Proton Nuclear Magnetic Resonance Studies of Spin Delocalization in Low-Spin Chelates of Chromium(II) and Iron(III) with Symmetrically Substituted o-Phenanthrolines and α,α'-Bipyridines

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Abstract: Narrow, well-resolved proton nmr spectra have been observed for a series of substituted tris o-phenanthroline and α,α'-bipyridine chelates of Cr(II). The isotropic shifts are interpreted as arising from a combination of direct π spin delocalization of metal unpaired spins, and negative σ spin delocalization, which results from an exchange polarization interaction between the unpaired metal spins and the ligand donor σ electrons. The absence of sizable π delocalization indicates that the Cr(II) chelates do not derive their marked stability from π bonding alone, and demonstrates that the "spin-only" magnetic moments for these compounds must be attributed to a strong trigonal distortion of the ligand field rather than to delocalization of magnetic electrons. A reinterpretation of the previously reported isotropic shifts for the analogous Fe(III) complexes suggests that they arise primarily from negative σ spin delocalization. This reinterpretation constitutes the most convincing evidence to date for the existence of the exchange polarization delocalization mechanism. It is also shown that this effect can be observed in other complexes in the literature. The relative contact shift magnitudes for the Cr(II) and Fe(III) chelates indicate that the former possess higher π covalency, while the latter exhibit larger σ covalency, which may be related to the higher energies of the Cr(II) d orbitals relative to Fe(III).

The analysis of the ligand proton magnetic resonance spectra of paramagnetic transition metal complexes can lead to useful information about their electronic structure.[1] The isotropic shifts arising from the scalar contact interaction, which results from spin delocalization, are given by the equation[2]

$$\left(\frac{\Delta H}{H_0}\right) = -A\frac{\gamma_e}{\gamma_H}\frac{g\beta S(S+1)}{3kT} \quad (1)$$

where all notations are standard.[1,2] In the favorable case where the spin-containing ligand orbital possesses π symmetry, the hyperfine coupling constant, A, derived from eq 1 can be related to the unpaired spin density, ρ, at the aromatic carbon by

$$Q\rho/2S = A \quad (2)$$

where Q is a constant.[3]

A second mechanism, the proton–electron dipolar interaction, can also lead to isotropic shifts, which are given by

$$\left(\frac{\Delta H}{H_0}\right) = \frac{\beta^2 S(S+1)}{3kT}\left(\frac{3\cos^2\chi - 1}{R^3}\right)F(g) \quad (3)$$

where $(3\cos^2\chi - 1)/R^3$ is the usual geometric factor, and $F(g)$ is some function of the components of the diagonal g tensor which depends on the relative magnitudes of the electron relaxation time, T_{1e}, the tumbling time of the complex in solution, τ, and the Zeeman anisotropy energy.[2,4]

To date, extensive high-resolution proton nmr studies on complicated paramagnetic compounds have been

restricted primarily to the ions Ni(II),[1,5] Co(II),[6] V(III),[7,8] and Fe.[5c,7,9–11] In each case the well-resolved proton spectra resulted from very short electron relaxation times. Though the factors leading to short T_{1e}'s are only incompletely understood at this time, it has been suggested[12] that two electronic properties of the complex, namely an orbitally triply degenerate ground state, or spin multiplicity, $(2S + 1) > 2$, preferably both, can lead to appropriately short T_{1e}'s. In its usual trivalent state, chromium possesses a $^4A_2$ ground state, and the proton spectra of such complexes are characterized by broad lines in most cases, permitting analysis only when the coupling constants, A, are very large,[13] or when the number of nonequivalent protons is small.[7] However, the reduced, divalent state, Cr(II), d⁴, when placed in a strong ligand field,

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gives rise to a $^3T_1$ ground state, for which a short T_{1e} and hence narrow proton nmr lines may be anticipated.

A particularly promising group of complexes with this apparent ground state is the tris o-phenanthrolines (phen) and the tris α,α'-bipyridines (bipy) of chromium(II) halides.[14-18] These compounds are stable against oxidation in an inert atmosphere in both solid and solution. Magnetic moments of these trigonally distorted octahedral chelates are essentially "spin only," falling in the range 2.8–3.3 BM,[16,17] in spite of their apparent $^3T_1$ ground states. This anomaly has received considerable attention, and two contrasting explanations have been forwarded. One analysis[17] invokes extensive delocalization of the magnetic electrons into the vacant antibonding ligand π orbital. The alternate interpretation postulates[18] a strong trigonal distortion to quench the orbital contribution to the magnetic moment, and requires only a modest delocalization of the unpaired spins. Inasmuch as the observed contact shifts can be related to the delocalized spin densities on the ligand, it should be possible to experimentally choose between these two interpretations.[1]

Moreover, as paramagnetic tris chelates with these two ligands are known[14] for a large number of transition metals in a variety of oxidation states, of which the proton nmr shifts for some of the Co(II),[19,20] Ni-(II),[19,20] and Fe(III) chelates[9] have already been reported, it would be fruitful to compare spin delocalization into the ligand for different metals. Since the proton nmr shifts for the well-characterized,[14] low-spin tris α,α'-bipyridines of ferric trihalides have not been reported, these complexes were also included in this investigation. Furthermore, the ability of the phen and bipy to stabilize low oxidation states of the early first-row transition metals has been attributed[14,17,21,22] to the superior π acceptor properties of these ligands. Estimates of the extent of π delocalization in the Cr(II) complexes should allow one to judge the π acceptor capabilities of the ligands.

Experimental Section

Complexes. All reactions and handling of Cr(II) complexes were carried out under N_2 using only thoroughly degassed solvents. The $CrCl_2$ complexes were prepared by mixing dry stoichiometric amounts of chromous chloride (Alfa Inorganics, Inc.) and the appropriate ligand (G. F. Smith Chemical Co., and K and K Laboratories, Inc.). Addition of water initiated the reaction by dissolving the complex. Filtering removed any insolubles, and the complex was recovered by the addition of sodium chloride. The samples were dried under vacuum. The bromide and iodide complexes were prepared by metathesis, where addition of an excess of the appropriate sodium halide to a dilute water solution of the $CrCl_2$ complex quantitatively yielded the CrX_2 chelate. The well-

characterized tris complexes of ferrous chloride were prepared in a similar fashion.

The results of elemental analysis for some of the new isomers are given in Table I. Fair agreement could be achieved by postulating one to two water molecules of hydration. However, the postulated water content is not considered significant in view of the possible oxidation or reaction of these very air-sensitive complexes during the excessive handling during analysis. Similar difficulties with analyses of some of these complexes have been experienced by other workers.[16] The nmr spectra are consistent with hydration of most complexes inasmuch as the solvent proton peak intensity increased upon dissolving the complex, and this intensity increase was minimized by first recrystallizing the complex from D_2O. Additional evidence for the structure of the complexes arises from the fact that when unsymmetrically substituted ligands were used, the nmr spectrum gave rise to four equally intense resonances per set of protons, which is indicative of the statistical mixture of *cis* and *trans* isomers which results from a tris complex of an unsymmetrical bidentate ligand (*vide infra*).

Table I. Elemental Analyses of Complexes

Complex	Calculated, % C	Calculated, % H	Found, % C	Found, % H	μ^a
(phen)₃CrBr₂	57.5	3.22	57.6	3.4	2.62 ± 0.2
(4,7-phen)₃CrCl₂·2H₂O	64.5	6.13	63.7	4.5	2.90 ± 0.2
(5,6-phen)₃CrCl₂·H₂O	65.6	5.48	65.1	5.1	2.87 ± 0.2
(bipy)₃CrCl₂·H₂O	59.1	4.92	59.0	4.9	2.94 ± 0.2
(bipy)₃CrBr₂·H₂O	51.5	3.70	51.1	4.2	2.73 ± 0.2
(4,4'-bipy)₃CrCl₂·H₂O	62.3	6.05	58.7	5.1	2.76 ± 0.2

^{a} Magnetic moment in BM, determined by a nmr method, ref 23.

The magnetic moments for some of the Cr(II) complexes in methanol were determined by a nmr method.[23] In view of the uncertainty of the water of hydration in the solid and the difficulty in handling and preparing the samples, the recorded moments in Table I can be considered accurate only to within ±0.2 BM.

The nmr samples were prepared by dissolving the Cr(II) chelates in d_4-methanol (Mallinckrodt Chemical Works) or deuterium oxide (Bio-Rad Laboratories), and sealing them under N_2. The Fe(III) samples were prepared by bubbling chlorine gas through a D_2O solution of the ferrous chelate in the absence of light. The characteristic color change from red to deep blue was observed. Though ~0.05 M solutions were generally used, varying the concentration had no significant effects on the chemical shifts.

For the sake of brevity, the ligands will be abbreviated to phen for o-phenanthroline, and to bipy for α,α'-bipyridine, and substituents are identified according to the numbering schemes[24] in I

I   II
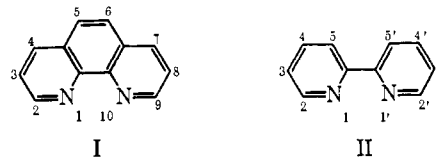
and II, respectively. Since primarily methyl-substituted complexes were studied, the substituted complexes will be simply designated by the number(s) of the position(s) of the methyl group(s); *i.e.*, 3,4,7,8-tetramethyl-o-phenanthroline will be written 3,4,7,8-phen. Other substituents will be designated by name.

Nmr Spectra. The proton nmr spectra were recorded on a Varian HR-100 spectrometer, modified to operate with variable modulating frequency from 0 to 50 kHz, and employing the usual audio-side-band technique for calibration. Unless specified otherwise, the solution temperature was maintained at 33°. The internal calibrant employed was TMS for the d_4-methanol, and sodium 3-(trimethylsilyl)-1-(propanesulfonate) for the D_2O solutions. The proton spectra of methanol solutions of (phen)₃CrCl₂ and (bipy)₃-CrCl₂ were run from −50 to 70°. The Cr(II) samples remained stable over a period of weeks and after temperature changes be-

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Table II. Isotropic Shifts for $L_3Cr^{II}X_2$ in d_4-Methanol[a]

Ligand	X	2,9	3,8	4,7	5,6
phen	Cl	+30.00 (~700)[b]	−4.77 (48)	−10.53 (46)	+3.57 (23)
phen	Br	+29.82 (~750)	−4.97 (50)	−10.61 (50)	+3.46 (..)
4,7-phen	Cl	+29.65 (~750)	−3.95 (40)	[+6.83][c] (39)	+4.02 (19)
5,6-phen	Cl	+30.63 (~800)	−6.10 (50)	−10.25 (48)	[+0.35] (21)
3,4,7,8-phen	Cl	+29.00 (~800)	[+10.02] (46)	[±6.20] (115)	+3.71 (36)
3,5,6,8-phen	Cl	+28.10 (~650)	[+9.48] (30)	−7.39 (53)	[+0.60] (16)
5-phen	Cl	+30.56 (~1000)	−5.23 −5.56	−6.78, −7.44 −8.61, −9.27 −10.87, −11.50 −12.72, −13.42	d

Ligand	X	2,2′	3,3′	4,4′	5,5′
bipy	Cl	+28.00 (700)	−11.43 (63)	−8.96 (55)	+3.77 (70)
bipy	Br	+27.45 (...)	−11.50 (..)	−9.20 (..)	+3.78 (..)
bipy	I	+27.90 (...)	−11.40 (..)	−8.96 (..)	+3.77 (..)
4,4′-bipy	Cl	+28.62 (700)	−10.89 (54)	[+5.11] (32)	+1.87 (65)
4,4′-bipy	Br	+28.67 (700)	−10.95 (50)	[+5.08] (31)	+1.90 (63)
4,4′-bipy	I		−10.97 (85)	[+2.84] (..)	+1.91 (..)
4,4′-Di-Ph-bipy[e]	Cl	+27.75 (...)	−13.45	(o) −2.43 (m) +0.48 (p) −2.09	+3.20 (..)

[a] Shifts in ppm, at 33°, referenced against diamagnetic ligand. [b] Proton line width, in Hz at 100 MHz, given in parentheses. [c] Shifts for methyl groups are enclosed in brackets. [d] The 5-CH_3 and 6-H peaks could not be identified at this time. [e] 4,4′-di-Ph-bipy represents 4,4′-diphenylbipyridine, where o, m, and p designate the ortho, meta, and para protons of the phenyl substituent.

Table III. Isotropic Shifts for L_3FeX_3

Ligand	X	2,2′	3,3′	4,4′	5,5′
bipy[a]	Cl	+52.25 (500)[b]	+7.70 (50)	+6.90 (40)	+1.55 (60)
4,4′-bipy[a]	Cl	+52.10 (450)	+7.75 (45)	[−12.75][c] (20)	+0.65 (55)

Ligand	X	2,9	3,8	4,7	5,6
phen[d]	ClO₄	+56.02	+10.52	−0.46	+6.53
4,7-phen[d]	ClO₄	+55.18	+10.95	[−13.49]	+2.96
5,6-phen[d]	ClO₄	+53.77	+10.69	−0.76	[+1.40]
3,4,7,8-phen[d]	ClO₄	+54.17	[+1.83]	[−14.32]	+4.84
3,5,6,8-phen[d]	ClO₄	+54.82	[+1.72]	−0.59	[+0.44]

[a] Shifts in ppm, recorded at 100 MHz, in D_2O solution at 33°, and referenced against diamagnetic ligand. [b] Line widths, in Hz at 100 MHz, given in parentheses. [c] Methyl shifts are enclosed in brackets. [d] Data taken from ref 9. Shifts are in ppm, recorded at 56.4 MHz, in D_2O solution at 25°.

tween −50 and 100°. On the other hand, the Fe(III) chelates all decomposed slowly at room temperature, becoming very unstable at higher temperatures. The positions of the peaks of the desired Fe(III) complex were not affected by the decomposition reaction, which produced green solutions.
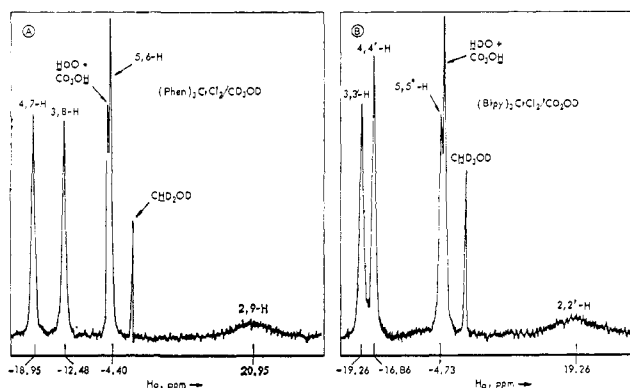

Figure 1. Proton nmr traces for (A) (phen)₃CrCl₂ and (B) (bipy)₃CrCl₂ in d_4-methanol, referenced against TMS.

The isotropic shifts are defined as the difference in the resonance position for a proton in the paramagnetic complex and in the diamagnetic ligand, such that an upfield shift is considered positive, and are all reported in parts per million. The line widths, defined as the peak width at half-height, are reported in hertz at 100 MHz.

Results

The proton nmr traces for d_4-methanol solutions of (phen)₃CrCl₂ and (bipy)₃CrCl₂ are illustrated in Figure 1, and the temperature dependence of their isotropic shifts is shown in Figure 2. Tables II and III list the observed isotropic shifts for the Cr(II) complexes in methanol and for the Fe(III) chelates in D_2O, respectively, each referenced against the diamagnetic ligand. The line widths for the Cr(II) peaks and for the new Fe(III) peaks are given in parentheses in Tables II and III, respectively. The isotropic shifts for the Cr(II) complexes are essentially identical in methanol and water, though their line widths differ considerably in some cases. The line-width dependence on temperature of the 4,7-H in (phen)₃CrCl₂ and 4,4′-H in (bipy)₃CrCl₂, both in methanol, is exhibited in Figure 3.

Discussion

As illustrated in Figure 1, the line widths are 20–75 Hz, except for the protons closest to the metal (~750 Hz), and indicate an electronic relaxation time comparable to that of octahedral V(III) or tetrahedral Co(II) complexes, both of which have been extensively investi-
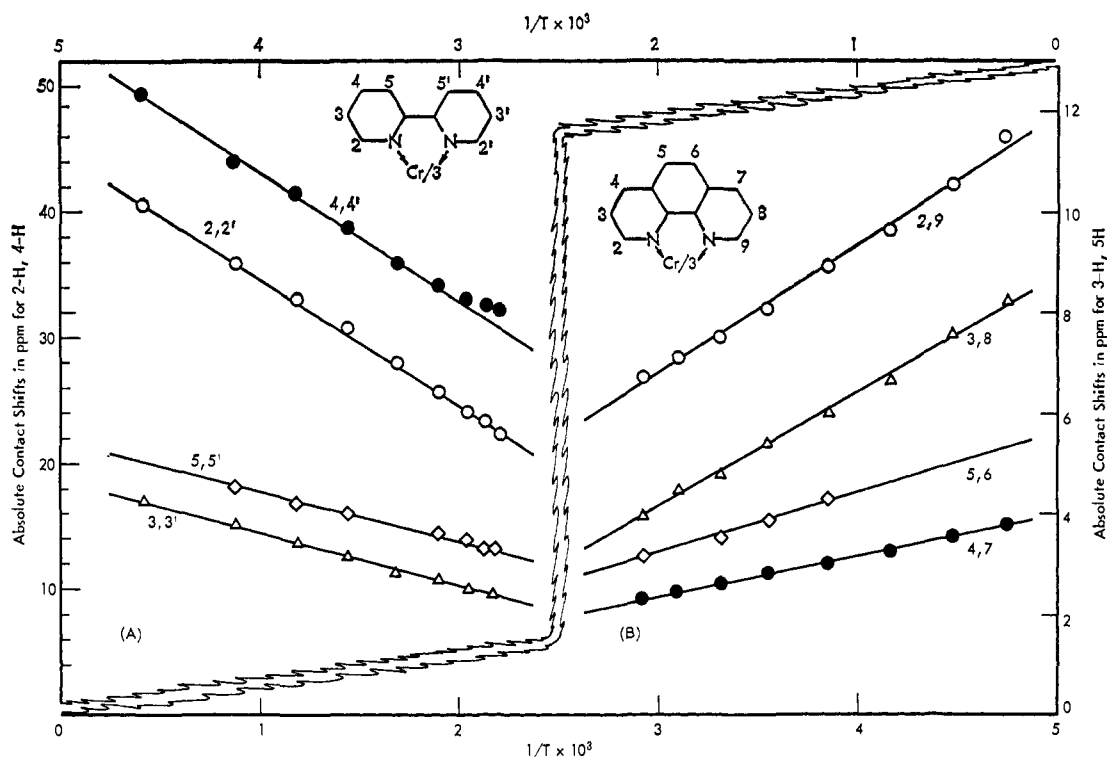
Figure 2. Curie plots for d_4-methanol solutions of (A) (bipy)$_3$CrCl$_2$ and (B) (phen)$_3$CrCl$_2$.

gated by proton nmr.[6b,c,8] Separate resonances for all nonequivalent sets of protons are resolved. Variations of the temperature from −50 to 70° for the chelates in Figure 1 show that the isotropic shifts generally obey the Curie law,[1,2] as shown in Figure 2. The minor deviations are more likely to arise from the referencing to the diamagnetic ligand[25] than from significant magnetic anomalies. The line widths and shifts for the Fe(III) chelates with bipy resemble those of the previously reported phen complexes.[9]

In the presence of free ligand, all Cr(II) complexes exhibited separate peaks for coordinated and free ligand. The temperature dependence of the 4,7-H and 4,4'-H line widths for the complexes in Figure 1 is illustrated in Figure 3. Ligand exchange is sufficiently slow so as to contribute[26] only negligibly to the observed line widths at 33°. Ligand exchange appears to occur at a faster rate at a given temperature for the bipy than for the phen complexes, and may be related to the greater rigidity of the phen ligand. If oxygen is admitted to a sample, the peaks increase in width until they become too broad to detect, but their positions remain as in the oxygen-free sample. Thus the rate of electron exchange between the Cr(II) species and the oxidized form, presumably the analogous Cr(III) complex, must be fairly slow. This is in contrast to the rapid electron transfer between the phen chelates of Fe(II) and Fe(III).[9]

For the phen chelates of Cr(II), all proton signals could be unambiguously assigned by methyl substitution at three of the four nonequivalent positions. For the bipy complexes of Cr(II) in methanol, as for the Fe(III) chelates in D$_2$O, it was feasible to introduce sub-
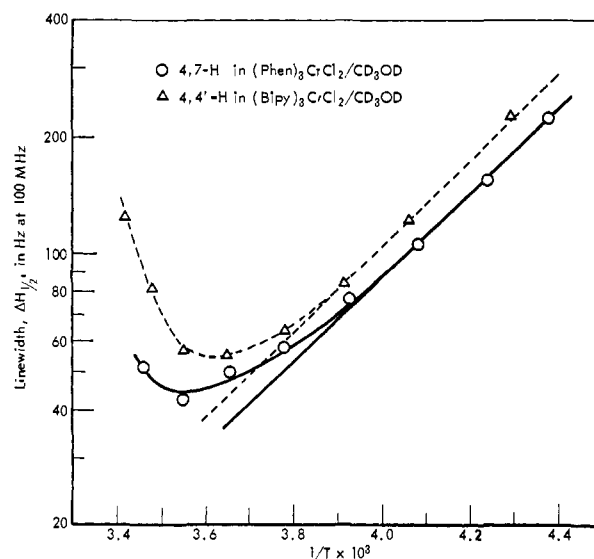
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Figure 3. Plot of line width vs. T^{-1} for 4,7-H in (phen)$_3$CrCl$_2$ and 4,4'-H in (bipy)$_3$CrCl$_2$ in d_4-methanol.

stituents only at the 4,4' positions. However, a convincing assignment for the remaining peaks could be effected from an analysis of the line widths and by comparison with the phen chelates. As is evident in Figure 1 and Tables II and III, the farthest upfield peak shows essentially the same shift for all complexes of a given metal ion and is always considerably broader than any other signal. Since the electron–proton dipolar relaxation mechanism often dominates the proton line widths in paramagnetic complexes, the relative line widths for nonequivalent protons will be largely determined by their relative values of R^{-6}, where R is the proton–metal distance.[27] Using the reported ligand

Table IV. Calculated Relative Line Widths and Dipolar Shifts[a]

Position	$\left(\dfrac{3\cos^2\chi - 1}{R^3}\right)$[b]	Rel[c] dipolar shift	Rel[d] R^{-6}
2-H	+0.02422	+1.000	25.9
3-H	+0.00336	+0.139	1.79
4-H	−0.00167	−0.069	1.00
5-H (phen)	−0.00395	−0.163	0.75
5-H (bipy)	−0.00838	−0.345	3.00
3-CH$_3$	+0.00278	+0.125	0.73
4-CH$_3$	−0.00114	−0.047	0.42
5-CH$_3$ (phen)	−0.00247	−0.102	0.34

[a] All values are valid for both phen and bipy, except the 5-H and 5-CH$_3$, which are so designated. Bond distances and angles taken from ref 28, and the M–N distance was estimated at 2.05 Å. [b] In cm^{-3} × 10^{24}. [c] The largest dipolar shift, 2-H, is normalized to 1.00. [d] The 4-H line width is normalized to 1.00.

distances[28] and estimating N–M = 2.05 Å,[29] we obtain the relative line widths (R^{-6}) listed in Table IV.

For the methanol solution of Cr(II), the calculated relative line widths in Table IV completely corroborate the assignments for phen reached on the basis of substitution, confirming the validity of the approach. For bipy complexes of both Cr(II) and Fe(III), the assignments from relative R^{-6} values are consistent with the 4,4' substitution and with the assignments for phen for protons in analogous positions on the heterocyclic ring. Thus the 2-H, 3-H, and 4-H shifts in phen and bipy complexes are very similar, as anticipated.

It should be stressed here that the assignments of peaks for either phen or bipy complexes of Cr(II) on the basis of line widths are valid only for the methanol solutions; the assignments can be extended to the D$_2$O solutions only because the isotropic shifts, though not the line widths, are essentially the same in the two solvents. For the D$_2$O solutions, the line widths, particularly for substituted phen complexes, appear to be dominated by a novel contact exchange mechanism, which will be discussed in more detail elsewhere.[30]

For the bipy chelates of Cr(II), the data in Table II show that the isotropic shifts are independent of the counterions; for the 4,4'-bipy, the iodide does differ somewhat from the other halides, though this is probably due to some decomposition, since its line widths are very broad and increase with time. For phen, the Cl and Br complexes have identical spectra, while the I complex is not sufficiently soluble. This is in contrast to the difference in magnetic moments reported for the solid complexes, where small differences with halogen were noted.[16] The solution magnetic moments indicate that they are all equal within the sizable limits of error, and they appear to discount moments as large as 3.3 BM, as observed in the solid. The solid-state magnetic moment differences may well arise from differences in molecular distortion resulting from crystal packing, as is also evidenced by the dependence of the observed moment in the solid on the extent of hydration of the crystal.[16,18]

Since the data in Tables II and III confirm that there exist sizable interactions between protons and the

metal electrons, it is instructive to consider the possible contributing mechanisms.[1]

Analysis of the Cr(II) Complex Shifts

π-Spin Delocalization. Since the ability of phen and bipy to stabilize low oxidation states has been attributed[17,21,22] to their possession of low-lying vacant π orbitals, it might be expected that the observed shifts would be indicative of extensive π delocalization. The t_{2g} π-bonding orbitals split into a_1^{π} and e^{π} under a trigonal distortion ($O_h \rightarrow D_3$), while $e_g^{\sigma}(O_h) \rightarrow e^{\sigma}(D_3)$. The π MO's for a symmetric bidentate ligand can be classified[31] either (+) or (−), depending on whether they remain unchanged or reverse sign upon rotation about their C_2 axis. The (−) MO's can interact only with the metal e orbitals, while the (+) MO's can interact with both a_1 and e orbitals. Since in a high-spin t_{2g}^4 subshell at least one unpaired spin must reside in the e^{π} d orbitals, π spin delocalization into any ligand orbital is symmetry allowed. However, since every t_{2g} orbital is at least singly occupied, π delocalization must result in net positive (α) spin density on the ligand, since the metal possesses only α spin to donate to vacant ligand orbitals. Alternatively, the π symmetry metal d orbitals can accept only negative (β) spin density from filled ligand MO's, again leaving a net α imbalance on the ligand. This is to be contrasted[8] with V(III), where the filled ligand orbitals could donate either α or β spin density to the metal π-bonding orbitals.

For both phen and bipy, the 4-H and 4-CH$_3$ shifts have approximately equal magnitudes and opposite signs, which can be taken as evidence that the π mechanism dominates at those positions.[32] For phen, a similar sign reversal for 3-H and 3-CH$_3$ must also reflect π spin density. Though methyl substituents at the 3 position in bipy were not available, the similarity of the 3,3'-H bipy shift and the 3,8-H phen shift suggests that both arise from the same mechanism. For the 5 position in phen, however, both proton and methyl group display positive shifts, indicating that at least one mechanism in addition to π delocalization must be operative. Unfortunately, methyl substitution at the 2 position inhibits formation of these complexes.

In order to assess whether π delocalization alone can account for the observed shifts, the Huckel π eigenvectors were calculated, correcting for correlation by the method of McLachlan,[33,34] and using the parameters $\alpha_N = \alpha_C + h\beta_{CC}$, and $\beta_{CN} = \beta_{CC}$, where h was varied from 0.0 (biphenyl or phenanthrene) to 1.0. The calculated spin densities for $h = 0.5$ for both phen and bipy are given in Table V. In addition to the highest bonding ligand orbitals, ψ_7 and ϕ_6 for phen and bipy, respectively, the two lowest vacant antibonding orbitals, ψ_8, ψ_9 and ϕ_7, ϕ_8, are also considered. For bipy, ϕ_8 is significantly higher in energy than ϕ_7, and is therefore unlikely to interact with d orbitals appreciably. However, for phen, ψ_8 and ψ_9 are much closer in energy, so that ψ_9 could conceivably accept some metal spin.

(27) N. Bloembergen and L. O. Morgan, *J. Chem. Phys.*, **34**, 842 (1961).

(28) L. L. Merritt and E. D. Schroeder, *Acta Cryst.*, **9**, 801 (1956).

(29) S. Herzog and R. Taube, *Z. Chem.*, **2**, 208 (1962).

(30) G. N. La Mar and G. R. Van Hecke, *J. Chem. Phys.*, **50**, 537 (1969).

(31) L. E. Orgel, *J. Chem. Soc.*, 3683 (1961).

(32) In the case of π spin density, eq 2 is applicable to both protons and methyl groups. The reversal of signs arises from the fact that Q_{CH} is negative and Q_{CCH_3} is positive.

(33) A. D. McLachlan, *Mol. Phys.*, **3**, 203 (1960).

(34) The method of ref 33 has been extended to apply to heteroatomic systems, where two-center repulsion integrals or atom-bond polarizabilities must also be introduced: G. N. La Mar and J. H. Schachtschneider, submitted for publication.

Table V. Calculated Spin Densities for phen and bipy[a]

phen position	ψ₇⁻ (−0.6594β)[b] HMO[c]	M-HMO	ψ₈⁺ (+0.5528β) HMO	M-HMO	ψ₉⁻ (+0.6180β) HMO	M-HMO
1,10	+0.054	+0.030	+0.050	+0.031	+0.157	+0.328
2,9	+0.075	+0.128	+0.123	+0.164	+0.015	−0.126
3,8	+0.003	−0.211	+0.001	−0.053	+0.103	+0.218
4,7	+0.094	+0.190	+0.135	+0.188	+0.103	+0.075
5,6	+0.197	+0.391	+0.149	+0.178	+0.006	−0.148

bipy	φ₆⁺ (−0.7645β)		φ₇⁻ (+0.5858β)		φ₈⁺ (+0.8842β)	
1,1′	+0.037	−0.150	+0.139	+0.195	+0.106	+0.170
2,2′	+0.071	+0.099	+0.002	−0.052	+0.141	+0.276
3,3′	+0.156	+0.312	+0.123	+0.153	+0.000	−0.159
4,4′	+0.001	−0.193	+0.060	+0.043	+0.136	+0.235
5,5′	+0.135	+0.257	+0.043	+0.018	+0.111	+0.095

[a] Parameters used are: $\alpha_C = \alpha$, $\alpha_N = \alpha + 0.5\beta$, $\beta_{CC} = \beta_{CN} = \beta$, with the correlation parameter $\lambda_C = 1.2$, $\lambda_N = 1.25$. [b] Orbitals are numbered in increasing energy, where the sign indicates whether the orbital is even (+) or odd (−) upon rotation about its C_2 axis. The orbital energy is given in parentheses. [c] HMO and M-HMO designate the Hückel and McLachlan-Hückel spin densities, respectively.

The most apparent feature of the spin densities for phen and bipy in Table V is their inability to account for the sizable positive 2-H shifts. Although the 2,9-H and 2,2′-H shifts are the largest by a factor of ~3, the calculated spin densities are the smallest positive or even negative values at these positions for both the highest bonding and lowest antibonding orbitals. Only for ϕ_8 on bipy is a sizable 2,2′-H shift predicted, and even in this case it should be comparable in magnitude to the 4,4′-H shift. However, it is unlikely that this high-lying MO can interact with metal d orbitals to any extent. Moreover, since the observed shift patterns for phen and bipy complexes are nearly identical, it is most likely that similar interactions dominate the shifts in both complexes, such that neither ϕ_8 or ψ_9 are expected to contribute to the shifts significantly. Thus π delocalization into either the highest bonding or lowest antibonding MO is incapable of accounting for the observed 2-H shifts. In addition, no single ligand MO considered can predict the observed negative 3-H and 4-H shifts. This last discrepancy may well arise from a simultaneous π delocalization into more than one ligand MO, or from some exchange polarization effects within the π system. Such a combination of mechanisms, however, does not appear to be able to account for the 2-H shifts.

For bipy, the reliability of the MO calculations is confirmed, at least for the LAO, since the spin densities for ϕ_7 agree well with the relative coupling constants reported[35] for the anionic free radical, which are 0.54/4.58/1.05/1.20 G for 2,2′-H/3,3′-H/4,4′-H/5,5′-H, respectively. Very good agreement in both magnitude and sign between the calculated spin densities and hyperfine constants derived from the nmr spectrum of the closely related biphenyl radical[36] ($h = 0.0$) is also noted. Esr data for phenanthroline have not been reported, though the calculated spin densities for phenanthrene ($h = 0.0$) agree well with the coupling constants for that radical.[37]

Thus the π spin delocalization, though definitely operative, cannot alone account for the observed isotropic shifts in these complexes.

The Dipolar Interaction. Inasmuch as these complexes should possess a $^3T_1$ ground state if they retain

a ligand field of octahedral symmetry, magnetic aniosotropy and resultant dipolar shifts might be anticipated.[2,4,6d,e] As is evident from eq 3, the relative dipolar shifts for nonequivalent sets of protons in a given complex are determined solely by the geometry of the complex, and are proportional to their geometric factor, $(3 \cos^2 \chi - 1)/R^3$. For these D_3 chelates, these geometric factors can be readily estimated[28,29] with the results listed in Table IV, where the dipolar shift for the 2-H is normalized to 1.00. An analysis of the calculated dipolar shifts in Table IV and the observed shift patterns leads us to exclude the dipolar interaction as a significant factor in the observed isotropic shifts for the following reasons.

(a) Table IV predicts dipolar shifts of opposite direction for the 2 and 5 positions, though both protons display upfield shifts. If the 5-H and 5-CH₃ shifts reflect a dipolar contribution, then the *contact* contribution to the 2-H shift must be larger than the observed shift. Alternatively, if the 2-H shift arises from magnetic anisotropy, then both the 5-H and 5-CH₃ contact shifts, which could not be rationalized by π delocalization, must be more positive than the observed shifts. Thus, though a small dipolar contribution to the observed shifts *may* be present, it cannot consistently account for the 2-H, 5-H, and 5-CH₃ shifts.

(b) The dipolar interaction predicts shifts with the same sign and nearly the same magnitude for protons and methyl groups at both the 3 and 4 positions. It is thus doubtful that the dipolar contributions to the observed shifts can be significant since for both positions the proton and methyl groups experience shifts of comparable magnitude but opposite signs, as predicted for π spin density.

(c) The essentially "spin-only" magnetic moments[16,18] of 2.8 BM are consistent[38] with $g_{av} = 2$. The g values required[39] by eq 3, if we assume that the ~30-ppm 2-H shift arises from magnetic anisotropy, are $g_{\parallel} = 1.3$ and $g_{\perp} = 2.4$. Inasmuch as the observed π shifts are rather small, it must be concluded that a strong trigonal distortion is most likely to give rise to the "spin-only" magnetic moments.[17,18] However, for

(35) J. C. Henning, *J. Chem. Phys.*, **44**, 2139 (1966).
(36) G. W. Canters, private communication.
(37) E. de Boer and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 4549 (1958); J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 280 (1963).

(38) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 142.
(39) From the observed 2,9-H line width, we calculate (ref 12, 27) $T_{1e} \sim 2 \times 10^{-12}$ and $\tau \sim 10^{-10}$ sec. Since the dipolar shift can be shown to be small, $1/\tau \gg |g_{\parallel} - g_{\perp}| \beta H_0 \hbar^{-1}$, and $\tau \gg T_{1e}$, such that $F(g) = (3g_{\parallel}^2 + g_{\parallel}g_{\perp} - 4g_{\perp}^2)$ in eq 3.

trigonally distorted T ground states,[40] where the separation between split e and a_1 components is large compared to the spin–orbit coupling constant, as is likely the case here, $g_{\parallel}$ is expected to be 2.0. Thus with a g_{av} of ~2, we must also have $g_{\perp} \sim 2$, and hence the dipolar shift (eq 3) reduces to near zero.

(d) The formation of a tris chelate from the unsymmetrically substituted 5-phen leads to both *cis* and *trans* isomers[8] in the statistical ratio 1:3. In the former isomer, all three ligands are equivalent, while in the latter isomer, each of the three ligands on a metal is different. As a result, the statistical mixture is expected to exhibit a proton spectrum with four equally intense peaks per nonequivalent ligand position. As indicated in Table II, eight resonances are observed for the combined 4,7-H protons, spread over ~6.7 ppm, while the 2,9-H resonance appears once with intensity eight times that of one of the 4,7-H peaks, and at essentially the same position as found in the symetrically substituted chelates. Since the *trans* isomer possesses no symmetry, it could be expected that if significant magnetic anisotropy were present in the symmetric chelates, then its magnitude would be increased, or at least dramatically altered, upon lowering the symmetry. Since the 2-H has by far the largest geometric factor, in rhombic[6b] as well as in axial[2,4,6c] symmetry, due to its proximity to the metal, a dipolar mechanism would predict a large shift difference between the *cis* and *trans* isomers at 2,9-H. However, no observable difference in shifts is noted, suggesting that the dipolar shift is negligible compared to the contact shift at those positions, and hence is negligible at the remaining ligand positions. On the other hand, the dramatic effect of unsymmetrical methyl substitution on the observed 4,7-H shifts, which should be least affected by the dipolar mechanism, strongly suggests changes in spin delocalization rather than anisotropy as the origin of these shift alterations.

The great similarity of the phen and bipy shift patterns, particularly for 2,9-H and 2,2'-H, implies that the dipolar mechanism is probably also negligible in the latter chelates. We therefore conclude that the observed shifts arise primarily from a contact interaction.

σ **Spin Delocalization.** Since low-spin d^4 complexes in an octahedral field possess no σ bonding e electrons,[41] it could be considered unlikely that σ spin delocalization can even occur. However, as was first pointed out by Orgel[42] for d^3 Cr(III) systems, it would be energetically profitable for the paired bonding electrons donated to the empty e^σ d orbitals to unpair slightly. This would place a net amount of positive (α) spin density in the metal e^σ orbitals, whose exchange interaction is more favorable with the unpaired (α) e^π, a_1^π, electrons, and thereby induce a net negative (β) spin density in the ligand σ system. This type of exchange polarization is analogous to that invoked to explain proton hyperfine splittings in aromatic free radicals.[3] Though it was first considered that this exchange polarization

was operative in the metal bis-cyclopentadienes,[43] more recent nmr work[11,44] has showed that the variation in the magnitude and direction of the isotropic shift with metal for these sandwich complexes instead arises from a variation in the relative extent of spin delocalization into the ligand carbon in-plane and out-of-plane p orbitals. Thus this effect has no reported experimental verification to date.

The σ delocalization of this negative (β) spin density on the ligand will produce contact shifts with all the characteristics of direct σ delocalization[5f,6a,45] previously observed in systems containing unpaired e^σ spins, except that the direction for all the shifts will be reversed. Thus for the phen chelates[20] of Ni(II) where the observed shifts arise primarily from direct σ spin delocalization, the largest downfield shift is observed for 2,9-H (2,2'-H in bipy), in agreement with the sizable *upfield* shifts at this position in the Cr(II) compounds. In addition, the direct σ downfield shifts[20] for both 5,6-H and 5,6-CH$_3$ in the Ni(II) chelates, as well as for 3,8-H, leads us to anticipate similar upfield shifts in the Cr(II) chelates, as observed at least for the 5,6 position.

Since the σ spin delocalization is expected to attenuate[5f,6a,45] by a factor of 3–4 from 2-H to 3-H, it is not surprising that the complementary π delocalization mechanism becomes dominant at the 3 and 4 positions. Some evidence for the presence of a small negative (β) σ spin density at the 3 position can be derived from the relative proton and methyl shifts. For 3,8-H, Q in eq 2 is usually accepted as a constant,[1] -22.5 G, while for the methyl group theory requires Q_{CH_3} to be positive, and values up to $+30$ G have been observed.[1,5a,6a,6b,46] If we make the reasonable assumption that a methyl group has no significant effect on the ligand π orbitals, the observed 3,8-H and 3,8-CH$_3$ shifts yield a $Q_{CH_3} = +60$, nearly twice the magnitude consistent with previous observations.[1] The direct π delocalization yields downfield 3,8-H and upfield 3,8-CH$_3$ shifts; the negative σ delocalization will produce upfield shifts for both 3,8-H and 3,8-CH$_3$. The presence of the latter mechanism thus has the effect of decreasing the dominant 3,8-H π shift and increasing the 3,8-CH$_3$ π shift. Such a combination of π and σ spin density at the 3,8 position would lead to a value of Q_{CH_3} which is larger than that expected for only π spin density.[47] For the 4,7 and 4,4' positions, for which σ spin delocalization should be even smaller than for 3,8-H, the observed proton and methyl shifts yield Q_{CH_3} values of $+13$ to $+15$ G, well within the expected range for only π spin density. Further support for postulating negative σ spin delocalization in the Cr(II) chelates to account for the 2,9-H, 5,6-H, and 5,6-CH$_3$ shifts can be derived from a reinterpretation of the phen complexes of Fe(III).[9]

Analysis of the Fe(III) Complex Shifts. The new data on the bipy complexes are given in Table III, where the previously reported shifts for the phen complexes are also reproduced.[9] As for the Cr(II) chelates, the

(40) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964).

(41) Under D_3 symmetry, the e^π orbitals may mix with the e^σ orbitals, so that there is probably a finite amount of positive unpaired spin density available for direct σ delocalization. However, such an effect is not expected to be very great, and can result in only downfield σ shifts. Such *direct* δ delocalization is therefore judged to be negligible.

(42) L. E. Orgel, *Discussions Faraday Soc.*, **26**, 92 (1958); *J. Chem. Phys.*, **31**, 1617 (1959).

(43) D. A. Levy and L. E. Orgel, *Mol. Phys.*, **3**, 583 (1960).

(44) M. F. Rettig and R. S. Drago, *Chem. Commun.*, 191 (1966).

(45) D. R. Eaton, A. D. Josey, and R. E. Benson, *J. Am. Chem. Soc.*, **89**, 4040 (1967).

(46) S. I. Weissman, T. R. Tuttle, and E. de Boer, *J. Phys. Chem.*, **61**, 28 (1957); I. Bernal, P. H. Rieger, and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 1484 (1962); D. B. Chesnut, *ibid.*, **29**, 43 (1958).

(47) It should be mentioned that the unexpectedly large Q_{CH_3} can be similarly rationalized by positive dipolar shifts at the 3,8 position. However, this is considered unlikely, since such shifts predict sizable downfield 5,6-H and 5,6-CH$_3$ shifts, contrary to observation.

isotropic shift patterns for the phen and bipy complexes resemble each other, indicating that the observed shifts probably arise from similar interactions.[48]

π Spin Delocalization. No consistent interpretation of the reported phen shifts has been attempted, though they were attributed[9] to a π delocalization mechanism on the basis of the fact that low-spin d^5 octahedral metal complexes do not possess any σ bonding electrons. However, inspection of Table III reveals that for none of the phen positions, and only for the 4,4' position in bipy, is there a sign reversal between the proton and methyl shifts, which is characteristic of π spin density.[32] This anomaly was interpreted[9] as arising from the methyl groups inducing a spin density at the aromatic carbon with a sign opposite to that present for a proton. Previous work,[5a,b,g,6b] however, has demonstrated that methyl substitution does not significantly alter the π eigenvectors, so electron–proton interactions other than π delocalization must be operative in the Fe(III) compounds. A comparison of the predicted spin densities in Table V with the shifts in Table III confirms the inability of π delocalization to account for observed shifts for much the same reasons as for the Cr(II) chelates. However, owing to the lack of sign reversal for H and CH_3 shifts at any phen position, it appears that π delocalization plays an even smaller part in determining the isotropic shifts in the Fe(III) than in the Cr(II) chelates.

The Dipolar Interaction. It has already been postulated that the magnetic anisotropy for the ferric chelates can be only minor[9] and should not significantly affect the isotropic shifts, since the reported magnetic moment[49] of 1.79 BM for the phen chelate is consistent[58] with an average g value of ∼2. Further justification for discarding the dipolar mechanism as dominant at any ligand position can be deduced along similar lines as for the Cr(II) chelates.

(a) As for Cr(II) chelates, eq 3 predicts shifts of opposite direction for 2,9-H and 5,6-H or 5,6-CH_3, contrary to observation.

(b) The relative shifts for protons and methyl groups at any position are in total disagreement with the predictions in Table IV.

(c) The maximum anisotropy[50] consistent with $g_{av} = 2$, $g_∥ = 0$, and $g_⊥ = 3$ can only account for a +27-ppm 2-H dipolar shift, though the observed 2-H shift is ∼+50 ppm. An upper limit to a more reasonable anisotropy of $g_∥ - g_⊥ = 0.5$ leads to a dipolar 2-H shift of +5.5 ppm, with the dipolar contribution at the remaining positions ∼1 ppm or less. The isotropic shifts for the Fe(III) chelates are therefore also primarily contact in origin.

σ Spin Delocalization. The observed Fe(III) shift patterns,[9] particularly for the phen compounds, are, however, consistent with negative (β) σ spin delocalization originating in the exchange polarization mechanism.[42] Two characteristics of σ spin delocalization, whether positive (α) or negative (β), are that the contact shifts attenuate rapidly with the number of bonds from the metal, and that replacing a proton by a methyl

(48) The comparison between (phen)₃Fe(ClO₄)₃ and (bipy)₃FeCl₃ appears warranted, in spite of the difference in counterions, since the isotropic shifts for (4,7-phen)₃Fe(ClO₄)₃ and (4,7-phen)₃FeCl₃ were identical.
(49) A. Simon and H. Knauer, *Z. Elektrochem.*, **45**, 678 (1939).
(50) We calculate (ref 39) $T_{1e} \sim 8 \times 10^{-13}$, $\tau \sim 10^{-10}$ sec, such that $F(g) = (3g_∥^2 + g_∥ g_⊥ - 4g_⊥^2)$.

group leads to a sharp shift attenuation *without* change in direction.[5f,6a,45] A predominantly direct σ spin delocalization mechanism has been established for the (phen)₃Ni²⁺ chelates, where only the 4,7 position experiences secondary π spin density. These contact shifts,[20] reproduced in Table VI, attenuate with distance from the nickel, and the expected σ effect for 5,6-H and 5,6-CH_3 shifts is observed. The relative Ni(phen)₃²⁺ shifts, with the 2,9-H shift normalized to −10.00, for 2,9-H/3,8-H/4,7-H/5,6-H are −10.00/ −2.83/−0.61/−1.14, which compare well with the *relative* shifts for the same positions in the Fe(III) chelates, which are +10.00/+1.88/−0.08/+1.17, except that their directions are opposite, as predicted.[42] The attenuation of upfield shifts without sign reversal upon replacing a proton by a methyl group at the 3,8 and 5,6 positions in the Fe(III) chelates further confirms the predominance of the σ spin density. We therefore conclude that the contact shifts for (phen)₃-Fe³⁺ chelates arise primarily from negative σ spin density in the ligand σ system, contrary to previous interpretation.[9] This reinterpretation of the (phen)₃-Fe³⁺ contact shifts therefore represents the first conclusive evidence for the existence of the exchange polarization delocalization mechanism.[42,43]

For the bipy chelates, lack of methyl substituents at any but the 4,4' position, where secondary π spin density is evident, prevents a more detailed analysis of the contact shifts. However, the relative Fe(III) shifts for 2,2'-H/3,3'-H/4,4'-H/5,5'-H, +10.00/+1.48/ +1.32/+0.29, do resemble the patterns for the relative Ni(II) shifts,[19] which are −10.00/−2.62/−0.43/−3.70, except for sign reversal. Agreement between the Ni(II) and Fe(III) bipy shift patterns cannot be expected to be as good as for the phen chelates, since the 4,4'-H and 4,4'-CH_3 shifts for Fe(III) indicated that, unlike for phen, a sizable π spin density is present in the ligand which will modify the shift pattern arising solely from σ spin density. However, the dominant spin-transfer mechanism in both phen and bipy chelates of Fe(III) must involve negative (β) σ delocalization.

Table VI. Isotropic Shifts for L₃Ni^II^X₂[a]

L	X	2,9	3,8	4,7	5,6
phen[b]	Cl	−147.0	−41.65	−8.95	−16.65
4,7-phen[b]	Cl	...	−37.5	[+11.75][c]	−18.36
5,6-phen[b]	Cl	...	...	−8.31	[−0.95]
		2,2'	3,3'	4,4'	5,5'
bipy[d]	Cl	−142.0	−37.1	−6.05	−52.5

[a] Shifts in ppm in D₂O referenced against diamagnetic Fe(II) chelate. [b] Data reproduced from ref 20. [c] Methyl shifts are enclosed in brackets. [d] Data reproduced from ref 19, except for 2,9-H peak.

Comparison of Cr(II) and Fe(III) Shifts. From the magnitudes of the 2,9-H or 2,2'-H σ shifts in Cr(II) and Fe(III) chelates, it appears that the σ delocalization is more extensive in the ferric than the chromous chelates. This can be attributed to the fact that the d orbitals for Fe(III) are lower in energy than for Cr(II), and are therefore more favorably placed for interacting with the relatively low-lying nitrogen lone-pair electrons. The relative σ shifts, however, are not likely to be

proportional only to the extent of σ covalency, since the exchange interaction which places the negative (β) spin density in the ligand σ system probably depends on the number of unpaired t_{2g} electrons.[42] Since Cr(II) has one more unpaired spin than Fe(III), it might be expected that a slightly greater amount of unpairing of the e^{σ} bonding electrons takes place in the former complexes, such that the observed difference in 2-H σ shifts would underestimate the difference in σ covalency.

For the ferric phen chelates, there is only indirect evidence for some π spin density at the 4,7 position, while for Cr(II), the π spin density at the 4,7 position is quite marked, and even dominates the 3,8 position. The apparent increase in π delocalization in the Cr(II) over the Fe(III) chelates may again be related to the higher d-orbital energies for the former ion, which would favor interaction with the vacant antibonding π orbitals. These conclusions are consistent with those forwarded for the tris acetylacetonates of first-row transition metals.[7] At the present, it is not possible to compare the σ covalencies of the Cr(II) or Fe(III) chelates with those of Ni(II), since the Ni(II) shifts arise from direct spin delocalization, while Cr and Fe must rely on the exchange polarization mechanism.

Negative (β) σ spin transfer to a ligand is not restricted only to the Fe and Cr complexes of interest here, but appears to be a general property of octahedral metal complexes with vacant e^{σ} orbitals and partially filled t_{2g} subshells. Thus the very large *positive* shifts observed for the azomethine protons in tris salicylaldimines[8b] and pyrrole-2-aldimines[8c] of V(III), as well as the α-H shifts in V(III) tris β-ketoimines,[8b] are comparable in magnitude but *opposite* in direction to the shifts for the same protons in the analogous bis Ni(II) chelates,[5b,d,e] where their origin was definitely attributable to direct σ spin delocalization. Since these sizable upfield shifts for the d^2 V(III) chelates are inconsistent with either π spin density or dipolar shifts,[8] they may also be associated with the σ delocalization of negative (β) σ spin *via* the exchange polarization mechanism.[42]

For the bipy chelates of Cr(II), though both π and σ mechanisms are operative, it is possible to obtain an estimate to the extent of π spin delocalization by comparing the hyperfine coupling constants for the free radical[35] with the coupling constants obtained from eq 1 for the essentially completely π-dominated 4,4'-H shifts. Such a comparison leads to $\sim$0.04 spin per ligand, indicating that the unpaired spins are primarily in antibonding d orbitals. The reported[17] orbital reduction factor of 0.6, necessary to account for the magnetic moments by delocalization of magnetic electrons, indicates[51] transfer of $\sim$0.3 spin to each ligand, if a reasonable Cr–N overlap of 0.1 is assumed.[18] The relatively minor amount of π spin delocalization in the Cr(II) chelates is also evidenced by the fact that the 4,7-H and 4,7-CH$_3$ π spin densities are of essentially the same magnitude in the Cr(II) and Ni(II) phen chelates,[20] in spite of the fact that Ni(II) unpaired electrons are capable of π bonding only by virtue of the trigonal distortion. The present study therefore strongly favors the sizable trigonal distortion hypothesis[18] over extensive π delocalization of d electrons[17] as the most plausible explanation for the lack of a significant orbital contribution to the observed magnetic moments.[52] In addition, it is suggested that phen and bipy are relatively inefficient[17,21,22] π acceptors in these complexes, such that the stability[17] of the Cr(II) oxidation state to oxidation cannot be attributed primarily to π bonding. A current investigation of spin delocalization in the isoelectronic d^4 (bipy)$_3$V^{I}ClO$_4$ chelates may shed further light on the bonding in these chelates.

(51) Reference 38, p 166.
(52) Since none of the three considered ligand orbitals leads to negative π spin density at the 4,7 position in phen complexes of Cr(II), it appears as if some indirect polarization mechanism may also be operative in the π system.