HFEPR Studies of Titanium(II) Coordination Complexes

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Introduction

Early transition metals are usually found in low electron count complexes. Group 4 metals are often found in the diamagnetic 4+ (nd^0) oxidation state, and sometimes in the paramagnetic 3+ ($3d^1$, S = 1/2) oxidation state. The 2+ (nd^2) oxidation state is extremely rare, and such complexes of Group 4 ions are usually diamagnetic due to having a low energy, doubly occupied MO. An exception are the complexes $TiCl_2(py)_4$ and $TiCl_2(tmeda)_2$, where py = pyridine,[1] tmeda = tetramethylethylenediamine.[2] Very limited magnetic studies indicated that these complexes each exhibited an S = 1 ground state. As part of efforts by the Mindiola group to understand reactive, paramagnetic early transition metal ion complexes,[3] we have investigated these two complexes by HFEPR and other spectroscopic techniques.

Experimental

The very air- and moisture sensitive Ti(II) complexes were prepared at Indiana U. The NHMFL EMR Facility with the superconducting 17-T magnet was used to study them only in the solid state. Unfortunately, these complexes are relatively insoluble in suitable solvents, as well as being much more reactive in solution than in the solid state.

Results and Discussion

HFEPR spectra of solid, polycrystalline $TiCl_2(tmeda)_2$ is shown in Figure 1. The spectrum is clearly from a spin triplet and was easily observable over the range 5 – 60 K, and even at 273 K. The field/frequency dependence of the signals was investigated and allowed extraction of the following frequency-independent spin Hamiltonian parameters: D = –5.24(1) cm^{-1}, E = –0.879(5) cm^{-1}, **g** = [1.878(3), 1.968(3), 1.783(5)]. Additional features due to unidentified decomposition products were also seen. The reactive nature of the Ti(II) complexes means that di- and polynuclear complexes of Ti(II) and Ti(III) could form. The complex $TiCl_2(py)_4$ gave no interpretable spectra; only very broad signals that may be indicative of relaxation effects. The same complexes will also be investigated by variable temperature magnetic susceptibility and magnetic circular dichroism (MCD) spectroscopy.

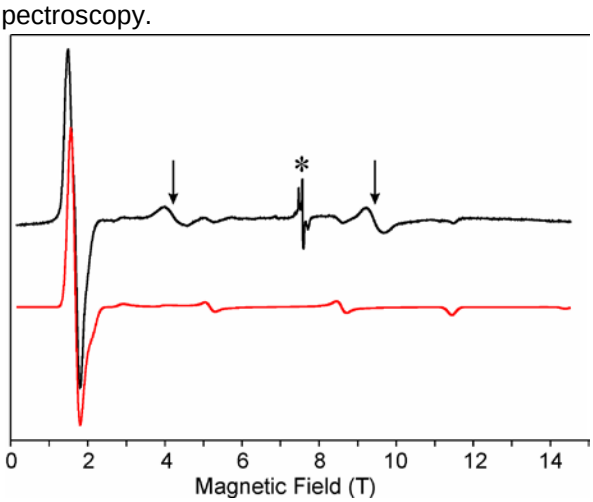

Figure 1. HFEPR spectrum of $TiCl_2(tmeda)_2$ recorded at 203 GHz and 30 K (black trace) and its simulation (red trace) using following spin Hamiltonian parameters: S = 1, D = –5.19 cm^{-1}, E = –0.84 cm^{-1}, **g** = [1.88, 1.95, 1.78]. The group of resonances at ca. 7.5 T indicated with an asterisk belongs to a mononuclear Ti(III) impurity. The origin of the two resonances marked with the arrows remains undetermined, but may be from di- or polynuclear, Ti(II, III) decomposition species.

Conclusions

HFEPR has now been successfully applied to what is one of the exceedingly rare Group 4 metal ion complexes with an S > 1/2 spin ground state, $TiCl_2(tmeda)_2$. The relatively small size of molecule under study means that *ab initio* computational methods can be applied to it. The current results will open the way for a better understanding of reactive, early transition metal ion complexes with relevance to chemical catalysis and energy conversion.

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References

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