HFEPR Studies of Aminocarboxylate Complexes of Vanadium(III) in Frozen Aqueous Solution

J. Telser (Roosevelt U., Biological, Chemical and Physical Sciences); C.-C. Wu, K.-Y. Chen, H.-F. Hsu (National Cheng Kung U., Taiwan, Chemistry); A. Ozarowski, J. Krzystek (NHMFL, EMR)

Introduction

As an extension of investigating model complexes for the vanadium-containing nitrogenase enzyme (V-N_2ase),[1] we have pursued studies of complexes formed by the vanadium(III) ion ($3d^2$, $S = 1$) with ligands of biological relevance belonging to the well known class of aminocarboxylates.[2] The biological relevance of aminocarboxylate complexes of V(III) stems from two disparate areas: they are analogous to those in ascidian (sea squirt) blood cells,[3] and are also employed as insulin mimics.[4] Perfecting the methodology of recording HFEPR spectra in frozen solution was the focus of the current study, since such experimental conditions are more relevant to biological samples than are solid-state studies.

Experimental

The EMR facility with a 17T superconducting magnet was used in this specific work. The solutions were prepared in degassed water with the pH adjusted to ~ 7. The V(III) concentrations were ~200 mM.

Results and Discussion

All three of the investigated V(III) complexes (with nta, edta, and trdta ligands) gave HFEPR spectra in frozen aqueous solution at multiple frequencies and temperatures. A representative spectrum for the trdta complex is shown in Fig. 1. As also indicated in the Fig. 1 caption, full spin Hamiltonian parameters were extracted for multiple species of this complex, which can be related to possible isomerism in solution, resulting from aqua versus carboxylato ligand coordination.[2,3]

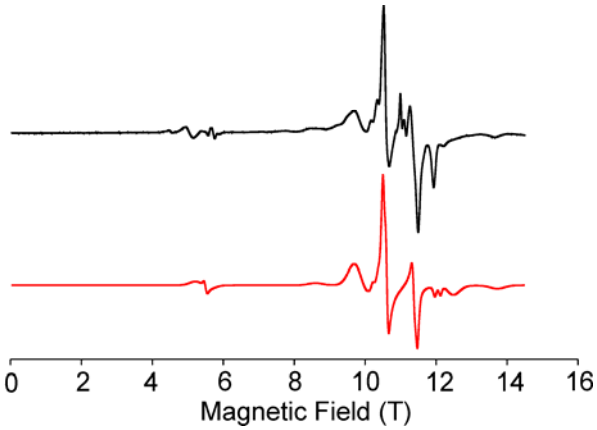

Figure 1. HFEPR spectrum of aqueous $[V(trdta)]^-$ recorded at 305 GHz and 20 K (black trace) together with a simulation (red trace) assuming an ideal powder pattern, which is the sum of equal amounts of three individual triplet species. Spin Hamiltonian parameters used in the simulations: all $S = 1$; one species with $D = +0.68$ cm^{-1}, $E = 0$, $g_{x,y} = 1.98$, $g_z = 1.95$; one species with the same except, $D = +0.87$ cm^{-1}; one species with the same except: $D = +2.35$ cm^{-1}, $g_{iso} = 1.95$. The sharp peaks appearing near 11 T in the experimental trace are due to a minor V(IV) impurity.

Conclusions

We have shown the ability of HFEPR to determine spin Hamiltonian parameters for the non-Kramers ion V(III) in frozen aqueous solutions. HFEPR is uniquely able to identify multiple species in solution, which optical measurements cannot distinguish. This demonstrates the potential of this technique for application to actual biological conditions.

Acknowledgements

We thank the National Science Council of Taiwan, Roosevelt University, and the NHMFL User Collaboration Grants Program for support.

References

[1] Chu, W.-C., *et al.*, Inorg. Chem. **45**, 3164-3166 (2006).
[2] Chen, K.-Y., *et al.*, NHMFL Research Report (2007); Telser, J., *et al.*, J. Inorg. Biochem., under review.
[3] Kanamori, K., *et al.*, Inorg. Chem. **33**, 5547-5554 (1994).
[4] Monga, V., *et al.*, Inorg. Chem. **44**, 2678-2688 (2005).