ence of a significant contribution of the latter mechanism is the probable origin of the facile outer-sphere reducing properties of these chelates. In part III of this study, we seek to interpret[24] the bonding characteristics of the ligand reflected in our "spectrochemical" order.

A more general use of nmr in paramagnetic chelates with perturbed orbitally degenerate ground states can also be envisaged, as suggested previously.[4,5] A particularly promising related application is that recently reported by Shulman, *et al.*,[11] where the analysis of the contact shifts of the porphyrin ring in oxidized cyanomyoglobin [low-spin Fe(III)], (a perturbed E orbital ground state) yielded the form of the orbital ground state of the ferric myoglobin and hence the "in plane" magnetic axes.

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Proton Nuclear Magnetic Resonance Studies of the Electronic Structure of Outer-Sphere Reducing Agents of Chromium(II). III. Elucidation of a π Spectrochemical Series and Metal–Ligand Bonding in Mixed α-Diimine Chelates

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Abstract: The bonding properties of a series of symmetrically substituted *o*-phenanthroline ligands, L, L′, in mixed ligand chelates of Cr(II) have been investigated by molecular orbital theory. The specific bonding property probed is revealed in the postulated 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, which has the property of determining the orbital ground-state symmetry of any mixed ligand complex, such that if L is above L′, ML_2L' has the A and MLL'_2 has the B ground state in C_2 symmetry. The effects of $\sigma,\pi(M \rightarrow L)$ and $\pi(L \rightarrow M)$ bonding on the relative energies of the A and B orbital states are evaluated in the LCAO approximation using interaction energies. From the known effects of the substituents on the three interaction energies and the experimentally determined orbital ground states, we conclude that the spectrochemical series is consistent with either increasing ligand basicity or decreasing π acceptor capability. A detailed analysis of the relative effects of the various methyl substituents with ligand position indicates that the π acceptor properties may be dominant. The significance of M → L and L → M π bonding is discussed in relation to the interesting outer-sphere electron transfer properties and magnetic moments of these complexes. The validity of using the free ligand basis functions to describe the observed spin distribution in the complex is also discussed.

The investigation[2a] in part I of the proton nmr spectra of a series of mixed ligand (m.l.) chelates of outer-sphere reducing agents of Cr(II) with symmetrically substituted *o*-phenanthrolines (phen), ML_2L', MLL'_2, has revealed that their contact shifts, particularly at the 4,7 position, differ dramatically from those in the parent tris (p.t.) complexes,[2b] ML_3, ML'_3. The relative effects of variable ligands, L′, on the contact shift of a fixed ligand, L, in a series of m.l. complexes led us to define[2a] a unique "spectrochemical" series[3]

$$\text{phen} < 5,6\text{-}Me_2\text{phen} < 3,5,6,8\text{-}Me_4\text{phen} < 4,7\text{-}Et_2\text{phen} \sim 4,7\text{-}Me_2\text{phen} < 3,4,7,8\text{-}Me_4\text{phen} \quad (1)$$

with the properties that in any m.l. chelate, the "weaker" ligand tended to exhibit negative $C_{4,7}$ spin density,[4] while the "stronger" ligand tended to exhibit positive $C_{4,7}$ spin density. This change in the sign of the spin density was concluded[2a] to arise from two competing π delocalization mechanisms which nearly cancel in the p.t. chelates.

In part II of this study,[5] we demonstrated that these large contact shift changes in the m.l. complexes were accompanied by strong deviations[6-8] from Curie behavior, which resulted from the lifting of the orbital degeneracy[6-10] of the ground state, $E(D_3) \rightarrow A,B(C_2)$. The spin delocalization into the nonequivalent ligands, L, L′, differs for the A and B orbital states,[5,6,11] so that

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Table I. Interaction Energies for C_2 Symmetry Orbitals in a Mixed Ligand Complex, MLL$'_2$[a]

d orbital	ϕ_1	ϕ_2	ψ_1	ψ_2
d_1[b]	$c_{L'}\beta_{ML'}$	0	0	$(\sqrt{3}/3)(2c_L{}^*\beta_{ML}{}^* + c_{L'}{}^*\beta_{ML'}{}^*)$
d_2	0	$^1/_3(2c_L\beta_{ML} + c_{L'}\beta_{ML'})$	$\sqrt{3}c(_{L'}{}^*\beta_{ML'}{}^*)$	0

[a] Coordinate system in Figure 3 of ref 8 was used. [b] The C_2 symmetry-adapted basis functions are defined in ref 13.

by virtue of the thermal population of both states, the characteristic deviations from Curie behavior predicted for the A and B ground states allowed[5] the assignment of the orbital ground state of all m.l. chelates. Furthermore, it was demonstrated[5] that the nature of the orbital ground state for any m.l. chelate was uniquely determined by the relative positions of the two ligands in the spectrochemical series 1. Thus if L is above L′ in the spectrochemical series, MLL$'_2$ possesses the B ground state and ML$_2$L′ possesses the A ground state; if L is below L′, then the A and B ground states are reversed. The ground state symmetry assignments in the m.l. chelates depended on a knowledge of the ligand π MO's involved in spin delocalization. From the similarity between phen and bipy m.l. chelates and an analysis of the ligand MO's of these two ligands, we postulated[5] a L → M charge transfer mechanism which placed negative $C_{4,7}$ spin density into a symmetric, ϕ-type π MO, and a M → L charge transfer mechanism which delocalized positive $C_{4,7}$ spin density into an antisymmetric ψ-type ligand π MO. Furthermore, in a given m.l. chelate, the difference in spectrochemical positions for the two ligands was concluded to determine the sign and magnitude of the separation between the A and B states.

In the strong field limit (neglecting spin-orbit coupling[12]) the A and B states correspond to the configurations $(d_1)^2(d_2)(d_3)$ and $(d_1)(d_2)^2(d_3)$, respectively,[13] so that the difference is primarily whether d_1 or d_2 is singly occupied, or, alternatively, whether d_2 or d_1 is higher in energy, respectively. Therefore, the relative energies of d_1 and d_2 are determined by the position of the component ligands in the spectrochemical series, so that an analysis of the various metal–ligand interactions which affect these orbital energies is expected to shed light on the particular bonding properties of these ligands which is reflected in the spectrochemical series. As indicated previously,[6] the simplest method for estimating the relative d orbital energies within the LCAO–MO approximation is the use of interaction energies, as discussed by Orgel,[11] which are defined as, $E = \int \phi_m H \phi_L d\tau$, where $\phi_L = \Sigma_i c_i(2p_i)$ for the ligand π MO, and ϕ_m is the symmetry d orbital on the metal. A resonance integral β is defined, $\beta_{ML} = \int d(t_{2g})H(2p_N)d\tau$ which corresponds to the equivalent interactions between the metal t_{2g} and ligand $2p_N{}^\pi$ atomic orbitals of a given ligand L. Thus in a m.l. chelate, two resonance integrals are required, as discussed elsewhere.[6] The interaction energies involving the C_2 symmetry-adapted d orbitals and the ligand ϕ- and ψ-type MO's for the m.l. chelate MLL$'_2$ are given in Table I.

Since interactions with vacant π MO's stabilize d orbitals, while interaction with filled MO's destabilizes the d orbitals,[14] a separate knowledge of whether the σ, π, or π^* interaction increases or decreases upon methyl substitution should allow us to determine whether M → L or L → M π bonding or σ bonding is dominant in deciding the relative d_1 and d_2 orbital energies.

Experimental Section

Extended Hückel molecular orbital calculations were performed on the ligand phen, 3,8-Me$_2$phen, 5,6-Me$_2$phen, and bipy, using the method described by Schachtschneider, *et al.*[15] The geometry reported for Zn(phen)Cl$_2$ was used,[16] and the C–C single bond taken as 1.54 Å. The orbital exponents were taken from the work of Clementi and Raimondi,[17a] and the valence state ionization potentials and their charge dependences were abstracted from the tables of Clementi.[17b] Calculations were performed on a Univac 1108 computer. Inasmuch as we are interested only in the orbital symmetries and the relative changes in orbital energies upon methyl substitution at various positions, no attempt was made to optimize the parameters.

Results and Discussion

Inasmuch as the directions of the m.l. chelate shifts as well as the non-Curie temperature dependence can be consistently interpreted[3a,5,6] on the assumptions of insignificant M–L covalency changes, by considering only the different spin distributions for the A and B orbital states, we will attempt to determine what ligand property is most probably reflected in our spectrochemical[3] series by considering the substituent effects on the ligand MO's and how they in turn affect the ordering of the metal d orbitals.

For this analysis, we will make the assumption that the ligand MO's determined[5] to be the most likely to be involved in M–L covalency in part II are indeed the correct MO's, where the filled MO is of type ϕ and exhibits negative $C_{4,7}$ spin density, while the vacant MO is of type ψ and displays positive $C_{4,7}$ spin density. Comparison of the calculated π eigenvectors and the observed contact shifts indicated[5] a poor quantitative fit, although the signs of the $C_{4,7}$ spin densities are probably correct. The discrepancies could arise from inherent shortcomings in the calculations,[15] other contributions[2a] to the 3,5,6,8-substituent shifts or from perturbations of the ligand eigenvectors due to relatively strong interaction with the metal orbitals (*vide infra*).

Effects from π Bonding. Since the large spin densities in the π system indicate strong covalency, we will

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(12) The effect of ignoring spin–orbit coupling has been discussed previously (footnote 16 in ref 5, footnote 10 in ref 6, and ref 9).

(13) The C_2 symmetry adapted basis functions are: $d_1 = (1/\sqrt{2})(d_{xz} - d_{yz})$, $\phi_1 = (1/\sqrt{2})(\phi_B - \phi_C)$, $\psi_2 = (1/\sqrt{6})(2\psi_A - \psi_B - \psi_C)$; a: $d_2 = (1/\sqrt{6})(2d_{xy} - d_{xz} - d_{yz})$, $\phi_2 = (1/\sqrt{6})(2\phi_A - \phi_B - \phi_C)$, $\psi_1 = (1/\sqrt{2})\cdot(\psi_B - \psi_C)$, where the coordinate system of Figure 3 in ref 8 is used, ϕ and ψ are the symmetric and antisymmetric ligand π MO's. The unique ligand in the mixed ligand chelates ML$_2$L′, MLL$'_2$ (L′ and L, respectively) are taken as ligand A, while the two equivalent ligands are taken as ligands B and C The use of only the $(d_1{}^2d_2d_3)$ and $(d_1d_2{}^2d_3)$ orbital configurations is justified for the qualitative analysis undertaken here (see footnotes 16 and 17 in ref 5).

(14) Reference 3, particularly p 133.

(15) J. H. Schachtschneider, R. Prins, and P. Ros, *Inorg. Chim. Acta*, **1**, 467 (1968).

(16) C. W. Reimann, S. Block, and A. Perloff, *Inorg. Chem.*, **5**, 1185 (1966).

(17) (a) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963); (b) E. Clementi, *IBM J. Res. Develop.*, **9**, 2 (1965).

first attempt to interpret the spectrochemical series in terms of the different π bonding properties of the ligand, assuming that different σ bonding does not split the E state. As indicated earlier,[5] the d-orbital energy for Cr^{2+} is expected to be between that of the lowest vacant and highest filled MO's, as pictured in Figure 1. It has been experimentally demonstrated in numerous cases[4] in both free radicals and transition metal complexes that simple methyl substitution does not significantly alter the π eigenvectors, as measured by their spin densities. However, as has been discussed by Day and Sanders,[18] methyl substitution does alter the ligand orbital energies, as evidenced by the effects of methyl substitution on the position of the charge-transfer bands for $(phen)_3Fe^{2+}$ and $(phen)_3Fe^{3+}$ complexes. In particular, methyl substitution has the effect of *raising* the energies of all π MO's, with the relative energy increase for a given MO proportional to the spin density at the position(s) of methyl substitution. The effect on the relative ligand MO energies upon methyl substitution are illustrated in Figure 1. It has been shown that the extent of metal–ligand interaction depends inversely on the energy separation between the metal and ligand levels. Upon methyl substitution we therefore expect[19] a *decrease* in the interaction between d orbitals and the vacant π^* MO's due to a larger energy separation, and simultaneously an *increase* in the interaction between the d orbitals and the filled π MO's due to a smaller energy separation. The two effects, decreasing M → L and increasing L → M π bonding both result in a destabilization of the spin containing orbitals.[14]

The different effects on the energies of the d_1 and d_2 orbitals in a m.l. chelate are given by the interaction energies[11] between the d orbitals and the various ligand π MO's, listed in Table I. The interaction with π^* MO's stabilizes the d orbitals (a negative contribution), while interaction with π MO's destabilized the d orbitals[14] (positive contribution). Thus for the MLL'_2 complex (L = ligand A, L′ = ligands B, C), we get

$$E(d_1) = c_{L'}\beta_{ML'} - \sqrt{3}(\tfrac{2}{3}c_{L}^*\beta_{ML}^* + \tfrac{1}{3}c_{L'}^*\beta_{ML'}^*)$$

$$E(d_2) = \tfrac{2}{3}c_{L}\beta_{ML} + \tfrac{1}{3}c_{L'}\beta_{ML'} - \sqrt{3}c_{L'}^*\beta_{ML'}^*$$

where $E(d_1) = E(d_2)$ when L = L′. For the particular complex, $(4,7\text{-}Me_2phen)(phen)_2CrCl_2$, where L is above L′, the above reasoning leads to the conclusion that $\beta_{ML'} > \beta_{ML}$ and $\beta_{ML'}^* < \beta_{ML}^*$. If we let $\beta_{ML'} - \beta_{ML} = \epsilon$ and $\beta_{ML'}^* - \beta_{ML}^* = -\delta$, where both ϵ and δ are small and positive, re-formulating the energies in terms of the parameters for phen leads to

$$E(d_1) = \beta_{ML'} - \sqrt{3}\beta_{ML'}^* + \frac{2\sqrt{3}}{3}\delta$$

$$E(d_2) = \beta_{ML'} - \sqrt{3}\beta_{ML'}^* + \tfrac{2}{3}\epsilon$$

Since we have concluded from the temperature dependence that $E(d_1) > E(d_2)$, we must have $\sqrt{3}\delta > \epsilon$, or $(\sqrt{3}\delta - \epsilon) > 0$. This dictates that the ligands must differ more in their π M → L than in the π L → M bonding properties, with phen the better π acceptor. Thus in a series of m.l. chelates $ML(phen)_2$, where L is varied, the relative energies for d_1 and d_2 obtained from the temperature dependence always leads to a positive value for $(\sqrt{3}\delta - \epsilon)$, but whose value must increase monotonically as L increases in the spectrochemical series. Thus increasing position in the spectrochemical series appears to reflect decreasing π acceptor capabilities of the ligand. An identical result is obtained if we consider any other series of m.l. chelates.

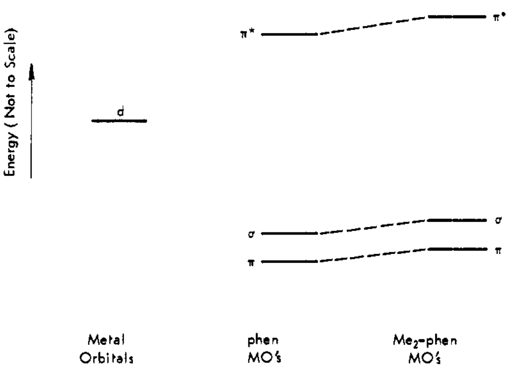

Figure 1. Relative energies of metal and ligand orbitals.

As indicated above, the decrease in β^* and increase in β upon methyl substitution is predicted[18] to be proportional to the spin density in the π^* and π MO's, respectively. The calculated[2,5] spin densities in Table I of ref 5, though probably correct in the sign of the $C_{4,7}$ spin density, are obviously a poor quantitative approximation, since spin densities of comparable magnitudes are indicated for all ligand positions (*vide infra*). However, experimentally, the 4,7 position exhibits[2a] the largest shifts, both upfield and downfield, so that both the ϕ and ψ MO's exhibit their largest spin densities at that position. The spectra in part I revealed[2a] that the 3,8-H, $3,8\text{-}CH_3$ shifts are also consistent with π spin density, but are much smaller than for the 4,7 position, while the shifts for 5,6-H, $5,6\text{-}CH_3$ are the smallest of the observable signals; hence the observed π spin densities appear to fall in the order $C_{5,6} < C_{3,8} < C_{4,7}$. Therefore, compared to phen, $4,7\text{-}Me_2phen$ should produce the largest, $5,6\text{-}Me_2phen$ the smallest, and $3,8\text{-}Me_2phen$ an intermediate $\sqrt{3}\delta - \epsilon$, which is completely consistent with our spectrochemical series. The larger effect of $3,8\text{-}CH_3$ compared to $5,6\text{-}CH_3$ is noted by the fact that the $5,6\text{-}Me_2phen$/phen m.l. chelates yield 4,7-H shifts only slightly shifted from the positions in the p.t. chelates, while in the $3,5,6,8\text{-}Me_4phen$ chelates, the 4,7-H shift in phen is shifted almost as far as for the $4,7\text{-}Me_2phen$/phen chelates.[2a]

The decreasing π acceptor capabilities upon methyl substitution are not unexpected, since alkyl groups are electron-releasing compared to protons, and would tend to destabilize M → L back bonding. The decreasing stabilities of the $(L)_3Fe^{2+}$ chelates (L = phen or substituted phen), upon increasing methyl substitution, as measured[20] by the decrease in the redox potentials, whose values are given in Table II, are also consistent with decreasing back bonding, though the trend can equally well be interpreted[20] in terms of increased stability of the ferric state due to the increasing ligand basicities,[21] which are also reproduced in Table II.

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[20] W. W. Brant and G. F. Smith, *Anal. Chem.*, **21**, 1313 (1949).

[21] W. A. McBryde, *Can. J. Chem.*, **43**, 3472 (1965); M. Charton, *J. Org. Chem.*, **31**, 3739 (1966); D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworth, London, 1965.

Table II. Redox Potentials of $Fe^{2+}L_3/Fe^{3+}L_3$ Couple and Ligand Basicities as a Function of Substituents

L	$E_{1/2}$[a]	Log pK_a[b]
phen	1.10	<4.98
3,8-Me_2phen	1.03	5.23
5,6-Me_2phen	1.00	5.60
3,5,6,8-Me_4phen	0.93	5.54
4,7-Me_2phen	0.88	5.95
3,4,7,8-Me_4phen	0.85	6.30

[a] Taken from ref 20. [b] Taken from ref 21.

Table III. Extended Hückel σ Energies for phen and bipy Ligands[a]

Ligand	$\sigma(\theta)$		$\sigma(\chi)$	
	Energy	$C_{N_{2s}}$[b]	Energy	$C_{N_{2s}}$[b]
phen	−9.819	0.103	−9.726	0.086
5,6-Me_2phen	−9.741	0.102	−9.653	0.083
3,8-Me_2phen	−9.727	0.100	−9.665	0.085
4,7-Me_2phen	−9.704	0.103	−9.608	0.085
bipy	−9.901	0.105	−9.799	0.089

[a] Energies in eV's. [b] Coefficient of nitrogen 2s orbital in MO.

However, Cr(II)[22] is more reducing than Fe(II),[20] so that π back-bonding effects can be expected[23] to be much more important in the present chelates.

Effects from σ Bonding. Even in the p.t. chelates, the e^{π} orbitals (d_1 and d_2 in C_2 symmetry), are no longer symmetry forbidden from interacting[24] with the ligand σ orbitals, as is the case in octahedral symmetry. Though the extent of interaction between the d_1 and d_2 orbitals and the lone pair σ orbitals is not known, the splitting between the d_1 and d_2 orbitals in the m.l. chelates could in principle arise from a difference in the basicities[21] of the component ligands. The ligand σ basis functions, like the π MO's, are divided into those which are symmetric, θ, and those which are antisymmetric, χ, with respect to the ligand C_2 axis. d_1 can interact with $(1\sqrt{2})(\theta_B - \theta_C)$ and $(1\sqrt{6})(2\chi_A - \chi_B - \chi_C)$, d_2 can mix with $(1\sqrt{6})(2\theta_A - \theta_B = \theta_C)$ and $(1\sqrt{2})(\chi_B - \chi_C)$. The interaction energies are similar in form to those given[11] for the π interaction. In these bidentate ligands, only the filled σ MO's need to be considered, so that all interactions destabilize[14] the d orbital energies. The relative energies for d_1 and d_2 for the m.l. chelate MLL'_2 are

$$E(d_1) = \alpha_{ML'} + \sqrt{3}(^2/_3\alpha_{ML}^* + {}^1/_3\alpha_{ML'}^*)$$

$$E(d_2) = {}^2/_3\alpha_{ML} + {}^1/_3\alpha_{ML'} + \sqrt{3}\alpha_{ML'}^*$$

where α and α^* are the interaction energies with the θ and χ σ MO's. Since the basicities of the ligands are known,[21] and a stronger base leads to a stronger σ interaction[3] we have for a complex with L above L′, in particular, (4,7-Me_2phen)(phen)$_2$$CrCl_2$, that $\alpha_{ML'}^* < \alpha_{ML}^*$ and $\alpha_{ML'} < \alpha_{ML}$. Letting $\alpha_{ML'} - \alpha_{ML} = \eta$ and $\alpha_{ML'}^* - \alpha_{ML} = \gamma$, the relative energies, expressed in terms of the parameters for phen, are

$$E(d_1) = \alpha_{ML'} + \sqrt{3}\alpha_{ML'}^* + \frac{2\sqrt{3}}{3}\gamma$$

$$E(d_2) = \alpha_{ML'} + \sqrt{3}\alpha_{ML'}^* + {}^2/_3\eta$$

Since we determined[5] $E(d_1) > E(d_2)$, we must have $\sqrt{3}\gamma > \eta$. This requires that the antisymmetric lone-pair orbital interacts more strongly with the e^{π} d orbitals than the symmetric lone-pair orbital. Analysis of the calculated[15] eigenvectors for phen and the three dimethyl-substituted isomers, given in Table III, show that in each case, the χ lone-pair orbital is higher in energy than the θ lone-pair orbital, and that the former orbital also has a larger coefficient at the nitrogens than the latter orbital. Since the σ MO's are expected to be below the d orbitals in energy, both energy and overlap considerations dictate[19] that the antisymmetric χ lone-pair orbitals will interact more strongly with the d orbitals. The ligand basicities, as measured by the pK_a values,[21] given in Table II tend to parallel our spectrochemical series (with some discrepancies) so that the different basicities could lift the e^{π} degeneracy and give rise to our spectrochemical series.

Origin of Spectrochemical Order. It is thus apparent that either π or σ bonding properties of the ligands could determine the orbital ground state of a given m.l. chelate, and thereby give rise to our spectrochemical series. If the σ or basicity effect is dominant, our spectrochemical series is identical in principle with that more conventionally derived from the optical spectra[3] of the chelates; although not new in principle, our method here would greatly increase the resolution of the series among very similar ligands. If it could be established that π bonding determines the orbital ground states in the mixed-ligand chelates, then the present technique could provide the basis for the determination of a π spectrochemical series.

It is not possible to establish with certainty that π bonding effects are dominant. However, inspection of the effect on basicity or σ orbital energy and π MO energies upon methyl substitution suggests that the spectrochemical ordering is unlikely to reflect solely σ bonding properties. The data in Table II show that the introduction of methyl substituents at any position significantly affects the ligand basicity, with the exact position of the methyl groups of only secondary importance. The extended Hückel σ energies, given in Table III, for both the symmetric and antisymmetric MO's also tend to show that altering the methyl positions in the ligand influences the energies considerably less than the initial introduction of two methyl groups. The σ overlaps are not affected by substitution, since the N coefficients appear to be independent of substituent, Table III. Furthermore, both the experimental basicities,[21] Table II, and the σ energies, Table III, predict the trend phen < 3,8-Me_2phen < 5,6-Me_2phen < 4,7-Me_2phen. However, our spectrochemical ordering indicates[2a] that the effect of methyl position at different ligand positions can be more important than the initial introduction of methyl groups (the difference between phen and 5,6-Me_2phen is considerably less than that between 5,6-Me_2phen and 4,7-Me_2phen, for example). Also, the present nmr data indicate[25] that the order is phen < 5,6-Me_2phen < 3,8-Me_2phen < 4,7-Me_2phen.

On the other hand, the energies for any one π MO,

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(22) B. Baker and B. Dev Metha, *Inorg Chem.*, **4**, 848 (1965); M. C. Hughes and D. J. Macero, *Inorg. Chim Acta*, **4**, 327 (1970).

(23) L. E. Orgel, "Introduction to Transition Metal Chemistry-Ligand Field Theory," Wiley, New York, N. Y., 1960, Chapter 9.

(24) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, Chapter 5.

(25) Although the 3,8-Me_2phen chelate was not available, the data in Tables I and II of ref 2a clearly show that the 3,8-CH_3 has a greater effect than the 5,6-CH_3.

Table IV. Extended Hückel π MO Energies for phen and bipy Ligands[a]

Ligand	$\pi_6(\phi)$	$\pi_7(\psi)$	$\pi_8(\phi)$	$\pi_9^*(\psi)$
phen	−10.942	−10.737	−8.073	−8.071
5,6-Me_2phen	−10.882	−10.552	−7.956	−8.029
3,8-Me_2phen	−10.778	−10.675	−8.028	−7.987
4,7-Me_2phen	−10.826	−10.634	−7.999	−7.943
	$\pi_5(\psi)$	$\pi_6(\phi)$	$\pi_7^*(\psi)$	$\pi_8^*(\phi)$
bipy	−11.476	−10.915	−8.157	−7.372

[a] Energies in eV's.

given in Table IV, depend very strongly on the position of the methyl substituents. In particular, for π_9^*, the acceptor orbital proposed[5] to be dominant in determining the spectrochemical ordering of the ligands, $E(\pi)$ follows the pattern

$$\text{phen} < 5,6\text{-Me}_2\text{phen} < 3,8\text{-Me}_2\text{phen} < 4,7\text{-Me}_2\text{phen}$$

identical to that in the spectrochemical series, with the differences between 5,6-Me_2phen and 4,7-Me_2phen larger than between 5,6-Me_2phen and phen, consistent with observations. Therefore, though the π^* interaction may not be the sole factor in determining the spectrochemical position of the ligands, we suggest that it is probably dominant.

The reason why phen and bipy are interchangeable[2a,5] in the spectrochemical order is not clear. An analysis of the different contributions from π, π^*, and σ contributions along the lines carried out for different phen ligands is not possible, since going from phen to bipy may cause large changes in all orbitals. The calculated σ energies for the lone pairs in these two ligands are very similar, Table III, and the overlaps are also about the same. We have already shown[5] that π MO's of the same symmetry and the same sign $C_{4,7}$ and $C_{4,4'}$ spin densities, and with comparable energies are available, so that very similar bonding is to be expected. However, the fact that there appears to be less difference between phen and bipy than between phen and 5,6-Me_2phen is surprising. It may well be possible that the similarity between phen and bipy occurs due to offsetting different contributions of σ and π effects.

Solvation Effects. The effect of water on the spectrochemical position of a 4,7 substituted ligand,[26] noted in part I,[2a] cannot be unambiguously interpreted at this time. It was noted[2a] that this solvent–ligand interaction lowered the position of a 4,7-alkyl-substituted ligand in the spectrochemical series. Thus if increasing position in the spectrochemical series indicates decreasing π-acceptor tendencies for the ligand, the specific solvation effect of water appears to increase the π acceptor capabilities of the 4,7-substituted ligands. In another investigation[27] of the general solvation of these outer-sphere reducing agents by proton nmr line width, we suggest that the solvation may involve some sort of hydrogen bond between water and the 4,7 position, which is slightly negatively charged in these chelates (*vide infra*). Since such hydrogen bonding would stabilize the delocalized negative charge, the π-acceptor capabilities would be enhanced. This solvent interaction will be treated in more detail elsewhere.[27]

Metal–Ligand Bonding. It is gratifying to find evidence of significant M → L back bonding in these chelates, inasmuch as their abilities to stabilize reduced metal ions has been attributed[23,28,29] to their superior π-acceptor properties. Hence the earlier data on the p.t. chelates which suggested[2b] only minor π covalency must be revised in light of the present investigation. This points out the danger in attempting to draw conclusions on covalency from hyperfine coupling constants if the participating MO's are not fully understood. Thus the "spin-only" magnetic moments[28–31] for these chelates probably do result from strong π bonding, but not so much from the delocalization of the magnetic electrons[28,29] as from the trigonal distortion[2b,30,31] resulting from the different π- and π^*-bonding effects, as proposed by Orgel[11] to account for the diamagnetism of the isoelectronic d^4 chelate (bipy)$_3$Ti(0), and also observed for (phen)$_3$Ti(0).[32]

In particular, the sizable positive spin density in what we postulate to be an antibonding ligand MO appears to be concentrated not only on the periphery of the complex, but at two specific positions in a ligand, $C_{4,7}$, though comparable contributions at $C_{2,9}$ cannot be ruled out (*vide infra*). This novel observation may not only account for the facile reducing properties of these complexes in outer-sphere electron transfer reactions,[33] but may be directly related to the reported stereospecificity for the electron transfer reaction[34]

$$(\text{phen})_3\text{Cr}^{\text{II}} + (\text{phen})_3\text{Co}^{\text{III}} \rightarrow (\text{phen})_3\text{Cr}^{\text{III}} + (\text{phen})_3\text{Co}^{\text{II}}$$

where the use of an optically active oxidant yielded optically active (phen)$_3$Cr^{III}. The concentration of spin density at the 4,7 positions suggests that these may be the "active sites" for the transfer of the electron in the outer-sphere redox reaction. If direct overlap between the $C_{4,7}$ p_z orbitals for the reactants is to be optimized for electron transfer, molecular models[35] suggest that the contact between two chelates along their C_3 axes is more favorable if the two complexes possess the same chirality than when they are mirror images. However, solvent mediated electron transfer process, which still may be stereospecific, cannot be definitely ruled[27] out at this time.

The significantly different spin distributions in ligands L and L′ in a given m.l. chelate indicate that any ligand–ligand overlap, which can arise from $2p_z$ overlap of the three ligands at $C_{2,9}$ must be relatively unimportant. This type of interligand π bonding has been postulated[36] in the analysis of the optical spectra of optically active tris chelates of phen and bipy with a variety of metal ions. If the interligand covalency were of sufficient magnitude, the spin distributions for the three ligands would be averaged, even though the symmetry re-

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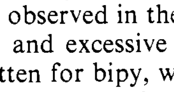
strictions on M–L delocalization in a given orbital state for the m.l. chelates persist.

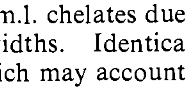
Ligand Basis Functions. In the analysis[5] of the directions of the shifts and the deviations from Curie behavior for the m.l. chelates, we made some assumptions about the validity of employing the ligand π MO's as basis functions, which, with the Cr^{2+} d orbitals, were used to construct the molecular orbitals for the whole complex.[19] The size and complexity precluded a calculation of the eigenvectors for the whole chelate. In particular, we assumed[5,37] that the symmetry of the ligand π MO's, and at least the *signs* of the $C_{4,7}$ and $C_{4,4'}$, spin densities were correctly predicted. The different symmetries and signs of the $C_{4,7}$, $C_{4,4'}$ spin densities could be experimentally demonstrated from the shifts and the temperature dependence, so that the assignments of the *relative* orbital ground states did not depend on any assumptions as to the exact ligand π MO's involved. Only in assigning the A or B ground state to given m.l. chelates in the pair ML_2L', MLL'_2 was knowledge of the specific ligand MO's required. The use of the free ligand π MO's was dictated by the lack of any suitable alternative. However, the ability to obtain such a consistent interpretation of the data in terms of the symmetries and spin densities for the relevant ligand π MO's in Table I of part II suggests that our assumptions are reasonable.

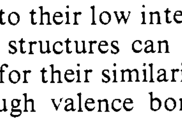
The calculated magnitudes[2,3] of the spin densities, however, are in generally poor agreement with the relative contact shifts. Part of this problem could arise from the fact that the dipolar shift contributes[2,4] to the observed shifts at positions closer to the metal; the sign reversal between the 3,8-H and 3,8-CH_3 shifts, however, suggests[2] that π spin density is dominant. The most notable discrepancy between the theoretical and experimental spin density appears at the 4,7 (4,4′) position, where considerably more spin density is found than is predicted.

The conventional approach in analyzing[4] nmr contact shifts in terms of M–L covalency is to compare the observed contact shift pattern with the calculated spin densities in a number of plausible ligand π MO's. In a number of idealized cases,[38] very good agreement between the experimental and theoretical spin densities has been reported, indicating that primarily a single MO was involved in the M–L covalency, and that the ligand π MO's served as valid basis functions for constructing the MO's for the whole complex. The apparently perturbed ligand π MO's in the present complexes probably result from the extensive M–L π covalency indicated by the large contact shifts, which could be expected to alter the magnitudes of the spin densities at some ligand positions (*vide infra*). In $(bipy)_3Cr^{III}$,[39] π bonding is thought to be unimportant, with the highest antibonding MO's highly localized on the ligand, so that the bipy π MO's are unperturbed; in $(bipy)_3Cr^0$,[39] the ligands are reported to resemble[40] bipy$^-$, so that the antibonding MO's are mostly ligand in character, and could also be described by the basis functions for bipy$^-$, which do not differ much from bipy. However, for chelates with intermediate valence states, the antibonding MO's must exhibit significant covalency. For such a complex, the resultant π MO's for the complex[19] could no more be realistically constructed from ligand π MO's and metal d orbitals than can the π MO's of pyridine *N*-oxide[41] be constructed from pyridine π MO's[42] and oxygen p orbitals. Though the covalency in these Cr(II) complexes is considerably smaller than in pyridine *N*-oxide,[41] significant perturbations on the ligand π MO's could be expected for our phen ligands.

Though the optical spectra for $(bipy)Cr^{2+}$ has been interpreted[39] in terms of relatively unperturbed ligand π–π transitions, ambiguities in the assignments of bands and the assumption of O_h symmetry, even though a very large trigonal distortion is indicated,[2,31] makes some of these conclusions doubtful. Furthermore, relatively little is known[43] about how much a given perturbation of the eigenvectors affects the position of the presumably ligand π–π^* bands.


Ia


Ib


Ic

Since a more complete MO calculation for the complex is not feasible at this time, the possible effects of M–L covalency, particularly M → L charge transfer, on the spin-density distribution on the ligands will be qualitatively probed by considering the resonance structures[44] for a fragment of which the metal is an integral part. Some of the more important valence bond structures for this fragment are illustrated for M → L charge transfer, I. It is seen that the unpaired spin will be concentrated primarily at $C_{4,7}$ and $C_{2,9}$, which is consistent with the observed spin concentration at the 4,7 position. The 2,9-H shifts, which are known to be very sizable in the p.t. chelates, are unfortunately not observed in the m.l. chelates due to their low intensity and excessive widths. Identical structures can be written for bipy, which may account for their similarity in the spectrochemical series. Though valence bond structures placing the spin at $C_{3,8}$ and $C_{5,6}$ can be written, their contribution to the electron structure will be much less important. However, although the valence bond picture gives some insight into the observed spin distribution, the attractive features of the simple MO picture, namely the symmetry properties[11]

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[37] It should be stressed that the presence of the two spin-delocalization mechanisms, one of which places positive, the other negative spin density on $C_{4,7}$, has been experimentally demonstrated (ref 2a). Furthermore, the fact that the two ligand MO's involved are one each symmetric, ϕ, and antisymmetric, ψ, about the ligand C_2 axis, has also been demonstrated by the observed non-Curie temperature dependence (ref 5). The MO calculations were used only to determine whether the ϕ- or ψ-type MO exhibits the positive spin density, and which of the two MO's was filled or vacant in the free ligand. For bipy, the only two available MO's exhibited both the correct spin density signs and symmetries; the interchangeability of phen and bipy in a m.l. chelate indicates very similar MO's must be available in phen, as found in the analysis (ref 5). Thus the assumed assignments of the participating ligand MO's appear reasonable.

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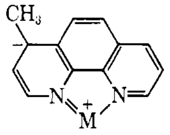
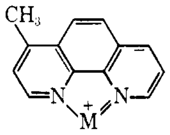
of the component MO's which were necessary to interpret[5] the temperature dependence, are lost. Since this M → L bonding is postulated to determine the spectrochemical ordering of the ligand, at least if π bonding effects are dominant, it is expected that methyl substitution at the 4,7 position will destabilize structures such as Ic. Due to the lesser importance of resonance structures placing the spin at $C_{3,8}$ or $C_{5,6}$, the relative destabilizing effects on M → L back bonding would be phen < 5,6-Me_2phen, 3,8-Me_2phen < 4,7-Me_2phen, as observed. Structure Ic can create pockets of electron density in the otherwise cationic complex, which have been invoked[27] to explain the apparent participation of water in some sort of hydrogen bonding interaction at the 4,7 position.

Another line of evidence which suggests that the delocalized spin density is not adequately described by the unperturbed ligand π MO's is seen from the m.l. chelates MLL'_2, where the two 4,7-CH_3 peaks in L′ display[2a] very different shifts, often one upfield and the other far downfield, although the spin densities in these symmetric ligands should yield[2b] very similar C_4 and C_7 shifts. A similar effect was noted[7] for the shifts in the trans isomer of the tris chelates with unsymmetrically methyl substituted phen ligands, where in the same ligand, the 4-CH_3 shift indicated very large positive spin density, while the 7-H shift indicated sizable negative spin density. Again, these differences within a given ligand can be rationalized by resonance structures, where structure IIa would be expected to be less stable than structure IIb. We are therefore forced to conclude that in phen or bipy complexes where significant M–L π bonding is postulated, the observed ligand spin densities are very unlikely to be quantitatively interpretable by the calculated ligand eigenvectors.



IIa



IIb

Summary

In summary, we have arrived at a number of qualitative conclusions concerning the electronic structure of these interesting Cr(II) chelates.

1. Extensive π bonding is present, though not obvious in the tris chelates[2a] with symmetric ligands due to near cancellation of two contributions of opposite sign. Thus the net hyperfine coupling constants in the tris chelates are poor indices of the actual M–L π covalency.

2. Both M → L and L → M charge transfer delocalization mechanisms are operative, though *net* spin transfer is small. The probable MO's in phen involved are π_6 and $\pi_9{}^*$, of which the former is symmetric and the latter antisymmetric about the ligand C_2 axis. Similar MO's are available in bipy.

3. The "spin-only" magnetic moments of these chelates probably arise from the trigonal distortion which results from the π bonding with symmetric and antisymmetric ligand π MO's, as discussed by Orgel.[11]

4. The "spectrochemical" series defined in parts I and II reflects, at least in part, the π-acceptor capabilities of the ligands, though ligand basicity differences could produce a similar effect.

5. The highly localized spin density at $C_{4,7}$ in these complexes must facilitate their acting as effective reducing agents and may account for their apparent stereospecific behavior in some outer-sphere electron transfer reactions.

6. The M–L π covalency appears to be sufficiently strong so that the free ligand eigenvectors are not valid for quantitatively describing the delocalized spin density.

7. The 4,7-substituted chelates interact specifically with water at the 4,7 position, probably *via* some sort of hydrogen bonding interaction. This novel solvation phenomenon increases the π acceptor capabilities of the ligand.

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