NMR relaxation studies of counter ion nuclei in solution

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Introduction

Non covalent interaction between counter ion nuclei and metal center can affect the reactivity and chemical structure of the metal complex in solution.¹ Many metal complexes accompanied counter ion to counterbalance its electric charge. However, nature of the counter ion and its effect on properties such as geometry, vibrations, nuclear spin content, and electronic spin magnitude has yet to be investigated.² Previous NMR studies on unsubstituted [Co(Tpm)₂]²⁺ with BF₄⁻ or PF₆⁻ counter ions has shown that BF₄⁻ counter ions are strongly associated with the metal center.³ In this project, Series of substituted cobalt (II) bis-trispyrazolylmethane ([Co(Tpm)₂]²⁺) complexes was studied to understand the effect of counter ion on NMR relaxation, geometry and the spin cross over. Here we report temperature dependent relaxation rates of counter ion nuclei and distance between counter ion nuclei (BF₄⁻ and PF₆⁻) and the metal center.

Figure 1. Variable-temperature ¹⁹F spectra of counter ion of (A) [Co(Tpe)₂][BF₄] and (B) [Co(Tpm^{3,5me})₂][PF₆]

Table 1. Calculated and measured Co—¹⁹F distances of Tpm complexes in solution and crystal structure

Complex	Distance of crystal structure (Å)	Distance of crystal structure (Å)
[Co(Tpe) ₂](BF ₄) ₂	6.172	8.973
[Co(Tpm ^{3,5me}) ₂](PF ₆) ₂	6.005 8.409	11.80
[Co(Tpm ^{3,5me}) ₂](BF ₄) ₂	8.220	9.454
[Co(Tpm ^{4me}) ₂](BF ₄) ₂	6.9005	8.034

$$r = \left[\frac{2}{15} \left(\frac{\mu_0}{4\pi} \right) \frac{\gamma_N g_e \mu_B S(S+1)}{T_{1M(dip)}^{-1}} (3\cos^2\theta - 1) \left(\frac{7\tau_c}{1 + \omega_S^2 \tau_c^2} + \frac{3\tau_c}{1 + \omega_I^2 \tau_c^2} \right) \right]^{1/6}$$

Equation 1. Modified Solomon-Bloembergen and Morgan equation

Figure 2. Temperature dependence of ¹⁹F spin-lattice relaxation time (T₁) at 300 MHz for Tpe [BF₄], 4me [BF₄]₂, 3,5me [PF₆] and 3,5me [BF₄]

Figure 4. calculated temperature dependence of distances between counter ion nuclei and metal center (BF₄ and PF₆) in solution for Tpe [BF₄], 4me [BF₄]₂, 3,5me [PF₆] and 3,5me [BF₄]

[Co(Tpm^{3,5me})₂][PF₆]

[Co(Tpe)₂][BF₄]

[Co(Tpm^{4me})₂][BF₄]

[Co(Tpm^{3,5me})₂][BF₄]

Conclusion

The BF₄⁻ counterion nuclei relax faster and are more tightly associated with the cobalt metal center compared to PF₆⁻ ion in solution. NMR studies of substituted Tpm complexes suggest that counter ion nuclei in solution have a weak interaction with metal center compared to the crystal structure.

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