High-Frequency and -Field EPR Studies on Nitrogen Oxide Complexes of Manganese

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Introduction

Nitric oxide (NO) is one of the most important small molecules in biology, because it is directly involved in a variety of cellular regulation and signaling processes. Part of this function derives from its ability to bind strongly to transition metal ions. Because NO is paramagnetic (\( ^2\Pi \) ground state), the nature of the species formed upon binding of NO to a transition metal ion is non-trivial and has been the subject of extensive computational work. We have begun a project to investigate the electronic structure of coordination complexes of transition metal ions with coordinated NO and with its derivatives such as \( \text{NO}_2 \), which represent oxidation products that would result from biological processes.

The complexes studied employ the tropocoronand (TC) class of ligands which have the structure shown to the left in their neutral, acid form, \( \text{H}_2\text{TC} \); they generally bind metal ions as dianions with loss of the two protons. The macrocyclic core size of the ligand can be tuned by varying the number of methylene groups in the two spacer chains. We investigated the NO and NO\(_2\) complexes of manganese coordinated by the symmetric TC ligand TC-5,5. The latter, \([\text{Mn(TC-5,5)(NO\(_2\))}] \), could be described as a conventional complex of Mn(III) \( (S = 2) \), whereas the former, \([\text{Mn(TC-5,5)(NO)}] \), shows ambiguous magnetic susceptibility in terms of the ground state being \( S = 1 \) or \( 2 \).

Experimental

The EMR Facility with the superconducting 12.5 and 17-T magnets was used to study polycrystalline samples of the highly air sensitive complexes, \([\text{Mn(TC-5,5)(NO\(_2\))}] \) and \([\text{Mn(TC-5,5)(NO)}] \).

Results and Discussion

\([\text{Mn(TC-5,5)(NO\(_2\))}] \) produced spectra that were consistent with those expected from an \( S = 2 \) spin state (Fig. 1). Its spin Hamiltonian parameters are similar to those in four- and five-coordinated Mn(III) as found, e.g., in porphyrins. On the other hand, initial spectra of \([\text{Mn(TC-5,5)(NO)}] \) suggest behavior that cannot be easily classified according to a defined spin ground state, in keeping with the magnetometric measurements. Investigation of these complexes has so far been hampered by lack of sufficient amounts of material of these synthetically challenging complexes. Work is in progress at MIT to rectify this situation.

Conclusions

This project has thus far not provided publishable results; however, the importance of metal-NO coordination chemistry, as well as the dedication of the synthetic and computational workers involved, means that the project will move forward. Particularly, HFEPR studies will be continued on \([\text{Mn(TC-5,5)(NO)}] \) once sufficient amounts of material are in hand.

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References