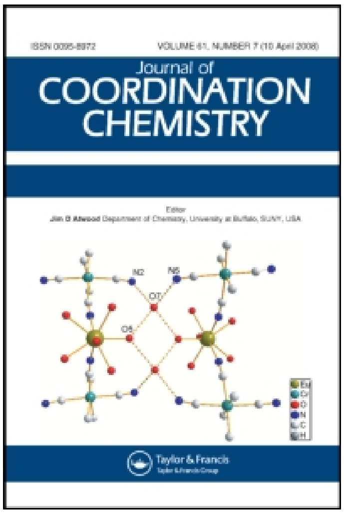

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NUCLEAR MAGNETIC RESONANCE SPECTRAL ANALYSIS OF PARAMAGNETIC NICKEL(II)-8-HYDROXYQUINOLINE COMPLEXES

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Chemical substitution has enabled ^{1}H nmr spectral assignments of paramagnetic Ni(II)-8-hydroxyquinoline complexes in d^6-dmso solution to be made. The complexes were found to be fluxional with a free energy of activation, ΔG^*, of 74 kJ mol^{-1} in dmso. INDO MO calculations enabled the observed proton chemical shifts to be interpreted in terms of a π-mechanism of spin delocalization, involving a transfer of spin from the metal into a π antibonding orbital of the ligand.

Keywords: Nmr, 8-hydroxyquinolines, nickel(II), fluxionality, delocalization

INTRODUCTION

Nuclear magnetic resonance spectra can, with a few exceptions, be recorded for paramagnetic complexes in solution.[1,2] The technique is a sensitive probe of solution structure and bonding. Unpaired spin density gives rise to substantial isotropic chemical shifts. These chemical shifts can arise *via* a dipolar mechanism if the complex is anisotropic or *via* a Fermi contact mechanism, which reflects spin delocalization in the ligand system.[3] Inter- and intramolecular exchange phenomena also play a part in determining spectral characteristics.

The Fermi contact interaction may arise from electron density donation from metal *d*-orbitals into vacant antibonding orbitals of the ligand which have σ- or π-character. This mechanism has been found to contribute to the isotropic shift for the pyridine, pyridine-*N*-oxide and picoline adducts of many 3*d* metal complexes.[4–6] Alternatively, electron density in the highest occupied orbitals of the ligand may be transferred into unfilled metal *d* orbitals. This mechanism is more likely for highly charged 3*d*-metal ions.

In the analysis of paramagnetic spectra, the Fermi contact resonance shifts are of interest since these can be interpreted in terms of a spin-transfer mechanism (σ or π), whereby the unpaired electrons are delocalized from the paramagnetic metal into the ligand system. The contact shift can be mathematically related to the spin density through the hyperfine coupling constant, which is directly proportional to spin density at the nucleus (N):[3]

$$A_N = (k|\varphi_{sN}(r_N)|^2)\rho_{sN}$$

where $k = (4\pi/3)gh\beta\gamma_n{<}S_Z{>}^{-1}$, ${<}S_Z{>}$ is the average spin, ρ_{sN} is the spin density in the valence s orbital on nucleus N, and $|\varphi_{sN}(r_N)|^2$ is the density at the nucleus N.

The factor $k|\varphi_{sN}(r_N)|^2$ is a constant for each type of magnetic nucleus and has the value 539.86 Gauss for the hydrogen atom.

Recently nmr spectral analysis of paramagnetic nickel-8-hydroxyquinoline complexes [Ni(R-oxine)$_2$] have been reported.[7] These spectra were recorded at 90 MHz where relatively simple spectra were found. We have extended this study to higher field strength, demonstrating the fluxionality of the complexes. The data is analyzed in terms of structure and, using INDO MO calculations,[8] in terms of bonding.

EXPERIMENTAL

Substituted *bis*(8-hydroxyquinoline)nickel(II) dihydrate complexes were prepared as described previously.[9] Purity of all complexes was established spectroscopically and by microanalysis (C,H,N). ^{1}H nmr spectra were recorded as d_6-dmso solutions on a Varian VXR-200 spectrometer in the region −20 to 160 ppm. For wide sweep width spectra, a short acquisition delay was used to prevent pulse breakthrough.

INDO open shell computations were performed on a Sperry-Univac 1100/81 computer using the CNINDO/74 program of Dobosch.[10] Geometric parameters were taken from X-ray crystallographic data.[11] Additional bond lengths and bond angles were taken as follows: C–H (aromatic) 1.08 Å; O–H 0.96 Å; N–H 0.99 Å; ∠COH 109°47′; ∠CNH 120°. In all cases the geometry of the free ligand was retained. Methyl groups were considered to rotate freely thus leading to an average spin density for the three protons.

RESULTS AND DISCUSSION

Analysis of ^{1}H-NMR Spectra

Initial ^{1}H nmr assignments were made at 393.1K using chemical substitution. Variable temperature studies allowed room temperature assignments to be made. The ^{1}H nmr spectra for the complexes [Ni(R-oxine)$_2$(H$_2$O)$_2$] at 393.1 K are shown in Fig. 1 and the ^{1}H nmr chemical shifts for these compounds are given in Table I. As

TABLE I

^{1}H nmr chemical shifts for [Ni(R-ox)$_2$(H$_2$O)$_2$] in dmso-d_6 at 393.1K.

	Chemical shift[a]						
R	2-H	3-H	4-H	5-H	6-H	7-H	2-CH$_3$
H	n.o.[b]	15.5	34.6	17.8	14.6	7.4	
5-Cl	n.o.[c]	14.2	36.0		12.7	5.1	
5,7-di-Cl	n.o.[d]	14.8	34.2		13.6		
5,7-di-Br-2-Me		13.7	39.8		13.5		−5.1
$\Delta\nu^{con}$	−160[e]	−8.1	−26.4	−10.5	−7.2	−0.3	

[a] Relative to dmso-d_6 (ppm); [b] n.o. = not observed; [c] Two broad peaks at δ 153 and δ 176 were observed at $T = 297.5$K; [d] Broad peak at δ 168.0 was observed at $T = 297.5$K; [e] Estimated to be approximately −160 ppm from superscript d above. Negative sign indicates a downfield shift relative to the diamagnetic position.

dmso coordinates readily with nickel, it is expected to replace the water molecules, which occupy the axial positions in the above complexes. Octahedral nickel(II) species are magnetically isotropic and hence the observed shifts are assumed to be purely contact in origin. Five peaks shifted from the diamagnetic positions are observed in the Ni(oxine)$_2$ complex (Fig. 1). The sharp singlet at δ 17.8 can be assigned unambiguously to H-5 as it is absent in the spectra of the 5-Cl-, 5,7-di-Cl- and 5,7-di-Br-2-Me-substituted complexes. The broad peak at δ 7.4 is readily assigned to H-7 as it is present in the 5-chloro-substituted complex, but disappears in the spectra of both the 5,7-di-Cl- and 5,7-di-Br-2-Me-substituted analogues. A peak, shifted substantially downfield from dmso, is expected for H-2, since this proton would be most directly affected by spin delocalization through the nitrogen atom of the ligand. However, no such peak was observed for any of the complexes at 393.1 K. A peak at δ 168 was observed in the spectrum of Ni(5,7-di-Cl-oxine)$_2$ at 297.5K, whilst two peaks were observed at δ 153 and δ 176 in the spectrum of Ni(5-Cl-oxine)$_2$. These peaks are assigned to H-2. The fact that two peaks are observed for the Ni(5-Cl-oxine)$_2$ complex where only one peak is expected, can be explained by the non-fluxional behaviour of this complex at 297.5K. Comparison with the results for Ni(II) pyridine[12] suggests the assignment of H-4 to the peak at δ 34.6. The two remaining peaks at δ 15.5 and δ 14.6 are tentatively attributed to H-3 and H-6, respectively. Attempts to confirm these assignments by variable temperature extrapolation failed because the diamagnetic chemical shift range was too small.

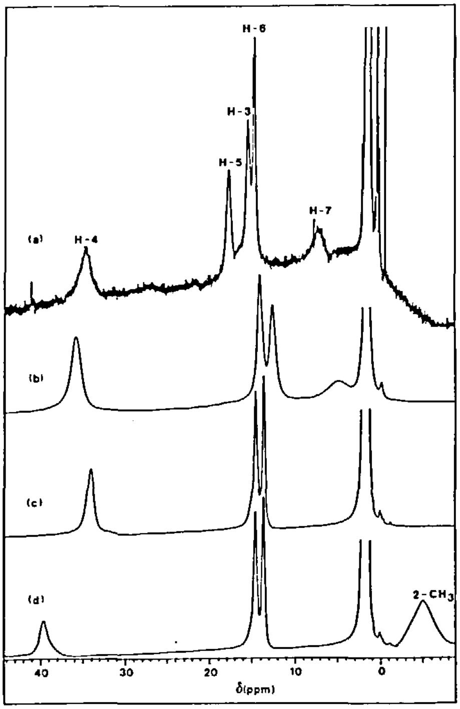


FIGURE 1 ^{1}H nmr spectra of the complexes [Ni(R-oxine)$_2$(H$_2$O)$_2$] in d_6-dmso at 393K: (a) R = H; (b) R = 5-Cl; (c) R = 5,7-di-Cl; (d) R = 5,7-di-Br-2-Me.

Fluxional Behaviour of Ni(R-oxine)$_2$ Complexes

Variable temperature ^{1}H-nmr (Fig. 2) reveals that the Ni(oxine)$_2$ complex is fluxional in solution. At ambient temperatures two signals (of unequal intensity) are seen for several of the oxine protons implying that, at this temperature, there are at least two isomers of the complex coexisting in solution. As the temperature is raised, these peaks coalesce. Chemical substitution confirms that at ambient temperature protons H-3, H-4 and H-6 each give rise to more than one nmr signal. A plot (Fig. 3) of chemical shift *vs* $1/T$ established a Curie behaviour for protons H-5, H-7 and 2-CH$_3$. Curie behaviour for H-3, H-4 and H-6 was only seen when the average chemical shifts of these protons was plotted against $1/T$.

TABLE II

Typical $\Delta G^{\ddagger}$ values for the *trans/cis* isomerization process.[a]

Complex	$\Delta G^{\ddagger}$/kJ mol^{-1}	Reference
[Co(en)$_2$(OH$_2$)Br]$^{2+}$	94.7	16
[Co(en)$_2$(OH$_2$)N$_3$]$^{2+}$	68.6	16
[Co(en)$_2$(OH$_2$)Cl]$^{2+}$	68.2	16
[Co(en)$_2$(OH$_2$)$_2$]$^{3+}$	101.8	17
[Co(en)$_2$(OAc)(OH$_2$)]$^{2+}$	98.8	17
[Cr(CO)$_2$(dpm)$_2$]	76.8	18
[W(CO)$_2$(dpm)$_2$]	72.5	18
[Mo(CO)$_2$(dpm)$_2$]	80.2	18
[W(CO)$_2$(dpe)$_2$]	78.7	18
[Co(en)(dmso)Cl]$^{2+}$	88.6	19
[Cr(mal)$_2$(H$_2$O)$_2$]$^-$	103.5	20
[Ni(R$_2$-ati)$_2$]^b (R = Et)	−12.2	21
(R = Ph)	−4.1	21
(R = Bz)	−3.4	21
[Mo(CO)$_4$(PPh$_3$)$_2$]	112.1	22
[Mo(CO)$_4$(P-*n*-Bu$_3$)$_2$]	109.4	23
[Co(diars)$_2$Cl$_2$]$^+$	100.0^c	24
[Cr(ox)$_2$(OH$_2$)$_2$]$^-$	92.1	25
[Co(acac)$_2$(NO$_2$)py]	98.3	26

[a] Here en = 1,2-diaminoethane; dpm = *bis*(diphenylphosphino)-methane; dep = 1,2-*bis*(diphenylphosphino)ethane; mal = malonato; R$_2$-ati = *bis*(*N*-alkylbenzoylacetoneiminato); Et = ethyl; Ph = phenyl; Bz = benzoyl; P-*n*-Bu$_3$ = *tris*-(*n*-butyl-phosphine); ox = oxalato; acac = acetylacetonato; py = pyridine; *n*-Pr = *n*-propyl; diars = Nyholm's diarsine; dmso = dimethylsulphoxide; OAc = CH$_3$CO$_2$$^-$. [b] Planar to tetrahedral isomerization. [c] In methanol.

There are five possible geometric isomers for the octahedral Ni(R-oxine)$_2$ complex in solution. The crystal structure[13] of [Zn(oxine)$_2$(H$_2$O)$_2$] has shown that the two oxinate anions coordinate to the metal by forming a *trans*-(H$_2$O), *trans*(N), *trans*(O) structure of C_{2v} symmetry. It seems likely that this is the structure of the most predominant Ni(R-oxine)$_2$ complex in solution. The rate of chemical exchange between different possible isomers was studied using computer-aided, bandshape analysis.[14,15] The Gibbs free energy of activation, $\Delta G^{\ddagger}$ was estimated to be 74 kJ mol^{-1}. Table II lists typical $\Delta G^{\ddagger}$ values for *cis-trans* isomerization which, with

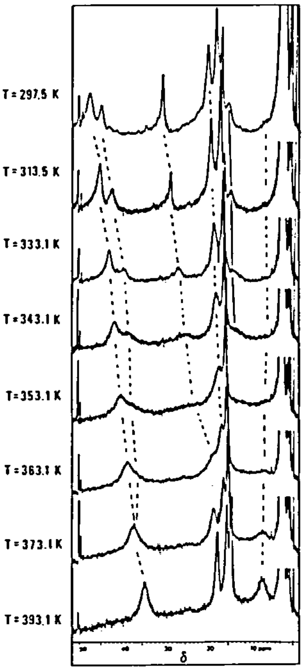
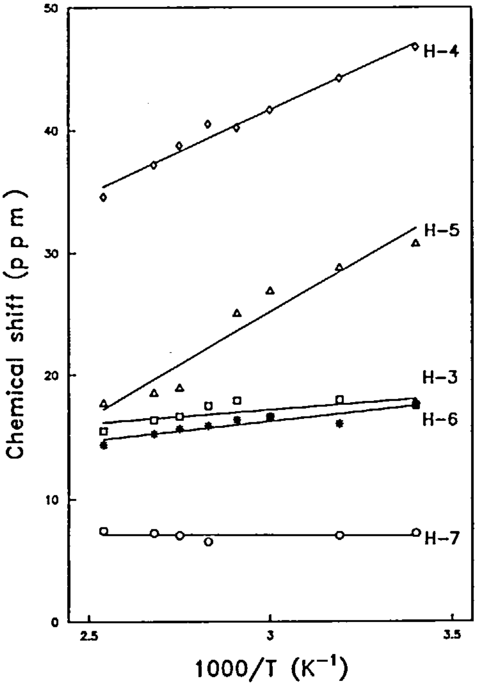


FIGURE 2 ^1H nmr spectra of $[Ni(oxine)_2(H_2O)_2]$ in d_6-dmso at different temperatures.



IGURE 3 Temperature dependence of the isotropic chemical shifts for $[Ni(oxine)_2(H_2O)_2]$ in d_6-dmso.

the exception of square planar/tetrahedral isomerization of Ni(II) complexes, are all in the range 70 to 115 kJ mol^{-1}. Hence, we conclude that the Ni(R-oxine)$_2$ (R = H, 5-Cl) complexes are undergoing *cis-trans* isomerization. A "Bailar twist" mechanism[27] would provide a low-energy path for this stereochemical rearrangement. An alternative mechanism involving bond rupture and dissociation of one of the solvent molecules is discounted on the basis of the low observed $\Delta G^{\neq}$ value and the fact that the Ni(R-oxine)$_2$ (R = 5,7-di-Cl and 5,7-di-Br-2-Me) complexes are not fluxional.

INDO Spin Density Calculations

Net spin density can arise on the ligand of a paramagnetic metal complex as a result of electron transfer from either the metal atom to the ligand or the ligand to the metal atom. If a whole electron is transferred from the metal atom to the ligand, then an anionic ligand radical with unpaired spin density in a previously empty (antibonding) orbital of the ligand is produced. If, however, the transfer is from the ligand to the metal, a cationic radical with unpaired spin density in a previously fully occupied (bonding) orbital is produced. A comparison of the NMR contact shifts (and hence experimentally determined spin densities and hyperfine coupling constants) for a complex with the calculated cationic or anionic spin densities can suggest the direction of electron transfer, and moreover, the type of ligand orbital containing the transferred spin density.

The observed isotropic hyperfine coupling constants (calculated from the observed contact shifts) for Ni(oxine)$_2$ and Ni(5,7-di-Br-2-Me-oxine)$_2$ complexes together with the calculated isotropic hyperfine coupling constants for the cationic and anionic species are given in Table III. The INDO calculations predict a downfield shift for all the protons except H-6 for the cationic species and a downfield shift for all the protons for the anionic species as is experimentally observed. Hence, the correlation between the calculated and observed hyperfine coupling constants is better in both sign and magnitude for the anionic ligand radical. This indicates that spin delocalization involves the transfer of spin from the metal into the antibonding π^* orbital of the ligand. It is noteworthy that the agreement between calculated and observed values for H-2 is particularly poor. One would expect this proton to be the most affected (and hence the most shifted) by spin delocalization because of its close proximity to the metal. However, INDO calculations for the anionic ligand radical predict that H-4 should shift most from its diamagnetic position. This discrepancy may be due to the fact that the Ni(R-oxine)$_2$ complexes are *not* purely octahedral as dmso molecules occupy the axial positions. If there is distortion from an idealized octahedral symmetry, one can no longer assume that the isotropic shifts are purely contact in origin. There may be a significant dipolar contribution to the shift which will become attenuated as the distance from the metal is increased. This could explain why H-2 is shifted significantly more than is theoretically expected.[3] An alternative explanation derived from considering the ligand as either a cation or anion, as in our case, is an oversimplification. Such an observation has been reported by Scarlett *et al.*[12] The neglect of the metal orbitals in the INDO calculations is only justifiable if the relative energies of the ligand orbitals do not change upon complexation.

The observed hyperfine coupling constants are numerically smaller than the calculated hyperfine coupling constants. INDO calculations are performed on the assumption that a whole electron is transferred. It is therefore possible to estimate the percentage electron transferred by comparing the magnitude of the observed and calculated hyperfine coupling constants. In the Ni(oxine)$_2$ complex, the percentage electron transferred was estimated to be 3%.

TABLE III
Calculated and observed hyperfine coupling constants for the oxine and 2-methyl oxine cation and anion radicals.

	Nucleus	oxine		2-methyl oxine	
Species	^{1}H	A_{H} (Gauss)	A_{H} (rel.)	A_{H} (Gauss)	A_{H} (rel.)
		calculated			
cation	2	−0.931	0.321		
	3	−0.033	0.011	−2.781	1.000
	4	−2.903	1.000	−6.911	2.485
	6	−7.449	2.566	−6.911	2.485
	7	−3.410	1.175	−2.824	1.015
	2-Me			1.982	−0.713
anion	2	−2.299	0.324		
	3	−0.755	0.106	−0.462	0.064
	4	−7.104	1.000	−7.259	1.000
	5	−3.076	0.433	−3.035	0.418
	6	−0.288	0.041	−0.244	0.034
	7	−0.663	0.093	−0.652	0.090
	2-Me			4.392	−0.605
		observed			
	2	~−1.067	~6.063		
	3	−0.054	0.307	−0.042	0.199
	4	−0.176	1.000	−2.211	1.000
	5	−0.070	0.398		
	6	−0.048	0.273	−0.041	0.194
	7	−0.002	0.011		
	2-Me			0.024	−0.114

INDO spin density calculations can also predict the type of spin delocalization (σ or π) in a selected system. Spin density in the p_z orbitals of the ligand atoms indicates a π-bonding mechanism, whereas if the spin density is concentrated mainly in the s, p_x and p_y orbitals of the ligand atoms, spin delocalization *via* a σ-bonding mechanism is implied. INDO spin densities for the oxine anion ligand radical reveal that spin density is concentrated mainly in the p_z orbitals. From this it appears that delocalization occurs predominantly *via* a π-mechanism. Substitution of H-2 by a methyl group, in Ni(5,7-di-Br-2-Me-oxine)$_2$, resulted in the methyl protons being shifted in the opposite direction to the substituted proton. This is characteristic of π-spin delocalization. There is no evidence for π-bonding through the phenolic oxygen atom.

It has been proposed[17,28] that certain features of a paramagnetic spectrum are unique to either σ- or π-spin delocalization. For σ-spin delocalization, proton resonances were thought to all shift in the same direction, upfield for delocalization of positive (antiparallel) spins and downfield for negative spin delocalization.

Isotropic shifts attenuate rapidly with increasing distance from the paramagnetic metal. On substitution of a proton by a methyl group, the methyl group protons are all shifted in the same direction as the substituted proton, but the shifts are generally smaller. π-Delocalization was thought to be characterized by both upfield and downfield shifts which alternated in direction between adjacent positions.[4] In addition, these shifts are not as rapidly attenuated. Often the largest shifts occur at positions far removed from the coordination site.

In contrast to the above discussion, Scarlett and colleagues[12,29] have shown that the manner in which the spin density is distributed through the ring system may not necessarily be indicative of a particular spin delocalization mechanism. These workers have shown that in the pyridine–*N*-oxide cation, the unpaired spin density lies in a σ-orbital, even though the sign of the spin density alternated through the conjugated system. Now we have shown that a π-spin delocalization mechanism is predominant in the Ni(oxine)$_2$ complex even though all six proton resonances are shifted downfield from their diamagnetic positions.

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