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Notes

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Solution Dynamics of Tris(acetylacetonato)chromium(III)

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Studies of the solution dynamics of transition metal complexes are important in understanding the catalytic activity of metal ions in both biological and nonbiological systems.[1] In particular, we are interested in the chemical dynamics of first and second coordination sphere exchange of ligands with bulk solvent molecules. Such studies are capable of exploring the rate, order, and preferential orientation of exchanging species in the first and second coordination sphere and relating these parameters to intrinsic properties such as ion size and charge, steric factors of association between the metal ion complex and solvent molecules, and dipole moment and hydrogen-bonding ability of the solvent.[2-4]

Certain paramagnetic complexes such as tris(acetylacetonato)chromium(III), Cr(acac)$_3$, have been used extensively as spin relaxants in carbon-13 Fourier-transform NMR studies. The controversy and questions which have arisen over their use are intimately associated with the first and second coordination sphere behavior of the solvent and solute molecules about the paramagnetic complex.[5-11] It has been postulated that while the spin–lattice and spin–spin relaxation times of the carbon-13 species are reduced in the presence of Cr(III) complexes and the NOE (nuclear Overhauser effect) is quenched, the chemical shift is unaffected. Our previous studies of the solution dynamics of tris(ethylenediamine)chromium(III) and hexakis(dimethyl sulfoxide)chromium(III) indicate that this assumption may not be true.[12,13]

Here we report the dependence of the chemical dynamics of first and second coordination sphere exchange of Cr(acac)$_3$ with four solvents on various properties of the solvents such as dipole moment, basicity, and hydrogen-bonding ability. In addition to its role as a spin relaxant, Cr(acac)$_3$ was chosen for the present study because of its well-known kinetic and thermodynamic stability and because of the nature of the d^3 isotropic electronic ground state which makes the interpretation of the NMR of its solutions less complicated. The changes in carbon-13 and hydrogen-1 chemical shifts upon addition
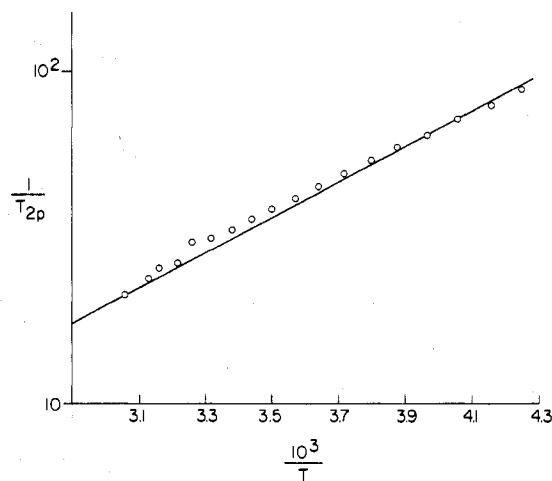

Figure 1. Line broadening of the methyl protons of acetonitrile for 0.1 M Cr(acac)$_3$ in acetonitrile.

of the Cr(acac)$_3$ are reported for the solvents.

Experimental Section

Proton line broadening and chemical shift measurements and carbon-13 chemical shift and T_1 measurements were made on each of the four solvents, benzene, acetonitrile, methanol, and dimethyl sulfoxide (DMSO), in the absence and presence of Cr(acac)$_3$. Data resulting from the temperature dependence of the proton line broadening were analyzed using the methods of Swift and Connick.[14] All data were normalized to 0.1 M Cr(acac)$_3$ where the concentration of Cr(acac)$_3$ ranged from 0.05 to 0.1 M. The proton NMR data were obtained using Varian A-60A and EM-390 spectrometers. The carbon-13 data were obtained using a Bruker HX-90 FT spectrometer with a Nicolet 1085 data system. TMS was used as an internal reference for the chemical shift studies.

All solvents were of spectrochemical quality. The Cr(acac)$_3$, obtained commercially, was purified by recrystallization.

Results and Discussion

Figure 1 shows a Swift–Connick plot for Cr(acac)$_3$ in acetonitrile. The results for acetonitrile are also typical of the results for benzene and DMSO. The plot is linear with positive slope; ΔH^* for the single process observed is 2.44 kcal/mol. From the temperature dependence of the relaxation rate, T_{2p}^{-1}, and the value of ΔH^*, exchange is fast as defined by the Swift–Connick relationship.[14] In the fast-exchange region, the Swift–Connick equation reduces to $1/T_{2p} = f/T_{2m}$, where f
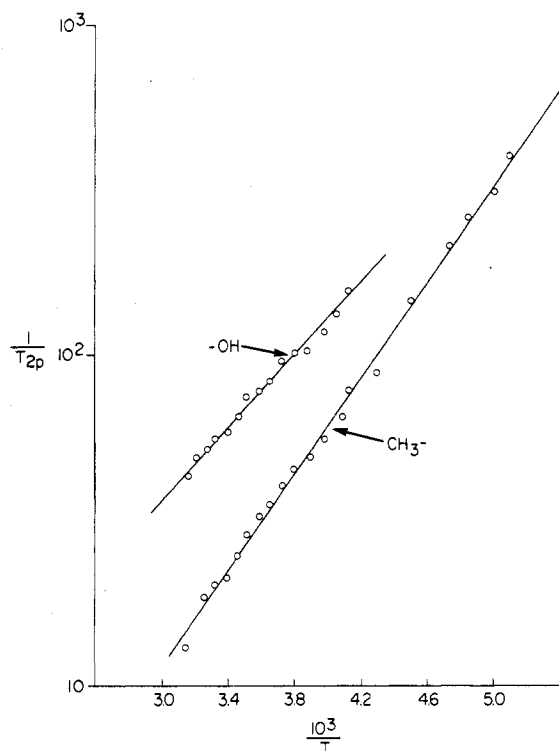
Figure 2. Line broadening of the methyl and hydroxyl protons of methanol for 0.1 M Cr(acac)$_3$ in methanol.

Table I. Second Coordination Sphere Parameters for Some Chromium Complexes in Dimethyl Sulfoxide

Complex	A_n, Hz	$k^{\ddagger}$ (25 °C), s^{-1}	$\Delta H^{\ddagger}$, kcal/mol
Cr(DMSO)$_6$$^{3+}$	-1.2×10^5	1.3×10^3	6.9
Cr(en)$_3$$^+$	-3.0×10^5	1.0×10^3	6.6
Cr(acac)$_3$	$\sim 10^3$		3.4

is a probability factor and $1/T_{2m}$ is the relaxation rate of the coordinated resonating nucleus. In the fast-exchange region, $1/T_{2m}$ is independent of the mean lifetime of the coordinated ligand. The exchange process is expected to be second coordination sphere because of the well-known ligand stability of Cr(acac)$_3$. The $\Delta H^{\ddagger}$ values for exchange for benzene and DMSO are 2.96 and 3.41 kcal/mol, respectively, and are also expected to be second coordination sphere processes.[15]

Methanol poses an interesting case since the line broadening of both the methyl and the hydroxyl protons may be monitored as a function of temperature. Figure 2 summarizes the results of the line broadening study. The hydroxyl proton relaxation is more rapid than the methyl proton relaxation. Since the outer-sphere dipole–dipole relaxation depends upon the Cr–H distances as $1/r^3$, this evidence indicates that the hydroxyl proton is closer to the chromium ion than the methyl proton. This suggests a preferential alignment of the methanol molecule in the second coordination sphere of the metal ion. Fackler,[16] by IR studies, has shown that methanol does bind by hydrogen bonding to the acetylacetonate. Interestingly, the slopes of hydroxyl and methyl plots are different [$\Delta H^{\ddagger}$ = 2.5 kcal/mol (OH) vs. 3.16 kcal/mol (CH$_3$)]. If line broadening for both hydroxyl and methyl protons occurred by the same mechanism, i.e., dipolar coupling to the Cr^{3+}, the T_{2p}^{-1} values at the same temperatures should be different due to the $1/r^3$ dipole relationship. However, the slopes ($\Delta H^{\ddagger}$'s) would be the same. Therefore, the hydroxyl proton is experiencing an additional relaxation process. Eaton,[17] by contact shift and molecular orbital calculations, showed a significant amount of unpaired spin density to be delocalized onto the Cr(acac)$_3$ oxygen. Thus the modulation of the unpaired spin density transfer between the acetylacetonate oxygen and the hydrogen-bonded hydroxyl proton could account for the additional process observed. This proposal is supported by the fact that the hydroxyl proton is the only solvent proton which possesses a contact shift.

The DMSO exchange with Cr(acac)$_3$ can be adequately explained by invoking an outer-sphere dipolar mechanism

although there is evidence of small contact shifts at high Cr(acac)$_3$ concentrations. It is interesting to contrast the results of the Cr(acac)$_3$ study with our previous studies of tris(ethylenediamine)chromium(III), Cr(en)$_3$$^{3+}$, and hexakis(dimethyl sulfoxide)chromium(III), Cr(DMSO)$_6$$^{3+}$, in DMSO (Table I). The Swift–Connick plots for Cr(DMSO)$_6$$^{3+}$ and Cr(en)$_3$$^{3+}$ in DMSO are complex and can be resolved into both first coordination sphere processes at high temperatures ($\Delta H^{\ddagger} \simeq$ 25 kcal/mol) and second coordination sphere processes at lower temperatures, as shown in Table I. An examination of the large $\Delta H^{\ddagger}$'s and hyperfine coupling constants, A_n, and the measurable exchange rates, $k^{\ddagger}$, for Cr(DMSO)$_6$$^{3+}$ and Cr(en)$_3$$^{3+}$ indicates that second coordination sphere bonding of DMSO is more significant than in the case of DMSO in solutions of Cr(acac)$_3$ where small $\Delta H^{\ddagger}$ and A_n values are noted and where only a lower limit to the exchange rate can be calculated.[14] The differences in the kinetic parameters are directly affected by the charge on the chromium complex and are consistent with similar findings by Frankel[2] and Langford.[4]

Second Coordination Sphere Structure and Exchange Mechanism. The Swift–Connick relationship reduces to $1/T_{2p} = f/T_{2m}$ under fast-exchange conditions. The value of T_{2m}^{-1} may be determined as

$$\frac{1}{T_{2m}} = \left\{ \frac{4}{3} \, \frac{\gamma_I^2 \beta^2 g^2 S(S+1)}{r_i^6} \right\} \tau_c$$
(inner sphere)

$$+ \frac{16\pi}{9} \left\{ \frac{\gamma_I^2 \beta^2 g^2 S(S+1)\rho \, [m] N}{r_o^3 \times 10^3} \right\} \tau_c$$
(outer sphere)

$$+ \left\{ \frac{4}{9} I(I+1) S(S+1) \frac{A_n^2}{\hbar^2} \right\} \tau_c$$
(contact shift)

where

$$\frac{\Delta \nu}{\nu} = \frac{-A_n \gamma_e g S(S+1)}{\gamma_n (3kT)}$$

and γ_I, γ_e, g, S, k, T, A_n, and $\hbar$ have their usual meaning.[18] In the case of Cr(acac)$_3$, the first term, which represents first coordination sphere exchange, may be neglected. The third term, the contact shift term, is unimportant for DMSO, benzene, and acetonitrile solutions and only slightly influences the methanol results. The second term representing outer-sphere dipolar relaxation may be considered the most important contribution to T_{2m}^{-1}. The distance between the Cr^{3+} ion and the resonating proton, r_o, may then be calculated for each solvent. $1/\tau_c$ is defined as $1/T_{2e} + 1/\tau_r + 1/\tau_e + 1/\tau_H$.[19] $1/\tau_e$, the electronic exchange rate, and $1/\tau_H$, the ligand exchange rate, are negligible compared to $1/\tau_r$, the rotational correlation rate in these systems. $1/T_{2e}$, the electronic transverse relaxation rate, is also small compared to $1/\tau_r$ for chromium solutions.[12] Thus, τ_c may be considered to be the rotational correlation time τ_r for the solvent molecule in the chromium ion system and is calculated using the Stokes–Einstein equation. A summary of the calculated distances is given in Table II. The table also gives a comparison of these distances with distances determined from space-filling models and x-ray crystallographic data taking as a standard distance

Table II. Summary of Model and Calculated Distances
(Cr–O = 2.0 cm = 1.99 A[20])

Molecule	Model dist, A	calcd dist, A	Orientation
Methanol	3.85 (OH)	3.7	Preferential
(OH first)	4.80 (CH$_3$)	4.7	
DMSO	5.15	5.0	Preferential
(S=O first)			
Benzene	4.6	5.1	Random
(flat and cleft)			
Acetonitrile			Preferential, favors
(N first)	5.28	3.72	CH$_3$ first
(CH$_3$ first)	3.09		

Cr–O = 1.99 Å = 2.9 cm.[20] Several orientations for each molecule were assumed. While the distances should not be taken as absolute values, the good agreement between the calculated distances and distances assuming a given orientation should be indicative of preferential ordering in the outer solvation sphere. For example, methanol is preferentially ordered due to the molecule being oriented along its dipole[2] due to its participation in hydrogen bonding with the acetylacetonate oxygen. The methyl proton distance is very close to that calculated. Agreement for the hydroxyl proton is not as good due to the contribution of the contact term to $1/T_{2m}$ and to the contribution of the additional relaxation mechanism to $1/T_{2p}$. Best agreement for DMSO is obtained by assuming preferential orientation with the oxygen atoms pointed into the octahedral face of the Cr(acac)$_3$. For benzene, a random orientation of the flat and cleft positions best fits the data. The acetonitrile molecule, from the NMR calculations, has a mildly preferred orientation with the methyl group pointing into the octahedral face of the Cr(acac)$_3$. This unexpected orientation is probably stabilized by weak hydrogen bonding between the methyl protons and acetylacetonate oxygens. The methyl protons become capable of hydrogen bonding as a result of the electron-withdrawing nature of the cyano group. The preferential orientation of the methyl group of acetonitrile is further supported by the carbon-13 chemical shift and T_1 data. The methyl carbon is shifted 0.3 ppm downfield [0.1 ppm Cr(acac)$_3$] while the cyano carbon is unshifted. The corrected T_1's for the methyl and cyano carbons are 0.72 and 0.93 s, respectively. Since T_1 is proportional to $1/r^6$ for the electronic–nuclear dipole mechanism,[10] the methyl protons must be closer to the paramagnetic center.

Although the proton chemical shifts for each solvent were small upon addition of 0.1 M Cr(acac)$_3$, the carbon-13 chemical shifts were larger and of the magnitude reported previously.[5] Each of the carbon-13 chemical shifts, except that of the cyano group of the acetonitrile, moves downfield upon addition of the Cr(acac)$_3$, the range being 0.1–0.3 ppm.

Registry No. Cr(acac)$_3$, 13681-82-8; Cr(en)$_3^{3+}$, 15276-13-8; Cr(DMSO)$_6^{3+}$, 19122-76-0.

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Intermediate-Spin (S = $^3/_2$) Porphyrinatoiron(III) Complexes

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There is much current interest in the synthesis of new iron porphyrin complexes having unusual electronic states or coordinations. The most common types of iron porphyrins are the pentacoordinate high-spin ($S = ^5/_2$) iron(III) complexes Fe(P)X (P = porphyrinato dianion, X = anionic group), hexacoordinate low-spin ($S = ^1/_2$) iron(III) complexes Fe(P)L$_2$X (L = amine base), and hexacoordinate low-spin ($S = 0$) iron(II) complexes Fe(P)L$_2$. Recently, preparations of a few iron porphyrin derivatives containing high-spin ($S = 2$) and intermediate-spin ($S = 1$) iron(II) have been reported.[1-5] The former are thought[2,3] to be pentacoordinate with the iron atom substantially out of the plane of the porphyrinato nitrogen atoms, while the latter are tetracoordinate with a planar FeN$_4$ core.[3]

The only apparently unknown ground state for either iron(II) or iron(III) porphyrins is the unusual intermediate-spin ($S = ^3/_2$) iron(III) state. Although this ground state is not known to occur in natural iron prophyrins, there is evidence for a low-lying $S = ^3/_2$ state in some heme proteins,[6a] and a new iron–sulfur cluster with $S = ^3/_2$ has recently been discovered in nitrogenase.[6b] Moreover, the preparation and characterization of $S = ^3/_2$ tetraaza iron(III) systems has recently been reported.[7]

The criterion for obtaining the $S = ^3/_2$ state for a d^5 ion is essentially the same as that for obtaining the $S = 1$ state for a d^6 ion: the d$_{x^2-y^2}$ antibonding orbital must lie well above the other d orbitals and be unoccupied, while the remaining four d orbitals must fill by Hund's rules. This requires strong bonding in the equatorial (xy) directions and very weak bonding (or none) in the axial direction so that d$_{z^2}$ remains close in energy to the t$_{2g}$ orbitals. It therefore seemed likely that the $S = ^3/_2$ state could be stabilized in Fe(P)X type complexes if X were a sufficiently weak-field anion.

Ogoshi et al.[8] have reported the preparation of octaethylporphyrinatoiron(III) perchlorate, Fe(OEP)ClO$_4$, and three of its monoamine adducts. The magnetic moments of all four complexes at 288 K were intermediate between those expected for high-spin and low-spin iron(III). These results, augmented by IR and reflectance spectra, were interpreted in terms of a $^6A_1-^2T_2$ spin equilibrium.[8] Although the temperature dependence of μ_{eff} for the three adducts appears to support this interpretation, only a single μ_{eff} value at 288 K was reported for Fe(OEP)ClO$_4$. We have now prepared this complex and its bis(ethanol) solvate by a new route and present clear evidence that in both compounds the iron(III)