Multifrequency EPR Study of $S = 1$ Vanadium (III) Complexes with Nitrogen Containing Ligands

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Introduction

Vanadium is essential to bacterial enzyme systems that fix nitrogen from the atmosphere and is believed to interact with proteins in mammalian organisms. We have investigated a series of model complexes formed by vanadium(III) with nitrogen containing phenantroline and pyridine ligands with the ultimate aim of understanding the relationship between structural, magnetic, and electronic properties of vanadium(III)-containing enzymes such as vanadium nitrogenase. A parallel motivation has been to characterize magnetic properties of V(III)-nitrogen/oxygen coordination complexes as building blocks for molecular magnets. This report contains the results of both magnetometric, and resonance studies. Preliminary theoretical calculations of spin Hamiltonian parameters using ORCA at BP86/DZVP level of theory were also performed.

Experimental

Standard magnetic susceptibility and magnetization measurements on the polycrystalline materials were performed on a SQUID at the U. Barcelona. EPR experiments were conducted at the NHMFL using either the Mn and Sub-mm Wave Facility associated with the 25 T “Keck” resistive magnet, or the EMR Facility and its 17 T superconducting magnet. Parallel-mode X-band EPR measurements were done at UC Davis.

Results and Discussion

Fig. 1 shows the 2-D map of EPR resonances in $[\text{V(III)Phen(Ox)}](\text{ClO}_4)$. The lines were plotted using best-fit spin Hamiltonian parameters: $D = +4.39(4)$, $E = +0.20(5)$ cm$^{-1}$; $g_\perp = g_\parallel = 1.900(3)$. The related complex $[\text{V(III)Bipy(Ox)}](\text{ClO}_4)$ yielded following parameters: $D = +4.43(2)$; $E = +0.01(1)$ cm$^{-1}$; $g_\perp = 1.887(3)$, $g_\parallel = 1.81(1)$.

Magnetometric studies resulted in very similar parameters for both complexes. DFT calculations yielded smaller values of $D$: +2.05, and +2.24 cm$^{-1}$, respectively.

Conclusions

Magnetometric and resonance experiments yield a very consistent set of spin Hamiltonian parameters for the ground state of the two octahedral complexes with a $\text{N}_2\text{O}_4$ coordination sphere with zfs consensus parameter $D \sim 4.0$ – 4.4 cm$^{-1}$. This value of $D$ falls in between the $\text{O}_6$ coordination as in V(acac)$_3$ ($\sim 7$ cm$^{-1}$)$^1$ and $\text{N}_2\text{O}_5$ coordination as in NaV(edta)$\cdot$3H$_2$O ($\sim 2$ cm$^{-1}$)$^2$. Attempts to calculate ab initio the zfs parameters have met with limited success. DFT-type calculations tend to underestimate the magnitude of zfs, although they give the correct sign of $D$.

References