Proton Nuclear Magnetic Resonance Studies of the Electronic Structure of Outer-Sphere Reducing Agents of Chromium(II). I. Metal–Ligand Covalency in Mixed α-Diimine Chelates

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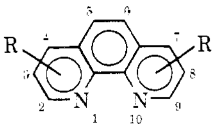
Abstract: The proton nmr spectra of the outer-sphere reducing agents (α-diimine)$_3$Cr^{2+} have been investigated in order to elucidate their electronic structure in relation to the mechanism of electron transfer in redox reactions. The spectra in d_4-methanol solution of a large series of mixed-ligand chelates, ML$_2$L′, MLL′$_2$ of chromous chloride with symmetrically substituted *o*-phenanthrolines and α,α'-bipyridines, have been recorded and assigned. These paramagnetic mixed-ligand chelates exhibit isotropic shifts which differ significantly from those of the related tris chelates, ML$_3$, ML′$_3$, particularly at the 4,7 position in phenanthroline and the 4,4′ position in bipyridine, where large increases in magnitudes and some changes in direction are observed. Analysis of the magnetic origin of these shifts reveals that they are contact shifts resulting from at least two competing spin delocalization mechanisms into the π system, one of which places positive, while the other places negative spin density on $C_{4,7}$ or $C_{4,4'}$. The relatively small contact shifts in the parent tris chelates, ML$_3$, ML′$_3$, are concluded to result from the near cancellation of very large positive and negative contribution, with the shifts in the ML$_2$L′, MLL′$_2$ chelates increasing due to an imbalance of the two mechanisms in the reduced symmetry. This indicates that the ligand hyperfine coupling constant or net spin density need not be a direct index of the metal–ligand π covalency. The relative tendencies of ligands L′ in inducing the dominance of either one or the other spin delocalization mechanism in ligand L in ML$_2$L′ and MLL′$_2$ lead us to postulate a "spectrochemical" ordering for the phenanthroline ligands which correctly predicts the shift changes for both L and L′ on going from ML$_3$, ML′$_3$ to ML$_2$L′, MLL′$_2$. The proton nmr spectra of the same mixed ligand chelates in aqueous solution reveal that for the 4,7-methyl substituted ligands there exists a strong solvent interaction specifically at the 4,7 position, causing the ligand to change its position in our "spectrochemical" order in a consistent manner.

The tris chelates of chromium(II) with *o*-phenanthrolines (I) and α,α'-bipyridines (II) possess a number of unusual chemical, electronic, and magnetic characteristics which have been the subject of renewed interest in the recent literature. Although the facility of these complexes in acting as outer-sphere reducing agents in inorganic redox reactions has been recognized[2] for some time, only recently has evidence been presented[3] which indicates that the outer-sphere reduction of (phen)$_3$Co^{3+} by (phen)$_3$Cr^{2+} proceeds stereospecifically. Thus the use of an optically active oxidant and racemic (phen)$_3$Cr^{2+} yielded[3] optically active (phen)$_3$Cr^{3+} as the main product. Inasmuch as the facile electron transfer properties of these low-valent chelates are generally attributed[4] to extensive M → L π bonding (π back-bonding), a nonspherically symmetric spatial distribution[3] for the "reducing" electron was suggested to account for the asymmetric induction.



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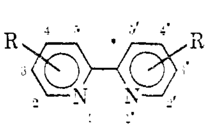

II

The two subject ligands, I and II, are considered[4] good π acceptors due to the fact that they stabilize low valent states for a wide variety of first-row transition metal ions.[5] In particular, the observed[6] spin-only magnetic moments for the tris chelates of Cr(II), which possess a ^{3}T ground state in an octahedral field, have been interpreted[6a] as arising from extensive π delocalization of the magnetic electrons. More recent analyses, however, indicate[6b] that these moments can also be rationalized by a strong trigonal distortion with only modest delocalization of spin.

The general invariance of the Cr–N vibrational frequencies in the series of chelates (bipy)$_3$Cr^{n+}, with n = 3, 2, 1, and 0, has also been interpreted[7] in terms of increasing M → L π bonding to compensate for the decreasing L → M σ donation as the oxidation state is lowered. To contrast the general consensus of these studies in invoking significant π bonding, an analysis[8] of the optical spectra for the same series (bipy)$_3$Cr^{n+}, n = 3, 2, 1, and 0, lead to the conclusion that Cr(II) is a valid oxidation state, with relatively insignificant M → L π bonding. However, this latter analysis[8] was based on the assumption of a strictly octahedral chromophore, which does not appear totally consistent with either the most recent susceptibility data[6b] or the present, as well as earlier,[9] proton nmr data on these systems.

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The appearance of ligand nuclear hyperfine structure in the esr spectrum[10a] or the observation of large ligand contact shifts in the nmr spectrum[10b] of a paramagnetic transition metal complex is generally considered to be direct evidence of metal–ligand covalency involving the spin-containing metal d orbitals. On the other hand, the absence of ligand hyperfine interactions for other than experimental reasons, such as low resolution, is usually taken as evidence for the lack of significant metal–ligand covalency. Thus in complexes of a reduced metal ion such as Cr(II) with ligands which are considered good π acceptors, phen or bipy, it may be reasonable to expect that if some of the metal t_{2g}^{π} electrons are unpaired in the octahedral complex, they will be partially delocalized by such π bonding, and the pattern and magnitudes of the resultant contact[10b] shifts should yield the nature of the ligand π molecular orbital (MO) which mixes with the d orbitals and the extent of the covalency. Such a detailed mapping of the unpaired "reducing" electron may be expected to shed light on the origin of the stereospecificity[3] in the outer-sphere electron transfer.

In an attempt to characterize the π covalency in these species, we had earlier investigated[9] the proton nmr spectra of a series of tris Cr(II) chelates with symmetrically substituted phen and bipy ligands. Although the paramagnetic shifts were demonstrated[9] to be primarily π contact in origin, at least for the 3,4,7,8 position in phen and the 4,4′ position in bipy, the shifts were found to be unexpectedly small, with magnitudes comparable to those reported[11,12] for analogous chelates with Co(II) and Ni(II), for which π bonding is expected to be much less important. In addition, the hyperfine coupling constants for the various nonequivalent ligand protons were of comparable magnitudes,[9] so that the delocalized spin density appeared to be more or less spherically distributed over the complex.

However, upon extending those studies to tris chelated with *unsymmetrically* substituted phen ligands, it was observed[12,13] that the *contact* shifts at the 4 and 7 positions in the trans isomer became considerably larger than in the complex with the analogous symmetrically substituted ligand, and in some cases even changed sign. This led us to suggest[12] that probably two or more π-delocalization mechanism were simultaneously operative, with the two mechanisms cancelling spin density in the trigonal chelates. Similar conclusions are suggested by the analysis of the temperature dependence of the contact shifts for the mixed-ligand chelates of 4,7-dimethylphenanthroline (4,7-$\mathrm{Me_2}$phen) and 4,4′-dimethylbipyridine (4,4′-$\mathrm{Me_2}$bipy).[14]

In view of the evidence that the small shifts in the trigonal chelates may result from cancellation of competing π-bonding mechanisms[12] and that lowering the symmetry may permit a characterization[13,14] of the component mechanisms, we have extended our investigation of the contact shifts in these complexes in order to shed some light on the metal–ligand bonding responsible for some of the novel properties of this class of compounds. We wish to present here a systematic nmr investigation of a large series of mixed ligand chelates, $\mathrm{MLL'_2}$, $\mathrm{ML_2L'}$, where L, L′ are different, symmetrically-substituted phen or bipy ligands. In part I of this study, we will analyze the relative abilities of a variety of ligands L′ to induce changes in the contact shifts of a fixed ligand L, as referenced to the parent tris chelate, $\mathrm{ML_3}$, and show that these large shift changes arise from changes in the relative contributions of two competing π-delocalized mechanisms, each of which must involve considerable metal–ligand π covalency. The relative ability of a ligand L′ in inducing the dominance of one or the other delocalization mechanism in the ligand L leads us to postulate a "spectrochemical" ordering for the ligands. In part II, we will consider[15] the temperature dependence of the observed shifts as it relates to the orbital ground state of a given mixed ligand chelate and our "spectrochemical" series, and in part III we will attempt to interpret[16] this "spectrochemical" series in terms of the postulated electronic structure of these complexes.

Experimental Section

All complexes used in this investigation have been previously characterized.[5,6,9,17] The mixed ligand chelates were not isolated due to their lability, being prepared *in situ* by mixing solutions containing two different chelates, $\mathrm{ML_3}$ and $\mathrm{ML'_3}$ according to the reaction

$$\mathrm{ML_3 + ML'_3 \rightleftharpoons ML_2L' + MLL'_2} \qquad (1)$$

as done previously.[14] The mixed ligand species could be detected by their proton nmr signals, and assigned by varying the relative amounts of $\mathrm{ML_3}$ and $\mathrm{ML'_3}$ in solution. All handling of the complexes and sample preparation was carried out under nitrogen in a Vacuum Atmospheres Corporation Dri-Lab to prevent any oxidation. Solutions of the parent tris chelates with the ligands phen, bipy, 5,6-$\mathrm{Me_2}$phen, 4,7-$\mathrm{Me_2}$phen, 4,4′-$\mathrm{Me_2}$bipy, 3,5,6,8-$\mathrm{Me_4}$phen, and 3,4,7,8-$\mathrm{Me_4}$phen, were prepared in d_4-methanol (Diaprep, Inc.), at concentrations approximately 0.1 molar. The mixed ligand chelates were prepared by mixing the two appropriate stock solutions in the volume ratios 2:1, 1:1, and 1:2, which were then sealed under nitrogen in nmr tubes.

Stock solutions (~0.08 *M*) of the tris chelates of 4,7-$\mathrm{Me_2}$phen, phen, 3,4,7,8-$\mathrm{Me_4}$phen, bipy and 4,4′-$\mathrm{Me_2}$bipy were also prepared in $\mathrm{D_2O}$, (Bio-Rad Laboratories), and similar 2:1, 1:1, and 1:2 mixtures were sealed under $\mathrm{N_2}$. TMS was used as marker for the methanol solutions. However, the sodium 3-(trimethylsilyl)-1-(propanesulfonate) marker was found unsatisfactory for the aqueous solutions, since it obscured too many peaks of interest; in a few cases, it appeared that the marker may have decomposed since its signal diminished with time. Hence 0.1% methanol was added, and its methyl peak used as reference, which was later calibrated to TMS in the absence of the metal chelate. The position of the methyl peak of the added methanol with respect to the unstable ionic marker was found to be the same in the presence and absence of the metal chelates.

The proton nmr spectra were recorded on a Varian HR-100 spectrometer, using the usual audio sideband technique for calibrating the shifts. Spectra were recorded at a number of temperatures for the purpose of optimizing resolution. Temperature control was effected by a Varian V-4343 Temperature Control Unit. The isotropic (contact) shifts were reported in ppm at 100 MHz,

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(17) The C, H analyses of some of the complexes previously analyzed but not reported (ref 8) are (3,5,6,8-$\mathrm{Me_4}$phen)$_3$$\mathrm{CrCl_2 \cdot 2H_2O}$, C, 66.1, H; 5.9 (calcd) and C, 66.2, H, 5.9 (found); (3,4,7,8-$\mathrm{Me_4}$phen)$_3$-$\mathrm{CrCl_2 \cdot H_2O}$, C, 67.4, H, 5.85 (calcd) and C, 67.4, H, 5.9 (found); (4,7-$\mathrm{Et_2}$phen)$_3$$\mathrm{CrCl_2 \cdot 2H_2O}$, C, 66.5, H, 6.0 (calcd) and found, C, 66.9; H, 5.9.

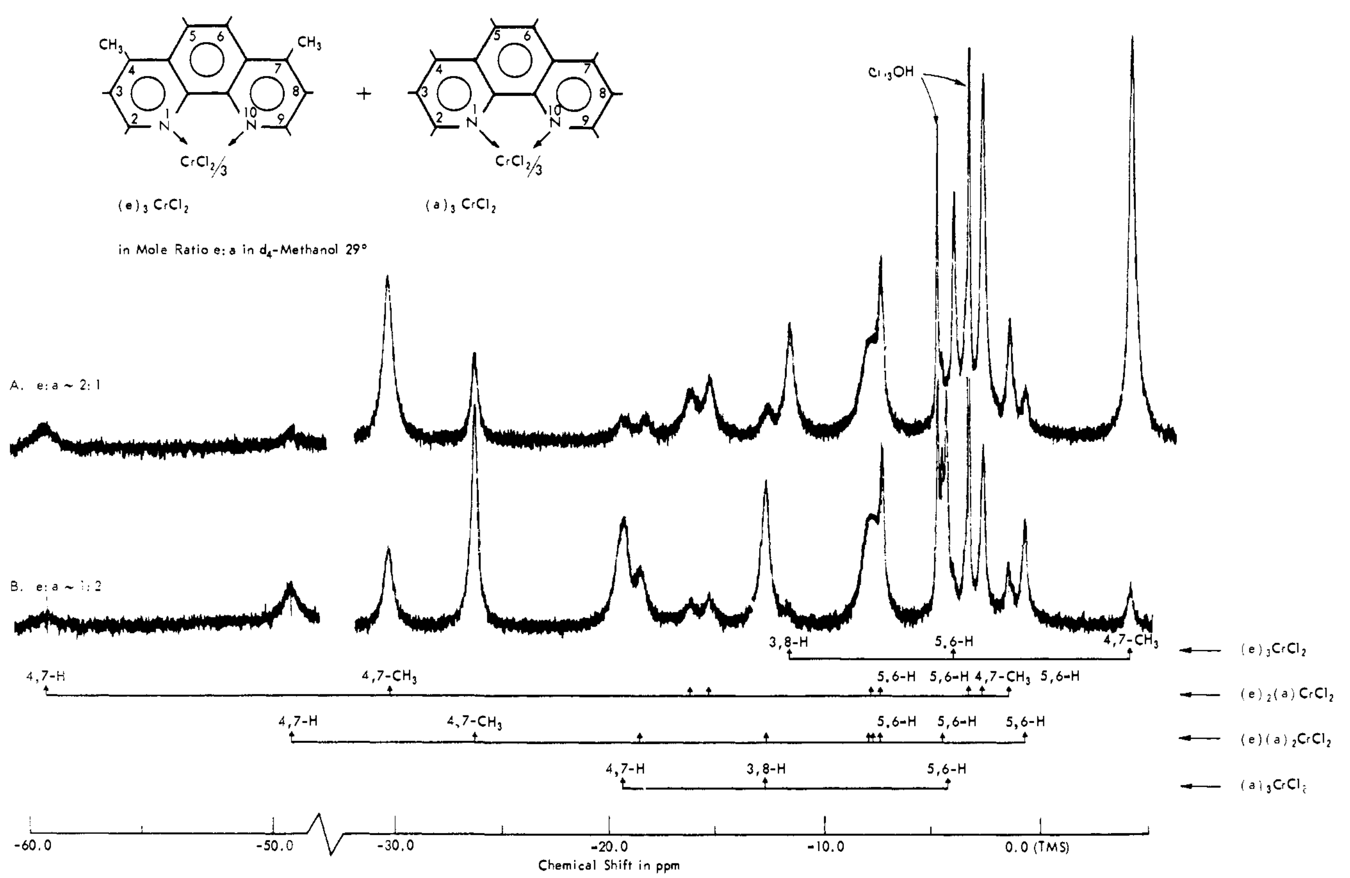

Figure 1. Proton nmr trace of mixed ligand chelates of (4,7-$Me_2phen)_3CrCl_2$ and $(phen)_3CrCl_2$.

and for a given ligand L are referenced against the analogous tris chelate of Fe(II), L_3Fe^{2+}.

Results and Discussion

The proton nmr spectra of 3 of the 20 different pairs of mixed ligand chelates (hereafter abbreviated to m.l. chelates) are illustrated[18] in Figures 1–3. It is immediately obvious from inspection of these spectra that, although the parent tris chelates (hereafter abbreviated to p.t. chelates) displayed shifts for any one ligand position which were essentially independent of the presence of substituents at any other ligand position, these m.l. chelates exhibit shifts which are very different from either of the p.t. chelates, and are extremely sensitive to the nature of the substitution on both ligands. Thus, while the range of 4,7-H (4,7-CH_3) shifts in the p.t. chelates covered only ~3 ppm (~1 ppm), this range is expanded to ~80 ppm (~60 ppm) in the m.l. chelates. This poses a problem in assigning the many resonances observed in these spectra, since the shifts for ligand positions other than the one substituted are drastically altered. Though the resonances are easily assignable to the MLL'_2 or ML_2L' m.l. chelate by varying the ratio of the two reactants in eq 1, the only resonances which can be immediately assigned are the methyl peaks.

For a given m.l. chelate, ML_2L', L′ will give rise to four resonances, one for each nonequivalent position in the free ligand, while L will yield eight resonances, since the ligand C_2 axis is removed by chelation. Thus, because there are two L ligands, a total of twelve resonances of equal intensity should be observed for a given m.l. chelate if neither ligand is substituted. In a mixture containing both p.t. and both m.l. chelates, 32 signals, in four sets, are anticipated.[19] The relative intensities of these four sets of peaks depends on the relative amounts of the p.t. chelates used to make the mixture, as illustrated in Figure 1. A random mixture of species corresponds to an equilibrium constant, $K = 9$. As previously shown,[9,12] the 2,9-H and 2,2′-H resonances are very broad (~700–1000 Hz) in the p.t. chelates and sometimes difficult to detect.[20]

Since we are interested primarily in monitoring the effect on the spin delocalization or π covalency in a given ligand upon altering the second ligand in a m.l. chelate, it is not necessary to assign all peaks in each spectrum, and instead it will suffice to focus on those ligand positions which are most sensitive to the nature of the other ligand, and for which the interaction giving rise to the observed contact shift in the p.t. chelate is best understood. In our m.l. chelates, it is the 4,7 or

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[18] In Figures 1–3 only the positions are indicated for peaks which could not be unambiguously assigned to a specific ligand in a mixed ligand chelate. For brevity, the ligands in the figures are designated by lower case letters.

[19] In the mixed ligand chelates involving L = 4,7-Et_2phen, the CH_2 peak in MLL'_2 but not ML_2L' is split into two resonances of equal width and intensity (separated by 25–75 Hz), at low temperatures (−10°). This is not unexpected since such methylene protons are diastereotropic in these complexes, though it is not understood why this effect is larger in the chelates containing only a single 4,7-Et_2phen ligand, particularly since the CH_2 shifts in MLL'_2 and ML_2L' are of comparable magnitude.

[20] In a solution containing a random mixture of p.t. and m.l. chelates, where a given m.l. chelate can account for only ~30% of the total metal ion concentration, and for which three different 2,9-H and/or 2,2′-H peaks are expected, the orders of magnitude reduction in effective concentration per nonequivalent 2,9-H (2,2′-H) peak precludes their detection and resolution for experimental reasons.

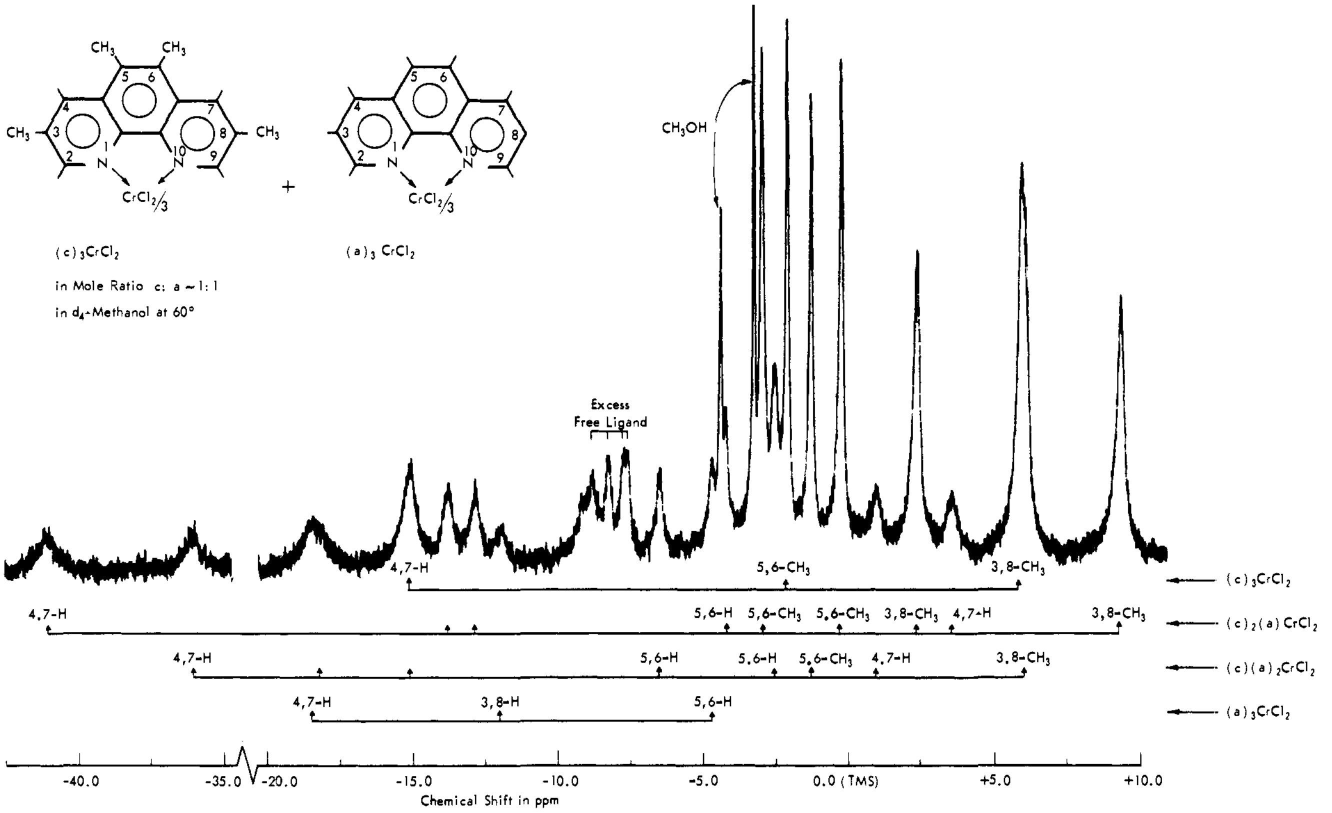

Figure 2. Proton nmr trace of mixed ligand chelates of $(3,5,6,8\text{-}Me_4phen)_3CrCl_2$ and $(phen)_3CrCl_2$.

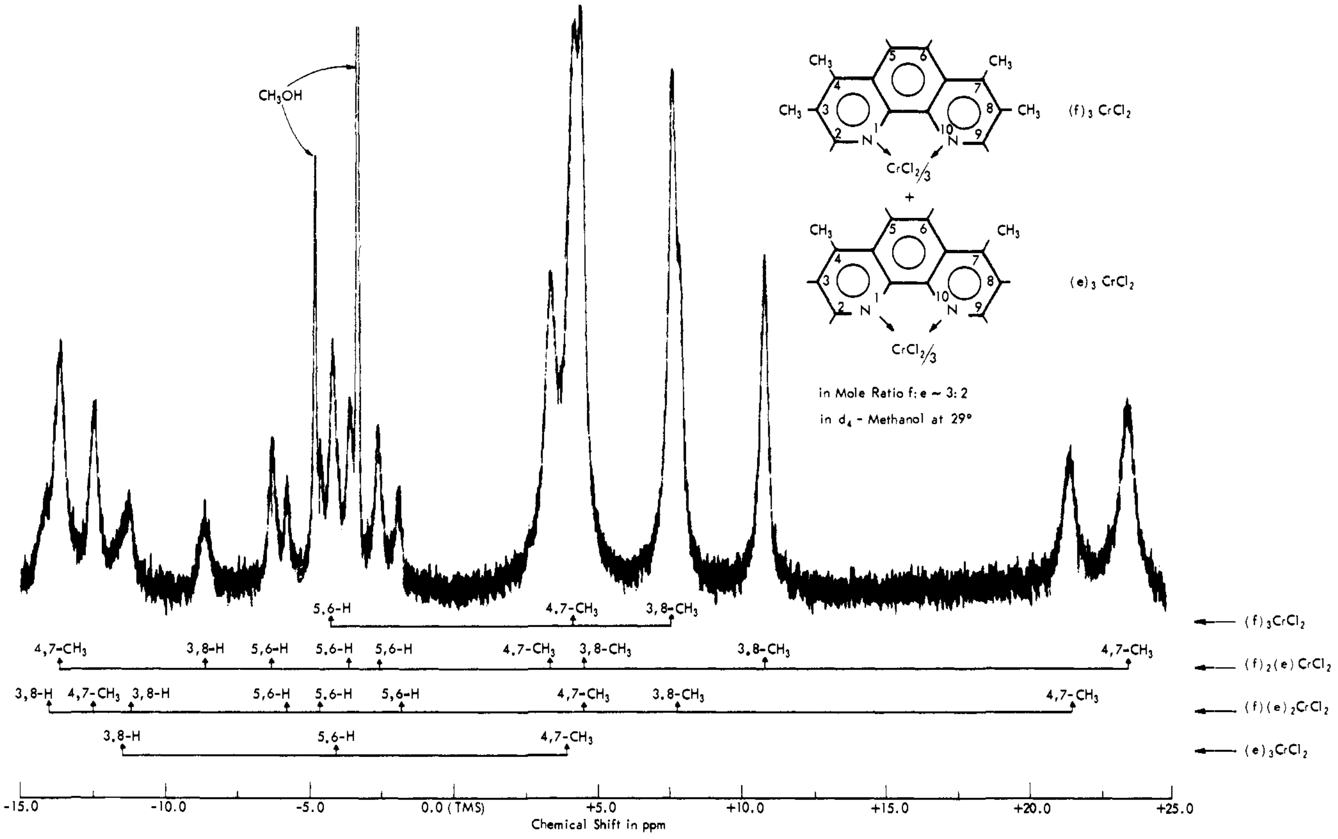

Figure 3. Proton nmr trace of mixed ligand chelates of $(4,7\text{-}Me_2phen)_3CrCl_2$ and $(3,4,7,8\text{-}Me_4phen)_3CrCl_2$.

4,4′ position which will be shown to be affected most, and it has already been shown[9] that the contact shifts in the p.t. chelates arise from π spin density. Other ligand positions need be assigned only to support the 4,7 peak assignments.

Unambiguous assignments of at least one of the 4,7-

Table I. Range of Observed Shifts in m.l. and p.t. Chelates[a]

Positions	p.t. chelates	m.l. chelates
3,8-H (CH_3)[b]	~−12 (~+7)[b]	−8 to −15 (+2 to +10)[b]
5,6-H (CH_3)	~−4 (~−2)	−7 to 0 (−5 to 0)
4,7-H (CH_3)	~−17 (~+5)	−73 to +5 (−27 to +24)

[a] Shifts in ppm at 29°, referenced against TMS. [b] Methyl shifts in parentheses.

Table II. Contact Shifts for L as a Function of L′ in MLL'_2[a]

		Ligand L′					
Ligand L	Position in L	phen	5,6-Me_2phen	3,5,6,8-Me_4phen	4,7-Et_2phen	4,7-Me_2phen	3,4,7,8-Me_4phen
phen	4,7-H	−10.40	−14.65	−38.75	−49.05	−51.45	−64.10
5,6-Me_2phen	4,7-H	−5.94	−9.88	−30.01			
3,5,6,8-Me_4phen	4,7-H	+12.60	+11.10	−7.06		−18.70	−34.85
4,7-Et_2phen	4,7-CH_2	−20.90			+4.59	*b*	
4,7-Me_2phen	4,7-CH_3	−23.26	−21.75	−4.55	*b*	+7.14	+26.35
3,4,7,8-Me_4phen	4,7-CH_3	−30.05		−17.70		−9.68	+8.10
bipy	4,4′-H	*b*			−46.35	−48.50	−58.80
4,4′-Me_2bipy	4,4′-CH_3	−24.05	−22.30	−6.24		+5.34	

[a] All shifts in ppm at 100 MHz, at 29°, referenced against appropriate ligand, L, in $L_3Fe(II)$, M = $CrCl_2$. [b] Spectra recorded, but peaks of m.l. chelates and p.t. chelates were not resolved.

Table III. Contact Shifts for L as a Function of L′ in ML_2L'[a]

		Ligand L′			
Ligand L	Position in L	phen	3,5,6,8-Me_4phen	4,7-Me_2phen	3,4,7,8-Me_4phen
phen	4,7-H	−10.40	−32.80	−40.10	−48.55
			b	*b*	*b*
3,5,6,8-Me_4phen	4,7-H	+15.90	−7.06	−16.45	−29.60
		b		*b*	−6.49
4,7-Me_2phen	4,7-CH_3	−27.35	−3.67	+7.14	+24.35
		+0.28	+4.45		*b*

[a] All shifts in ppm at 100 MHz, at 29°, referenced against appropriate ligand, L, in $L_3Fe(II)$, M = $CrCl_2$. [b] Second of two L resonances not unambiguously assignable due to overlap with other (3,8-H, 3,8-CH_3) resonances.

H (4,4′-H) and/or 4,7-CH_3 (4,4′-CH_3) peaks for each ligand in all m.l. chelates were obtained by using relative intensities, relative line widths, and noting the effect of systematic methyl substitution at all but the 2,9 position. The arguments invoked to effect these assignments are lengthy and involved, and will not be reproduced here in detail.[21] However, a detailed analysis of the 20 pairs of m.l. chelates reveals that the shifts for the 3,8 and 5,6 substituents in a given ligand are relatively insensitive to the nature of the other ligand in a m.l. complex. On the other hand, the shifts for the 4,7 substituents are extremely sensitive to the nature of the second ligand in the m.l. chelate, with the isotropic shifts changing in magnitude by up to a factor of 7, and in addition changing sign in a number of cases, as illustrated in Figures 1–3. The ranges of the observed shifts for the various ligand positions are indicated in Table I. The actual isotropic shifts for the 4,7 substituents in the m.l. chelates are tabulated in Tables II and III.[22]

Hence the 4,7 (4,4′) position is found to be the most sensitive to the composition of the m.l. chelate. A similar sensitivity of these positions to stereochemistry was found[12] earlier in the tris chelates with unsymmetrically methyl-substituted phen ligands. Due to the overlap of many of the 5,6 and 3,8 substituent peaks, only the 4,7 (4,4′) substituent peaks could be assigned in all cases. We therefore will concern ourselves solely with the 4,7 (4,4′) substituent shifts, as listed in Tables II and III.

Observations of note for the 4,7 substituent shifts in the m.l. chelates follow.

(a) In all m.l. chelates, ML_2L', MLL'_2, the shift for one ligand, L′, maintains the same sign as in the p.t. chelate, ML'_3, but increases dramatically in magnitude, while the shifts for the other ligand, L, change sign from that in the p.t. chelate, ML_3, and similarly increase in magnitude. This effect is clearly exhibited in Figures 1–3. For example, in Figure 2, the 4,7-H shift is upfield for 3,5,6,8-Me_4phen and downfield for phen in (phen)(3,5,6,8-Me_4phen)$_2$$CrCl_2$, while in Figure 3, the 4,7-CH_3 shift is upfield for 4,7-Me_2phen and downfield for 3,4,7,8-Me_4phen in (4,7-Me_2phen)$_2$(3,4,7,8-Me_4phen)$CrCl_2$.

(b) The pattern of observed shifts is totally inconsistent with significant dipolar contributions to the shifts,[23] such that the shifts are primarily contact in

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(21) The spectra of five additional pairs of m.l. chelates on whose basis the complete peak assignments listed in Tables II and III can be achieved, in addition to other supporting evidence, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-9042. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(22) The complete set of shifts for the MLL'_2 complexes for fixed L′ as a function of L reflect the identical trend observed in Table II, and therefore only a few examples are given in Table III. The shifts for the remaining m.l. complexes will appear following these pages in the microfilm edition of this volume of the journal, see ref 21.

(23) The geometric factors for all positions in the m.l. chelate MLL'_2 have been calculated considering both the axial and rhombic contributions, G. N. La Mar, W. D. Horrocks, Jr., and L. C. Allen, *J. Chem. Phys.*, 41, 2126 (1964). The complete tabulation of the calculated relative dipolar shifts are found elsewhere, ref 21. The major reasons for discounting the dipolar term as a prime source of the dramatic changes in 4,7-substituent shifts are: (a) the dipolar shifts predict the

both the p.t. as well as the m.l. chelates. Hence the changes in magnitude and sign of the shifts must reflect changes in the nature of the spin delocalization mechanism(s).

(c) The ligands can be arranged in a unique "spectrochemical" series,

$$\text{phen} < 5,6\text{-Me}_2\text{phen} < 3,5,6,8\text{-Me}_4\text{phen} < 4,7\text{-Et}_2\text{phen} \sim 4,7\text{-Me}_2\text{phen} < 3,4,7,8\text{-Me}_4\text{phen} \quad (2)$$

such that the relative positions of any two ligands in a m.l. chelate completely determine for which ligand the contact shift increases, and for which ligand the contact shift changes sign.[24] Thus in a series of m.l. complexes, MLL'_2 (ML_2L'), where L is held fixed, the relative position in eq 2 of arbitrary L′ with respect to L is determined by the sign and magnitude of the L shift in the m.l. chelate relative to that in the p.t. chelate, ML_3. Our choice of the term "spectrochemical" order[25] for eq 2 will be shown to be appropriate in part III,[16] since these shifts are an index of the different extents of interaction between the ligands and the d orbitals; under certain conditions, our series will be identical to that usually determined from the position of optical transitions.[25]

The properties of this "spectrochemical" series reflected in eq 2 are that for the m.l. chelates ML_2L', MLL'_2, with L above L′, the contact shift for L is of the same sign as in ML_3, but larger in magnitude; for fixed L, its shift increases monotonically as L′ increases its position in eq 2. The contact shift for L′ decreases in magnitude and changes sign from that in ML'_3; for fixed L′, its shift will monotonically increase with changed sign as L increases its position in eq 2. These relative variations in contact shift trends are clearly demonstrated by the data in Table II, where the shifts for a fixed L in MLL'_2 are given as a function of L′. A similar tabulation is obtained keeping L′ fixed and varying L; a few examples are reproduced[22] in Table III.

One further observation of note is that the ligands phen and bipy (4,7-Me_2phen and 4,4′-Me_2bipy) can be interchanged in any m.l. chelate without markedly altering the shifts for the other ligand, as shown in Table II. Similar effects were noted upon interchanging phen and bipy in a number of cases. Indeed, the spectrum of the phen/bipy m.l. chelates exhibitied no resolvable shifts from those in the p.t. chelates. This interchangeability between phen and bipy is seen to have important ramifications in the interpretation of the temperature dependence[15,16] of the shifts in these m.l. chelates and the type of ligand π MO involved in the spin-delocalization mechanism.

Since the redistribution of spin density reflected in the significant changes in contact shifts upon m.l. complex formation appears primarily at the 4,7 position, the contact interaction would have to involve predominantly π rather than σ ligand molecular orbitals.[26] A similar conclusion[12] has been reached for the 4,7-substituent shifts in the tris chelates with unsymmetrically methyl substituted ligands. This is consistent with the fact that these low-spin chelates have their unpaired spins in d orbitals which are primarily π bonding in character.

Direct evidence for the dominance of π spin delocalization can be derived from considering the shifts of certain pairs of m.l. chelates. It is observed that in (phen)(4,7-Me_2phen)$_2$$CrCl_2$, the 4,7-H shift in phen is downfield (−51.45), while the 4,7-CH_3 shift in 4,7-Me_2phen is also shifted downfield (−27.35), and actually changes sign from that in (4,7-Me_2phen)$_3$$CrCl_2$. That this change in sign of the methyl contact shift represents a change in the sign (from − to +) of the effective $C_{4,7}$ π spin density can be demonstrated by showing that if 4,7-Me_2phen in that m.l. chelate is replaced by a ligand close to it in the spectrochemical series, but which is *unsubstituted at the 4,7 position*, such as (phen)(3,5,6,8-Me_4phen)$_2$$CrCl_2$, the 4,7-H peak in phen is similarly downfield (−38.75 ppm), but the 4,7-H shift in 3,5,6,8-Me_4phen is *upfield*, having also changed sign from that in the p.t. chelate. This is also indicative of a change of effective $C_{4,7}$ π spin density from − to +. An identical change in sign between 4,7-H and 4,7-CH_3 can be observed by comparing the 4,7-H shift of 3,5,6,8-Me_4phen (−29.60 ppm) and the 4,7-CH_3 shift of 4,7-Me_2phen (+24.35 ppm), in the complexes (3,4,7,8-Me_4phen)(4,7-Me_2phen)$_2$$CrCl_2$ and (3,4,7,8-Me_4phen)(3,5,6,8-Me_4phen)$_2$$CrCl_2$, where the 4,7-$CH_3$ resonances of 3,4,7,8-Me_4phen are both downfield at −9.68 and −17.70 ppm, respectively. Thus the major characteristic of π spin density,[27,28] namely the opposite sign for the proton and methyl contact shifts is clearly demonstrated, and this can be taken as direct evidence that the sizable 4,7-contact shifts originate from π spin density in the ligand.

Since it is well known that simple methyl substitution does not significantly alter the π eigenvectors of the ligand,[10b] the present data are strongly indicative of two π spin delocalization mechanisms, probably involving spin transfer into two different ligand π MO's, for which the $C_{4,7}$ spin densities exhibit opposite signs. The dominant mechanism in the p.t. chelates yields a net negative $C_{4,7}$ spin density (downfield 4,7-H, upfield 4,7-CH_3 shifts). However, as the symmetry is lowered in the m.l. chelates, the extent of spin delocalization by the two mechanisms becomes unbalanced, with one mechanism favored in one ligand, and the other mechanism predominant in the other ligand. We will show in part II[15] that this unbalancing of the two spin-delocalization mechanisms arises primarily not from changes in metal ligand covalency,

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smallest rather than the largest effect for 4,7 substituents; (b) the dipolar term predicts a fixed ratio for the 4,7-substituent shifts for the two nonequivalent ligands in a m.l. chelate, while the sign of the observed ratio depends critically on whether the substituent is a proton or methyl group.

(24) The 4,7-substituent peaks can be assigned directly to a given ligand in a given m.l. chelate only when only one ligand is methyl substituted (13 pairs of m.l. chelates). These chelates serve to establish the "spectrochemical" series in eq 2. The 4,7-substituent peaks in m.l. chelates where neither or both ligands are methyl substituted can be assigned to the correct ligand by noting that one of the two possible assignments is consistent with eq 2 for both ML_2L' and MLL'_2, while the alternate assignment is inconsistent with eq 2 for both m.l. chelates.

(25) C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, Chapter 10.

(26) It should be noted that since the contact shifts are largest at the 4,7 positions, this π spin density must arise from direct M–L π charge transfer, and not from spin polarization of the π system by unpaired spin delocalized into the ligand σ system, as found to be the case for the nickel(II) complexes of heterocyclic amines: W. D. Horrocks, Jr., and D. L. Johnston, *Inorg. Chem.*, **10**, 1835 (1971).

(27) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956); S. I. Weissman, *ibid.*, **25**, 890 (1956).

(28) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

but from the reduced symmetry affecting the spin populations of the various d orbitals.[13,14]

Our spectrochemical series therefore lists ligands L in their increasing propensity to induce spin delocalization into the L π MO with negative $C_{4,7}$ spin density, while decreasing position in the series favors spin delocalization into the π MO with positive $C_{4,7}$ spin density. Furthermore, in any m.l. chelate, MLL'$_2$, ML$_2$L', the stronger[29] ligand tends to exhibit positive $C_{4,7}$ spin density, while the weaker ligand tends to display negative $C_{4,7}$ spin density. In the p.t. chelates, these two competing spin delocalization mechanisms nearly cancel, leading to only a very small net contact shift.

The most significant result from this investigation is the conclusion that the net ligand hyperfine coupling constants are not necessarily valid indices of M–L covalency. Our present results dramatize a major difficulty in interpreting[10] contact shifts or hyperfine coupling constants in terms of metal–ligand covalency; the difficulty being that only the net spin density at any atom is observed in the nmr (or esr) experiment. Since a number of ligand MO's (π or σ) usually have energies favorable for significant interaction with the spin-containing d orbitals, the observed spin density represents the vector sum of the spin densities in all ligand MO's. In order to qualitatively interpret the hyperfine coupling constant, great care must be exercised in ensuring that only one spin delocalization mechanism is operative, or in clearly defining the contributions from different mechanisms, which may be very difficult both experimentally and theoretically. The present complexes, where the two contributing mechanisms place spin density of opposite sign at $C_{4,7}$, are an example of where the ligand hyperfine coupling constant in the p.t. chelates appears to be a very poor index of the covalency in the π system. Such combinations of spin delocalization mechanisms, plus the added possibility of σ spin delocalization, may be responsible for the obscure contact shift patterns found in phen and bipy chelates with Fe(III),[9,12,30,31] and suggest that a detailed analysis[31] of such poorly understood shifts is meaningless at this stage.

It should be noted here that, since only at the 4,7 positions do the π contact shifts increase dramatically upon m.l. complex formation, the two competing spin-delocalization mechanisms each reflect a ligand MO with a highly nonspherical distribution for the unpaired electrons. Such a nonspherical distribution for the reducing electron could be responsible for the asymmetric induction reported[3] in the outer-sphere redox reaction with (phen)$_3$Co^{3+}.

The present results demonstrate that these complexes exhibit significant π covalency. The nature of the π MO's involved and the origin of the unbalancing of the two delocalization mechanisms can be understood by considering the anomalous temperature dependence of the contact shifts,[15] which will be taken up in part II.

Solvent Effects on Contact Shifts. A previous investigation has shown that, although the solvent can drastically affect the methyl line widths[32] in the p.t. chelates, their contact shifts[9] in CD$_3$OD and D$_2$O were essentially the same. A novel line broadening for methyl peaks in D$_2$O was found only for the p.t. chelates of 4,7-Me$_2$phen, 4,7-Et$_2$phen, and 3,4,7,8-Me$_4$phen, which was concluded[32] to originate at the 4,7 position. The related 4,4'-Me$_2$bipy chelate did not exhibit the line width effect. Since (4,7-Me$_2$phen)$_3$CrCl$_2$, for example, displayed these broad methyl signals only in D$_2$O and not in CD$_3$OD, a specific complex–solvent interaction is indicated which differs for the two solvents. Whether the broad methyl resonances are an electronic property of the metal complex and interaction with methanol eliminates this property, or whether the methyl line broadening results from a specific interaction between ligand and water has not been determined.

When d_4-methanol is used as a solvent for our m.l. chelates (Tables II and III), the contact shifts for all species are found to be independent of the total metal ion concentration and the relative amounts of the two ligands present in solution. When D$_2$O is used as the solvent, two types of behavior are observed. For m.l. chelates involving the ligand pairs[33] 4,4'-Me$_2$-bipy/phen, and 4,4'-Me$_2$bipy/bipy, the shifts for any one m.l. chelate are identical with those observed in d_4-methanol, and independent of the relative amounts of the two ligands in solution. However, when one of the ligands in the m.l. chelates is 4,7-Me$_2$phen or 3,4,7,8-Me$_4$phen, the contact shifts for the m.l. chelates are always different from those of the same species in CD$_3$OD, and the shift for a given m.l. chelate depends on the relative amounts of the two ligands present in solution. The contact shifts for (3,4,7,8-Me$_4$phen)$_2$-(phen)CrCl$_2$, in aqueous solution, with ligand ratios of approximately 1:2, 1:1, and 2:1 are given in Table IV. The dependence on the ligand ratio is such that as the fraction of either 4,7-Me$_2$phen or 3,4,7,8-Me$_4$-phen decreases, the contact shifts for the m.l. chelates in D$_2$O approach those in CD$_3$OD.

Table IV. Solvent and Ligand Composition Dependence of Contact Shifts in (3,4,7,8-Me$_4$phen)$_2$(phen)CrCl$_2$[a]

3,4,7,8-Me$_4$-phen:phen	Solvent[c]	4-7-H shift in phen	4,7-CH$_3$ shift in 3,4,7,8-Me$_4$phen
b	M	−55.2	−30.2
~1:2	W	−50.5	−26.6
~1:1	W	−49.5	−24.6
~2:1	W	−47.8	−22.9

[a] Shifts in ppm at 100 MHz at 60°, referenced against appropriate ligand L, in L$_3$Fe(II). [b] Shifts are independent of relative amounts of two ligands. [c] Solvents are W = d_2-water; M = d_4-methanol.

As the temperature of an aqueous solution is raised, the *difference* between the spectra in D$_2$O and CD$_3$OD decreases. This is illustrated in Table V, where the shifts in the two solvents are compared as a function of temperature. It is seen that the ratio of these two shifts, R, approaches 1.0 as the temperture is raised. A similar decrease of the methyl line widths in D$_2$O solution was noted[32] upon raising the temperature. Furthermore, when spectra for the m.l. chelates were obtained in mixed D$_2$O/CD$_3$OD solvents, the addition

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[29] By the "stronger" ligand we designate the one with the higher position in our postulated "spectrochemical" ordering of the ligands.

[30] R. E. DeSimone and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 2343 (1970).

[31] R. G. DeSimone and R. S. Drago, *Inorg. Chem.*, 11, 668 (1972).

[32] G. N. La Mar and G. R. Van Hecke, *J. Chem. Phys.*, **50**, 537 (1969); **52**, 5676 (1970).

[33] These ligands exhibited "normal" dipolar dominated line widths, ref 32.

Table V. Effect of Temperature on the Difference in Contact Shifts for $(phen)_2(4,7\text{-}Me_2phen)CrCl_2$ in Methanol and Water Solution[a]

T, °C	S[b]	4,7-CH_3 shift in 4,7-Me_2phen	R[c]	4,7-H shift in phen	R[c]
29	M	−23.3	0.89	−40.2	0.89
	W	−20.8		−35.7	
45	M	−20.8	0.92	−36.4	0.92
	W	−19.2		−33.4	
60	M	−19.1	0.94	−34.2	0.95
	W	−18.0		−32.5	

[a] Shifts in ppm at 100 MHz, referenced against appropriate ligand L in $L_3Fe(II)$. [b] Solvents are W = d_2-water; M = d_4-methanol. [c] R is ratio of shift in water to that in methanol.

of as little as 20% CD_3OD already suppressed[14] the difference in contact shifts between the two solvents.[34] From these observations, we suggest that the different m.l. chelate contact shifts in the two solvents must result from a specific interaction between water and the complex, which is either absent or considerably less important in methanol.

In terms of our spectrochemical series, the upfield bias of the phen 4,7-H shift in the 4,7-Me_2phen/phen or 3,4,7,8-Me_4phen/phen m.l. chelates in D_2O compared to CD_3OD solution indicates that the interaction of these methyl-substituted ligands with water *lowers* their position relative to phen.

The reasons for the dependence of the m.l. chelate shifts on the L/L′ ratio is not understood. A plausible explanation is that the extent of interaction between the water and 4,7-Me_2phen ligand differs substantially for the three species containing that ligand in solution, so that there is a competition for the water among the three species. Support for such a mechanism can be obtained from the observation that the difference in shifts between the aqueous and methanolic solutions increases with the number of 4,7-Me_2phen or 3,4,7,8-Me_4phen ligands in the m.l. chelate (Table IV). The details of this solvent–solute interaction, along with an investigation of the solvation of these complexes, will be treated elsewhere.[35] We tentatively suggest some type of hydrogen bond between water and specifically the 4,7 position.

In part II of this investigation,[15] we will analyze the temperature dependence of the observed shifts in these m.l. chelates and in part III[16] attempt to arrive at the electronic origin of our spectrochemical order.

Acknowledgment. The authors are indebted to P. C. Irwin for assistance in preparation of the complexes and nmr samples.

(34) A similar effect on the methyl line widths in mixed water–methanol solution has been observed: G. N. La Mar and G. R. Van Hecke, *Chem. Commun.*, 274 (1971).

(35) G. N. La Mar and G. R. Van Hecke, submitted for publication.

Proton Nuclear Magnetic Resonance Studies of the Electronic Structure of Outer-Sphere Reducing Agents of Chromium(II). II. Determination of Orbital Ground State in Mixed α-Diimine Chelates

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Abstract: Analysis of the non-Curie temperature dependence of the ligand contact shifts in a large series of mixed ligand complexes of Cr(II) with symmetrically substituted *o*-phenanthrolines (phen) has yielded the orbital ground states for each complex, provided a specific spin-delocalization mechanism is assumed. This non-Curie behavior arises from the lifting of the orbital degeneracy of the parent tris chelates, with the result that both orbital states are populated, each of which exhibits a different spin-delocalization pattern for the nonequivalent ligands. For each pair of mixed ligand chelates, ML_2L', MLL'_2, one is shown to possess the A while the other is shown to possess the B orbital ground state. The various ligands can be arranged in a "spectrochemical" series, phen < 5,6-Me_2phen < 3,5,6,8-Me_4phen < 4,7-Et_2phen ∼ 4,7-Me_2phen < 3,4,7,8-Me_4phen, with the property that if L is above L′, ML_2L' has the A, while MLL'_2 has the B orbital ground state. The spectrochemical series is thus concluded to reflect the relative signs and magnitudes of the C_2 distortion in the mixed ligand chelates. Two spin delocalization mechanisms are shown to be operative, one of which places negative $C_{4,7}$ spin density in a filled symmetric ligand π MO, with the other placing positive $C_{4,7}$ density into a vacant antisymmetric π MO. The interchangeability of phen and α,α'-bipyridine (bipy) in the spectrochemical series indicates that MO's of the same symmetry and spin density signs are involved in phen and bipy. This is qualitatively confirmed by an analysis of the Hückel and extended Hückel π eigenvectors for the two ligands.

In part I of this study,[2a] the contact shifts for the aromatic protons and methyl groups at the 4,7 position in *o*-phenanthroline (phen), or the 4,4′ position in bipyridine (bipy), in the mixed ligand (m.l.)

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(2) (a) G. N. La Mar and G. R. Van Hecke, *J. Amer. Chem. Soc.*, **94**, 9042 (1972), hereafter referred to as part I. (b) G. N. La Mar and G. R. Van Hecke, *ibid.*, **91**, 3442 (1969).