stretch, found at 303 cm.$^{-1}$ in ferrocene,[21] 298 cm.$^{-1}$ in $C_6H_6Cr(CO)_3$,[22] and 279 cm.$^{-1}$ in $(C_6H_6)_2Cr$,[23] is expected around 300 cm.$^{-1}$. This vibration would also involve a large change in polarizability and should, therefore, give rise to a strong Raman shift. The

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very strong polarized band at 330 cm.$^{-1}$ is most likely derived from this mode. This line is, however, broad and so may overlap a COT mode. In ferrocene, $C_6H_6Cr(CO)_3$, and $(C_6H_6)Cr$[23] the ring-tilt is found at 388, 330, and 333 cm.$^{-1}$, respectively. The weak band at 404 cm.$^{-1}$ may belong to this mode. The COT–Fe–$(CO)_3$ bending modes should be very low, below 100 cm.$^{-1}$, and were probably not observed in this work.

Electron Spin Density Distribution and Structure of Nickel(II) and Cobalt(II) Acetylacetonate Complexes with Pyridine N-Oxides by Nuclear Magnetic Resonance Isotropic Shifts[1]

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Pyridine N-oxide and its monomethyl derivatives form a series of isolable 2:1 complexes with nickel(II) and cobalt(II) acetylacetonates. Electron spin density distribution in the ligands was studied by n.m.r., and the data were compared with other experimental and calculated values. From pseudo-contact n.m.r. shifts it was ascertained that the pyridine N-oxide complexes have a M–O–N angle of 114–125° in solution. Evidence for hydrogen bonding with chloroform and the presence of other than 2:1 complexes in solution was also obtained.

Introduction

Nuclear magnetic resonance has been used in the determination of unpaired spin density distribution in the ligands of paramagnetic metal complexes in which the effective electron spin relaxation time is short.[2-7] More recently n.m.r. data on pairs of paramagnetic complexes, one essentially magnetically isotropic and the other anisotropic, have provided some details on the geometric structure of these complexes in solution.[2-4] Convenient systems for the study of these effects are the metal acetylacetonates of nickel(II) and cobalt(II) [bis(2,4-pentanedionato)nickel(II) and -cobalt(II), hereafter referred to as Ni(AA)$_2$ and Co-(AA)$_2$]. In solution these chelates exist as octahedrally coordinated polymeric species, but upon addition of

basic ligands an equilibrium mixture is formed in which the added ligand coordinates with the metal and reduces the degree of polymerization. With increasing ligand concentration there is generally formed a 2:1 complex in which the two acetylacetonate groups define an equatorial plane which includes the metal atom, and the two added ligands occupy positions axial to this plane.[8] The exchange rate of these ligands with the metal acetylacetonates has been found to be rapid. This results in a proton n.m.r. spectrum in which the observed chemical shifts are a number-average of the shifts of the coordinated and uncoordinated ligand. The deviations from the diamagnetic positions of the coordinated ligand proton resonances are dependent on the electron spin density at the proton and, in a magnetically anisotropic complex, the position of the proton relative to the molecular axis. Using the M(AA)$_2$ system, previous workers have determined that electron spin density is distributed by a σ mechanism in pyridine[4] and by a π mechanism in phenylisocyanide[2] and triphenylphosphine.[2] Furthermore all of these ligands form complexes in which the major ligand axis is coincident with the complex axis.

The present work is concerned with a study of the coordination of pyridine N-oxide and some of its methyl derivatives with Ni(AA)$_2$ and Co(AA)$_2$. These aromatic N-oxides are weakly basic substances[9] which coordinate readily with metal salts.[10] Several calculations of the π-electronic structures of these ligands have been published.[11,12] These ligands are shown to

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coordinate readily with Ni(AA)₂ and Co(AA)₂, and sizeable n.m.r. shifts in the pyridine ring proton resonances, due to spin delocalization in the ligand π orbital, are observed.

Experimental Section

Isolation of Metal Acetylacetonate–Amine N-Oxide Complexes. To 0.256 g. (0.001 mole) of anhydrous nickel acetylacetonate in 10 ml. of hot toluene was added 0.220 g. (0.002 mole) of γ-picoline N-oxide. After 3 days 0.33 g. of green 2:1 complex was isolated and dried *in vacuo* at 56°. *Anal.* Calcd. for $C_{22}H_{28}O_6N_2Ni$: C, 55.61; H, 5.94; N, 5.89. Found: C, 55.70; H, 5.61; N, 5.98.

Similarly prepared was the buff-colored 2:1 γ-picoline N-oxide–Co(AA)₂ adduct. *Anal.* Calcd. for $C_{22}H_{28}O_6N_2Co$: C, 55.58; H, 5.94; N, 5.89. Found: C, 55.13; H, 6.06; N, 5.77. A similar experiment using 0.256 g. (0.001 mole) of anhydrous Co(AA)₂ but only 0.108 g. (0.001 mole) of γ-picoline N-oxide in 10 ml. of toluene gave no precipitate after 3 days.

The 2:1 pyridine oxide–M(AA)₂ complexes were similarly prepared. *Anal.* Calcd. for $C_{20}H_{24}O_6N_2Ni$: C, 53.72; H, 5.41; N, 6.26. Found: C, 53.91; H, 5.35; N, 6.16. Calcd. for $C_{20}H_{24}O_6N_2Co$: C, 53.69; H, 5.41; N, 6.26. Found: C, 53.87; H, 5.84; N, 6.01.

The M(AA)₂ complexes with β-picoline N-oxide were quite soluble in toluene and methylcyclohexane–toluene was used as a solvent. With an excess of amine oxide the green 2:1 nickel complex was isolated. *Anal.* Calcd. for $C_{22}H_{28}O_6N_2Ni$: C, 55.61; H, 5.94; N, 5.89. Found: C, 55.91; H, 6.11; N, 5.54. The red-brown cobalt 2:1 complex was also isolated using this mixed solvent. *Anal.* Calcd. for $C_{22}H_{28}O_6N_2Co$: C, 55.58; H, 5.94; N, 5.89. Found: C, 56.26; H, 5.96; N, 5.62.

α-Picoline N-oxide formed 2:1 complexes with both Ni(AA)₂ and Co(AA)₂. These were recrystallized from chloroform and isolated as crystals containing chloroform. Drying at 56° *in vacuo* produced the desolvated complexes. *Anal.* Calcd. for $C_{22}H_{28}O_6N_2Ni$: C, 55.61; H, 5.94; N, 5.89. Found: C, 55.96; H, 5.92; N, 5.87. Calcd. for $C_{22}H_{28}O_6N_2Co$: C, 55.58; H, 5.94; N, 5.8.9. Found: C, 55.08; H, 5.97; N, 5.47.

With an excess of 2,6-lutidine N-oxide, Co(AA)₂ in methylcyclohexane–toluene formed a 1:1 complex. *Anal.* Calcd. for $C_{17}H_{23}O_5NCo$: C, 53.69; H, 6.10. Found: C, 53.25; H, 6.59. This became rapidly hydrated upon exposure to the atmosphere and the resulting pink 1:1:1 2,6-lutidine N-oxide–water–Co(AA)₂ complex was purified by drying at 56° *in vacuo* (to remove some liberated N-oxide) and rehydrating the anhydrous complex in the atmosphere. *Anal.* Calcd. for $C_{17}H_{25}O_6NCo$: C, 51.26; H, 6.33; N, 3.52. Found: C, 51.34; H, 6.41; N, 3.77. A light green 1:1:1 2,6-lutidine N-oxide–water–Ni(AA)₂ complex was isolated. *Anal.* Calcd. for $C_{17}H_{25}O_6NNi$: C, 51.29; H, 6.33. Found: C, 51.29; H, 6.63.

Spectra. Visible and near-infrared spectra were taken using a Cary Model 14 spectrophotometer. In-

frared spectra were taken as Nujol mulls in the range 4000 to 750 cm.$^{-1}$ on a Perkin-Elmer Model 237B grating spectrophotometer. The n.m.r. spectra were obtained using a Varian A-60 spectrometer. Samples were prepared for the n.m.r. by weighing out freshly dried M(AA)₂ and adding a 0.5- or 1-ml. aliquot of freshly distilled N-oxide (γ-picoline N-oxide was freshly recrystallized and dried at 56° *in vacuo*), weighed, and diluted to volume in a volumetric flask. Deuteriochloroform was the solvent and the probe temperature was approximately 36°. Most of the spectra were calibrated using a wide-range oscillator and frequency counter to impress calibrated side bands of the internal standard, 1% tetramethylsilane (TMS), onto the spectra. The concentration of M(AA)₂ was varied for each ligand concentration studied. The diamagnetic ligand proton resonances are: for 0.7 M pyridine N-oxide (α, β, γ) −492, −436, −436; 2.3 M, −497, −442, −438; 4.5 M, −500, −442, −440; for 0.8 M γ-picoline N-oxide (α, β, γ-CH₃) −484, −424, −141; 2.3 M, −489, −430, −142; for 0.8 M β-picoline N-oxide (α, β, β-CH₃, γ) −483, −424, −139, −424; for 0.8 M α-picoline N-oxide (α, α-CH₃, β, γ) −496, −154, −435, −435; and for 0.8 M 2,6-lutidine N-oxide (α-CH₃, β, γ), −152, −425, −425 (all in c.p.s. from TMS).

X-Ray Powder Patterns. These were taken using a 114.6-mm. camera and a nickel-filtered copper source. The samples were powdered and packed into a 0.3-mm. capillary tube, but care was taken not to powder the sample extensively in order to prevent crystal change or re-equilibration. All samples gave slightly diffuse grainy lines due to large crystal size, and the cobalt complexes also showed considerable fluorescence. In all cases corresponding Co(II) and Ni(II) complexes (described above) gave identical patterns. The pyridine N-oxide–Co(AA)₂ complex also showed a second crystal structure having no counterpart in the nickel series. Interplanar spacings in Å. and intensities are for bis(γ-picoline N-oxide)–bis(2,4-pentanedionato)cobalt(II): 9.26 (s), 7.35 (m), 6.60 (w), 6.31 (ms), 4.46 (ms), 3.89 (m), 3.58 (w), 3.37 (m), 3.03 (m), 2.60 (mw), 2.19 (w); for the corresponding nickel complex: 9.26 (s), 7.35 (m), 6.67 (mw), 6.31 (ms), 4.80 (w), 4.46 (s), 4.18 (w), 3.89 (m), 3.64 (w), 3.37 (m), 3.05 (m), 2.60 (mw), 2.25 (w), 2.21 (w).

Results

Pyridine N-oxide and the picoline N-oxides form crystalline 2:1 complexes with Ni(AA)₂ and Co(AA)₂ which, for a given ligand, are isomorphic and isometric. The infrared spectra of all these solid complexes show the typical strong acetylacetonate peaks at 1600 and 1520 cm.$^{-1}$ for the Ni(AA)₂ complexes and at 1582 and 1512 cm.$^{-1}$ for the Co(AA)₂ complexes.[13] The NO stretching frequency generally found near 1250 cm.$^{-1}$ (1275 cm.$^{-1}$ for β-picoline N-oxide) for the uncoordinated ligand is shifted to 1210–1220 cm.$^{-1}$ in the complex (1250 cm.$^{-1}$ in the β-picoline N-oxide complex). This is in agreement with coordination with the metal through the oxygen atom.[14] The 1:1:1 2,6-lutidine N-oxide–water–M(AA)₂ complexes show char-

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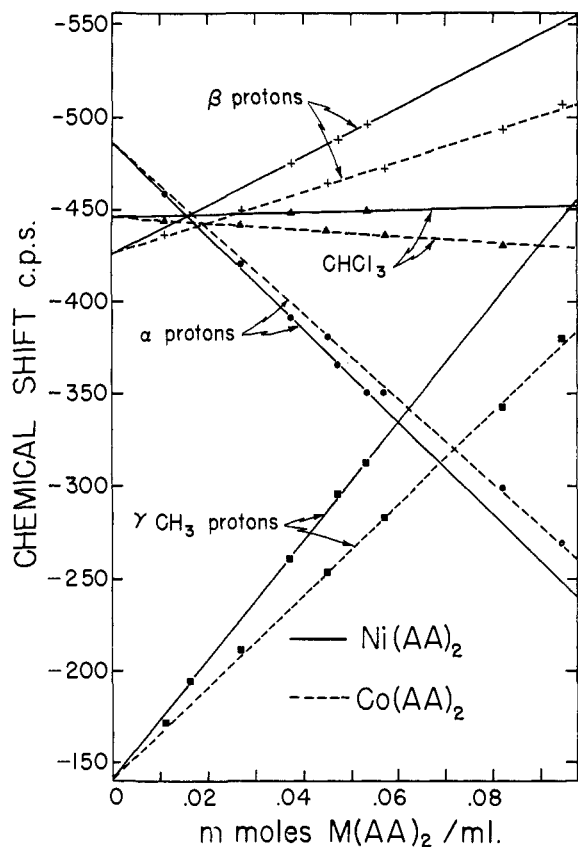(14) Y. Kakuiti, S. Kida, and J. V. Quagliano, *Spectrochim. Acta,* 19, 201 (1963).

Figure 1. Variation of chemical shifts of protons in a 0.8 M deuteriochloroform solution of γ-picoline N-oxide with increasing M(AA)₂ concentration.

acteristic broad absorptions at 3330 cm.⁻¹ (OH stretch) in addition to the above absorptions.

Optical studies on solutions of ligand and M(AA)₂ show the presence of species other than the isolated 2:1 complex in agreement with previous solution studies on the coordination of pyridine with M(AA)₂.[8] The visible and near-infrared spectra of Ni(AA)₂ (0.039 M) and α-, β-, or γ-picoline N-oxide in methylene chloride show two peaks: the first at 8550–8700 cm.⁻¹ (ε 6–7, units of l. mole⁻¹ cm.⁻¹ used throughout), and the second at 15,300–15,500 cm.⁻¹ (ε 7–8), which on the basis of an octahedral model correspond to ³A₂g → ³T₂g and ³A₂g → ³T₁g transitions. In addition an inflection was noted at 13,200 cm.⁻¹ (³A₂g → ¹Eg). At the same concentration 2,6-lutidine N-oxide absorbed at 8660 cm.⁻¹ (ε 9) and 14,320 cm.⁻¹ (ε 10) with inflections at 20,400 and 7000 cm.⁻¹. Typical of the N-oxide–Co(AA)₂ spectra (except for that of 2,6-lutidine N-oxide) is the spectrum of γ-picoline N-oxide (2.38 M in chloroform) containing Co(AA)₂ (0.0018 M). Readily observable features (cm.⁻¹) are a peak at 8800 (ε 5.4), a broad shoulder at 12,400 (ε 2.5), a shoulder at 18,000, and two peaks at 19,100 and 20,000 (ε 40, 43; these two peaks are superimposed on the base of a very strong ultraviolet peak, and the true extinction coefficients are probably ε <10). Using an octahedral model these absorptions can be assigned to the transitions ⁴T₁g → ⁴T₂g (8800 cm.⁻¹), ⁴T₁g → ⁴A₂g (18,000 cm.⁻¹), and ⁴T₁g(F) → ⁴T₁g(P) (19,100, 20,000 cm.⁻¹), the splitting of the latter peak probably being due to tetragonal distortion or spin–orbit coupling.[15] The shoulder at 12,400

cm.⁻¹ is presumably due to the presence of some 1:1 complex since its extinction coefficient decreases as the N-oxide–Co(AA)₂ ratio increases. This is confirmed by its absence in a mull spectrum of the pure 2:1 complex. From this shoulder can be constructed a peak with a maximum at 12,400 cm.⁻¹ (ε ~1). 2,6-Lutidine N-oxide (0.46 M) in methylene chloride with Co(AA)₂ (0.039 M) has a broad absorption at about 5600 cm.⁻¹, a peak at 12,200 cm.⁻¹ (ε 16), and peaks at 16,800, 18,200, and 20,800 cm.⁻¹ (ε 50, 35, 26). For this concentration and solvent, peaks and shoulders for γ-picoline N-oxide complexes were observed as before but the extinction coefficients indicate the presence of more 1:1 complex: 8800 cm.⁻¹ (ε 5), 12,500 (3), 18,000 (20), 19,000 (22), 20,000 (21).

Typical n.m.r. data are presented in Figure 1 which shows the observed chemical shifts to vary linearly, within experimental error, with increasing M(AA)₂ concentration at high ligand to metal ratios (total ligand concentration being constant). At lower ratios deviation from "linearity" is found with the chemical shifts asymptotically approaching constant values. The proton resonances of the pyridine and picoline N-oxides in the absence of added M(AA)₂ were found to be slightly concentration dependent with all absorptions shifting to lower fields at higher amine N-oxide concentrations. Isotropic shifts (see Discussion) were calculated using values only at high ligand to metal ratios and using the experimentally found ligand resonances (see Experimental Section) for that concentration. These data are included in Table I.

Assignment of the peaks was made on the basis of relative intensities and spin–spin splittings as well as the "linear" variation of the chemical shifts with metal concentration. For example, in the ligand pyridine N-oxide the β and γ protons form a complex A–B system. Adding small amounts of M(AA)₂ splits this AB system into two triplets, the upfield one of relative intensity one and the downfield triplet of relative intensity two. At higher metal concentrations the spin of the α protons is effectively relaxed owing to an increase in the average time this proton spends near the paramagnetic metal atom (i.e., the percentage of coordinated ligand is greater). Consequently the β proton is split only by the γ proton and is observed as a doublet. Likewise, the α proton which initially is a doublet of relative intensity two is rapidly converted to a broad single peak by increasing the metal concentration. At even higher metal concentrations all signals appear as broad single peaks.

Methyl resonances of the acetylacetonate (AA) groups are also observed in these systems. For Ni(AA)₂ complexes these absorptions are observed as broad peaks centered around −250 ± 5 c.p.s. (from TMS). At lower ligand to metal concentration ratios this peak broadens further and its center of gravity shifts further downfield (~10–15 c.p.s.). With 2,6-lutidine N-oxide this absorption is found at −306 c.p.s. The position of the acetylacetonate methyl peaks of the Co(AA)₂–amine N-oxide complexes is highly variable. For a given metal concentration the methyl peak is shifted downfield and the band width narrowed for an increase in ligand concentration. For various concentrations

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Table I. Contact Shifts and Pseudo-Contact Shifts

M^a	Lig.[b]	Concn., mole l.$^{-1}$ Lig.	M(AA)$_2$	Proton	$\Delta\nu_0$	β ratio (obsd.)	M–O–N angle	$\frac{3\cos^2\chi-1}{r^3}$ (Å.)$^{-3}$	Pseudo-contact shift	$\Delta\nu$ (cor.)^d	β ratio (cor.)^e
Ni	Py	4.54	0.194	α	+92	−0.598	...	...	0	+92	−0.586
				β	−54	+1.000	...	...	0	−54	+1.000
				γ	+113	−0.486	...	...	0	+113	−0.477
Co	Py	4.54	0.194	α	+150	−0.113	114° 15′	+0.00117	+45	+105	−0.582
				β	−17	+1.000	114° 15′	+0.00115	+44	−61	+1.000
				γ	+179	−0.095	114° 15′	+0.00136	+52	+127	−0.481
Ni	Py	2.35	0.097	α	+87	−0.540	...	...	0	+87	−0.540
				β	−47	+1.000	...	...	0	−47	+1.000
				γ	+106	−0.444	...	...	0	+106	−0.444
Co	Py	2.35	0.097	α	+130	−0.154	114° 45′	+0.00156	+38	+92	−0.543
				β	−20	+1.000	114° 45′	+0.00124	+30	−50	+1.000
				γ	+148	−0.135	114° 45′	+0.00142	+34	+114	−0.438
Ni	Py	0.744	0.125	α	+305	−0.532	...	...	0	+305	−0.532
				β	−162	+1.000	...	...	0	−162	+1.000
				γ	+385	−0.421	...	...	0	+385	−0.421
Co	Py	0.744	0.125	α	+341	−0.267	114° 0′	+0.000967	+53	+288	−0.528
				β	−91	+1.000	114° 0′	+0.001104	+61	−152	+1.000
				γ	+438	−0.208	114° 0′	+0.001325	+73	+363	−0.417
Ni	Gp	2.33	0.097	α	+95	−0.526	...	...	0	+95	−0.526
				β	−50	+1.000	...	...	0	−50	+1.000
				γ-CH$_3$	−119	+0.420	...	...	0	−119	+0.420
Co	Gp	2.33	0.097	α	+113	−0.248	114° 15′	+0.00117	+20	+93	−0.517
				β	−28	+1.000	114° 15′	+0.00115	+20	−48	+1.000
				γ-CH$_3$	−100	+0.280	114° 15′	+0.00065	+11	−111	+0.433
Ni	Gp	0.80	0.097	α	+247	−0.543	...	...	0	+247	−0.543
				β	−134	+1.000	...	...	0	−134	+1.000
				γ-CH$_3$	−314	+0.427	...	...	0	−314	+0.427
Co	Gp	0.80	0.097	α	+227	−0.356	114° 0′	+0.000967	+25	+202	−0.545
				β	−81	+1.000	114° 0′	+0.001104	+29	−110	+1.000
				γ-CH$_3$	−242	+0.334	114° 0′	+0.000627	+16	−258	+0.427
Ni	Bp	0.80	0.125	α	+284	−0.556	114°	+0.00097	0	+284	−0.556
				β	−158	+1.000	114°	+0.00110	0	−158	+1.000
				β-CH$_3$	+119	−1.328	114°	−0.0012	0	+119	−1.328
				γ	+348	−0.454	114°	+0.00132	0	+348	−0.454
Co	Bp	0.80	0.125	α	+306	−0.294	114°	+0.00070	+38	+268	−0.545
				α'	+350	−0.257	114°	+0.00149	+81	+269	−0.543
				β	−90	+1.000	114°	+0.00104	+56	−146	+1.000
				β'-CH$_3$	+123	−0.732	114°	−0.00005	−2	+125	−1.169
				γ	+406	−0.221	114°	+0.00132	+72	+334	−0.437

^{a} M = metal of M(AA)$_2$. ^{b} Lig. = ligand, Py = pyridine N-oxide, Gp = γ-picoline N-oxide, Bp = β-picoline N-oxide. ^{c} All geometric factors are for unrestricted rotation of the ligand except factors for M = Co, Lig. = Bp which are for restricted rotation. ^{d} Isotropic shift corrected for pseudo-contact shift to give contact shift. ^{e} β ratio is the ratio of the n.m.r. shift of the β-proton resonance to that of the proton resonance given.

of γ-picoline N-oxide and 0.047 M Co(AA)$_2$ in deuterio-chloroform the (AA) methyl absorption is shifted −843 (0.36 M), −930 (0.73 M), −1009 (1.46 M), and −1057 c.p.s. (2.43 M). The band width at half-height decreases 28, 23, 22, 20 c.p.s. at the same concentrations. Similarly pyridine N-oxide–Co(AA)$_2$ complexes have methyl resonances as low as −1180 c.p.s., β-picoline N-oxide as low as −1173 c.p.s. (although in pure β-picoline N-oxide the shift is only −1143 c.p.s.), and α-picoline N-oxide as low as −1269 c.p.s. The 2,6-lutidine N-oxide–Co(AA)$_2$ complex shows a relatively concentration invariant peak at −445 c.p.s. These shifts are in agreement with the presence of at least two structures in all systems except those of 2,6-lutidine N-oxide. This is also supported by the variance of $\Delta\nu$ calculated using eq. 3 (vide infra) and the data of Table I. It is further supported by the non-Curie behavior of Co(AA)$_2$ in the presence of excess γ-picoline N-oxide.

Discussion

In paramagnetic systems with electronic relaxation times sufficiently short for the observation of nuclear

resonance, the resonances of protons on the ligands can be shifted from their corresponding diamagnetic position (the isotropic shift). Such a shift can be caused by either of two types of interaction, a contact interaction or a pseudo-contact interaction.

Contact Shifts. The contact interaction results from the coupling of the electron spin density at the resonating nucleus with the effective electronic spin magnetization in the magnetic field of the n.m.r. experiment to produce a shift in the nuclear resonance frequency from its diamagnetic value. This effect is given quantitatively for a proton by[16]

$$\Delta\nu = -A_i \frac{\gamma_e}{\gamma_H} \frac{S(S+1)}{3kT} g\beta\nu \qquad (1)$$

where A_i is the electron–proton hyperfine interaction constant of the ith proton, γ_e and γ_H are the electronic and nuclear magnetogyric ratios, $\Delta\nu$ is the isotropic contact shift for the paramagnetic species, and ν is the frequency of the resonance. A_i is dependent on the

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Table II. Contact Shifts for Substituted Pyridine N-Oxides

Metal chelate	Metal concn., mole l.$^{-1}$	Ligand[a]	Ligand concn.	α	α-CH$_3$	β	β'	β-CH$_3$	γ	γ-CH$_3$
Ni (DPM)$_2$	0.125	Bp	0.80	+210	...	−124	...	+94	+266	...
Ni (AA)$_2$	0.125	Bp	0.80	+284	...	−158	...	+119	+348	...
Ni (DPM)$_2$	0.125	Gp	0.80	+238	...	−126	...	...	...	−311
Ni (AA)$_2$	0.125	Gp	0.80	+295	...	−159	...	...	...	−374
Ni (AA)$_2$	0.109	Ap	0.80	+250	−188	−85	−179	...	+299	...
Co (AA)$_2$	0.109	Ap	0.80	+86	−105	−96	−74	...	+348	...
Ni (AA)$_2$	0.125	L	0.80	...	−108	−63	...	...	+155	...
Co (AA)$_2$	0.125	L	0.80	...	−360	−98	...	...	+358	...

[a] Bp = β-picoline N-oxide, Gp = γ-picoline N-oxide, Ap = α-picoline N-oxide, L = 2,6-lutidine N-oxide.

magnitude of the electron spin density at the hydrogen nucleus. A_i for a proton attached directly to a π system is related to the π-orbital spin density, ρ_i, at the carbon to which it is attached by the relationship (eq. 2)[17] where Q is a "semiempirical" constant of

$$A_i = Q\rho_i/2S \qquad (2)$$

proportionality $Q = -22.5$ gauss ($Q = +5$ to $+30$ gauss for a proton of a methyl group attached to a π system). For a system in rapid equilibrium between a diamagnetic form (free ligand) and a paramagnetic form (complexed ligand), the observed isotropic shift ($\Delta\nu_0$) is the number-average of the isotropic shifts of the paramagnetic form ($\Delta\nu$) and the diamagnetic forms ($\Delta\nu_d = 0$)[18]

$$\Delta\nu_0 = N_p(\Delta\nu) + N_d(\Delta\nu_d) \qquad (3)$$

where N_p and N_d are the mole fractions of paramagnetic and diamagnetic species, respectively.

The isotropic shifts found for the nickel chelates are assumed to arise solely from a contact interaction. Similar conclusions have been reached for other nickel complexes.[2–7] Furthermore, in an essentially octahedral ligand field the ground state of the Ni(AA)$_2$ complexes is the orbitally nondegenerate $^3A_{2g}$ state which would not be expected to give rise to significant pseudo-contact shifts (vide infra). Such conclusions are supported by the relative invariance of the "β ratios" (the ratio of the isotropic shifts of the β to the other protons, i.e., β/α, β/γ) with varying ligand concentration for the nickel complexes (Table I). The fact that the α- and γ-proton resonances are shifted to higher fields whereas the β-proton absorptions are shifted to lower fields, while the reverse is true of the protons of methyl groups at these positions, indicates that spin is delocalized in a π orbital (Tables I and II).

Table III presents a comparison of the contact shifts observed in the present work with the spin densities and related data reported in the literature for pyridine N-oxide and several analogs. These data clearly support a π mechanism for spin delocalization but do not answer the question of whether spin is delocalized in the highest bonding π orbital or lowest antibonding π orbital. Using eq. 3 and a small extrapolation of the data in Table I, one can calculate that the isotropic shift of the α proton for the pure 2:1 pyridine N-oxide–

Ni(AA)$_2$ complex is about 1100 c.p.s. Using eq. 1 and a spin density of $+0.393$ (valence bond (V.B.) spin density for benzyl radical) for this position, one calculates a contact shift of about 50,000 c.p.s. indicating the observed ligand spin density involves delocalization of about $^1/_{50}$ of an electron spin into a ligand ring.

A comparison of the isotropic shift ratios (β ratios) for the various Ni(AA)$_2$ complexes (Table I and II) shows that these ratios are relatively insensitive to the ring substituent as has been previously noted.[2,5,7] On this premise Q_{CH_3} values could be calculated for the pyridine N-oxide ring and were found to be $+23$ gauss for the α-CH$_3$ and $+17$ gauss for the β-CH$_3$. An anomalous situation is found for the Ni(AA)$_2$–α-picoline N-oxide complex. Two peaks corresponding to β-proton resonances are noted indicating considerable asymmetry in the spin density distribution. Two β-proton resonances were also noted for the Ni(AA)$_2$–α-picoline complexes.[4]

Pseudo-Contact Shifts. Assuming the Ni(AA)$_2$ complex isotropic shifts are pure contact shifts and that spin delocalization in a given ligand should result in the same ratio of shifts regardless of the coordinating metal atom, then the deviations found in the ratios of the amine N-oxides–Co(AA)$_2$ complexes may be attributed to a pseudo-contact interaction (an electron spin–nuclear spin dipolar interaction).

For an axially symmetric system in which the electronic spin relaxation time is short compared to the molecular correlation time for tumbling in solution, a g-tensor anisotropy gives rise to an isotropic shift described by eq. 4,[19] in which r_i is the length of a

$$\Delta\nu_i = -\nu\frac{\beta^2 S(S+1)}{45kT}\left[\frac{3\cos^2\chi - 1}{r_i^3}\right](3g_{||}^2 +$$
$$g_{||}g_\perp - 4g_\perp^2) \qquad (4)$$

vector joining the ith proton and the metal atom, and χ is the angle between this vector and the principal molecular axis. The pseudo-contact shift is therefore dependent on the geometry of the complex as well as its anisotropy.

Because of the labile nature of the M(AA)$_2$ complexes and the lack of data on Co(II) g-tensor anisotropies, only relative shifts can be calculated. Table I includes the values for calculated geometric factors ($3\cos^2\chi - 1)r^{-3}$ which satisfactorily interpret the data. These were calculated using the molecular parameters: Co–O bond distance of 2.20 Å. (slightly less than H$_2$O–Co

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(18) B. B. Wayland and R. S. Drago, J. Am. Chem. Soc., 87, 2372 (1965).
(19) H. M. McConnell and R. E. Robertson, J. Chem. Phys., 29, 1361 (1958).

Table III. Contact Shifts and Spin Densities for Pyridine N-Oxide

Proton	$\Delta\nu_0$	$\Delta\nu_0{}^a$	V.B. ρ_i for $C_6H_5CH_2{}^b$	Hückel ρ_i for C_5H_5NO π bonding^c	π^* antibonding^c	A_i exptl. $C_6H_5O^d$
α	+87	+0.39	+0.393	+0.12 + 0.087	+0.12 + 0.17	6.6
β	−47	−0.21	−0.221	+0.007^e + 0.017^e	+0.02^e + 0.01^e	1.9
γ	+106	+0.47	+0.435	+0.14 + 0.13	+0.21 + 0.22	10.4

^{a} Restated as spin density, obtained by $\Delta\nu_0$ (0.00449). ^{b} Valence bond spin densities; H. H. Dearman and H. M. McConnell, *J. Chem. Phys.*, **33**, 1877 (1960); see also M. D. Curtis and A. L. Allred, *J. Am. Chem. Soc.*, **87**, 2554 (1965), Table II. ^{c} Hückel spin densities for two different sets of parameters; see ref. 11. ^{d} Experimental e.p.r. hyperfine coupling constants for phenoxy radical: T. J. Stone and W. A. Waters, *Proc. Chem. Soc.*, 253 (1962). ^{e} May become negative upon introduction of spin correlation.

bond[20] distance owing to some π bonding and greater ligand basicity); O–N bond distance of 1.35 Å.,[21] a pyridine ring which is a regular hexagon 1.39 Å. on a side (a simplification justified by the absence of much better data and the relatively small resulting error), C–H bond distances of 1.09 Å., and C–CH₃ distances of 1.52 Å. Average values were obtained assuming unrestricted rotation of the pyridine around the N–O bond and the methyl groups (where applicable) around the C–CH₃ bond. All calculations were made on an IBM 7094 computer except for several made using a geometric construction. The geometric factors (3 $\cos^2 \chi - 1)r^{-3}$ for the α, β, and CH₃ protons in these complexes vary considerably as the angle of rotation around the N–O bond sweeps through a 360° arc. Table IV presents these values for 30° rotations with an assumed Co–O–N angle of 114°. In all cases Table IV shows that the average values (Table I) are composed of positive and negative numbers.

Table IV. Effect of Rotation on Geometric Factor (3 $\cos^2 \chi - 1)r^{-3}$ for γ-Picoline N-Oxide Complexes^a

Angle of rotation	α proton	β proton	γ-CH₃
0	+1.78 × 10⁻²	+5.48 × 10⁻³	+1.63 × 10⁻³
30	+1.75 × 10⁻²	+5.12 × 10⁻³	+1.51 × 10⁻³
60	+1.61 × 10⁻²	+3.96 × 10⁻³	+1.16 × 10⁻³
90	+1.18 × 10⁻²	+1.89 × 10⁻³	+6.65 × 10⁻⁴
120	−1.58 × 10⁻⁴	−9.47 × 10⁻⁴	+1.23 × 10⁻⁴
150	−2.56 × 10⁻²	−3.70 × 10⁻³	−2.98 × 10⁻⁴
180	−4.54 × 10⁻²	−4.88 × 10⁻³	−4.58 × 10⁻⁴

^{a} Values are in Å.$^{-3}$.

Using these calculated ratios and an arbitrary proportionality factor, corrections were made for the pseudo-contact contribution to the isotropic shift in a manner previously described.[2] For the Co(AA)₂–pyridine N-oxide or γ-picoline N-oxide complexes, agreement with the contact shift ratios of the corresponding Ni(AA)₂ complex were obtained using pseudo-contact shifts based on a Co–O–N angle of 114°–114° 45′ and assuming $g_\perp > g_{\parallel}$ (Table I). The geometric factors are relatively sensitive to the Co–O bond length, but satisfactory pseudo-contact correction could still be made assuming a Co–O bond length as small as 2.00 Å. using a Co–O–N angle of about 118°. Considerable restriction in rotation of the pyridine ring may actually occur and models indicate that for several rotational positions around the Co–O bond, the plane of the pyridine ring

cannot be perpendicular to the plane of the AA ring. Such rotational restrictions hopelessly complicate the calculations, but its effect is to make the required Co–O–N bond angle smaller. Another model can be postulated in which rotation around the N–O bond is completely restricted due to N–O π-bond formation. In such a model the pyridine ring protons are always at perigee or apogee (*vide infra*) relative to the plane of the acetylacetonate rings, and the equivalence of the two α positions and the two β positions would be due to rapid ligand exchange. For such a model, based on the above bond angles and bond lengths, agreement with the contact shift ratios given in Table I for pyridine N-oxide can be obtained by assuming an M–O–N angle of about 125°. Therefore the pyridine N-oxide ring must coordinate with a Co–O–N angle of about 114–125° and more probably with an angle of about 115°. Analogies for such a bent structure are found in X-ray structures of pyridine N-oxide hydrochloride[21] and phosphine oxide complexes.[22]

For β-picoline N-oxide, although the nickel shifts appear to be normal, the cobalt shifts are anomalous in that they show the presence of two different α protons. Such a result is explicable on the basis of restricted rotation of the pyridine ring owing to interference of the β-CH₃ group with the Co(AA)₂ ring system. One can consider a rotamer in which the plane of the pyridine ring is perpendicular to the plane of the acetylacetonate ring; then the protons at apogee with respect to the metal will be defined as at 0° of internal rotation and those at perigee, at 180° rotation. By assuming the pyridine ring methyl spends only ¹⁵⁄₁₆ as much time at 150, 180, and 210° as it does at all the other 30° angular increments, new geometric factors were calculated which give reasonable contact shift ratios except for the β-CH₃ protons. In this case the computer program used did not allow calculation for restricted rotation around the C–CH₃ bond. Restriction of this rotation would make this factor positive and thus in agreement with experiment. A quantitative analysis of the isotropic shifts of α-picoline N-oxide was not made, but the data are in agreement with the α-CH₃ group spending considerably less of its time near perigee (180° rotation). The data for 2,6-lutidine N-oxide differ from the other data in that rather large differences are observed between the isotropic shifts of the Ni(AA)₂ and Co(AA)₂ complexes (Table II). Presumably, owing to steric hindrance, no proton spends much of its time at apogee or perigee. These complexes are principally 1:1 complexes, and the visible spectra suggest that the Co(AA)₂ complex is a pentacoordinate square

(20) G. J. Bullen, *Acta Cryst.*, **12**, 703 (1959).
(21) G. Tsoucaris, *ibid.*, **14**, 914 (1961).

(22) F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **85**, 2402 (1963).

pyramid while the Ni(AA)₂ complex is octahedrally coordinated.[23]

The large variation in the acetylacetonate methyl absorptions previously noted for the Co(AA)₂ complexes can also be explained on the basis of pseudo-contact shifts. Thus for the 2:1 ligand–Co(AA)₂ complex, the geometric factor for these protons is large and negative. For 1:1 complexes in which the (AA) group must take up the sixth coordination site, the positional average of the methyl group has a more positive geometric factor. The effect of this is to produce a more negative pseudo-contact shift as the ratio of (2:1)/(1:1) complexes increases, as is observed.

The chloroform proton absorption provides another example of pseudo-contact shift. Chloroform hydrogen bonds with the amine N-oxides in the absence of M(AA)₂ as evidenced by a downfield shift of this peak with increasing amine N-oxide concentration. (Figure 1 shows a downfield shift of about 10 c.p.s. from the diamagnetic CHCl₃ resonance.) It is also well known for its bonding to chelate compounds[24] with the presently reported chloroform solvate of the α-picoline N-oxide–M(AA)₂ 2:1 complex another example. Figure 1 shows that for increasing Ni(AA)₂ concentration (total ligand concentration being constant) the chloroform peak is shifted downfield as is expected for hydrogen bonding.[25] For the Co(AA)₂ complexes the shift of the chloroform peak is strongly upfield and is due to a positive pseudo-contact contribution. This limits the position of the hydrogen to a cone having $\chi < 54° \ 44'$. Assuming planar acetylacetonate rings and normal hydrogen bond lengths, the hydrogen bond can be localized to the vicinity of the six oxygen atoms.

(23) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, 4, 943 (1965); L. Sacconi, M. Campolini, and G. P. Speroni, *ibid.*, 4, 1116 (1965). In agreement with the octahedral configuration of the Ni(AA)₂ complex, only a green 2:1 2,6-lutidine N-oxide–Ni(DPM)₂ complex was isolated by the addition of an excess of N-oxide to Ni(DPM)₂ in methylcyclohexane. *Anal.* Calcd. for C₅₆H₅₄O₆N₂Ni: C, 64.57; H, 8.13; N, 4.19. Found: C, 64.29; H, 8.41; N, 4.17.

(24) J. F. Steinbach and J. H. Burns, *J. Am. Chem. Soc.*, 80, 1838 (1958); J. P. Fackler, Jr., T. S. Davis, and I. D. Chawla, *Inorg. Chem.*, 4, 130 (1965).

(25) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 15.

Miscellaneous. Some preliminary data on another interesting system bis(dipivaloylmethido)nickel(II) [Ni-[(CH₃)₃CCOCHCOC(CH₃)₃]₂, Ni(DPM)₂] are also presented in Table II. Ni(DPM)₂ is a red square-planar compound, monomeric in solution,[26] which associates with many ligands in solution particularly at low temperatures to give green and other colored compounds. Coordination of the amine N-oxides with Ni(DPM)₂ which can be observed visually results in spin delocalization in the ligand quite similar to that observed for Ni(AA)₂ although smaller for comparable concentrations. In addition, the effect of axial coordination on the position of the β-diketone C–H proton can be observed. Although at large ligand–Ni(DPM)₂ ratios this peak is not observed owing to broadening, at low ratios this proton is observed to shift from −324 to −279 c.p.s. (relative to TMS) while the chelate *t*-butyl methyl peak shifted from −59.0 to −68.3 c.p.s. For large ligand–Ni(DPM)₂ ratios the *t*-butyl methyl proton resonance is found at about −288 c.p.s. The observed CH shifts lead, by means of linear extrapolation, to the conclusion that at large ratios the CH absorption should be found at +780 c.p.s. (from TMS). This is in reasonable agreement with the analysis of Eaton[27] on the shifts of metal acetylacetonates which would suggest for this complex a ligand to metal β spin transfer with large upfield shift of the CH absorption and a small shift of indeterminant sign for the CH₃ protons. In the system Co(AA)₂–pyridine-N-oxide a broad peak of low intensity at +300 c.p.s. (ligand 0.80 *M*, Co(AA)₂ 0.2 *M*) was observed which may be the acetylacetonate CH proton. The methyl absorption is found at −950 c.p.s. and both of these peaks would be expected to be shifted downfield by a pseudo-contact term. The geometric factors for an acetylacetonate ring are CH = -1.2×10^{-2} and CH₃ = -0.8×10^{-2} Å.$^{-3}$, and therefore the pseudo-contact shift would be greater for the CH group.

Acknowledgment. Computations were carried out at the Princeton University Computer Center.

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(27) D. R. Eaton, *ibid.*, 87, 3097 (1965).

Fluoroolefin Complexes of Transition Metals

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Contribution No. 1103 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington 98, Delaware.
Received June 8, 1965

The tetrafluoroethylene complexes (AcAc)Rh(C₂F₄)(C₂H₄) (1), (Ph₃P)₂IrCl(CO)(C₂F₄) (4), and (Ph₃P)₃Ni(C₂F₄) (6) have been prepared and characterized. Various Lewis bases (L) displace ethylene from 1 to give complexes of the types (AcAc)Rh(C₂F₄)L₂ (2) and [(AcAc)Rh(C₂F₄)L]₂ (3). The dimeric complexes contain tridentate bridging acetonylacetotonate (AcAc) ligands. The spectra indicate that the C₂F₄–metal link in complexes 2–4 approaches the form of a σ-bonded three-membered ring. In complexes 1 and 6, the metal–olefin bond appears to have considerable π character.

Attempts to prepare fluoroolefin π complexes of transition metals analogous to the complexes formed by simple olefins have usually given σ-bonded fluoro-