initial complex. The reaction of Mo$_2$O$_4$(Cys)$_2^{2-}$ with cysteine, however, is an interesting situation in that the structural change is catalyzed by a molecule that is also a ligand in the complex. Cleavage of the dioxo structure in molybdenum(V) complexes produces monooxo-bridged and monomeric species that appear to be more reactive than the original material. In the case of monooxo-bridged molybdenum(V)-thioglycolate complexes, reduction by sulfhydryl compounds is found to occur.[6] For Mo-EDTA complexes the following sequence of reactivity and ease of reducibility is found:[29] monomeric > monooxo-bridged > dioxo-bridged.

Registry No. Na$_2$Mo$_2$O$_4$(cysteine)$_2$·5H$_2$O, 22723-22-4; cysteine, 52-90-4.

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Proton Nuclear Magnetic Resonance Studies of the Electronic Structure of Outer-Sphere Reducing Agents of Chromium(II). IV. Solvation of Tris(α-diimine) Chelates

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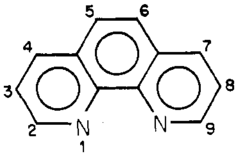
The anomalous proton nmr line broadening of the alkyl substituents in tris(*o*-phenanthrolines) of chromium(II) is interpreted in terms of a specific solvent–solute interaction which is characteristic of such complexes with reducing metal ions. The ligand line width study reveals that this interaction is highly specific to the 4,7 positions and is most important in aqueous solution. This solvent–solute interaction is postulated to involve some form of hydrogen bonding of the solvent to pockets of electron density on the ligand which result from extensive M→L π back-bonding. Analysis of the solvent line width in mixed aqueous–methanolic solutions reveals a distinct preference for water molecules penetrating within the "ionic radius" in the cationic chelates of the reducing chromium(II) ion but not for the more redox-stable nickel(II) ion.

Introduction

We have been interested in using proton nmr for investigating paramagnetic complexes of low-valent metal ions[2-4] inasmuch as this technique[5] is especially well suited for elucidating the anticipated important contributions to the electronic structure from metal-to-ligand π charge transfer.[6] Such π back-bonding has been considered to be characteristic[6] of a particularly interesting class of complexes of low-valent metal ions, the outer-sphere reducing agents.[7] The particular reducing agents of interest have been the tris chelates[2,3] of chromium(II) with substituted *o*-phenanthrolines, I (phen), and α,α′-bipyridines, II (bipy), and their mixed-ligand chelates,[8] whose redox properties,[9] magnetic susceptibilities,[10] electronic spectra,[11] and bonding[2,3,8,12-15] have been the subject of recent interest.



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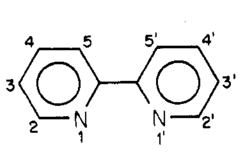

II

Analysis of the isotropic shifts for these low-spin (d^4, $S = 1$) chelates has shown[2,12] that they are primarily contact in origin, resulting from both L→M and M→L π charge transfer,[8,12,13] the latter mechanism imparting the facile outer-sphere reducing properties of these chelates. The detailed description of the spin-transfer mechanism was achieved[8,12,13] only after investigating the proton nmr spectra of mixed-ligand chelates, for which it was possible not only to characterize the bonding and assign the orbital ground state of each complex[8,12-13] but also to determine the relative π-acceptor abilities[12,13] of a variety of substituted diimines. It was demonstrated[8] that the M→L delocalized π spin density was centered predominantly at the 4,7 positions of phen (or 4,4′ positions in bipy), which were postulated[12,13]

[1] (a) University of California; Fellow of the Alfred P. Sloan Foundation, 1972–1974. (b) Harvey Mudd College.

[2] (a) G. N. La Mar and G. R. Van Hecke, *J. Amer. Chem. Soc.*, 91, 3442 (1969); (b) G. N. La Mar and G. R. Van Hecke, *Inorg. Chem.*, 9, 1546 (1970).

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

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to be the "active sites" during electron transfer. Such an asymmetric distribution of the "reducing" electron was shown[13] to be consistent with the recently reported[9] stereoselective outer-sphere reduction of $(phen)_3Co^{3+}$ by $(phen)_3Cr^{2+}$.

Although the prominent electronic, magnetic, and chemical properties of these reducing chelates could be interpreted consistently[13] in terms of the isotropic shifts reflecting the distribution of the metal spins in an isolated chromophore, it was noted earlier[15] that some unusual solvent–chelate interactions were also operative. Since the possible role of solvent-mediated electron transfer[16] has been raised in the case of a redox reaction involving the related tris(diimine) chelates of iron(II), we will address ourselves here to the role played by the solvent in either the electronic structure or chemical (redox) properties of the Cr(II) chelates. We present evidence here for a specific solvent–complex interaction which, in addition to stabilizing the π back-bonding, may play an important part in the mechanism of outer-sphere electron transfer in some inorganic redox reactions (*vide infra*).

The present investigation is based largely on our previously reported observations[15] of anomalously broadened methyl resonances for 4,7-dimethyl-substituted chelates. Although these methyl line width effects were initially suggested[15] to arise from intramolecular steric interactions, we have recently presented preliminary evidence[17] that these relaxation effects result from some form of intermolecular interaction which in turn depends on the unique reducing properties of Cr(II). We present here further data to substantiate this solvent–complex interaction and interpret this specific solvation in terms of the bonding in chelates with low-valent metal ions.

We have shown[2,15] previously that the dominant proton relaxation mechanism in these chelates is electron–nuclear dipolar relaxation, such that the line width, δ, is given[18] by

$$\pi\delta = T_{2\mathrm{H}}^{-1} = Br^{-6}\tau_c \tag{1}$$

where $B = 4\gamma_{\mathrm{H}}^2 g^2 \beta^2 S(S+1)/3$, r is the proton–metal distance, τ_c is the dipolar correlation time, and the other symbols have their usual meanings. For these Cr(II) chelates $\tau_c = T_{1e}$, the electron spin relaxation time.[2a] The geometry of these tris chelates and eq 1 require[2,15] a line width trend 2,9 H $>$ 3,8 H $\lessgtr$ 4,7 H $>$ 5,6 H, with a methyl signal predicted to be narrower than the aromatic proton at all but the 2,9 positions. Since τ_c can generally be expressed[15,19] as

$$\tau_c = \tau_c^{\,0} \exp(V/RT) \tag{2}$$

where V is the activation energy for the molecular motion giving rise to τ_c (T_{1e}), the combination of eq 1 and 2 predicts a series of parallel lines for nonequivalent protons in the plot of log δ *vs.* the reciprocal temperature. Such lines were observed[15] in aqueous solution with the unsubstituted chelates.

The anomalously broad 4,7 CH_3 peaks, however, exhibited[15] much steeper slopes than the aromatic protons in the log δ *vs.* T^{-1} plot, indicating that a different relaxation mechanism with a much higher activation energy was operative. The correlation time, τ^*, for the methyl proton relaxation was demonstrated to exhibit the magnetic field dependence expected[20] from the modulation of the contact shift. Such a correlation time was shown to be consistent with methyl rotation, since the coupling constant, A, and hence the contact shift depend on the angle, ϕ, between the HCC plane and the aromatic carbon p_z axis, according[21] to

$$A_{\mathrm{CH}_3} = B_2\rho \cos^2 \phi \tag{3}$$

where ρ is the carbon p_z π spin density and B_2 is a constant, ~120 MHz.

Although molecular models have indicated[15,22] a possible steric contribution to the barrier to methyl rotation, the observation[15] of hindered rotation in aqueous but not in methanolic solution suggested[17] an unspecified intermolecular contribution to the barrier. A clearer description of the intermolecular origin of the methyl line width effects can be achieved upon considering the influence on the line widths of different metal ions, other alkyl substituents, and variable solvent composition and the effect of the paramagnetic complex on proton relaxation of the solvent.

Experimental Section

The preparation and characterization of the chromous chelates used in this study, $(4,7\text{-}Et_2phen)_3CrCl_2 \cdot 2H_2O$, $(3,4,7,8\text{-}Me_4phen)_3CrCl_2 \cdot H_2O$, and $(4,7\text{-}Me_2phen)_3CrCl_2 \cdot 2H_2O$, have been reported previously.[2,8] All manipulations of the chelates and solutions were performed in a Vacuum Atmospheres Corp. glove box to prevent oxidation. Solutions ~0.065 M in complex in D_2O (Bio-Rad) and methanol-d_4 (Diaprep) were sealed under nitrogen in 5-mm nmr tubes. The proton nmr spectra remained reproducible over a period of several months. This is in contrast to the report[11] that much more dilute solutions of such chromous chelates decompose appreciably in a period of only minutes.

The complexes of Co(II) and Ni(II), also reported previously,[2,3] were handled in the open atmosphere. The Fe(III) chelates[2,23] were prepared from the Fe(II) species by oxidation with chlorine. The nmr spectra were identical with those presented earlier.[2,23] In the solution of mixed solvents, ~5 mol % undeuterated solvent was added before preparing the solvent mixtures in order to yield a strong hydroxyl proton signal which experienced negligible interference from the ligand resonances of the dissolved complexes.

Proton nmr spectra of the chelates were recorded on a Varian HR-100 spectrometer, modified to operate with variable-frequency modulation using a PAR HR-8 lock-in amplifier. Temperature calibration was effected by using the Varian V-4343 temperature-control unit which was precalibrated with methanol and ethylene glycol. Isotropic shifts are referenced against the analogous diamagnetic Fe(II) chelate.

Line widths for the chelate resonances, defined as the full peak width at half-height and recorded at radiofrequency power levels well below saturation, are reported in hertz at 100 MHz. The solvent hydroxyl proton line widths were similarly recorded on a Varian A-60 spectrometer and are given in hertz at 60 MHz.

Results and Discussion

Although it will be shown that the anomalous methyl line widths originate in some intermolecular solvent–complex interaction, the most reasonable physical interpretation of the dynamic process leading to the unusual methyl proton relaxation is still in terms of the modulation of the contact shift by methyl rotation.[15] The lines of evidence which support this hypothesis are threefold. First, the magnetic field dependence and temperature dependence of the methyl line widths predicted[20] for such a mechanism have been experimentally verified.[15] Although the demonstrated modulation of the 4,7 CH_3 contact shift does not necessarily have

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[16] J. G. F. Littler and R. J. P. Williams, *J. Chem. Soc.*, 6368 (1965).

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[22] The "CPK Atomic Models," Ealing Corp., Cambridge, Mass., were employed.

[23] D. W. Larsen and A. C. Wahl, *J. Chem. Phys.*, **41**, 908 (1964).

to originate in methyl rotation, the lack of any good alternative suggests that this is the most reasonable model. Second, the fact that the 3,8 CH_3 signal exhibits[15] this anomalous line width effect in $(3,4,7,8\text{-}Me_4phen)_3CrCl_2$, where the 3,8 and 4,7 methyl groups interact sterically, but not at all in $(3,5,6,8\text{-}Me_4phen)_3CrCl_2$, strongly suggests that the 3,8 methyl groups experience the hindered rotation only through the steric interaction with the severely hindered 4,7 methyl groups in the former chelate. These latter data provide the strongest evidence that the rotational barrier, or line width effect, originates at the 4,7 position, whatever its physical origin. Last, the inability to observe 4,7 H line width effects in aqueous solutions of the complexes without substituents at the 4,7 position, even though it is possible to show that water is interacting with that position, suggests that the angular dependence[21] of the contact shift for the methyl group serves as the unique probe.

A consistent and physically reasonable interpretation of the electronic origin of these methyl rotational barriers or line width effects can be obtained by considering the dependence of this phenomenon on the nature of the metal ion, the alkyl group, and the solvent.

Effect of Metal Ions. The only requirement[15] for the observation by nmr of the hindered methyl rotation is that there is spin density in the p_π orbital of $C_{4,7}$. Thus a number of related tris chelates with $4,7\text{-}Me_2phen$, specifically those of Ni(II), Co(II), and Fe(III), whose 4,7 H and 4,7 CH_3 reflect π spin density at $C_{4,7}$ either directly[2] or indirectly,[24] may be expected to exhibit similar 4,7 CH_3 line width effects if the barrier either is intramolecular in origin or reflects a solvent-chelate interaction which is characteristic of any chelated $4,7\text{-}Me_2phen$ ligand.

However, in spite of the apparent presence of p_π spin density at $C_{4,7}$, the narrower 4,7 CH_3 peak in comparison to the 4,7 H peak for all but Cr^{2+} (as predicted by simple dipolar relaxation), given in Table I for the complexes in aqueous solution, shows that the nature of the metal ion is important. The comparison is particularly dramatic for Cr(II) and Ni(II), where the π contact shifts are larger for the latter ion. The most distinguishing characteristic of the Cr(II) ion, in comparison to Co(II), Ni(II), and Fe(III), is that it is considerably more reducing. Hence the M-L bonding expected for reducing metal ions enhances the methyl rotational barrier, either directly or indirectly by facilitating the intermolecular solvent-complex interaction.

Effect of Alkyl Groups. Even though a purely intramolecular steric origin for the rotational barrier is unlikely in view of the solvent dependence, a comparison of the proton nmr spectrum of $(4,7\text{-}Et_2phen)_3CrCl_2$ in D_2O, illustrated in Figure 1, with that of $(4,7\text{-}Me_2phen)_3CrCl_2$[15] indicates that steric factors are probably negligible.[25] The 4,7 CH_2 resonance in the former chelate is broader than expected for dipolar relaxation, as was observed[15] for 4,7 CH_3 in the latter chelate. However, in the plot of log δ *vs.* T^{-1}, shown in Figure 2, the slope of the 4,7 CH_2 line width is considerably lower than for 4,7 CH_3.[15] The reduced rotational barrier for the ethyl relative to the methyl group is inconsistent with simple steric arguments, inasmuch as esr data[26] and molecular models[22] concur in predicting a larger steric barrier for the ethyl group. The absence of intramolecular steric effects therefore indicates that the barrier arises primarily due to solvent-complex interactions.

Table I. Isotropic Shifts and Line Widths for 4,7 H and 4,7 CH_3 in Tris(diimine) Chelates of Various Metals[a]

Complex	Isotropic shift[b]	Line width[c]
$(phen)_3CrCl_2$	−10.2	48
$(4,7\text{-}Me_2phen)_3CrCl_2$	(+6.84)	>1000
$(phen)_3NiCl_2$	−8.85	180
$(4,7\text{-}Me_2phen)_3NiCl_2$	(+12.3)	100
$(phen)_3CoCl_2$	−7.98	18
$(4,7\text{-}Me_2phen)_3CoCl_2$	(+3.55)	15
$(phen)_3FeCl_3$	−0.45	12
$(4,7\text{-}Me_2phen)_3FeCl_3$	(−13.75)	10

[a] At ~30° in D_2O solution. [b] Shifts in ppm at 100 MHz, referenced against diamagnetic Fe(II) chelate. [c] Line width in Hz at 100 MHz.

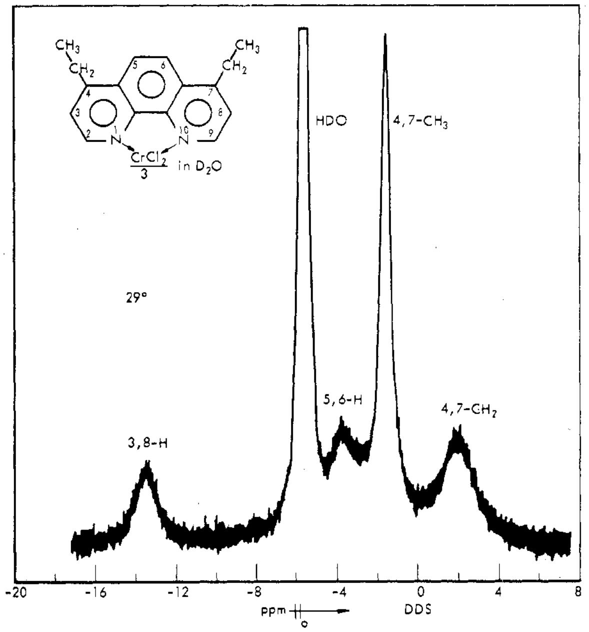

Figure 1. Proton nmr spectrum of $(4,7\text{-}Et_2phen)_3CrCl_2$ in D_2O (2,9 H peak omitted).

Effect of Solvent. The original observations[15] of these methyl line width effects in aqueous but not in methanolic solution suggested that the barrier is absent in methanol. Analysis of the line widths of $(3,4,7,8\text{-}Me_4phen)_3CrCl_2$ in CD_3OD, however, reveals that the barrier is present in both solvents, although considerably reduced in methanol. The proton nmr trace of $(3,4,7,8\text{-}Me_4phen)_3CrCl_2$ in CD_3OD, shown in Figure 3, exhibits broader 4,7 CH_3 than 3,8 CH_3 line widths, contrary to predictions of eq 1. The plot of log δ *vs.* T^{-1} for this complex, illustrated in Figure 4, reveals a higher slope for the 4,7 CH_3 line width, indicating[15] a contribution from another relaxation mechanism similar to that observed in D_2O solutions. Hence the line width effect, though present, is significantly attenuated in CD_3OD.

The effect of solvent composition on the shifts and line widths of $(4,7\text{-}Me_2phen)_3CrCl_2$ is illustrated in Figure 5. The effect on the shifts and the line width of the aromatic protons is small, while the change in the 4,7 CH_3 line width is very dramatic. The shape of the 4,7 CH_3 curve in Figure 5 suggests that the line width does not reflect the composition of the bulk solvent. However, since the dependence of the rotational barrier on the extent of solvent-complex interaction is not known, the shape of this curve cannot be

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

[25] The methyl line widths for the substituted chelates were found to be independent of the concentration of the chelate and insensitive to the presence of either excess chloride ions (from added NaCl) or excess ligand.

[26] M. D. Sevilla and G. Vincow, *J. Phys. Chem.*, 72, 3647 (1968).

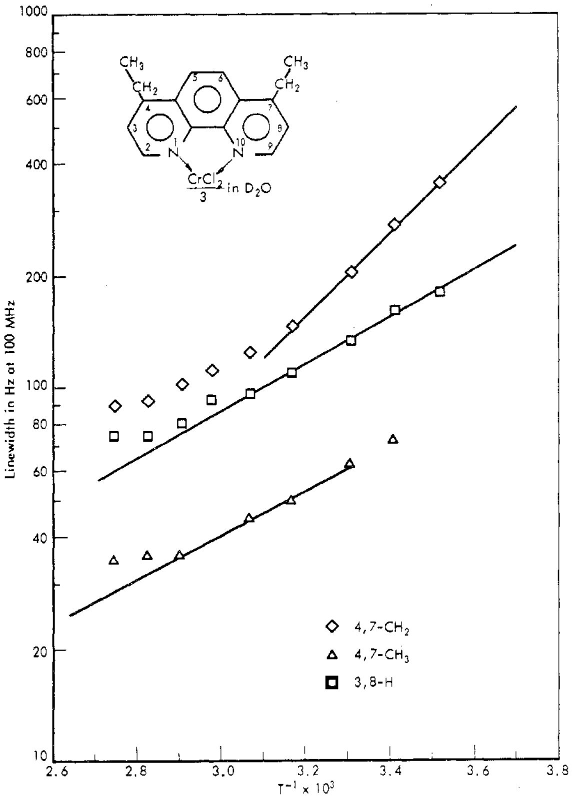

Figure 2. Proton line width dependence on temperature for (4,7-Et_2phen)$_3CrCl_2$ in D_2O.

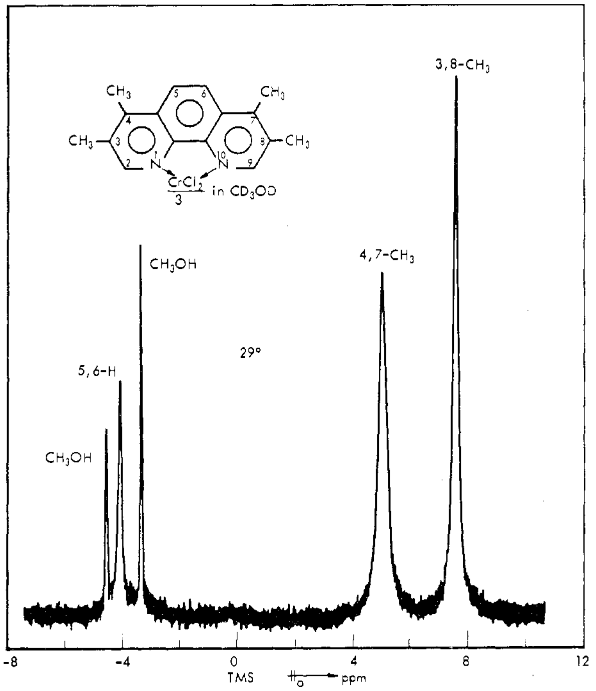

Figure 3. Proton nmr spectrum of (3,4,7,8-Me_4phen)$_3CrCl_2$ in CD_3OD (2,9 H peak omitted).

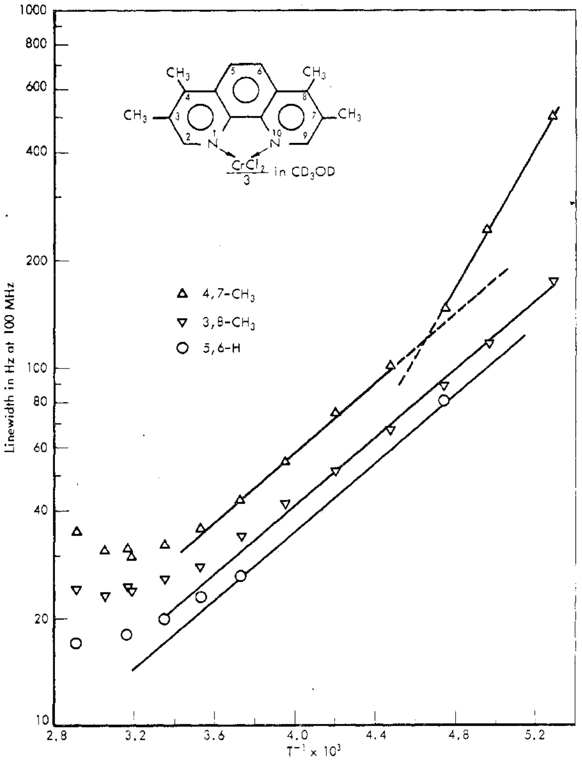

Figure 4. Proton line width dependence on temperature for (3,4,7,8-Me_4phen)$_3CrCl_2$ in CD_3OD.

interpreted in terms of the solvent preference in the vicinity of the 4,7 position in the complex.

The conclusions which can be reached at this stage, and which must be rationalized in terms of the electronic structure of these complexes, are that the methyl rotational barrier arises from solvent-solute interactions which are specific to the 4,7 positions, that the solvent interaction is stronger for D_2O than for CD_3OD and is facilitated by the bonding characteristic of reducing metal ions, and that the solvent-solute interaction is reduced by replacing a methyl by an ethyl group at the 4,7 position. It may be noted that these conclusions can be reached without specifically assuming that the line width effect reflects hindered rotation. Supporting evidence for a favored interaction with water can be derived from the solvent line widths.

Solvent Proton Line Widths. If the methyl line width effects for the 4,7 position are correctly interpreted as arising from a difference in the extent of solvent-solute interaction in water and methanol, it should be possible to find confirming evidence by considering the solvent resonance. Investigation of the position of the solvent peak positions shows that the methanol CH_3 shift is unaffected, while the residual OH peaks in both solvents are not significantly altered from the positions in related diamagnetic molecules. The small shifts[27] which are observed[2,3,8,12] cannot be interpreted in terms of paramagnetic interactions in view of the known variable effects of ionic species[28] on the OH resonance of such strongly hydrogen-bonded solvents. However, the small solvent shifts strongly argue against any direct coordination to the metal ion (*vide infra*). Hence we restrict our discussion to the observed line widths.

Bulk solvent proton line broadening for solutions of stable, coordinatively saturated paramagnetic complexes is determined by electron-proton dipolar relaxation[18] in the second coordination sphere,[29] SCS. Rapid exchange with bulk solvent averages the relaxation, such that the solvent line width, δ_s, increases over that of the pure solvent and is given by[18,29]

$$\pi\delta_s = Br^{-6}\tau_c f \tag{4}$$

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[27] The contact shifts in methanol and water were generally found to be the same.

[28] C. Deverell, *Progr. Nucl. Magn. Resonance Spectrosc.*, 4, 235 (1969).

[29] T. R. Stengle and C. H. Langford, *J. Phys. Chem.*, 69, 3299 (1965); S. Behrendt, C. H. Langford, and L. S. Frankel, *J. Amer. Chem. Soc.*, 91, 2236 (1969); L. S. Frankel, *J. Phys. Chem.*, 74, 1645 (1970).

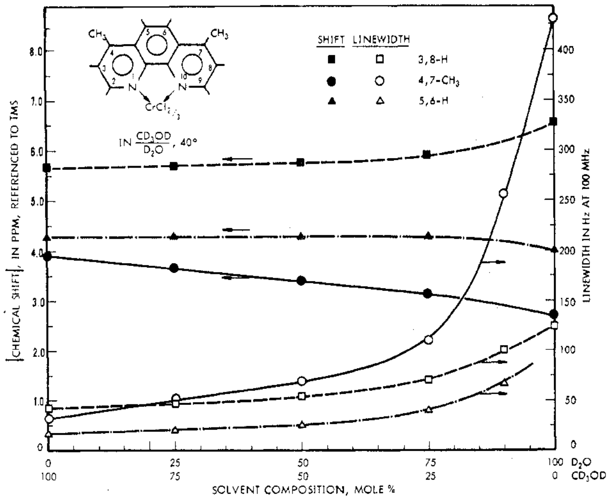

Figure 5. Effect of solvent composition on isotropic shifts and line width for (4,7-Me_2phen)$_3$CrCl_2 in mixed D_2O-CD_3OD solvents.

where f is the fraction of the solvent molecules accommodated in the SCS. For both water and methanol, the SCS for these cationic complexes is expected to consist of the solvent dipoles oriented with the negative end directed toward the metal, such that the OH protons in both solvents occupy comparable positions in the SCS. Hence, the relative proton line widths of the residual OH signals in methanol-d_4 and water-d_2 at equimolar concentrations of complex will be given by

$$\delta(\mathrm{M})/\delta(\mathrm{W}) = B_\mathrm{M} r_\mathrm{M}^{-6} \tau_\mathrm{M} f_\mathrm{M} / B_\mathrm{W} r_\mathrm{W}^{-6} \tau_\mathrm{W} f_\mathrm{W} \qquad (5)$$

where the subscripts refer to methanol, M, and water, W. $B_\mathrm{M} = B_\mathrm{W}$, since it depends only on the spin state of the chelate; $\tau_\mathrm{M}/\tau_\mathrm{W} \approx 0.8$, obtained directly from the relative proton line widths of (phen)$_3$CrCl_2 in CD_3OD[2] and D_2O.[15] If we assume very similar structures for the SCS in methanol and water (*i.e.*, the same r which places the solvent outside the "ionic radius"), with the number of molecules varying due to their different sizes, take into consideration the different fractions of molecules in the SCS based on this model, and use the reasonable value for the ionic radius[30] of the cationic chelate of 7 Å, we estimate $\delta(\mathrm{M})/\delta(\mathrm{W}) \approx 1.1 \pm 0.1$.

It is observed, however, that the residual OH signal in a CD_3OD solution 0.065 M in (4,7-Me_2phen)$_3$CrCl_2 is very narrow (~3 Hz) while the residual OH peak in D_2O solution is considerably broader (~13.5 Hz). The experimental ratio $\delta(\mathrm{M})/\delta(\mathrm{W}) \cong 0.25$ is well outside the range that can be predicted by dipolar relaxation for the solvents having a similar structure for the SCS. The contrast in relaxation in the SCS in the two solvents is demonstrated even more dramatically by the behavior of the averaged line width for D_2O and CD_3OD in mixed solvents, as illustrated in Figure 6. Thus the addition of approximately 3 mol % D_2O doubles the OH line width, although the spectrum of the dissolved chelate remains unchanged. The OH line widths in mixed solvents changed very little upon raising the temperature, such that they do not reflect some dynamic process involving proton exchange between solvents.

The dotted line in Figure 6 represents the expected averaged OH line width in mixed solvents if the solvent composition in the SCS of fixed structure is identical with that of the bulk solvent, allowing for the small difference in size of the solvent molecules and the fact that water contains two labile protons to the one of methanol.

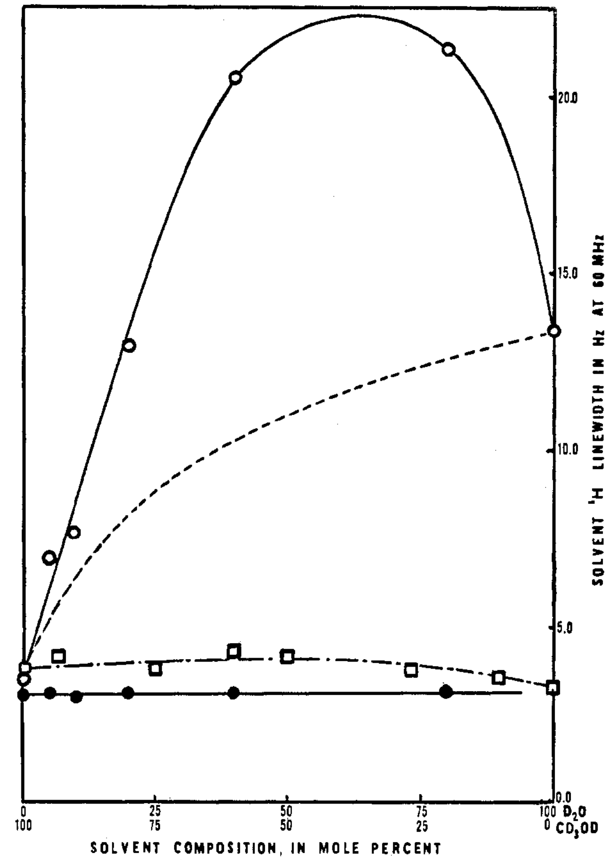

Figure 6. Effect of solvent composition on the residual solvent hydroxyl proton line width for a 0.065 M solution of (4,7-phen)$_3$CrCl_2 (–○–, OH; –●–, CH_3) and for a 0.13 M solution of (4,7-Me_2phen)$_3$NiCl_2 (– · –□ · –, OH) in mixed D_2O-CD_3OD solvents. The dotted line represents the predicted averaged OH line width if the second coordination spheres for the two solvents are identical.

The observed line width difference in pure solvents, given by eq 5 must represent significant differences in either the ratio $r_\mathrm{M}^{-6}/r_\mathrm{W}^{-6}$ or $f_\mathrm{M}/f_\mathrm{W}$. For identical SCS's (same r), the observed difference in line widths requires that more than 4 times as many water molecules fit into the SCS as into the methanol molecules, which is inconsistent with the relative sizes of the molecules and the assumed invariant structure for the SCS. The observed line width ratio therefore strongly supports the conclusion that $\langle r_\mathrm{M}^{-6}\rangle < \langle r_\mathrm{W}^{-6}\rangle$ (*i.e.*, $r_\mathrm{M} > r_\mathrm{W}$) or that water can approach the metal ion much more closely than methanol. Using the observed line width ratio and attributing the difference solely to differences in r, we estimate that water can penetrate the "ionic radius" $r_\mathrm{i} \approx 7$ Å for the complex by some 2 Å, if it is assumed that methanol is constrained to remain outside this "ionic radius." We therefore conclude that water molecules can enter into the "pockets" between the chelates (between the "propeller blades" of the chelate) much more easily than methanol.

The shape of the curve of the averaged OH line width in Figure 6 is consistent with a rapid dynamic equilibrium between $CD_3O\mathit{H}$ ($r > r_\mathrm{i}$), HDO ($r > r_\mathrm{i}$), and HDO ($r < r_\mathrm{i}$). Since there may be several nonequivalent sites which the water can occupy within these pockets and the number of molecules which can enter these sites is unknown, the equilibrium cannot be meaningfully interpreted at this time.

Two observations of note concerning the solvent line widths are that similar data are obtained for (phen)$_3$CrCl_2, so that the solvation effect is common to the Cr(II) che-

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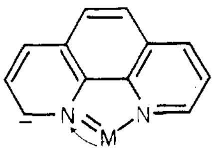
[30] D. H. Templeton, A. Zalkin, and T. Ueki, *Acta Crystallogr., Sect. A*, **21**, 154 (1966); M. Shiro and Q. Fernando, *Chem. Commun.*, 350 (1971).

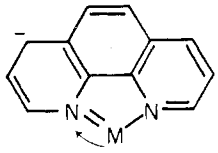
lates, and that these solvent line width effects are absent for the complexes of the less reducing metal ions. The OH line widths for $(4,7\text{-Me}_2\text{phen})_3\text{NiCl}_2$ in mixed solvent, also included in Figure 6, clearly show solvent relaxation must occur in very similar SCS's for methanol and water or that both solvents are either excluded from the pockets or have equal access to them.

Analysis of the solvent line widths has shown that water can enter the pockets within the ionic radius of the complexes, while the chelate line widths permitted us to locate the ligand site with which the water interacts. Both phenomena appear to be unique to the Cr(II) ion.

Nature of the Solvent-Complex Interaction. The failure to observe the anomalous line width effects for either the complex or solvent for all but the reducing chromous ion indicates that the characteristic bonding[6] in these chelates facilitates the solvent-complex interaction. We have shown elsewhere[8,12] that these chelates exhibit significant M→L π back-bonding, and that this delocalized charge is centered primarily at the 4,7 positions. The pertinent resonance structures for this type of bonding[13,31] can be written



IIIa

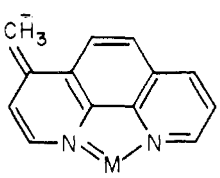


IIIb

The resonance structures related by the twofold axis are omitted. Comparably large $C_{2,9}$ spin densities cannot be discounted, since the 2,9 H peaks could not be located[8] in the mixed-ligand chelates. Structure IIIb is expected to make significant contributions[6] to the ground state only in complexes with reducing metal ions such as Cr(II) and Fe(II) but would be unimportant for Co(II), Ni(II), and particularly Fe(III).

The pockets of electron density generated at the 4,7 position in reducing chelates could act as a center for hydrogen bonding with the solvent. Such interactions have been considered by others[32] for the related Fe(II) chelates, although the lack of a suitable spectroscopic probe prevented the location of the sites of this interaction (*vide infra*). Water forms much stronger hydrogen bonds than methanol, which is consistent with the observation of a greater methyl line width effect in D_2O and a broader *H*DO solvent line width. Since these chelates are unstable in other solvents,[11] the effect of non-hydrogen-bonding solvents could not be determined. As ethyl groups are more electron releasing than methyl groups, the ethyl substituent would be expected to destabilize structure IIIb more than a methyl group, thus accounting for the reduced alkyl line width effect in $(4,7\text{-Et}_2\text{phen})_3\text{CrCl}_2$. These arguments suggest that this hydrogen-bonding effect should be strongest in the absence of 4,7 substituents; unfortunately, the absence of a suitable probe (eq 3) does not permit a direct comparison.[33] This novel H bonding to the 4,7 position may also play a minor role in increasing the stability of these chelates, inasmuch as the delocalized charge is stabilized by this interaction. Indeed, our earlier analysis of the contact shifts in the mixed-ligand chelates has demonstrated[8] that the interaction of water with the coordinated $4,7\text{-Me}_2\text{phen}$ ligand increases its π-acceptor capability.[13] This view is also supported by the reported observations that these chelates decompose[11] by disproportionation in solvents other than water and methanol.

The interpretation of the 4,7 CH_3 line widths in terms of hindered rotation[14] can be rationalized in that molecular models[22] suggest that interaction of the solvent at the 4,7 position could cause severe crowding of the methyl group. An alternate view, not considered as likely, is that the rotational barrier is due to the participation of resonance structure IV. The importance of such methyl group π-acceptor orbitals in stabilizing low-valent metal complexes has been considered elsewhere.[34] Structure IV would also be less stable for an ethyl than a methyl group at the 4,7 position and would be similarly stabilized by hydrogen bonding.



IV

Although these interesting chromium(II) chelates have not yet been subjected to the variety of physical measurements as have the related ferrous chelates, considerable insight into the relevance of the present line width observations can be gained by focusing on evidence for anomalous solvation effects reported[32,35] for the iron(II) system. These Fe(II) chelates are also reducing, although much less so than Cr(II). Since their electronic structure has also been interpreted[36] in terms of some contributions from M→L π back-bonding (structure III), solvent-complex interactions similar to those proposed for Cr(II) may also be present. The observation of similar line width effects for the ferrous chelates is unfortunately impossible, since our observations are intimately related to the paramagnetism of the chromous ion.

The entropy of one-electron reduction of cationic complexes (3+) which do not undergo structural changes in the first coordination sphere, $ML_n^{3+} + e^- \rightarrow ML_n^{2+}$, is generally large and positive[37] ($\geqslant$30 eu) due to the decrease in solvent ordering for the species with the lower charge. However, for the reaction in aqueous solution

$$(\text{phen})_3\text{Fe}^{3+} + e^- \rightarrow (\text{phen})_3\text{Fe}^{2+} \qquad (6)$$

George, *et al.*,[38] found that the entropy change was large and

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[31] R. K. Murmann and F. Basolo, *J. Amer. Chem. Soc.*, 77, 3484 (1955); V. H. Rosenberger, M. Pettig, K. Majeda, and G. Klose, *Ber. Bunsenges. Phys. Chem.*, 72, 847 (1968).

[32] B. Kratochvil and J. Knoeck, *J. Phys. Chem.*, 70, 944 (1966).

[33] Some support for water interacting with the 4,7 position in the unsubstituted chelates is derived from the observation that for the anhydrous *in situ* preparation of $(\text{phen})_3\text{CrCl}_2$ in CD_3OD, the 4,7-H line width increases with decreasing concentration, increases with temperature much faster than for the other positions, and increases with added chloride ion in the form of NaCl. The line widths for hydrated chelates in methanol or water are "normal" and independent of concentration and excess halide. These line width effects in anhydrous methanol were suppressed by excess ligand, suggesting some unspecified dynamic dissociation or disproportionation effect, and were eliminated upon addition of ~5% water. This latter observation supports our hypothesis that the solvent-complex interaction is specific to the 4,7 position and contributes to the solution stability of these chelates.

[34] J. D. Duncan, J. C. Green, M. H. L. Green, and K. A. McLauchlan, *Discuss. Faraday Soc.*, 47, 178 (1969); S. Evans, J. C. Green, M. H. L. Green, A. F. Orchard, and D. W. Turner, *ibid.*, 47, 112 (1969).

[35] S. Burchett and C. E. Meloan, *J. Inorg. Nucl. Chem.*, 34, 1207 (1972).

[36] P. Day and N. Sanders, *J. Chem. Soc. A*, 1530 (1966).

[37] A. J. de Bethune and N. S. Loud, "Standard Aqueous Electrode Potentials and Temperature Coefficients," C. A. Hampel Publishers, Skokie, Ill., 1964.

[38] P. George, G. I. H. Hanania, and D. H. Irvine, *J. Chem. Soc.*, 2548 (1959).

negative ($\Delta S = -21$ eu), suggesting that the solvent ordering was *more* extensive in the ferrous than in the ferric state. This study was extended by Kratochvil and Knoeck,[32] who found that this anomalous entropy of reduction was unique to water, with a "normal," positive $\Delta S = +25.4$ eu obtained in non-H-bonding acetonitrile. These results led the authors to postulate[32] some specific solvent-complex interaction, suggesting H bonding to some unspecified part of the chelate as the most reasonable interpretation.

An earlier study by Gere and Meloan[39] had demonstrated that water was tightly held by $(phen)_3Fe^{2+}$, in that extraction of an aqueous solution of the complex into nitromethane always resulted in the transfer of some ~60 molecules of water with every complex. Burchett and Meloan[35] subsequently showed that this extracted water in nitromethane was of two types. Infrared studies of this dissolved water yielded evidence for "normal" water, with bands at 3500-3600 cm^{-1}, as found by dissolving water in nitromethane, and some form of "bound" water, which exhibited characteristic absorption at 2900-3400 cm^{-1}. Since this "bound" water resembled strongly H-bonded water, and in the absence of any probe for locating the site of the interaction, these authors suggested[35] that the water must coordinate to the metal ion in the intact $(phen)_3Fe^{2+}$ species. This ir evidence[35] more likely reflects H bonding of the water to the 4,7 position, as suggested in our investigation, since molecular models[22] suggest that direct attachment to the metal in the tris chelate is unlikely.

The possible role of solvent-mediated electron transfer in outer-sphere redox reactions involving $(phen)_3Fe^{2+}$ has been raised.[16] This suggestion was based on the failure to detect[16] conductivity or charge-transfer bands in single crystals of $[(phen)_3Fe^{2+}][IrCl_6^{2-}]$, in spite of the fact that in aqueous solution the reaction

$$(phen)_3Fe^{2+} + IrCl_6^{2-} \rightarrow (phen)_3Fe^{3+} + IrCl_6^{3-} \qquad (7)$$

proceeds with a rate that is nearly diffusion controlled.[40] The solvent interaction in our Cr(II) chelates occurs[15] at the 4,7 position, which is the same position we have postulated[8,12,13] to be the "active site" for outer-sphere electron transfer. Such a specific active site was shown[13] to be consistent with the stereoselective electron transfer[9] in the redox reaction

$$(phen)_3Cr^{2+} + (phen)_3Co^{3+} \rightarrow (phen)_3Cr^{3+} + (phen)_3Co^{2+} \qquad (8)$$

where use of an optically active oxidant yielded nearly pure optically active $(phen)_3Cr^{3+}$. This suggests that the solvent molecule which is hydrogen bonded at this site may be implicated in some manner in the electron-transfer process in some reactions. The kinetic studies of Zwickel and Taube,[41] using $(bipy)_3Cr^{2+}$, did not yield any evidence for a solvent isotope effect in the case of the reduction of $(NH_3)_6Co^{3+}$, though such an effect was noted using the oxidant $(H_2O)(NH_3)_5Co^{3+}$. In the latter case, the isotope effect was attributed[41] primarily to the deuteration of the coordinated water. Investigation of some of these redox reactions in nonaqueous media would be particularly illuminating at this stage.

The present model for hydrogen bonding to pockets of electron density on the ligands of tris(diimine) chelates of reducing metal ions may also shed some light on the previously reported effect[42,43] of hydroxide, cyanide, and azide ions in accelerating the rate of decomposition of $(phen)_3Fe^{2+}$ but not $(phen)_3Ni^{2+}$. These observations have been interpreted[42,44] in terms of a tendency of these small anions to destabilize the metal-ligand bond of the ferrous but not the nickel complex, by interacting with the antibonding t_{2g} electrons in the iron chelate. However, these results are also consistent with our model for hydrogen bonding, inasmuch as any small anion which enters between the "propeller blades" of these chelates would destabilize the pockets of delocalized electron density ($M \rightarrow L\ \pi^*$ bonding) and hence weaken the M-L bond in Fe(II), but not in Ni(II).

Summary

The present analysis of the line widths for the 4,7 alkyl groups on the chelate and the solvent hydroxyl proton leads us to conclude the following points.

(1) Specific solvent-complex interactions occur at the 4,7 position of the chromous and probably of the ferrous chelates of α-diimines.

(2) This interaction is postulated to involve hydrogen-bonding to the pockets of electron density on the coordinated ligand.

(3) These pockets of electron density and hence the specific solvation are unique to chelates of reducing metal ions for which $M \rightarrow L\ \pi$ back-bonding makes important contributions to the ground-state electronic structure.

(4) The solvent-complex interaction appears to enhance $M \rightarrow L\ \pi$ back-bonding and thereby contribute to the stability of these chelates in solution.

(5) The specific solvation at the 4,7 positions, postulated to be the "active sites" in outer-sphere electron transfer, suggests the possibility of solvent-mediated electron transfer in some redox reactions of these chromous (and possibly ferrous) chelates.

Registry No. $(phen)_3CrCl_2$, 23856-31-7; $(4,7\text{-}Me_2phen)_3CrCl_2$, 23856-32-8; $(phen)_3NiCl_2$, 14356-44-6; $(4,7\text{-}Me_2phen)_3NiCl_2$, 33247-42-6; $(phen)_3CoCl_2$, 15136-98-8; $(4,7\text{-}Me_2phen)_3CoCl_2$, 29589-18-2; $(phen)_3FeCl_3$, 40273-22-1; $(4,7\text{-}Me_2phen)_3FeCl_3$, 40273-23-2; $(4,7\text{-}Et_2phen)_3CrCl_2$, 40273-24-3; $(3,4,7,8\text{-}Me_4phen)_3CrCl_2$, 23856-34-0.

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(43) L. P. Morgenthaler and D. W. Margerum, *J. Amer. Chem. Soc.*, **84**, 710 (1962).

(44) D. W. Margerum and L. P. Morgenthaler in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, p 481.