reported for the new complex dichlorobis[N-methyl-α-(2-pyridyl)nitrone]-nickel(II) and its methyl derivatives. The pyridylnitrone ligands represent a new class of bidentate chelating agents. The two remaining coordinating positions in the six-coordinate complexes are occupied by chloride ions in the solid state and by water molecules in aqueous solutions of the complexes. The pmr isotropic shifts are consistent with unpaired electron spin density being delocalized in the ligands through both σ and π molecular orbitals. The lowest energy antibonding π molecular orbital is most likely involved in the π spin delocalization, although exact correlation between calculated and observed spin densities is not achieved.

Introduction

Proton magnetic resonance (pmr) studies of pyridine and other heterocyclic amines coordinated to paramagnetic transition metals have shown that unpaired electron spin density is delocalized into these heterocyclic amine ligands by a mechanism principally involving the ligand σ molecular orbitals.[2] In contrast, the mechanism of unpaired spin delocalization in coordinated heterocyclic N-oxides involves a ligand π molecular orbital.[3] Recently Kluiber and Horrocks[4] studied the coordination of the N-oxide group in the compound N-methyl-α-phenylnitrone and again found unpaired spin delocalized through a π mechanism. The compound N-methyl-α-(2-pyridyl)nitrone, MPN contains both an N-oxide and a pyridine moiety, each of which when independently coordinated employs a different mechanism of unpaired spin delocalization. Different delocalization mechanisms in separate parts of a chelate have recently been reported for structurally similar ligands coordinated to nickel(II).[5] A pmr study of complexes containing MPN was therefore of interest. Since these complexes have not previously been reported, this paper describes the preparation and properties in addition to the pmr spectra of dichlorobis[N-methyl -α-(2-pyridyl)nitrone]nickel(II), Ni$(MPN)_2Cl_2$, and its methyl derivatives.



Experimental Section

Preparation of the Pyridyl Nitrones.—The following procedure represents a considerable improvement over the literature method[6] for the synthesis of N-methyl-α-(2-pyridyl)nitrone.

To a stirred solution of 10.0 g of methylhydroxylamine hydrochloride in 65 ml of 2 *N* sodium hydroxide 12.8 g of freshly distilled 2-pyridinecarboxaldehyde was added dropwise over a period of 10 min. The resulting solution was stirred for 10 additional min, saturated with sodium chloride, and extracted repeatedly with chloroform. The chloroform extract was dried over sodium sulfate, and the solvent was removed under reduced pressure. The resulting yellow oil solidified upon cooling, yielding 16.3 g of crude material. The crude solid was recrystallized from hot methylcyclohexane and dried over phosphorus pentoxide *in vacuo*, yielding 11.4 g of N-methyl-α-(2-pyridyl)nitrone, mp 61.5–62.5°; picrate, mp 149–150° dec; lit.[4] 147–148°. The compound readily adsorbed water when exposed to the atmosphere.

The N-methyl-α-(methyl-2-pyridyl)nitrones were prepared in the same manner starting with the appropriate methyl-2-pyridinecarboxaldehyde, the latter being either purchased or synthesized by the literature method.[7] The resulting nitrones were identified by their pmr spectra. Because of their hydroscopic nature they were not obtained in a highly purified form. The melting points of the products obtained from a single recrystallization from methylcyclohexane are: N-methyl-α-(3-methyl-2-pyridyl)nitrone, 3-CH_3-MPN, mp 64–66°; N-methyl-α-(4-methyl-2-pyridyl)nitrone, 4-CH_3-MPN, mp 52–56°; N-methyl-α-(5-methyl-2-pyridyl)nitrone, 5-CH_3-MPN, mp 81–83°; N-methyl-α-(6-methyl-2-pyridyl)nitrone, 6-CH_3-MPN, mp 58–59°.

Preparation of Complexes.—The complexes were synthesized by the following procedure described for Ni$(MPN)_2Cl_2$.

A solution of 5.00 g of N-methyl-α-(2-pyridyl)nitrone in 15 ml of methanol was added dropwise over a period of 30 min to a stirred solution of 4.36 g of nickel chloride hexahydrate in 15 ml of methanol on a water bath at 50°. The resulting solution was stirred for 1 additional hr at 50°. The product was precipitated as a brown solid by the addition of diethyl ether to the reaction solution. Recrystallization was achieved by dissolving the product in methanol at room temperature and adding diethyl ether to a point just short of precipitation of the solid. Allowing this solution to stand in the refrigerator for several hours resulted in separation of the product as well-formed brown crystals.

The methyl-substituted pyridylnitrone complexes were synthesized in an analogous manner except that in some instances the complex precipitated spontaneously from the reaction solu-

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(1) (a) This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research through Contract AF49(638)-1492 and by the National Science Foundation through Grant GP6321. (b) Princeton University.

(2) J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963); R. H. Holm, G. W. Everett, Jr., and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, **88**, 1071 (1966); R. W. Kluiber and W. D. Horrocks, Jr., *ibid.*, **88**, 1399 (1966); B. B. Wayland and R. S. Drago, *ibid.*, **88**, 4597 (1966); G. N. La Mar, *Inorg. Chem.*, **6**, 1939 (1967).

(3) R. W. Kluiber and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, **87**, 5350 (1965).

(4) R. W. Kluiber and W. D. Horrocks, Jr., to be submitted for publication.

(5) G. N. La Mar and L. Sacconi, *J. Am. Chem. Soc.*, **90**, 7216 (1968).

(6) B. Umezawa, *Chem. Pharm. Bull.* (Tokyo), **8**, 967 (1960).

(7) S. Ginsburg and I. B. Wilson, *J. Am. Chem. Soc.*, **79**, 481 (1957); N. Nishimoto and T. Nakashimo, *Yakugaku Zasshi*, **81**, 88 (1961); *Chem. Abstr.*, **55**, 13420*i* (1961).

tion shortly after the addition of the ligand was complete. The results of elemental analysis of the complexes are shown in Table I.

TABLE I

ELEMENTAL ANALYSIS OF COMPLEXES

Complex	Calcd		Found	
	% C	% H	% C	% H
$Ni(MPN)_3(BF_4)_2$	39.36	3.78	39.35	3.86
$Ni(MPN)_2Cl_2$	41.84	4.01	42.01	4.02
$Ni(3\text{-}CH_3\text{-}MPN)_2Cl_2$	44.69	4.69	44.92	4.87
$Ni(4\text{-}CH_3\text{-}MPN)_2Cl_2$	44.69	4.69	44.85	4.90
$Ni(5\text{-}CH_3\text{-}MPN)_2Cl_2 \cdot H_2O$	42.90	4.95	43.23	4.92
$Ni(6\text{-}CH_3\text{-}MPN)_2Cl_2$	44.69	4.69	44.71	4.70

Attempts to prepare the complex $Ni(MPN)_3Cl_2$ by the same procedure as above except using water as a solvent rather than methanol resulted only in the formation of an amorphous solid upon evaporation of the aqueous reaction solution. Attempted recrystallization of this solid from methanol–ether resulted in formation of $Ni(MPN)_2Cl_2$. The addition of sodium tetrafluoroborate to an aqueous solution of the above amorphous solid resulted in the precipitation of the complex $Ni(MPN)_3(BF_4)_2$ which was recrystallized from a small amount of hot water. This complex, however, was not sufficiently soluble to permit observation of a pmr spectrum in aqueous solution.

Spectra.—The pmr spectra were recorded on a Varian Associates A-60A spectrometer, which was modified to scan 5000 cps on either side of TMS, or on a Varian DP-60 spectrometer. Except as noted, the spectra were recorded at the ambient probe temperature which varied over a period of several months from 39 to 45°. The spectra were recorded from solutions of the complexes in deuterium oxide. The pmr frequencies are measured relative to the peak of the methyl protons of tetramethylammonium chloride, present in the solutions as an internal standard.

Visible and near-infrared spectra were recorded on a Cary 14 spectrometer on aqueous solutions or on Nujol or Halocarbon oil mulls smeared on filter paper.

Infrared spectra were recorded with a Perkin-Elmer 237B spectrometer on Nujol or Halocarbon oil mulls and calibrated with polystyrene.

Results

$Ni(MPN)_2Cl_2$ and Its 3-CH_3, 4-CH_3, and 5-CH_3 Derivatives. Ligand Field Spectra.—The energies of the observable ligand field bands for these compounds are shown in Table II. The similarity of the spectra in the solid state and in solution for the complex $Ni(MPN)_3(BF_4)_2$ indicates that the coordination in this complex involves three bidentate ligands forming an effective octahedral ligand field. Therefore the Δ value of 10,200 cm^{-1} observed for this complex may be taken as the strength of the ligand field for the pyridylnitrone ligands. The spectra of the bis(pyridylnitrone) complexes, however, indicate differences in coordination in aqueous solution from the coordination in the solid state. The spectra in aqueous solution may be interpreted in terms of an effective octahedral ligand field with the spectral bands assigned to the respective transitions $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^1E_g(^1D)$, and $^3A_{2g} \rightarrow {}^3T_{1g}(^3F)$ in O_h symmetry. The Δ value observed for the complex $Ni(MPN)_2Cl_2$ in aqueous solution is 9900 cm^{-1}. In solution the coordination sphere is undoubtedly occupied by two bidentate pyridylnitrone ligands and two coordinated water molecules. An average Δ value calculated as the sum of $^2/_3\Delta$ for the pyridylnitrone ligand and $^1/_3\Delta$ = 8500 cm^{-1} for H_2O[8] yields Δ = 9600 cm^{-1}, in reasonable agreement with that observed. In the solid state the two low-energy bands in the spectrum of $Ni(MPN)_2Cl_2$ can be interpreted as resulting from the splitting of the $^3T_{2g}$ state by a distorted ligand field, the coordination sphere being occupied by two O, two N, and two Cl atoms. These bands fall at lower energies in the mull spectra than in aqueous solution spectra, suggesting that the chloride ions (which lie low in the spectrochemical series)[9] are replaced by water molecules in the latter case. This is to be expected since octahedral nickel(II) complexes of monodentate ligands are substitutionally labile.

TABLE II

VISIBLE AND NEAR-INFRARED SPECTRA OF COMPLEXES

Complex	ν_{max}, cm^{-1} (ϵ_{max}, l. mol^{-1} cm^{-1})
$Ni(MPN)_3(BF_4)_2$	
H_2O solution	10,200 (8.1), 12,700 (3.0), *a*
Nujol mull	10,100, 12,600, 17,900[b]
$Ni(MPN)_2Cl_2$	
H_2O solution	9900 (6.2), 13,200 (1.7), 17,300[b] (8.2)
Nujol mull	8600, 10,200, *a*
$Ni(3\text{-}CH_3\text{-}MPN)_2Cl_2$	
H_2O solution	9900 (6.6), 13,100 (1.8), 17,000[b] (9)
Nujol mull	9400,[c] *a*
$Ni(4\text{-}CH_3\text{-}MPN)_2Cl_2$	
H_2O solution	9900 (6.2), 13,200 (1.7), 17,300[b] (8.2)
Nujol mull	8600, 10,200, *a*
$Ni(5\text{-}CH_3\text{-}MPN)_2Cl_2 \cdot H_2O$	
H_2O solution	9800 (6.6), 13,200 (2.0), 17,400[b] (9.0)
Nujol mull	8900, 10,200, *a*
$Ni(6\text{-}CH_3\text{-}MPN)_2Cl_2$	
H_2O solution	8850 (2.7), 14,000 (2.5), 15,200 (2.4)
Nujol mull	8000, 12,300, 13,700

[a] Higher energy bands are obscured by the intense charge-transfer band. [b] Shoulder. [c] Band is very broad but shows no definite splitting.

Infrared Spectra.—The infrared spectra of these complexes were in general too complex to permit a complete assignment of the bands; however, several important bands could be uniquely identified and are listed in Table III.

TABLE III

INFRARED BANDS FOR $Ni(MPN)_2Cl_2$ APPEARING IN THE REGIONS 1500–1650 AND 1100–1200 CM^{-1}

Assignment	ν, cm^{-1}	
	Free ligand	Complex
C=N str	1583	1625
Ring (ν_{8a})[a]	1575	1591
Ring (ν_{8b})	1563	1568
	1558 sh	
NO str	1165	1180
H bend (ν_{15})	1140	1163

[a] The frequency designations in parentheses refer to the corresponding normal modes of benzene: H. Shindo and B. Umezawa, *Chem. Pharm. Bull.* (Tokyo), **10**, 492 (1962); C. H. Kline and J. Turkevich, *J. Chem. Phys.*, **12**, 300 (1944).

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(8) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **2**, 134 (1959).

(9) D. M. L. Goodgame, M. Goodgame, and M. J. Weeks, *J. Chem. Soc.*, 5194 (1964).

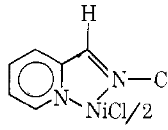
TABLE IV

PMR SPECTRA OF AQUEOUS SOLUTIONS OF COMPLEXES

	3-H	4-H	5-H	6-H[a]	7-H	N–CH$_3$
			Ni(MPN)$_2$Cl$_2$ (39°)			
Free ligand resonances, cps	−321[b]	−271	−245	−311	−263	−39
Isotropic shift, cps	−2000 ± 10[c]	−770 ± 10	−1525 ± 10	∼−7000	+1780 ± 15	−643 ± 5
A, G	+0.314	+0.121	+0.239	+1.10	−0.279	+0.101
			Ni(3-CH$_3$-MPN)$_2$Cl$_2$ (40°)			
Free ligand resonances, cps	(CH$_3$) +57	−271	−250		−291	−45
Isotropic shift, cps	−535 ± 5	−690 ± 10	−1500 ± 15		+2210 ± 20	−405 ± 15
A, G	+0.084	+0.108	+0.236		−0.348	+0.063
			Ni(4-CH$_3$-MPN)$_2$Cl$_2$ (45°)			
Free ligand resonances, cps	−307	(CH$_3$) +65	−228		−261	−39
Isotropic shift, cps	−1910 ± 10	+566 ± 3	−1430 ± 15		+1720 ± 15	−646 ± 5
A, G	+0.306	−0.090	+0.228		−0.275	+0.103
			Ni(5-CH$_3$-MPN)$_2$Cl$_2$·H$_2$O (87°)			
Free ligand resonances, cps	−321	−262	(CH$_3$) +57		−270	−41
Isotropic shift, cps	−1810 ± 20	−590 ± 10	−517 ± 5		+1560 ± 20	−504 ± 10
A, G	+0.328	+0.107	+0.093		−0.284	+0.091
			Ni(6-CH$_3$-MPN)$_2$Cl$_2$ (2°)			
Free ligand resonances, cps	−308	−260	−230	(CH$_3$) +54	−251	−39
Isotropic shift, cps	−1910 ± 20	−715 ± 5	−1480 ± 20	+625 ± 50	+2360 ± 50	−490 ± 10
A, G	+0.264	+0.099	+0.205	−0.086	−0.326	+0.068

[a] A peak resulting from the hydrogen in the 6 position was observed only for Ni(MPN)$_2$Cl$_2$. [b] Measured relative to the methyl proton peak of (CH$_3$)$_4$NCl. A negative frequency is at a lower applied field than the reference frequency. [c] A negative isotropic shift is a shift to a lower applied field.

For the free ligand the assignments of the C═N and NO stretching bands were made on the basis of the shifts observed for these bands in aqueous solutions of the compound. The bands at 1583 and 1165 cm^{-1} in the mull spectrum shifted to 1602 and 1159 cm^{-1}, respectively, in aqueous solution with relatively little effect on the other bands listed. Similar solvent effects have been noted for other nitrones.[10] The assignment of the two bands in the 1100–1200-cm^{-1} region was aided by a comparison with the spectrum of the analogous imine complex



The spectrum of the imine complex shows only a single band at 1150 cm^{-1} in the 1100–1200-cm^{-1} region. It would therefore seem more logical to assign the higher energy band in this region to the NO stretch in the spectrum of Ni(MPN)$_2$Cl$_2$. The shifts in the pyridine ring bands to higher energies, shown by Busch[11] to be indicative of pyridine coordination, and the shifts in the C═N and NO stretching bands indicate that the pyridylnitrone ligands coordinate in a bidentate manner.

Magnetic Moments.—The magnetic susceptibilities of the aqueous solutions of the complexes, measured by the Evans method,[12] at concentrations from 0.06 to 0.19 *m* at 40° yielded an effective magnetic moment of 3.18 BM for all of the complexes studied. This yields a value for the spectroscopic splitting factor of $g = 2.25$, calculated from the formula $\mu_{\text{eff}} = g\sqrt{S(S+1)}$.

Pmr Spectra.—The pmr spectrum of Ni(MPN)$_2$Cl$_2$ in deuterium oxide is shown in Figure 1, and a tabulation of the pmr results for all the complexes is listed in Table IV. The assignment of the resonance peaks was accomplished by a comparison of the spectrum of the parent complex with the spectra of its methyl derivatives. Ni(5-CH$_3$-MPN)$_2$Cl$_2$·H$_2$O was less soluble than the other complexes; hence, the solutions of this complex were heated to obtain sufficient solubility to observe a well-defined spectrum. The values of *A*, the hyperfine coupling constant in units of gauss, were calculated using[13]

$$\frac{\Delta\nu}{\nu} = -\frac{A}{2S}\left(\frac{\gamma_e}{\gamma_H}\right)\frac{g\beta S(S+1)}{3kT} \tag{1}$$

In eq 1 $\Delta\nu$ is the isotropic shift where $\Delta\nu = \nu_{\text{paramag}} - \nu_{\text{diamag}}$, ν is the frequency of the spectrometer, γ_e and γ_H are the magnetogyric ratios for the electron and the proton, respectively, g is the spectroscopic splitting factor, β is the Bohr magneton, and S is the total spin quantum number.

The pmr spectrum of a solution of Ni(MPN)$_2$Cl$_2$ containing excess MPN ligand showed separate peaks resulting from coordinated and uncoordinated ligands, indicating that the rate of chemical exchange of the ligand between the coordination sphere and the bulk solution is slow on the pmr time scale. An upper limit to the rate of exchange may be calculated from the width at half-height, $\Delta\nu_{1/2}$, of the coordinated ligand peaks. The effective transverse relaxation time, T_2, is given by $1/T_2 = \pi\Delta\nu_{1/2}$. Under the conditions of

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(10) H. Shindo and B. Umezawa, *Chem. Pharm. Bull.* (Tokyo), **10**, 492 (1962).

(11) D. H. Busch and P. E. Figgins, *J. Phys. Chem.*, **65**, 2236 (1961).

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

(13) H. M. McConnell and D. B. Chestnut, *J. Chem. Phys.*, **28**, 107 (1958).

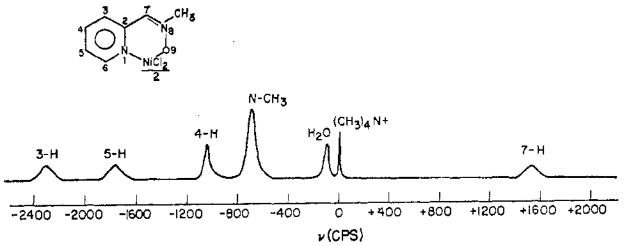

Figure 1.—The pmr spectrum at 60 Mcps of $Ni(MPN)_2Cl_2$ in deuterium oxide at 39°. The 6-H peak at −7000 cps with a half-width of ~1700 cps is not shown in the figure.

slow exchange T_2 is related to T_{2M}, the transverse relaxation time in the absence of exchange, and $1/\tau_M$, the rate of chemical exchange, by eq 2.[14] The narrowest paramagnetic peak in the spectrum of $Ni(MPN)_2Cl_2$ in a solution containing excess MPN had a width at half-height of 50 cps, corresponding to a value of $1/T_2 = \sim 160$ sec^{-1}, such that $1/\tau_M < \sim 160$ sec^{-1}.

$$1/T_2 = (1/T_{2M}) + (1/\tau_M) \qquad (2)$$

$Ni(6\text{-}CH_3\text{-}MPN)_2Cl_2$.—The presence of the methyl group in the 6 position on the pyridine ring exerts a steric hindrance which affects the properties of this complex. The fact that a crystalline complex containing two pyridylnitrone ligands exists indicates that this ligand is capable of acting as a bidentate ligand in spite of the steric hindrance of the 6-methyl group. This conclusion is supported by shifts in the infrared spectra of the ligand upon coordination similar to those observed for N-methyl-α-(2-pyridyl)nitrone. Some important peaks in the infrared spectra which could be assigned are listed in Table V.

TABLE V

INFRARED BANDS FOR $Ni(6\text{-}CH_3\text{-}MPN)_2Cl_2$ APPEARING IN THE REGIONS 1500–1650 AND 1100–1200 CM^{-1}

	ν, cm^{-1}	
Assignment	Free ligand	Complex
C═N str	1580	1629
Ring (ν_{8a})	1576	1587
Ring (ν_{8b})	1565	1565
	1557 sh	
NO str	1169	1179
H bend (ν_{15})	1142	1170

The ligand field spectrum of this complex in the solid state (reported in Table II) is best interpreted by assigning the bands at 8000, 12,300, and 13,700 cm^{-1} to the transitions $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^1E_g$ (^1D), and $^3A_{2g} \rightarrow {}^3T_{1g}$ (^3F), respectively, in O_h symmetry. The calculations of Liehr and Ballhausen[8] predict bands at 12,100 and 13,500 cm^{-1} for $\Delta = 8000$ cm^{-1}. An interpretation of these three bands as the split components of the $^3T_{2g}$ state of O_h due to the actual lower symmetry requires unreasonably large values for both the splitting parameters and Δ. The observed Δ value of 8000 cm^{-1} indicates a large reduction in the strength of the ligand field perhaps owing to the greater length of ligand–metal bonds resulting from the steric hindrance. The electronic spectrum of this complex in aqueous solution is quite similar to that of the hydrated nickel ion, consistent with the pmr results which indicate that the complex is largely dissociated in aqueous solutions (*vide infra*).

The pmr spectrum of $Ni(6\text{-}CH_3\text{-}MPN)_2Cl_2$ in deuterium oxide is shown in Figure 2, where two effects are apparent. The first is that partial dissociation of the complex occurs in aqueous solution. The pmr spectra at temperatures below 20° show peaks resulting from ligands in both diamagnetic and paramagnetic environments; that is, both uncoordinated and coordinated ligands are in solution. The second effect is that the rate of chemical exchange between the coordinated and uncoordinated ligands at temperatures above 20° becomes increasingly more rapid and is such that at temperatures above 70° the only peaks that are observed represent an average of the ligands in the two magnetic environments. No exchange effects are noted for solutions of the complexes of the other pyridylnitrones containing excess ligand. Thus the steric hindrance of the 6-methyl group results in a partial dissociation of the complex in solution as well as an increase in the rate of chemical exchange of the ligand.

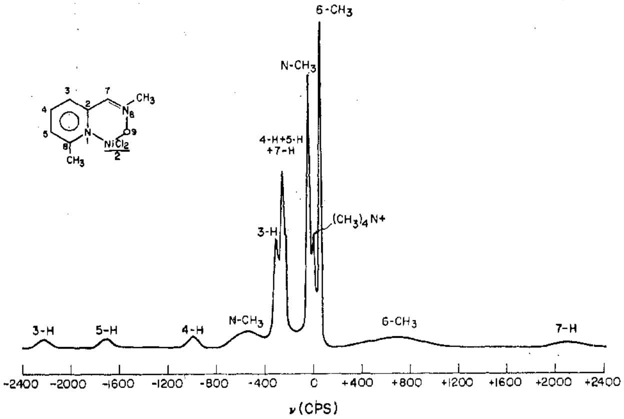

Figure 2.—The pmr spectrum at 60 Mcps of $Ni(6\text{-}CH_3\text{-}MPN)_2Cl_2$ in deuterium oxide at 2° showing the effects of decomposition in solution. The broad and sharp peaks result from the coordinated and uncoordinated ligands, respectively. Compared to the spectrum of the free ligand in solution, the sharp peaks are considerably broadened but are not shifted by more than 10 cps.

The degree of dissociation of the complex may be determined from both the low- and high-temperature spectra. A comparison of the areas under the diamagnetic peaks with the areas under the paramagnetic peaks for a 0.58 *M* solution of the complex at 1.5° indicates that 20% of the ligands are complexed at this temperature, such that ~40% of the nickel ions form complexes with the pyridylnitrone ligand if one assumes that no complexes containing more than a single chelate ligand exist. At 96° a comparison of the shifts observed with those expected for the paramagnetic species as extrapolated from the low-temperature data indicates that ~30% of the ligands are complexed.

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[14] L. H. Piette and W. A. Anderson, *J. Chem. Phys.*, **30**, 899 (1959).

Discussion

The observed isotropic shifts for the chelate protons may be confidently attributed to a Fermi contact interaction involving either spin delocalization or polarization, for it has been amply demonstrated that the dipolar shifts are generally negligible for magnetically isotropic octahedral nickel(II) complexes. The large downfield 3-H, 5-H, and 6-H shifts are very similar to those observed for various paramagnetic pyridine complexes,[2] where σ spin delocalization has been demonstrated to account for the shifts. The effect of methyl substitution at the 3 and 5 positions attests to the σ delocalization mechanism, since the shift magnitudes decrease by a factor of ~3, without reversal of shift direction. The observed 3-H to 5-H shift ratio of ~1.3 closely corresponds to that reported for tris(bipyridyl)nickel(II) (1.4)[15] and to the analogous ratio for picolinic acid complexes of nickel (1.3).[16] Substitution of a hydrogen atom in the 2 position by a carbon atom apparently increases the spin density at the adjacent hydrogen atom on a pyridine ring.

The sizable upfield shift for 7-H indicates, however, that some π spin delocalization must also occur. A very similar combination of spin delocalization mechanisms has also been observed for the acetylimine-substituted pyridine complex of nickel[5] with an analogous azomethine linkage. In addition, methyl substitution at the 4 position reveals that the pyridine ring also experiences a secondary π contribution to its shifts, but owing to the large σ shifts, the π mechanism dominates only at the 4 position, as noted previously.[2,5] In order to ascertain which ligand π orbital is responsible for the large 7-H shift, a Hückel–McLachlan spin density calculation,[17] where spin correlation is included,[18] was performed, using the accepted parameters $\alpha_O = \alpha + 2\beta$, $\beta_{NO} = 0.6\beta$, $\beta_{CN(8)} = 1.2\beta$, $\beta_{CN(1)} = 1.0\beta$, and $\alpha_N = \alpha + h\beta$, where h was varied from 0.5 to 1.0. The results were not affected qualitatively by the choice of h, and the calculated spin densities for $h = 0.5$ are given in Table VI. A noteworthy feature of the MO calculation is that only very small positive or sizable negative spin density is predicted for the 7 position for the highest bonding orbital (HBO), depending on the choice of parameters. The results presented in Table VI are for the calculation yielding the most positive value of the spin density at the 7 position for the HBO. Increasing the h parameter only makes this spin density more negative. Thus it appears that the lowest antibonding orbital (LAO) with a sizable positive 7-H spin density must be invoked to interpret the large positive 7-H shift. For the 4 and 6 positions, where methyl substitution indicates small negative π spin densities, agreement with either MO is poor, since the LAO accounts for the 6-CH_3 shift, while the HBO is in accord with the 4-CH_3 shift. What appears to be the most plausible rationalization here is that both ligand π orbitals contain some unpaired spin and that the π shifts at a given position are perhaps determined by the relative magnitudes of the spin densities in the two contributing orbitals.[19] Of interest is the fact that the LAO participates at all, since most other nickel complexes have displayed π shifts consistent with the HBO. Two possible reasons can account for the present observation. First, the energy of the LAO is very low, 0.5756β (0.3781β for $h = 1.0$), compared to many of the previously studied ligands; this would facilitate an M→L charge transfer for spin delocalization. Second, and perhaps more significantly, it should be remembered that not only the energy of a ligand MO but also the metal orbital–ligand atom orbital overlap determine the extent of metal–ligand orbital mixing, such that ligand MO's with zero coefficients at the bonding atom cannot interact covalently with the metal d orbitals, no matter how favorably they be placed energetically. This is the case for symmetrically substituted pyridines, where a node passes through the nitrogen in the HBO, precluding any direct spin delocalization into that orbital. It is probable that this is the reason for the almost complete absence of π shifts in pyridine-type ligands.[2] Inspection of Table VI shows that the squares of the coefficients of the N(1) and O(9) bonding atoms in the HBO are very small, particularly at the nitrogen, though quite sizable on at least one bonding atom (the nitrogen) in the LAO. Thus overlap considerations tend to favor M→L over L→M charge transfer for spin delocalization[19] in the present case.

Table VI

Calculated Spin Densities[a]

Position	HBO		LAO	
	HMO	MHMO	HMO	MHMO
N(1)	0.030	−0.329	0.157	0.189
C(2)	0.141	0.281	0.149	0.173
C(3)	0.160	0.153	0.051	−0.010
C(4)	0.002	−0.343	0.065	0.043
C(5)	0.190	0.394	0.139	0.131
C(6)	0.101	0.093	0.002	−0.065
C(7)	0.068	0.058	0.160	0.114
N(8)	0.243	0.554	0.263	0.407
O(9)	0.064	0.140	0.014	0.017

[a] HMO represents Hückel spin densities and MHMO represents the correlated McLachlan spin densities, calculated according to ref 17 and 18.

Another point relevant to the π delocalization is that the observation of π shifts does not necessarily reflect metal–ligand π bonding. Owing to the low symmetry of the complex and the possibility that the ligand is not planar, no rigorous σ–π separation exists. In such a case σ spin delocalization in the Ni–O bond could induce π spin density in other parts of the chelate owing to the nonorthogonality of the σ and π systems in nonplanar chelates.[20] Even for a planar ligand, rigorous σ–π separation may not obtain when the metal is included in the system. Horrocks, *et al.*, have

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(15) M. L. Wicholas and R. S. Drago, *J. Am. Chem. Soc.*, **90**, 2196 (1968).

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(18) The correlation was introduced by varying the coulomb integrals, as indicated in ref 17. However, both diagonal and off-diagonal elements were altered, which will be shown to be necessary for heteroatomic systems: G. N. La Mar and J. H. Schachtschneider, to be submitted for publication.

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shown[21] in an X-ray structure determination of bis(pyridine N-oxide)bis(2,4-pentanedionato)nickel(II) that the nickel atom does not lie in the plane of the pyridine N-oxide ligand molecule; hence, the metal–ligand bond and the ligand π system are not orthogonal. Even if the observed π shifts arose from direct metal–ligand π bonding, it would still be necessary to postulate some unpairing of the paired t_{2g} orbital electrons. Spin–orbit coupling can account for some unpairing, as discussed previously;[19] however, it does not seem fruitful to speculate further on the exact nature of the spin-transfer mechanism in view of the numerous possibilities, of which spin polarization might also be mentioned.[19,22] This last mechanism has been postulated[22] but still awaits documentation.[19,23]

Last, while the observed negative N–CH_3 shifts are consistent with either σ or π spin density in either HBO or LAO, this methyl group exhibits an upfield shift when the pyridine is replaced by a phenyl ring.[4]

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On the Preparation and Structure of Acetamidinium Tetrachlorocuprate(II)[1]

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Acetamidinium tetrachlorocuprate has been prepared and characterized. Optical spectra, thermochromism, and epr spectra of this compound are reported and discussed. A structural model is proposed in which $CuCl_4^{2-}$ layers are composed of strips of tetrahedral sites alternated with strips of tetragonal sites. These layers are separated from each other by the acetamidinium ions.

Introduction

As part of a program of investigating ligands similar in geometry to acetate ion, the coordination chemistry of acetamidine and some of its derivatives is under study. During this study a number of new chlorometalate salts have been prepared; this paper reports the investigations on one of these, acetamidinium tetrachlorocuprate(II), $[CH_3C(NH_2)_2]_2CuCl_4$.

Copper forms a great many double salts with other chlorides, and these display various structural forms. X-Ray crystal structures have been reported on a number of these[2,3] and considerable literature is available on spectra and magnetic properties of the various structural types.

A brief review of the structural variations which have been observed in tetrachlorocuprates may be useful. Cs_2CuCl_4 is an orange compound, which contains discrete distorted tetrahedral $CuCl_4^{2-}$ groups.[2,3a] Two tetraalkylammonium tetrachlorocuprates have also been investigated crystallographically and found to contain discrete, distorted tetrahedral $CuCl_4^{2-}$ ions.[3] In contrast, the large number of known monoalkylammonium tetrachlorocuprates[4] have a different structure in which the copper is coordinated in square-planar geometry to four chloride ions and exhibits weak bonding to two more chlorides in other $CuCl_4^{2-}$ groups.[5] The geometry of the copper site in these structures is the usual tetragonally distorted octahedron which has become so familiar.

The monoalkylammonium tetrachlorocuprates also exhibit thermochromism, a property which Cs_2CuCl_4 and $(R_4N)_2CuCl_4$ do not share. In particular, all of the monoalkylammonium salts which have been studied transform from yellow to green at low temperatures. The temperature of the transition varies with the alkyl group. In isopropylammonium tetrachlorocuprate it is above room temperature. The structure of the low-temperature green form has not yet been determined.

$[CH_3C(NH_2)_2]_2CuCl_4$ is bright yellow and thermochromic, and very large crystals can easily be prepared. It was felt that the structure could probably be easily deduced from its properties in the midst of this wealth of data. The results of this study have been both interesting and unexpected.

Experimental Section

Sample Preparation.—$[CH_3C(NH_2)_2]_2CuCl_4$ was prepared by mixing stoichiometric amounts of acetamidine hydrochloride and anhydrous copper(II) chloride in ethanol. This is the same procedure used by Remy and Laves[4] to prepare alkylammonium

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