Elucidation of Electronic Effects on Methyl Rotational Barriers in Reduced Chromium Complexes by ^{1}H Nuclear Magnetic Resonance Spectroscopy

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Summary The restricted rotation of alkyl groups in substituted 1,10-phenanthroline chelates with chromium(II) originates from an electronic rather than a steric effect, and can be rationalized by π back-bonding.

THE ability of 1,10-phenanthroline (phen) type ligands to stabilize[1] a wide range of low-valent metal ions has been attributed to the superior π acceptor properties of these ligands. However, for the reduced *tris* chelates of Cr^{II}, it was not possible to establish[2] sizable π back donation since the π contact shifts in these paramagnetic ($S = 1$) chelates were no larger than for the analogous Ni^{II} complexes, in which back-bonding would be less important. The failure to establish by n.m.r. spectra that $M \rightarrow L\ \pi$ bonding is the primary stabilizing factor in these Cr^{II} complexes may be due to simultaneous delocalization into two πMO's which have spin densities of opposite sign,[3] so that the *net* contact shift need not be a direct measure of the π covalency. In the n.m.r. spectra of $[(4,7\text{-}Me_2\text{-phen})_3Cr]^{2+}$, in D_2O, the methyl proton signal was anomalously broad. The relaxation mechanism was shown[4] to involve modulation of the average spin magnetization (contact shift) by rotation of the methyl group,[5] and the rotational barrier was calculated from the temperature dependence of the linewidth. It was suggested that the rotational barrier arose primarily from intramolecular steric hindrance by the 5- and 6-protons, since molecular models indicated some steric interaction.

We report here that the analysis of the ^{1}H n.m.r. linewidths and contact shifts of analogous chelates with Ni^{II} and other ions, and the Cr^{II} chelate with 4,7-diethyl substituents, reveals that the restricted rotation must be primarily electronic in origin, and is probably a characteristic of the unusual π bonding in the reduced Cr^{II} chelates.[1,6] The evidence *against* a simple steric barrier is based on three observations.

If the rotational barrier is primarily steric, it should be a property of the ligand, and depend only slightly on the co-ordinated metal ion. Thus we expect severe methyl line broadening in the n.m.r. spectrum of any paramagnetic 4,7-Me_2-phen complex which satisfies the requirements for the operation of this novel relaxation mechanism, namely that the substituents experience primarily π spin density. However, in aqueous solution, $[(4,7\text{-}Me_2phen)_3Ni]^{+2}$ does not exhibit any methyl line broadening indicative of hindered rotation. Since the π contact shifts in the Ni^{II} chelate are greater than for the Cr^{II} complex, more severe broadening is predicted[4] by a steric barrier. Therefore the rotational barrier is not a characteristic of the ligand, and must depend on the metal and metal–ligand bonding.

Upon substituting ethyl for methyl groups, more severe steric hindrance is expected on the basis of the molecular models, which is confirmed[7] by e.s.r. studies in free radicals of similar structure. However, the n.m.r. spectrum of aqueous $[(4,7\text{-}Et_2\text{-}phen)_3Cr]^{2+}$, although it exhibits the broadened 4,7-CH_2 lines indicative of restricted rotation, the actual barrier (*ca.* 5 kcal) is considerably less than for the analogous 4,7-Me_2phen chelate (*ca.* 18 kcal) and thus inconsistent with a simple steric origin.

The 4,7-Me barrier is solvent dependent, decreasing from 18 kcal in D_2O to < 3 kcal in CD_3OD. Analysis of the methyl linewidths in water–methanol shows that the addition of only 25% of methanol essentially totally suppresses the barrier such that a strong preference for methanol in the second co-ordination sphere is indicated.

A qualitative description of a possible electronic origin for the restricted 4,7-alkyl rotation can be traced to the strong M → L back-bonding expected[1] primarily in the chelates with the more reduced metal ions. One of the possible resonance structures of importance for these Cr^{II} complexes[8] which involves a double bond to the methyl group would be less stable for the ethyl than the methyl substituent, and the contribution from this structure would be expected to be somewhat solvent dependent owing to variable solvation of the charge on the periphery of the molecule. Similar π back donation to methyl groups in low-valent metal complexes has recently been proposed on the basis of anomalous H–D n.m.r. coupling constants in $-CH_2D$ groups,[9] and photoelectron[10] and vibrational spectroscopy.[11]

Alternatively a specific solute–solvent interaction could cause the barrier. Some resonance structures could create pockets of electronegativity at the 4 and 7 positions in the cationic complexes, which could facilitate hydrogen bonding interaction, impeding methyl rotation.[4] In either case, the mechanism would be expected to be dominant in reduced chelates exhibiting π back bonding. Further work, with other metal ions and solvents, is in progress.

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