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.

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[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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Received March 31, 1972

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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[1] Author to whom correspondence should be addressed at the University of California; Fellow of the Alfred P. Sloan Foundation, 1972–1974.

[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).

chelates ML_2L', MLL'_2, were shown to differ dramatically from the shifts in the parent tris (p.t) chelates[2b] ML_3, ML_3'. The sizable increase in shifts and the simultaneous change in sign for the shifts in some of the ligands were postulated[2a] to arise from the unbalancing in the m.l. chelates of two competing spin-delocalization mechanisms which nearly cancel in the p.t. chelate, one of which places positive spin density, the other negative spin density, at the 4,7 (4,4′) position. The relative effects of a series of ligands, L′, on the direction and magnitude of the 4,7 or 4,4′ shift in a fixed ligand L in ML_2L', MLL_2 led us to define[2a] a spectrochemical series for the phen ligands with

$$\text{phen} < \text{5,6-Me}_2\text{phen} < \text{3,5,6,8-Me}_4\text{phen} < \text{4,7-Et}_2\text{phen} \sim \text{4,7-Me}_2\text{phen} < \text{3,4,7,8-Me}_4\text{phen} \quad (1)$$

properties that increasing position for L′ favored the delocalization of *positive* spin density to $C_{4,7}$ in L, while decreasing position favored the delocalization of *negative* spin density to $C_{4,7}$ in L. Furthermore, in any given m.l. chelate, the ligand with the higher position tended to display positive $C_{4,7}$ spin density, while the ligand with the lower position always exhibited negative $C_{4,7}$ spin density.

It is considered unlikely that this observed increase of a factor of ~10 in the net spin delocalization into a given ligand in a m.l. chelate, when compared to the p.t. chelate,[2b] can arise primarily from changes in the metal–ligand π covalency, since it is deemed improbable that simple changes in the methyl substitution on one ligand could cause such a sizable perturbation on the electronic structure of the chelate. However, it was previously demonstrated[3–5] that the p.t. chelates are in the doubly degenerate E orbital ground state, which, if the symmetry (D_3) is lowered (C_2 in m.l. chelates or C_1 in chelates with unsymmetrically substituted ligands), will split into two closely spaced orbital states (E → A, B in C_2). Depending on the states the unpaired electrons are placed[6] into a d orbital which interacts differently with the nonequivalent ligands. Due to the small separation between these two states and their different spin-delocalization patterns, both states are populated in the accessible temperature range, leading to strong overall deviations from Curie behavior,[4,6] though the shifts for either state and the averaged spin magnetization follow the Curie law. The contact shifts[2b] and spin magnetization[7] for the p.t. chelates each follow the Curie law quite accurately.

Similar differences in shifts between resonance positions in m.l. chelates and the p.t. chelates have been reported[5] for the 4,7-Me_2phen/4,4′-Me_2bipy system, where it was also demonstrated that these shift differences were accompanied by sizable deviations from Curie behavior which could be interpreted consistently by only considering the effect of lifting the E degeneracy[6] and without invoking any sizable covalency changes in the m.l. chelates. These complexes provided an ideal test for the capability for obtaining information on the orbital ground states of a given m.l. chelate by virtue of the fact that they were the only m.l. chelates where not only could all eight 4,7-CH_3, 4,4′-CH_3 resonances be located and observed over a broad temperature range, but all peaks could be unambiguously assigned to the appropriate ligand within a given m.l. chelate. This latter assignment of the peaks to a given ligand was made possible by the dramatically different methyl line widths[8] for the two component ligands in aqueous solution. The complete consistency between the observed deviations from Curie behavior for *all resonances* and that predicted for the ground states for the two m.l. chelates indicated[5] the validity of the technique for this class of Cr(II) complexes. In our present chelates, though in no case could all the 4,7 (4,4′) resonances be unambiguously assigned, those resonances which are observed will be shown to suffice in order to clearly differentiate between the two possible orbital ground states. Although the relative orbital ground states for any two m.l. chelates can be experimentally determined, the association of a given ground state with a particular m.l. chelate again necessitates some assumptions[5] as to the nature of the particular molecular orbital(s) into which the spin is delocalized.[9] However, in the earlier analyses[4,5] it was possible to interpret the temperature dependence by assuming only a single spin delocalization mechanism, since all methyl shifts in CD_3OD solution exhibited the same sign as in the p.t. chelates. For the present m.l. chelates, we have already shown[2a] in part I that at least two distinct spin delocalization mechanisms are operative.

This technique for determining[4–6] the orbital ground-state symmetry from the relative extents of spin delocalization into the three ligands in the m.l. complexes is very similar in principle to the well-established esr method for obtaining the orbital ground state for substituted benzene anion radicals.[10] A related approach has been used by Shulman, Glarum, and Karplus[11] to determine the form of the orbital ground-state functions of oxidized myoglobin. In this case, the splitting of the E state by spin–orbit coupling was found to be large compared to kT.

We will consider here the temperature dependence of the 4,7 (4,4′) contact shifts reported[2a] in part I for the purpose of determining the orbital ground states of the m.l. chelates. We will here demonstrate that the direction and magnitudes of the observed shifts are determined by the nature of the orbital ground-state symmetry, so that the relative positions of two ligands in the spectrochemical series determine the orbital ground state for a given m.l. chelate.

Experimental Section

The mixed ligand complexes employed in this investigation were identical to those described[2a] in part I; d_4-methanol (Diaprep) was

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(3) G. N La Mar and G. R. Van Hecke, *Inorg. Chem.*, **9**, 1546 (1970).

(4) G. N. La Mar and G. R. Van Hecke, *J. Amer. Chem. Soc.*, **92**, 3021 (1970).

(5) G. N. La Mar and G. R. Van Hecke, *J. Magn. Resonance*, **4**, 384 (1971).

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

(7) A. Earnshaw, L. F. Larkworthy, K. C. Patel, K. S. Patel, R. L. Carlin, and E. G. Terezakis, *J. Chem. Soc. A*, 511 (1967); Y. M. Udachin and M. E. Dyatkina, *J. Struct. Chem.* (*USSR*), 8, 325 (1967).

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

(9) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, 1, 103 (1965).

(10) R. G. Lawler, J. R. Bolton, G. K. Fraenkel, and T. H. Brown, *J. Amer. Chem. Soc.*, **86**, 520 (1964); see also A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, Chapter 6.

(11) R. G. Shulman, S. H. Glarum, and M. Karplus, *J. Mol. Biol.*, 57, 93 (1971).

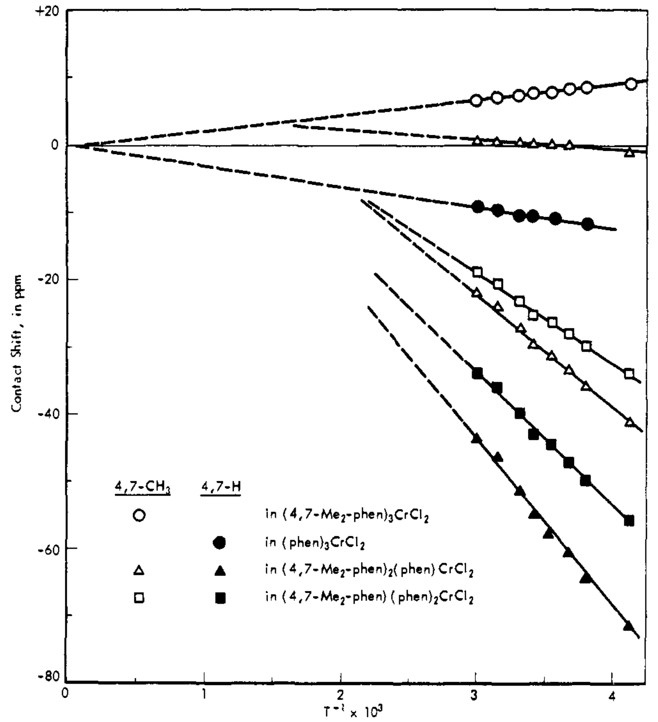

Figure 1. Temperature dependence of 4,7-CH_3 and 4,7-H shifts in mixed ligand complexes of (4,7-Me_2phen)$_3$CrCl$_2$ and (phen)$_3$CrCl$_2$ in d_4-methanol.

the only solvent used. All spectra were recorded on a Varian HR-100 spectrometer modified to operate with variable modulating frequency. The shifts were calibrated by the conventional side-band technique, using TMS as internal calibrant. The spectra of all complexes were recorded over a temperature range *ca.* +60 to −35°, using a Varian V-4343 temperature control unit which was precalibrated with methanol and ethylene glycol. The exact upper temperature was determined by the appearance of line broadening arising from bulk ligand exchange or intramolecular racemization, while the low temperature limit was determined by lack of resolution due to excessive line widths.

All shifts are reported in ppm, referenced against the appropriate ligand in the diamagnetic tris ferrous chelate.

Extended Hückel calculations were carried out on phen and bipy to obtain the π eigenvectors and associated spin densities, using a method described by Schachtschneider, *et al.*[12] Hückel calculations of the effect of the charge on nitrogen on the orbital energies were carried out using parameters described previously.[2b]

Results and Discussion

Typical plots of contact shifts *vs.* T^{-1} for 4,7-H (4,4′-H) and 4,7-CH_3 peaks are illustrated in Figures 1–3. In each case, very large deviations from Curie behavior are observed for all positions whose shifts differ significantly between the m.l. and p.t. chelates, suggesting that this temperature dependence must be related to those shift changes and also probably to the spectrochemical ordering of the ligands.[2a] For these m.l. complexes, typical intercepts at $T^{-1} = 0$ for the strongly shifted resonances are ~30 ppm or 3 KHz at 100 MHz. Such deviations are an order of magnitude larger than those usually observed where questions of proper diamagnetic referencing or temperature dependent solvent–solute interactions may be raised.[9] The 4,7 shifts for the p.t. chelates follow Curie behavior[13,14] quite accurately, as shown in Figures 1–3.

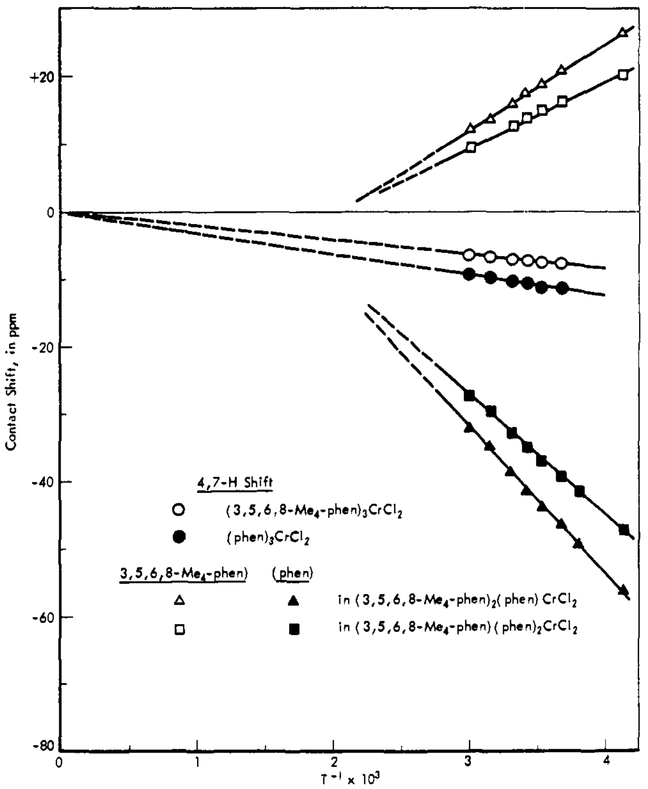

Figure 2. Temperature dependence of 4,7-H shifts in mixed ligand complexes of (3,5,6,8-Me_4phen)$_3$CrCl$_2$ and (phen)$_3$CrCl$_2$ in d_4-methanol.

Any non-Curie behavior for the spin magnetization in the m.l. chelates can be discounted by the fact that the solution susceptibility[15] of a composite solution is the volume averaged susceptibility of the two p.t. chelates, and this susceptibility followed the Curie law within experimental error. Furthermore, any non-Curie behavior for the spin magnetization on the metal would necessarily affect all ligand *contact* shifts in the same manner.

We have previously shown,[4,5] however, that non-Curie behavior can be expected for such mixed ligand chelates resulting from the lifting of the orbitally degenerate E ground state; this state corresponds to the strong field configuration $(e)^3(a_2)$ for the p.t. chelate of D_3 symmetry. On forming m.l. chelates, $E(D_3) \rightarrow A,B(C_2)$, which correspond to the configurations $(d_1)^2(d_2)(d_3)$ and $(d_1)(d_2)^2(d_3)$, respectively;[16] the C_2 symmetry-adapted basis functions contributing to the MO's in question are *b:* $d_1 = 1/\sqrt{2}(d_{xz} - d_{yz})$, $\phi_1 = 1/\sqrt{2}(\phi_B - \phi_C)$, $\psi_2 = 1/\sqrt{6}(2\psi_A$

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

(13) Deviation from Curie behavior for the 4,7 position in the p.t. chelates was found only for 4,7-CH_2 in (4,7-Et_2phen)$_3$CrCl$_2$, presumably due to the restricted rotation (ref 9), which would change the average hyperfine coupling constant with temperature E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 37, 1326 (1962). All other 4,7 or 4,4′ peaks followed the Curie law accurately.

(14) The other positions also exhibit deviations from Curie behavior, but the extent of this deviation is considerably smaller. Though the temperature dependence of the 3,5,6,8 peaks in the p.t. and m.l. chelates differ slightly, the problem encountered in referencing these small shifts to the proper diamagnetic position precludes any further analysis. The fact that the 5,6-H peak in the p.t. chelates follows the Curie law exactly while deviations from the $1/T$ behavior are observed for the m.l. chelates indicates that the prominent effect noted for the 4,7 resonances is also operative at the other positions but to a much smaller extent.

(15) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(16) These two states, $(d_1{}^2d_2d_3)$ and $(d_1d_2{}^2d_3)$, are actually mixed slightly by spin-orbit coupling, but the effect has been shown [W. C. Lin and L. E. Orgel, *Mol. Phys.*, 7, 131 (1963)] to be small, as also discussed previously (ref 5). Neglect of this mixing does not affect the qualitative conclusions reached here.

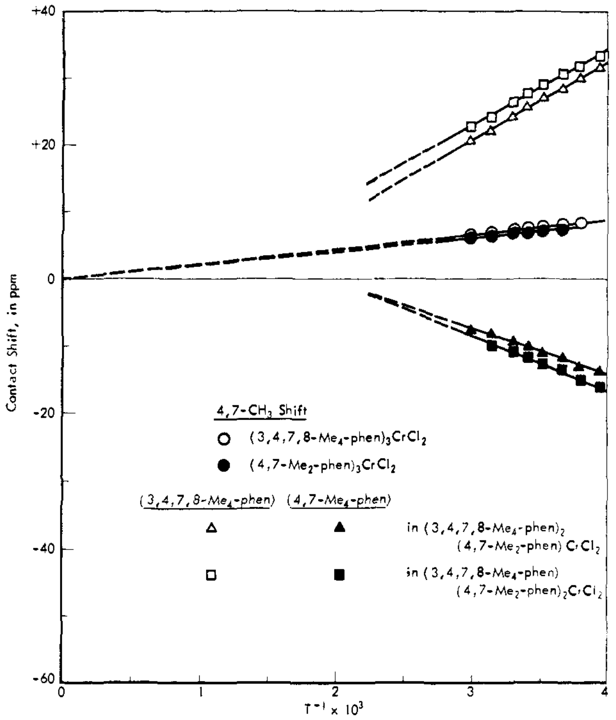

Figure 3. Temperature dependence of 4,7-CH shifts in mixed ligand complexes of $(3,4,7,8\text{-Me}_4\text{phen})_3\text{CrCl}_2$ and $(4,7\text{-Me}_2\text{phen})_3\text{CrCl}_2$ in d_4-methanol.

$- \psi_B - \psi_C$); 1*a:* $d_2 = 1/\sqrt{6}(2d_{xy} - d_{xz} - d_{yz})$, $\phi_2 = 1/\sqrt{6}(2\phi_A - \phi_B - \phi_C)$, $\psi_1 = 1/\sqrt{2}(\psi_B - \psi_C)$; and 2*a:* $d_3 = 1/\sqrt{3}(d_{xy} + d_{xz} + d_{yz})$, $\phi_3 = 1/\sqrt{3}(\phi_A + \phi_B + \phi_C)$.[17,18] ϕ and ψ refer to the ligand π MO's, characterized[6] by whether they are symmetric (ϕ) or antisymmetric (ψ) upon rotation about the isolated ligand C_2 axis. Thus, if the orbital ground state for a m.l. chelate is B, d_1 will be singly occupied,[16] so that if the ligand π MO receiving the spin density is of type ϕ, ligand A is symmetry forbidden from interacting with d_2, while ligands B and C would receive 50% more spin density than in the p.t. chelate, assuming no changes in covalency. If the splitting between the A and B orbital states was small enough, raising the temperature equalized the d_1 and d_2 spin populations (so that the spin delocalization resembles that of the p.t. chelate, where d, d_2 are degenerate), while lowering the temperature will produce an increase in unpaired spin density in ligands B and C and a decrease in ligand A. d_3 is singly occupied in both the A and B states, so that the spin delocalization involving covalency with this d orbital will be identical in the A and B states of the m.l. chelates and in the E state for the p.t. chelate. Thus, the temperature dependent population of the two orbital states will produce non-Curie behavior even if both states exhibited Curie behavior. A similar non-Curie behavior is predicted for the A ground state, providing the ligand interaction is with the π MO is of type ψ.

However, it is obvious that while such spin-delocalization mechanisms into one ligand π MO are capable of explaining non-Curie behavior, they can only explain[5] changes in shift *magnitudes*, and do not directly lend themselves towards understanding changes in both *magnitudes and signs* of contact shifts, such as observed[2a] in the present complexes, *i.e.*, the change in shift direction observed for the upfield $4,7\text{-CH}_3$ of $(4,7\text{-Me}_2\text{phen})_2(\text{phen})\text{CrCl}_2$ in Figure 1. Furthermore, since all ligand π MO's of a given type (ϕ or ψ) affect the relative extends of spin delocalization into the two nonequivalent ligands in the same way, delocalization into two or more ligand MO's of the *same type* is also incapable of accounting for changes in sign. On the other hand, we will now demonstrate that if, of the two delocalization mechanisms, one involves a ϕ type MO and the other a ψ type MO, the present non-Curie behavior can be qualitatively accounted[19] for in a satisfactory manner.

In the forthcoming discussion we will assume that the metal–ligand π covalency for any given ligand is essentially unaltered on forming the m.l. chelate by methyl substituting one or two of the ligands in a tris chelate. This can be considered reasonable since simple methyl substitution is unlikely to produce covalency changes of a magnitude comparable to the dramatic contact shift changes. In particular, covalency changes could not by themselves account for any non-Curie behavior.[20] Also, the m.l. chelates with metal ions which do not possess[3,4] this E orbital ground state [Fe(III) and Ni(II)] do not exhibit[21] shifts which differ significantly from the p.t. chelates, as also found[3,4] for the complexes with unsymmetrical ligands. The tendency of the shifts of the m.l. chelates of $4,7\text{-Me}_2$-phen and $4,4'\text{-Me}_2$bipy to converge[5] to those observed in the p.t. chelates as the temperature is raised suggests that covalency changes are relatively unimportant and indicates that the shift changes arise primarily from the different symmetry properties of the spin containing d orbitals in the A and B orbital states.

Determination of Orbital Ground States. We know that of the two spin-delocalization mechanisms operative in these complexes,[2a] one exhibits negative $C_{4,7}$ spin density while the other displays positive $C_{4,7}$ spin density. We will *assume* at this time that the ligand π MO with the *negative* $C_{4,7}$ spin density is of type ϕ, so that the MO with the positive $C_{4,7}$ spin density must be of type ψ. Justification for this choice will be given later, and the consequences of reversing the assignment will be discussed. The ability of two such delocalization mechanisms to account for changes in both magnitudes and *signs* of spin densities will be demonstrated for the m.l. chelate MLL'_2. If this complex possesses the B ground state, for example, d_1 will contain the unpaired electron, which can be delocalized only into $(1/\sqrt{2})(\phi_B - \phi_C)$ and $(1/\sqrt{6})(2\psi_A - \psi_B - \psi_C)$. (Since d_3 is singly occupied in all states of interest, it will not be

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(17) The 1a and 2a orbitals are energetically well separated, as indicated by the very large trigonal splitting [ref 2, 4, and P. M. Lutz, G. J. Long, and W. A. Baker, Jr., *Inorg. Chem.*, 8, 2529 (1969)] and are, therefore, assumed not to interact significantly. Thus, 2a remains singly occupied whether the A or B orbital state is lower in energy (eliminating significant contributions from terms such as $d_1d_2d_3{}^2$) and can be ignored in our analysis.

(18) For the m.l. chelates $\text{ML}_2\text{L}'$ and MLL'_2, the unique ligand, L′ and L, respectively, is designated as ligand A, while the two equivalent ligands are designated ligands B and C in the basis functions and in coordinate system in ref 4.

(19) It is possible that other minor spin delocalization mechanisms are also operative; however, they do not dominate the observed shifts and may, therefore, be neglected in our qualitative analysis of the temperature dependence on the shifts.

(20) The direct change in sign of one of the $4,7\text{-CH}_3$ peaks in $(4,7\text{-Me}_2\text{phen})_2(\text{phen})\text{CrCl}_2$ (Figure 2) cannot be rationalized by simple changes in metal–ligand covalency.

(21) G. N. La Mar, unpublished observations.

considered further.) Compared to the p.t. chelate, where d_1 and d_2 are degenerate, delocalization of *unpaired* spin into the ϕ MO will be *greater* in ligand B and C and *less* in ligand A, while spin delocalization into the ψ MO will *simultaneously decrease* into ligands B and C and *increase* into ligand A. Therefore, if the small spin density observed for the 4,7 position in the p.t. chelates results from the near cancellation of sizable positive and negative spin density contributions in ligand π MO's of different symmetry, decreasing the symmetry to C_2 has the effect (for the B ground state) of making the ϕ delocalization mechanism more prominent in ligands B and C (negative $C_{4,7}$ spin density) and increasing the relative contribution of the ψ delocalization mechanism in ligand A so that it also can become dominant (positive $C_{4,7}$ spin density). Whether the negative spin density in ligand A just decreases or actually changes sign and becomes positive depends on the relative magnitudes of the positive and negative spin density contributions and the splitting between the A and B states. The A ground state can similarly account for sign changes for one type of ligand. The exact temperature dependence predicted by a given ground state is determined by whether the 4,7 position is substituted or not.

If in the m.l. chelate ML_2L', L′ but not L possesses 4,7-CH_3 substituents, the B ground state with the spin in d_1 predicts that the 4,7-H shifts in L will be downfield and increasing faster than Curie behavior, while the 4,7-CH_3 shift in L′ will become less positive, perhaps change sign, and then increase in the negative direction, again faster than Curie behavior. The A ground state, with the spin in d_2, predicts only upfield 4,7-CH_3, and decreasing negative or even positive 4,7-H shifts. Inspection of spectra typical of these chelates, as in Figure 1, reveals that only the former temperature dependence is observed so that ML_2L', where L′ but not L is 4,7-methyl substituted, always possesses the B orbital ground state.

For the other m.l. chelate, MLL'_2, where only L′ is 4,7-CH_3 substituted, the A ground state with the spin in d_2 predicts downfield 4,7-H shifts which increase faster than Curie behavior and either decreasing upfield or downfield shifts for 4,7-CH_3 in L′. The B ground state reverses the directions of the 4,7-H and 4,7-CH_3 shifts from those predicted for the B state. The data in Figure 1 are consistent only with the A orbital ground state for MLL'_2.

When neither ligand is substituted at the 4,7 position, such as in the 3,5,6,8-Me_4phen/phen m.l. chelates, the B ground state for (3,5,6,8-Me_4phen)(phen)$_2$$CrCl_2$ correctly predicts that the 4,7-H shift in 3,5,6,8-Me_4phen is either negative and increasing slower than Curie behavior or positive and increasing faster than Curie behavior (the latter is observed), while the 4,7-H shift in phen remains negative and increases faster than Curie behavior, as illustrated in Figure 2. The A ground state would incorrectly reverse the shift directions for the two ligands. For the other m.l. chelate, (3,5,6,8-Me_4phen)$_2$(phen)$CrCl_2$, the A ground state correctly predicts the downfield 4,7-H shift for phen and the upfield shift for 4,7-H each of which increase faster than Curie behavior. An identical analysis of the other m.l. chelates permits a similar determination of the orbital ground state.

For the complexes where both ligands possess 4,7-CH_3 substituents, only the B ground state is consistent with the temperature dependence of (3,4,7,8-Me_4phen)(4,7-Me_2phen)$_2$$CrCl_2$, while only the A ground state is in accord with the deviations from Curie behavior noted for (3,4,7,8-Me_4phen)$_2$(4,7-Me_2phen)$CrCl_2$, illustrated in Figure 3.

Closer analysis of all the orbital ground states determined in this manner for all m.l. chelates of phen and its methyl-substituted isomers reveals that the m.l. complexes *ML_2L' (MLL'_2) possess the B (A) orbital ground state if L′ is above L in the spectrochemical series*[2a] and that for any pair of m.l. chelates ML_2L', MLL'_2, one possesses the A ground state, while the other exhibits the B ground state. The different ground states for the pair of m.l. chelates have been shown[5] to be expected from simple MO considerations. Thus the relative positions of any two ligands in the spectrochemical series determines the ground state, which indicates very strongly that the spectrochemical series is some index of the "strength" of a given ligand.[22] The closer the spacing between the A and B states, the more equal their populations so that the shifts should approach those of the p.t. chelate, where A and B are degenerate; alternatively, the farther apart the A and B states are, the more the spin density distribution in a given ligand resembles that of the pure A or B state.[23] Thus based on the assumption of no actual covalency changes, this leads us to the conclusion that our spectrochemical series is an index of not only the sign of the A,B splitting but also its magnitude. However, slight covalency changes do occur, so that both effects are operative. A more detailed analysis of the temperative dependence, which could yield the magnitude of the C_2 distortion, would require a more detailed knowledge of the splitting between the A and E term in the p.t. chelates, as well as a consideration of spin-orbit coupling. However, as indicated previously, our simple model[5,11,16] is sufficient to yield the qualitative information on the *relative* energies of the A and B orbital states in the m.l. chelates.

The above assignments of the orbital ground states were based on our assumption that the negative $C_{4,7}$ spin density arose through a delocalization mechanism involving ϕ type ligand MO's and that the positive $C_{4,7}$ spin density then must originate in a delocalization mechanism into a ψ type MO. It is easily shown that if this assignment is reversed, *i.e.*, the ϕ MO exhibits positive $C_{4,7}$ spin density and the ψ MO negative $C_{4,7}$ spin denisty, the only consequence will be that the A and B ground state assignments will be interchanged for each m.l. chelate; the relationship to the spectrochemical ordering will remain in that the relative positions of two ligands in the series always determine the ground state and separation from the other component of the E state in the p.t. chelates.

As demonstrated in part I, the ligands phen and bipy (or 4,7-Me_2phen and 4,4′-Me_2bipy) are interchangeable in any m.l. chelate without significantly affecting the shifts of the other ligand, so that they are essentially indistinguishable in our spectrochemical series. In addition, their temperature dependences

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[22] C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, Chapter 10.

[23] This is strictly true only if spin-orbit coupling effects are totally neglected (ref 16).

are very similar, which indicates that the same delocalization mechanisms must be operative, namely, positive spin density to $C_{4,7}$ or $C_{4,4'}$ in a ϕ type MO. If in one ligand (bipy) a ϕ MO and in the other ligand (phen) a ψ MO were involved, then interchanging phen and bipy should produce[5] spin densities of opposite sign for $C_{4,7}$ and $C_{4,4'}$ and a temperature dependence inconsistent with the experimental data.

Ligand π-Molecular Orbitals. Molecular orbital calculations for the two ligands phen and bipy were performed[12] for the purpose of determining if similar MO's are available for bonding in both ligands as required by the nature of the deviations from Curie behavior for analogous phen and bipy m.l. chelates. Since the interpretation of our spectrochemical series[24] in part III requires knowledge of both the σ and π MO energies, extended Hückel spin densities[12] and energies were obtained, which are given in Table I for those phen and bipy π MO's with energies anticipated to be favorable for interaction with metal d orbitals. We had previously reported[2] the Hückel spin densities for these two ligands which were corrected for correlation by the method of McLachlan[25] so that negative spin densitives could be predicted. In general, excellent agreement between the Hückel and extended Hückel eigenvectors is observed, such that similar conclusions are reached from either method. Analysis of the charge transfer bands of a variety of divalent and trivalent metal chelates has shown[26-28] that the most important ligand π MO's involved in bonding are the highest filled and lowest vacant π MO's. The dominant M → L bands in the divalent ions and the predominance of L → M bands in the trivalent ions has placed[27,28] the energies of the d orbitals between those of the highest filled and lowest vacant π MO's.

Table I. Extended Hückel Spin Densities for phen and bipy[a]

Ligand	Position[b]	$\pi_6(\phi)$	$\pi_7(\psi)$	$\pi_8{}^*(\phi)$	$\pi_9{}^*(\psi)$
phen	N_1	0.194	0.073	0.090	0.238
	C_2	0.089	0.102	0.117	0.021
	C_3	0.118	0.003	0.001	0.068
	C_4	0.069	0.112	0.123	0.094
	C_5	0.007	0.165	0.130	0.002
	Energy, eV	−10.942	−10.737	−8.073	−8.071
		$\pi_5(\psi)$	$\pi_6(\phi)$	$\pi_7{}^*(\psi)$	$\pi_8{}^*(\phi)$
bipy	N_1	0.092	0.157	0.225	0.155
	C_2	0.157	0.005	0.006	0.122
	C_3	0.007	0.134	0.088	0.015
	C_4	0.099	0.028	0.065	0.116
	C_5	0.141	0.062	0.024	0.096
	Energy, eV	−11.476	−10.915	−8.157	−7.372

[a] Taken from calculations described in part III (ref 24). [b] Positions according to structural formulas I and II in part I (ref 2a).

For bipy, it was concluded[27,28] that only two MO's have energies favorable for participation in significant covalency, the highest filled MO, π_6, of type ϕ, and the lowest vacant MO, $\pi_7{}^*$, which is of type ψ. The present extended Hückel spin densities agree very well with the McLachlan–Hückel calculations,[2b] where it was shown that the small $C_{4,7}$ spin density in π_6 becomes negative when correlation is introduced; the $C_{4,7}$ spin density in $\pi_7{}^*$ is positive. The MO's above $\pi_7{}^*$ and below π_6 are well separated[2b] in energy and unlikely to interact with the metal significantly. Thus, bipy appears to possess two π MO's of different symmetry and $C_{4,7}$ spin densities of opposite signs which are capable of accounting for the two postulated spin delocalization mechanisms required to interpret the non-Curie temperature dependence.

Phen, on the other hand, has been shown to be more complicated in that, though the highest filled, π_7, and the lowest vacant, $\pi_8{}^*$, MO's have energies very similar to those of bipy, two additional MO's, one below the highest filled, π_6, and one above the lowest vacant, $\pi_9{}^*$, are very close and can be expected to also participate[2b,27,28] in metal–ligand bonding. Of these four π MO's, only π_6 exhibits[29] a small $C_{4,7}$ spin density, which becomes negative upon the introduction of correlation, and is of type ϕ. Even though π_7 may be energetically more favorably placed relative to the d orbitals, the interaction with π_6 would be considerably larger than with π_7, (compare N coefficients in Table I), which could well account for π_6 receiving more spin density than π_7. The dominant participation of π_6 rather than the expected π_7 in L → M transfer has also been noted in the related $(phen)_3Fe^{3+}$ chelates.[27]

The two vacant MO's in phen, $\pi_8{}^*$ and $\pi_9{}^*$, are nearly degenerate. Calculations show that the increase in positive charge on the nitrogens resulting from coordination[28] actually depresses $\pi_9{}^*$ below $\pi_8{}^*$, making the latter the lowest vacant MO in the complex. Even if $\pi_8{}^*$ and $\pi_9{}^*$ are sufficiently close in energy so that both could interact equally with the d orbitals, the latter MO, $\pi_9{}^*$, would receive considerably more spin density by virtue of its more favorable overlap (N coefficients in Table I). $\pi_9{}^*$ is of type ψ and exhibits positive $C_{4,7}$ spin density. The dominant participation of $\pi_9{}^*$ instead of $\pi_8{}^*$ in M → L charge transfer has been noted[27] for the related $(phen)_3Fe^{2+}$ chelates.

Thus for both phen and bipy ligands, we find that the π MO's expected to be prominently involved in metal–ligand covalency are a filled MO of type ϕ, which exhibits negative $C_{4,7}$ spin density, and a vacant ψ type MO which displays positive $C_{4,7}$ spin density. Other ligand π MO's may participate in M–L covalency, but their contributions[19] to spin delocalization must be secondary to the two important MO's.

We therefore conclude that the spectrochemical series given in eq 1 can be interpreted in terms of the nature of the orbital ground state for a given m.l. chelate. The lowering of the chelate symmetry thereby permits the "factoring" of the two competing spin-delocalization mechanism involving π MO's of different symmetry.

The two spin delocalization mechanisms are concluded to arise from simultaneous L → M π charge transfer from a filled ligand MO, and M → L π charge transfer[30] into a low-lying vacant π^* MO. The pres-

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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$_2$phen < 3,5,6,8-Me$_4$phen < 4,7-Et$_2$phen ~ 4,7-Me$_2$phen < 3,4,7,8-Me$_4$phen, which has the property of determining the orbital ground-state symmetry of any mixed ligand complex, such that if L is above L′, ML$_2$L′ 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$_2$L′, 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]

$$\text{phen} < \text{5,6-Me}_2\text{phen} < \text{3,5,6,8-Me}_4\text{phen} < \text{4,7-Et}_2\text{phen} \sim \text{4,7-Me}_2\text{phen} < \text{3,4,7,8-Me}_4\text{phen} \quad (1)$$

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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