Proton Magnetic Resonance Studies on Paramagnetic Quinoline 1-Oxide and Isoquinoline 2-Oxide Complexes[1]

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Abstract: Complexes of isoquinoline 2-oxide and quinoline 1-oxide with $Ni(AA)_2$ and $Co(AA)_2$ have been isolated. Solution nmr studies of these complexes in the presence of excess ligand indicate that unpaired electron spin delocalization from the metal to the ligand occurs through a π mechanism involving the highest filled bonding ligand orbital. In corresponding complexes of isoquinoline and quinoline, spin is delocalized by a σ mechanism. Pseudocontact shifts assumed for the $Co(AA)_2$–isoquinoline 2-oxide complex are in qualitative agreement with restricted rotation around the N–O bond and a Co–O–N angle of 115–130°. The observed nmr chemical shifts of the N-oxide ligand appear to vary linearly with $M(AA)_2$ concentration, and extrapolation to zero concentration gives the chemical shifts of the diamagnetic ligand protons.

An interpretation of nmr spectra of complexes of pyridine N-oxide and picoline N-oxides with nickel(II) and cobalt(II) acetylacetonates [bis(2,4-pentanedionato)nickel(II) or -cobalt(II), $Ni(AA)_2$ or $Co(AA)_2$] in terms of contact and pseudocontact shifts has recently been presented.[2] These studies have now been extended to complexes of quinoline 1-oxide and isoquinoline 2-oxide with $Ni(AA)_2$ and $Co(AA)_2$. In addition to complementing the conclusions previously reached, the results allow assignment of the ligand orbital into which spin delocalization occurs and demonstrate a method for the assignment of nmr chemical shifts in otherwise complicated proton spectra of diamagnetic ligands.

Experimental Section

Isolation of Complexes. To a solution of 0.85 g of $Ni(AA)_2$ (0.0033 mole) in 15 ml of chloroform was added 1 g (0.0069 mole) of isoquinoline 2-oxide prepared by the method of Ochiai.[3] A green crystalline precipitate was isolated, washed with chloroform, and air dried. Drying at 56° resulted in a weight loss of 30.4% (calculated for $C_{28}H_{28}O_6N_2Ni \cdot 2CHCl_3$: 30.38% $CHCl_3$). The resulting desolvated complex was yellow. Identical material could be obtained by the direct interaction of $Ni(AA)_2$ and excess isoquinoline 2-oxide in toluene. *Anal.* Calcd for $C_{28}H_{28}O_6N_2Ni$: C, 61.45; H, 5.16. Found: C, 61.28; H, 4.94.

Analogously, the 2:1:2 isoquinoline 2-oxide–$Co(AA)_2$–$CHCl_3$ solvated complex was isolated as orange needles. *Anal.* Calcd for $C_{28}H_{28}O_6N_2Co \cdot 2CHCl_3$: C, 45.83; H, 3.85; N, 3.56. Found: C, 45.98; H, 4.19; N, 3.58. Desolvation at 56° (1 mm) resulted in a buff-colored powder. *Anal.* Calcd for $C_{28}H_{28}O_6N_2Co$: C, 61.42; H, 5.15. Found: C, 61.18; H, 5.35. This solid complex has a magnetic moment of 4.83 BM measured by the Gouy method. Both the nickel- and cobalt-solvated complexes slowly lost chloroform upon standing over a period of several months, but could be resolvated with additional chloroform. The desolvated complexes react readily with water.

The dihydrate of $Ni(AA)_2$, 0.5 g (0.0017 mole), was dehydrated by azeotropic distillation of the water in toluene. Quinoline 1-oxide, 1 g (0.0069 mole), was added to the hot solution and the solution allowed to cool. The red 1:1 $Ni(AA)_2$–quinoline 1-oxide complex which crystallized was removed by filtration and dried at 56° (1 mm) for 1.5 hr. *Anal.* Calcd for $C_{19}H_{23}O_5NNi$: C, 56.76; H, 5.27; N, 3.48. Found: C, 56.88; H, 5.12; N, 3.44. Analogously prepared was the red 1:1 $Co(AA)_2$–quinoline 1-oxide complex. *Anal.* Calcd for $C_{19}H_{23}O_5NCo$: C, 56.72; H, 5.26; N, 3.48. Found: C, 56.87; H, 5.29; N, 3.34.

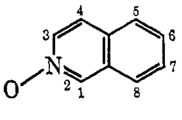
Spectra. Infrared spectra were obtained using a Perkin-Elmer 237B grating spectrometer and samples prepared as Nujol mulls. Visible and near-infrared spectra were obtained using a Cary Model 14 recording spectrophotometer. Spectra were obtained using both solutions and Nujol mulls.

Nmr Spectra. These were obtained using a Varian A-60 nmr spectrometer (60 Mc) with a probe temperature of 37°, deuteriochloroform as solvent, tetramethylsilane as an internal standard, and the techniques previously described.[2] Because of the insolubility of the isoquinoline complexes in deuteriochloroform, spectra on this ligand in the presence of $M(AA)_2$ were generally obtained using supersaturated solutions, and care was taken to use only data from solutions which did not precipitate the complex during measurement.

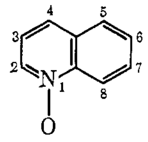
X-Ray Powder Diffraction Patterns. These were obtained as before[2] on lightly powdered samples in a 0.3-mm capillary tube using a 114.6-mm diameter camera and a nickel-filtered copper source. Virtually identical powder patterns were obtained for the chloroform solvates of the $Ni(AA)_2$– and $Co(AA)_2$–isoquinoline 2-oxide complexes and also for the 1:1 $Ni(AA)_2$– and $Co(AA)_2$–quinoline 1-oxide complexes. The interplanar *d*-spacings obtained from the powder patterns of the desolvated 2:1 isoquinoline 2-oxide–$Ni(AA)_2$ and –$Co(AA)_2$ complexes showed that these crystals were not isomorphous.

Results

Like pyridine N-oxide and its methyl derivatives, isoquinoline 2-oxide (A) and quinoline 1-oxide (B) form isolable complexes with $Ni(AA)_2$ and $Co(AA)_2$. As deposited from solution these nickel and cobalt complexes form isostructural pairs as evidenced by the X-ray data. Superficially one would expect isoquinoline 2-oxide to behave like β-picoline N-oxide, because it has a substituent β to the heterocyclic nitrogen, and quinoline 1-oxide to behave like α-picoline N-oxide. However, in forming a stable chloroform solvate of a 2:1 N-oxide–$M(AA)_2$ complex, the isoquinoline 2-oxide behaves more like α-picoline N-oxide, and quinoline 1-oxide, in forming only a 1:1 complex, behaves more like 2,6-lutidine N-oxide.[2]



A



B

The infrared spectra of the solvated isoquinoline 2-oxide–$Ni(AA)_2$ and –$Co(AA)_2$ complexes are similar as are the spectra of the two desolvated complexes and the

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[1] This research was supported by the National Science Foundation through Grant No. NSF GP 3397.

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

[3] E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).

two quinoline 1-oxide complexes. In addition to the two strong acetylacetonate peaks in the 1500–1600-cm^{-1} region, the chloroform solvates of the isoquinoline 2-oxide complexes have a strong absorption at 745 cm^{-1} ($CHCl_3$). In the 1200-cm^{-1} region where the N–O stretching frequency is expected, isoquinoline 2-oxide has peaks at 1325, 1260, and 1250 cm^{-1}, which are almost unchanged by coordination. A relatively strong peak at 1180 cm^{-1} is shifted to 1165 cm^{-1} upon coordination, suggesting that this frequency has a significant N–O stretching component. Similar shifts were previously reported for acid salts of isoquinoline 2-oxide.[4] The visible and near-infrared spectra of these complexes are in agreement with an octahedral structure for all of these complexes. Thus the isoquinoline 2-oxide–$Ni(AA)_2$ complex forms a yellow solution in chloroform with low intensity maxima at 8100 and 15,500 cm^{-1} (${}^3A_{2g} \rightarrow {}^3T_{2g}$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}$). The corresponding $Co(AA)_2$ complex showed a broad absorption which could be crudely resolved into peaks at 9000 and 12,000 cm^{-1} (possibly due to the splitting of the ${}^4T_{1g}$ and ${}^4T_{2g}$ states of an octahedral complex by a tetragonal distortion or the presence of 1:1 complex) and shoulders at 18,000 and 22,000 cm^{-1}.[5] Similar peaks appear to occur in the solution spectra of the red quinoline 1-oxide complexes, although in both spectra a strong charge-transfer band obscures the higher frequency peaks. This indicates a difference between the 2,6-lutidine N-oxide–$Co(AA)_2$ 1:1 complex which appears to be pentacoordinate in solution[2] and the corresponding quinoline 1-oxide complex which, if it is a 1:1 complex in solution, is probably associated. Small but significant shifts in the peaks observed in the visible, near-infrared, and infrared region of the spectrum were observed for mull spectra of the isoquinoline 2-oxide complexes and the corresponding chloroform solvates as could be expected from the color changes observed upon desolvation, but as these do not add to the discussion of the nmr data they will not be considered further here.

The nmr experiments were carried out using a constant volume of 0.8 M amine oxide solution to which was added small increments of $Ni(AA)_2$ or $Co(AA)_2$. The exchange of ligand is rapid in these systems, and only an average resonance position for each ligand proton is observed.[2,6] Assignment of the nmr chemical shifts and coupling constants in the uncomplexed ligand is trivial for the 1 and 3 protons in isoquinoline 2-oxide and the 2, 3, and 8 protons in quinoline 1-oxide. The observed shifts for these protons (Table III) are in agreement with previously reported data,[7] although it should be noted that some of these, particularly the chemical shifts of the 2 proton of quinoline 1-oxide, are concentration dependent. Assignments of the observed peaks in the spectra of solutions containing paramagnetic complexes were made principally on the basis of the nuclear spin–spin splitting patterns, broadening of resonance signals due to the proximity of the paramagnetic center, the near-linear dependence of chemical shift on complex concentration, and the calculated direction of the isotropic shifts (*vide infra*).

For isoquinoline 2-oxide the 1 proton has a resonance absorption which is a quartet in the diamagnetic ligand ($J_{1,3}$ = 1.7 cps; $J_{1,8}$ = 0.7 cps). This resonance shifts upfield linearly with increasing $M(AA)_2$ concentration and becomes very broad. Likewise the 3 proton has an nmr signal observed in the uncomplexed ligand as a quartet ($J_{3,4}$ = 7.2 cps; $J_{1,3}$ = 1.7 cps) which is shifted upfield and becomes a singlet not as broad as the 1-proton signal. The 4-proton resonance, originally unresolvable, appears downfield at higher complex concentration. It is a slightly broadened singlet, owing to the rapid relaxation of the 3-proton resonance. Both the 5- and 8-proton resonances are doublets and cannot be independently identified, but all quantum mechanical calculations (*vide infra*) indicate that the 8-proton resonance should be shifted upfield. Therefore the doublet shifted downfield ($J_{5,6}$ = 7.5–8 cps) is assigned to the 5 proton and the upfield resonance is assigned to the 8 proton ($J_{7,8}$ = 8.0 cps). This is supported by the greater broadening of the upfield doublet as the 8 proton is closer to the metal atom (*vide infra*). The upfield doublet is skewed toward the downfield triplet, allowing assignment of this triplet to the 7-proton resonance. The remaining resonance which becomes a triplet shifted upfield ($J_{6,7} \sim 7.51$ cps) at higher complex concentration is assigned to the 6-proton resonance by the process of elimination, and this assignment is supported by the skewing of the 5-proton resonance. The signs of these isotropic shifts are in agreement with those previously reported for the ring protons of the 2-naphthyl group in nickel(II) chelates of substituted aminotroponimines.[8]

For quinoline 1-oxide the 2-proton resonance is observed as a quartet ($J_{2,3}$ = 5.9 cps; $J_{3,4}$ = 1.1 cps) which becomes a broad single peak shifted upfield with increasing metal concentration. The 3-proton resonance appears as a quartet ($J_{2,3}$ = 6.0 cps; $J_{3,4}$ = 8.5 cps) which shifts downfield and becomes a semiresolved doublet. The 4-proton resonance, originally not resolved, shifts upfield and can be observed as a doublet at low metal concentrations ($J_{3,4}$ = 8.5 cps). The 5-proton resonance is shifted upfield as a doublet ($J_{5,6}$ = 8.0 cps). The 6-proton resonance is a triplet shifted downfield, while the 7-proton resonance is generally observed as a peak having almost no structure. The 8-proton resonance appears to be a quadruplet in the diamagnetic complex which is unsymmetrically broadened. Addition of $Ni(AA)_2$ lowers the frequency of this resonance peak and rapidly broadens the peak to a structure less absorbance. Of all the isotropic shifts observed, only those of the 8 proton of quinoline 1-oxide have different signs for the $Ni(AA)_2$ and $Co(AA)_2$ complex, the resonance being shifted upfield upon addition of $Co(AA)_2$.

The nmr spectra of the heterocyclic bases, in contrast to the N-oxides, show only downfield shifts of the proton resonance in the presence of $Ni(AA)_2$. Thus nmr spectra of solutions containing $Ni(AA)_2$ and an excess of isoquinoline show that the 1- and 3-proton resonances are broadened rapidly with increasing metal concentration and shifted strongly downfield. A

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(4) M. Szafran, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, **11**, 503 (1963); *Chem. Abstr.*, **60**, 7574 (1964).

(5) Similar cobalt(II) complex spectra are reported by L. Sacconi, M. Ciampolini, and G. P. Speroni, *Inorg. Chem.*, **4**, 1116 (1965).

(6) W. D. Horrocks, Jr., R. C. Taylor, and G. N. LaMar, *J. Am. Chem. Soc.*, **86**, 3031 (1964).

(7) K. Tori, M. Ogata, and H. Kano, *Chem. Pharm. Bull.*, **14**, 681 (1963).

(8) D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips, and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4100 (1962).

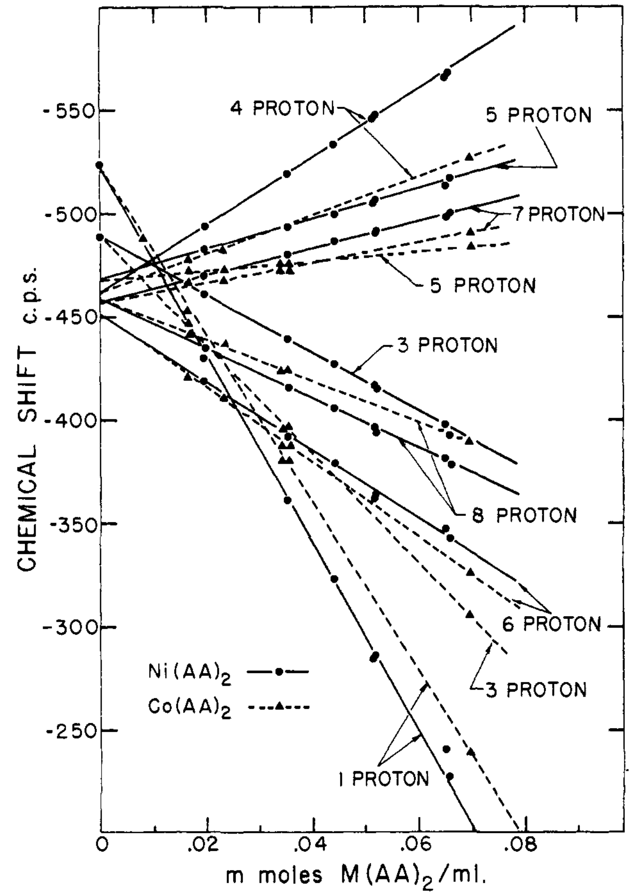

Figure 1. Observed nmr chemical shifts relative to tetramethylsilane at 60 Mc for protons of 0.8 M isoquinoline 2-oxide in deuteriochloroform with added M(AA)$_2$.

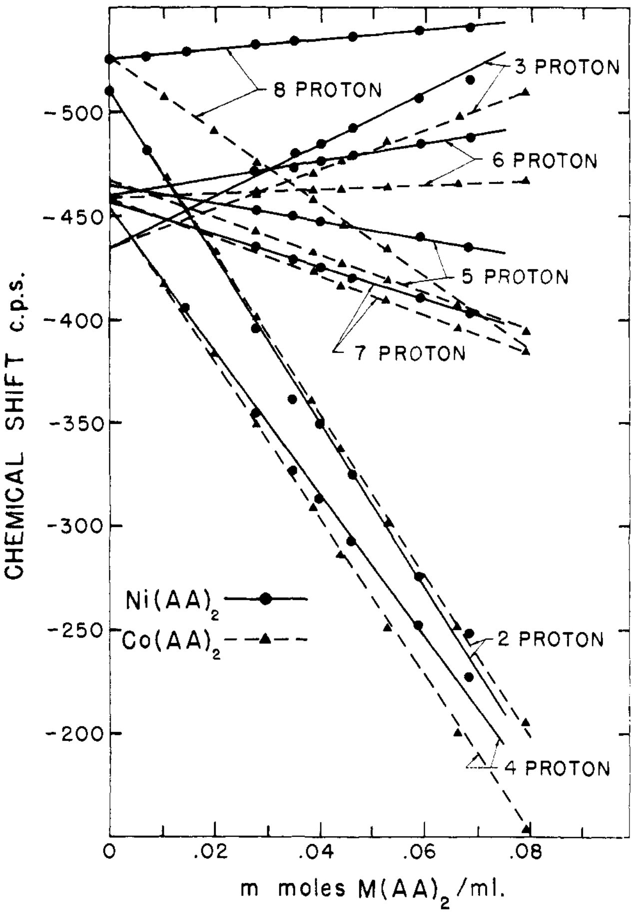

Figure 2. Observed nmr chemical shifts relative to tetramethylsilane at 60 Mc for protons of 0.8 M quinoline 1-oxide in deuteriochloroform with added M(AA)$_2$.

second proton resonance which may be that of the 4 proton is shifted downfield much less strongly, and the remaining proton resonances are shifted downfield to a smaller extent. For quinoline in the presence of Ni(AA)$_2$, the nmr spectra indicate that the 2-proton resonance is shifted strongly downfield, while the other resonances are shifted downfield much less strongly with the 5-proton resonance, identified as a doublet, being shifted very little and the 6-proton resonance, a triplet, being virtually unshifted.

Discussion

Nmr isotropic shifts, $\Delta\nu_i$ (the deviation between the chemical shift of a proton in a paramagnetic complex and the same proton in a diamagnetic environment), of octahedrally coordinated nickel compounds are generally accepted as being due to contact shifts, $\Delta\nu_c$ (a shift due to direct coupling of the electron and nuclear spins).[9]

The contact shift is related to the epr isotropic hyperfine coupling constant A by eq 1, for nuclei $I = {}^1/_2$.[10] For a system in which unpaired electron spin

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

density is distributed by a π mechanism and in which the proton is attached directly to a carbon atom in the π system, the π-spin density ρ of the carbon to which the proton is attached is related to A by eq 2, where Q is a

$$A = \frac{Q\rho}{2S} \qquad (2)$$

proportionality constant of about -22.5 gauss.[11] Thus nmr experiments involving coordinated Ni(AA)$_2$–aromatic ligand systems can provide data on the distribution of spin density in the aromatic system.

The present experimental data (Table I, Figures 1 and 2) clearly support spin delocalization in the N-oxide ligands by a π mechanism in agreement with earlier work on the pyridine N-oxides.[2] This is in contrast to the heterocyclic amines themselves which by analogy with the pyridines[12] have spin distributed principally by a σ mechanism. Spin delocalization in a π orbital can involve either the highest filled π bonding orbital or the lowest-unfilled π antibonding orbital. In principle these can be distinguished by comparing the observed isotropic shifts with spin densities calculated by molecular orbital (MO) or valence bond

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[9] A more complete discussion and many leading references can be found in (a) G. N. LaMar, W. D. Horrocks, Jr., and L. C. Allen, *J. Chem. Phys.*, **41**, 2126 (1964); (b) B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, **87**, 3272 (1965).

[10] (a) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958); (b) H. M. McConnell and C. H. Holm, *ibid.*, **27**, 314 (1957).

[11] H. M. McConnell and D. B. Chesnut, *ibid.*, **28**, 107 (1958); R. E. Robertson in "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, Chapter 10; J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963).

[12] J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

(VB) methods.[8,13] For the pyridine N-oxide–Ni(AA)$_2$ system, it was not possible to distinguish between these two mechanisms using the available literature calculations because of the similarity in spin distribution in the π bonding and antibonding orbitals. In the present case, however, Table I shows that a much better correlation can be made between the experimental data and the spin density distribution calculated for the highest filled ligand π bonding molecular orbital.[14] The one-electron nature of the MO calculations does not allow spin correlation to be introduced directly, but low calculated spin densities could be expected to become negative in this model if spin correlation were introduced. On this basis the correlation of the present nmr shifts and spin density delocalization into the highest filled π bonding orbital becomes evident particularly by comparing the calculated spin density distributions with the observed nmr shifts in the homocyclic ring. This assignment is further substantiated by the valence bond (VB) calculations for the α- and β-methylnaphthenyl radicals.[15] These calculations describe the spin density distribution in the highest filled bonding π orbital, and spin correlation is an integral part of the calculation. Moderately good agreement is obtained between these values and the experimental by assuming that the all carbon π systems for which the calculations were made and the amine N-oxide systems presently studied differ in that the homocyclic ring of the N-oxide has less than half the spin density calculated for the corresponding ring in the methylnaphthenyl radical.

Table I. Contact Shifts and Spin Densities of Ni(AA)$_2$ Complexes

Proton position	Isotropic shift[a]	MO ρ π bonding[b]	MO ρ π antibonding[b]	VB ρ[c]
		Isoquinoline 2-Oxide		
1	+325	0.202	0.216	+0.394
3	+100	0.033	0.027	+0.196
4	−116	0.010[d]	0.220	−0.127
5	−53	0.015[d]	0.102	−0.133
6	+118	0.073	0.048	+0.209
7	−46	0.000[d]	0.057	−0.108
8	+86	0.072	0.098	+0.182
		Quinoline 1-Oxide		
2	+287	0.141	0.123	+0.368
3	−89	0.027[d]	0.013[d]	−0.204
4	+245	0.173	0.172	+0.354
5	+31	0.059	0.099	+0.200
6	−31	0.006[d]	0.043	−0.100
7	+56	0.045	0.055	+0.195
8	−17	0.023[d]	0.096	−0.122

[a] Measured at 9 mg of Ni(AA)$_2$/ ml and 0.8 *M* in ligand. [b] "Spin densities" are squares of the atomic orbital coefficients reported in ref 14. [c] For α- or β-methylnaphthenyl radical; see ref 15. [d] These values may become negative upon introduction of spin correlation.

The contact-shift data presented in Table I represent the average contact shifts for the ligand protons which, owing to the labile nature of these complexes in solution and the presence of excess ligand, are rapidly exchanging between diamagnetic and paramagnetic environments. An approximate value for the contact shifts of the pure complexes can be obtained using eq 3[9b] in which $\Delta\nu_0$ is the observed isotropic shift $\Delta\nu_i$, is the

$$\Delta\nu_0 = \Delta\nu_i N_P + \Delta\nu_D N_D \qquad (3)$$

isotropic shift for the pure complex, N_P is the mole fraction of ligand complexed to a paramagnetic site, $\Delta\nu_D$ is the isotropic shift of the ligand at a diamagnetic site (which by definition is zero), and N_D is the mole fraction of ligand at such a site. Based on this equation the isotropic shift of the 1 proton in the pure isoquinoline 2-oxide–Ni(AA)$_2$ complex should be about 1900 cps, assuming essentially complete 2:1 complex formation under the conditions described in Table I. Using a spin density for this position of 0.3, eq 1 and 2 give a calculated isotropic shift of approximately 38,000 cps for a system having one unpaired electron delocalized into the ligand π bonding orbital. This indicates that in the observed complexes slightly less than 0.05 of an electron spin is found on the N-oxide ligand. This is higher than the 0.02 of electron spin estimated to be delocalized in the π system of pyridine N-oxide.[2]

The isotropic shifts observed for the Co(AA)$_2$ complexes differ in magnitude and relative ratio but, in general, not in sign from the shifts on the corresponding Ni(AA)$_2$ complex. This indicates that in the cobalt complexes the isotropic shifts are also due principally to spin delocalization in the π bonding orbital. To a first approximation the spin density introduced onto the coordinated ligand should distribute itself throughout the ligand in the same ratio regardless of the metal atom, although the magnitude of the spin introduced can vary. However, contact shifts may arise by spin delocalization in the ligand σ bonding, π bonding, or π antibonding orbitals or any combination of these. In addition, for magnetically anisotropic complexes, a pseudocontact term can also contribute to the isotropic shifts. Thus the ratio of isotropic shifts observed in a ligand is dependent on the relative contribution of each of these mechanisms and is known to vary as the nature of the coordinating metal atom changes.[9a,16]

For systems involving ligands coordinated to Ni(AA)$_2$ and Co(AA)$_2$, considerable success has been achieved by basing this difference solely on the pseudocontact term. This term is dependent on the geometry of a complex and the magnetic anisotropy. For an axially symmetric molecule in solution in which the electronic spin-lattice relaxation time is short compared to the molecular correlation time, the pseudocontact term can be calculated using eq 4,[10a] where χ is the angle between

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

the principal axis of the complex and a vector joining the metal and a given proton, and r is the length of this vector. For octahedral nickel(II) complexes which, having an A_2 ground state, are magnetically isotropic, the pseudocontact term becomes zero. Weak-field octahedral cobalt(II) complexes, having a T_1 ground state, become upon distortion magnetically anisotropic

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(13) R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Am. Chem. Soc.*, **86**, 379 (1964).

(14) T. Kubota, *Bull. Chem. Soc. Japan*, **35**, 946 (1962); T. Kubota, *Nippon Kagaku Zasshi*, **80**, 578 (1959).

(15) H. H. Dearman and H. M. McConnell, *J. Chem. Phys.*, **29**, 1361 (1958).

(16) D. R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965).

and are expected to possess a significant pseudocontact term. An attempt was made to resolve the difference in ratios of shifts between the $Ni(AA)_2$ and $Co(AA)_2$ complexes based on the premise that the ratio differences are due only to the pseudocontact shift of the $Co(AA)_2$ complex.

Table II. Pseudocontact Shifts for the Isoquinoline 2-Oxide–$Co(AA)_2$ Complex

Proton position	Isotropic shift[a]	Pseudocontact shifts: Exptl[b] (0.46)	Pseudocontact shifts: Exptl[b] (0.92)	Pseudocontact shifts: Calcd 116°[c]	Pseudocontact shifts: Calcd 127° 30′[d]
1	+291	+142	−9	−2	−6
3	+188	+142	+96	+93	+90
4	−64	−10	+43	+51	+53
5	−16	+8	+33	+23	+28
6	+129	+75	+20	+7	+13
7	−35	−14	+7	−3	+5
8	+72	+32	−7	−25	−10

[a] Observed at 9 mg of $Co(AA)_2$/ml, 0.8 *M* ligand concentration. [b] Calculated from given isotropic shift assuming contact shift is 0.46 or 0.92 times that in the corresponding $Ni(AA)_2$ complex. [c] Calculated by multiplying the geometric factor in A^{-3} by 3.62×10^4. Geometric factor calculated for a Co–O–N angle of 116°, a Co–O distance of 2.10 A, and slight restriction of rotation. [d] Calculated for a Co–O–N angle of 127° 30′, a Co–O distance of 2.20 A, and complete restriction of rotation and multiplying the calculated geometric factors by 1.60×10^4.

Table II presents data for the case of isoquinoline 2-oxide, which appeared more amenable to calculation because of its lower steric hindrance to free rotation around the N–O bond. Neither the relative amounts of spin delocalization in the $Ni(AA)_2$ and $Co(AA)_2$ complexes nor the *g* tensor anisotropy for the $Co(AA)_2$ complex are known. Therefore various pseudocontact shifts were deduced from the experimental data by scaling the $Ni(AA)_2$ shifts by an arbitrary constant and obtaining the difference between these numbers and the observed $Co(AA)_2$ complex isotropic shifts. Two sets of these shifts derived from the experimental data and based on the contact shift in the $Co(AA)_2$ complex being 0.46 and 0.92 times that observed for the corresponding $Ni(AA)_2$ complex (Table I), at the same ligand and $M(AA)_2$ concentration, are given in Table II. The ratios of pseudocontact shifts for the various protons of isoquinoline 2-oxide can be independently evaluated by calculating the geometric factor $[(3 \cos^2 \chi - 1)r^{-3}$, eq 4] for each proton. This was done using an IBM 7094 computer based on a model in which the planar isoquinoline ring rotates freely around the N–O bond, all C–C and C–N bond lengths are 1.40 A, all C–H bond lengths are 1.10 A, the N–O bond length is 1.35 A, the Co–O bond length varies from 2.00 to 2.20 A, and the bond angles are all 120° except for the Co–O–N angle which was varied from 110 to 180°. The rotation around the N–O bond gives rise to varying geometric factors. For example, for Co–O–N = 116° and Co–O = 2.10 A, the geometric factor for the 1 proton varies from 1.87×10^{-2} A^{-3} at apogee (proton 1 being situated at its farthest point from the plane of the acetylacetonate ring) to -4.57×10^{-2} A^{-3} at perigee (proton 1 being situated closest to the plane of the acetylacetonate ring with the plane of the isoquinoline ring being perpendicular to the plane of the acetylacetonate rings with proton 3 being at its farthest point). A reliable average value for each proton was obtained from the twelve geometric factors calculated for 30° increments of rotation of the isoquinoline ring around the N–O bond. The data indicate that the 1 and 3 protons cannot be symmetrically located around an axis of free rotation. In such a situation the pseudocontact shifts of the 1 and 3 protons would have to be equal. Such shifts (Table II, Pseudocontact shift, Exptl (0.46)) cannot be substantiated by calculated geometric factors obtained from any reasonable model, and therefore the isoquinoline 2-oxide ring must be distorted or restriction of rotation must occur.

Two sets of pseudocontact shifts obtained from calculated geometric factors using restricted rotation models are given in Table II. In the first case a Co–O–N angle of 116° and a Co–O length of 2.10 A was used, and the isoquinoline ring was assumed to rotate almost freely around the N–O bond with a small amount of rotational restriction being introduced by assuming protons 3, 4, and 5 spend only 0.53 times as much time at perigee as they do at the other eleven positions used in the average. Likewise protons 1, 6, 7, and 8 spend only 0.53 times as much time at apogee as at any of the other positions. The second model assumes a Co–O–N angle of 127° 30′ and an M–O bond length of 2.20 A with rotation around the N–O bond completely restricted owing to the N–O π-bond requirements. In this model, protons 3, 4, and 5 spend 0.6 of their time at apogee and 0.4 of their time at perigee, and the single resonance signal observed for each proton is due to rapid exchange of the complexed and uncomplexed ligand. In either case the agreement with the "experimental" pseudocontact shifts (0.92) is moderate, but refinements in the assumed structure of isoquinoline 2-oxide, such as the alternating bond lengths found in naphthalene,[17] the shorter C–N bond lengths in pyridine N-oxide,[18] and distortions of any or all angles from 120°, might be expected to improve the correlation. In either model the 1 proton is assumed to spend more time at perigee, which puts it closer to the central metal atom, than the 3 proton. This is in agreement with the greater broadening of the 1-proton nmr signal compared to the 3-proton resonance signal but is not that expected from simple steric requirements, *i.e.*, steric interaction of the benzo ring with the acetylacetonate ring. This suggests an asymmetric distortion of the isoquinoline ring in which the 3 proton presents more steric hindrance to rotation past the acetylacetone ring than the 1 proton. (Attractive forces such as hydrogen bonding to the coordinated oxygens are alternate but less well understood explanations.) Clearly, the models assumed herein are not the only solutions allowable by the pseudocontact shifts but they do indicate that the M–O–N angle is bent with a probable value of 115–130°. This is in agreement with data previously presented for pyridine N-oxide.[2]

A crude calculation of the magnetic anisotropy can be made assuming complete formation of a 2:1 complex and fixing $g_{\parallel} = 2$. The calculated geometric factors (2.57×10^{-3} A^{-3} for the 116° and 5.64×10^{-3} A^{-3} for the 127° 30′ model for the 3 proton) would require $g_{\perp}$ to be 3.7 for the 116° model and 3.0 for the 127° 30′ model. The values of $g_{\parallel}$ and $g_{\perp}$ demanded by either model are within the range reported for high-

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Table III. Diamagnetic Chemical Shifts of the Ligand Protons by Extrapolation[a]

	Isoquinoline 2-oxide		Quinoline 1-oxide	
Position	Ni(AA)$_2$	Co(AA)$_2$	Ni(AA)$_2$	Co(AA)$_2$
1	524^b	524^b	. . .	. . .
2	. . .	. . .	511^b	510^b
3	489^b	489^b	435^b	435^b
4	462	462	453	454
5	468	467	465	467
6	451	453	460	459
7	457.5	457	457	458
8	458.5	460	525^b	525^b

[a] Shifts are in cps at 60 Mc measured downfield from tetramethylsilane as internal standard using deuteriochloroform as solvent. [b] These shifts are directly measurable on the diamagnetic ligand solutions.

spin octahedral cobalt(II) complexes.[19] The self-consistancy of the data gives support to the original assumption that the differences in the Ni(AA)$_2$ and Co(AA)$_2$ complexes isotropic shift ratios are due principally to pseudocontact terms for the Co(AA)$_2$ complex.

The observed differences between the isotropic shift ratios of the Ni(AA)$_2$ and Co(AA)$_2$ complexes of quinoline 2-oxide (Figure 2) can be qualitatively explained by assuming pseudocontact shifts for the Co(AA)$_2$ complex for a model in which rotation of the quinoline ring is hindered. Because of the steric bulk of the benzo group, protons 5, 6, 7, and 8 spend less time near the acetylacetone plane than protons in positions 2 or 3.

Figures 1 and 2 indicate that the observed ligand proton chemical shifts vary "linearly" with metal complex concentration and can be extrapolated to their diamagnetic positions at zero metal concentration. This procedure was used in obtaining the isotropic shifts. Quantitatively this relationship is described by eq 3, where the $\Delta\nu$'s are redefined as chemical shifts rather than isotropic shifts, which is the expression defining chemical shifts of a system in rapid equilibrium.[20] Linearity can be expected in such a labile system in which each increment of added paramagnetic ion is completely converted to a single type of paramagnetic complex, to a constant ratio of different complexes, or to a variable ratio of complexes having identical stoichiometry and chemical shift. The validity of such a linear dependence is shown in the present work, within the limits of experimental uncertainties, using the chemical shifts readily available from the spectra of the diamagnetic ligands. The diamagnetic chemical shifts obtained by extrapolation are given in Table III. Although this method for obtaining chemical shifts should be applicable to any rapid equilibrium, it is particularly useful for molecules which coordinate with paramagnetic ions because of the very large shifts which are found in these systems. In the present work the shifts observed are due to spin delocalization by a π mechanism, and for the Co(AA)$_2$ complexes these shifts are also due to pseudocontact interactions. Earlier Phillips, Looney, and Ikeda[21] also noted a linear dependence of the methyl and methylene proton resonances in 1-propanol with paramagnetic metal ion concentration, a system which involves spin delocalization by a σ mechanism.

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Kinetic Studies of Exchange between Metallic Mercury and Mercury Compounds in Solution. II

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Abstract: Further investigations of the conditions affecting the exchange of diarylmercury in solution with metallic mercury have been performed using a variety of symmetrically monosubstituted mercury diaryls. Activation parameters ΔS^*, ΔH^*, ΔF^*, E_A, and log PZ have been determined for ten compounds, and the theories of Hammett and Leffler applied to show that all reactions follow a constant $S_{E}i$ mechanism throughout the series. Measurements of reaction surface area have been made and are considered in the light of log PZ values obtained.

In part I of this study, a report was made of an experimental technique for the exchange of diphenylmercury in benzene solution with a stirred metallic mercury layer.[2] This followed an initial report by Reutov and Ostapchuk.[3] Experimental parameters involved were investigated in turn by us, and the reaction was shown to proceed reproducibly and reversibly with first-order kinetics under conditions involving sufficient stirring. The reaction rate was shown to depend directly upon the mercury surface area, though no

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[1] Part of this material was taken from a thesis of D. R. Pollard in fulfillment of the degree of Ph.D., University of London, at Sir John Cass College.

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