

NMR Studies of Outer-Sphere Coordination to Tris(tropolonato)-chromium(III) in Organic Solvents

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Tris(acetylacetonato)chromium(III), Cr(acac)₃, is extensively used in NMR studies as a paramagnetic relaxation reagent (PARR).¹ The interaction of Cr(acac)₃ with surrounding molecules in organic solvents has previously been studied in detail.² It is well established that compounds with acidic protons (alcohols, halogenated hydrocarbons, etc.) effectively solvate Cr(acac)₃, forming hydrogen bonds with its oxygen atoms, whereas solutes incapable of hydrogen-bond donation form outer-sphere adducts with Cr(acac)₃, apparently as the result of to electrostatic and donor-acceptor interactions.² However, the question of the interaction mechanisms responsible for solute orientation in the outer sphere of PARR is not fully answered. In this connection, and investigation of outer-sphere solvation of paramagnetic, coordinatively saturated tris(tropolonato)-chromium(III), Cr(trop)₃, is presented. This chelate complex, like Cr(acac)₃, has an octahedral coordination core [CrO₆],³ but the ligands are not generated from 1,3-diketones in contrast with all other reported PARRs. In this report ¹H and ¹³C spin-lattice relaxation times have been used to investigate the interactions between Cr(trop)₃ and different organic molecules in solution.

Results and discussion

The relaxation rate observed for solute nuclei in the presence of PARR includes three contributions² [eqn. (1)]

$$R_1(\text{obs}) = 1/T_1(\text{obs}) = R_{1M} + R_{1V} + R_{1D} \quad (1)$$

where the first term is due to rapid dipole-dipole electron-nuclear relaxation in the second coordination sphere of PARR. The magnitude of this term is proportional to the

fraction of solute molecules which are bound to the metal complex and the relaxation rate of bound molecules. The second term is the electron-nuclear relaxation rate in bulk solution. The relaxation rate R_{1V} may easily be estimated using an inert reference compound which does not specifically interact with PARR [in our case cyclohexane or tetramethylsilane (TMS)]. The last term is due to the diamagnetic relaxation rate, i.e. the rate of relaxation observed in the absence of paramagnetic complexes.

A study of the dependence of proton relaxation rate of solvate S as a function of solvate concentration makes it possible to determine both an effective stability constant of PARR · S adducts (K_{eff}) and an effective relaxation rate of S protons for solute molecules in the second coordination sphere (R_{1M}°).⁴ In an inert solvent such as carbon tetrachloride we obtained $k_{\text{eff}} = 1.0 \pm 0.1 \text{ m}^{-1}$, $R_{1M}^\circ = (2.4 \pm 0.3) \times 10^4 \text{ Hz}$ for Cr(trop) · CHCl₃ adducts. The two values are very close to the corresponding parameters of Cr(acac)₃ · CHCl₃ adducts.⁴ Such a similarity seems somewhat surprising since the lone electron pairs of the oxygen atoms which are considered to participate in hydrogen bonding with CHCl₃ are shielded by methyl groups in Cr(acac)₃ whereas in Cr(trop)₃ the oxygens are much more accessible.

Unfortunately, Cr(trop)₃ is reasonably soluble only in halogenated hydrocarbons such as chloroform or dichloromethane. This condition does not permit the derivation of stability constants of adducts formed by Cr(trop)₃ with other outer-sphere ligands since the use of strongly interacting solvents suppresses outer-sphere interactions of solutes. By measuring T_1 values in CDCl₃ in the presence of Cr(trop)₃, however, the preferred orientation of solute molecules in the second sphere of the chelate can be determined.

The relaxation rate R_{1M}° according Solomon and Bloembergen⁵ is proportional to the inverse sixth power of the average distance r between the nucleus and the metal atom in outer-sphere adducts. Thus, one may consider to a first approximation the relaxation rates R_{1M} for two non-equivalent protons (or for two ¹³C nuclei) of a given solute molecule to be related as the corresponding geometric factors [eqn. (2)].

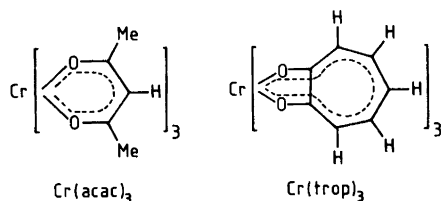


Fig. 1.

Table 1. Spin-lattice proton relaxation rates of methanol in chloroform solutions in the presence of paramagnetic chelates ($[M]=4.4\times 10^{-3}$ M).

[MeOH]/M	Nucleus	$R_1(\text{obs})/\text{Hz}$	R_{1M}/Hz	R_{1V}/Hz	R_{1D}/Hz
M = Cr(trop)₃					
1.0	Me	4.85	3.80	0.85	0.20
	OH	28.57	27.53	0.85	0.19
	CHCl ₃	7.94	6.96	0.85	0.13
	TMS	1.06	—	0.85	0.21
0.03	Me	6.13	5.03	0.90	0.20
	OH	38.46	37.38	0.90	0.18
	CHCl ₃	10.00	8.96	0.90	0.14
	TMS	1.12	—	0.90	0.22
M = Cr(acac)₃					
1.0	Me	3.69	2.52	0.97	0.20
	OH	20.41	19.25	0.97	0.19
	CHCl ₃	9.26	8.16	0.97	0.13
	TMS	1.18	—	0.97	0.21
0.03	Me	4.26	3.08	0.98	0.20
	OH	24.39	23.23	0.98	0.18
	CHCl ₃	10.43	9.30	0.98	0.14
	TMS	1.20	—	0.98	0.22

$$(R_{1M})_i/(R_{1M})_j = r_i^{-6}/r_j^{-6} \quad (2)$$

The observed relaxation rates of methanol protons in CDCl₃ solutions containing PARR [Cr(trop)₃ or Cr(acac)₃] are listed in Table 1. The comparison of T_{1M} for hydroxy and methyl protons shows that for both complexes the geometries of outer-sphere adducts are practically identical. This means that methyl groups of acetylacetonate li-

Table 2. Electron-nuclear ¹³C relaxation rates R_1^e for aromatic compounds in chloroform solutions containing paramagnetic chelates.^a

Compound	R_1^e/Hz				
	C-1	C-2	C-3	C-4	C-7
Cr(trop)₃					
Toluene	0.32	0.32	0.31	0.32	0.32
<i>N,N</i> -Dimethylaniline	0.29	0.31	0.31	0.28	0.38
Nitrobenzene	0.45	0.59	0.74	0.78	—
Pyridine	—	0.39	0.53	0.58	—
4-Methylpyridine	—	0.43	0.51	0.51	0.57
Cr(acac)₃					
Pyridine	—	0.43	0.47	0.54	—
4-Methylpyridine	—	0.41	0.45	0.38	0.52

^aConcentrations of substrates and chelates were 0.5 and 2.2×10^{-2} M, respectively.

gands in Cr(acac)₃ do not prevent these proton donors from occupying optimal positions for hydrogen bonding with the oxygen atoms of the chelate.

The present study also includes an investigation of paramagnetic nuclear relaxation of compounds not capable of hydrogen bonding. In Table 2 are summarized ¹³C relaxation data for some representative substrates. In this case it is more correct to analyze total electron-nuclear relaxation rates $R_1^e = R_{1M} + R_{1V}$ because outer-sphere complexation of these substrates is substantially suppressed by chloroform. Hence the R_{1M} and R_{1V} terms in eqn. (1) have comparable magnitudes.

The orientation of substituted benzenes in the solvation shell of Cr(acac)₃ has previously been studied in detail.^{6,7} It has been shown that aromatic molecules with a significant molecular dipole moment adopt a preferred outer-sphere orientation with the negative end of the dipole being directed away from the chelate. In the case of substituted aromatics with donor-type of substituents, the substrate undergoes practically random orientation in the outer sphere of the metal chelate.^{6,7} The analysis of the relation data for nitrobenzene, toluene and *N,N*-dimethylaniline (Table 2) shows that the same situation exists in the case of Cr(trop)₃.

The observed orientation of aromatic compounds in the outer sphere of PARR's may be regarded as a result of two types of interactions: electrostatic and steric. The investigation of the electron-nuclear relaxation rates for pyridine shows that the basic regularities in mutual orientation of aromatic substrates and PARR are retained. In this case the negative end of the molecular dipole coincides with the sterically unhindered, unsubstituted nitrogen atom and it is easily seen from the relaxation data that this end of the molecule points away from the metal both for Cr(acac)₃ and for Cr(trop)₃. Methyl substitution of the positive end of the dipole creates steric hindrance for such an orientation.

Conclusions

The experiments conducted showed that, in spite of known difference in the structure of Cr(acac)₃ and Cr(trop)₃ inner-sphere ligands, there is a striking similarity in the outer-sphere complexation properties for the two complexes. This condition suggests that the specific solvation is determined mainly by the interaction of solute molecules with the nearest coordination environment of the metal, i.e. the oxygen atoms and the highly polarized C–O bonds of the inner-sphere ligands.

Experimental

Cr(trop)₃ was prepared by refluxing Cr₂(SO₄)₃ and tropolone in water and was recrystallized from a chloroform–heptane mixture. Anal. C₂₁H₁₅CrO₆: C, H, O. Purity was confirmed by IR and ¹H NMR spectroscopy. Commercially available materials were used without further purification. NMR spectra were recorded on a Bruker AC-P 250 spec-

trometer at 25°C. The spin-lattice relaxation times were obtained from a conventional inversion-recovery pulse sequence. The estimated T_1 errors were to within $\pm 5\%$.

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