# HFEPR Studies on Vanadium(III) Complexes with Aminocarboxylate Ligands

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## Introduction

In the course of our investigation of model complexes for the vanadium-containing nitrogenase enzyme (V-$N_2$ase),[1] we have performed studies on another series of complexes that also contain the vanadium(III) ion ($3d^2$, $S = 1$). In the V-$N_2$ase model complexes, the V(III) ion is chelated by a phosphorus atom and three arylthiolates (PS3 series ligand).[1] In contrast, the complexes studied here employ well known aminocarboxylate ligands such as nta (nitrilotriacetate), trdta (1,3-diaminopropane-*N*,*N*,*N*′,*N*′-tetraacetate), and edta (1,2-diaminoethane-*N*,*N*,*N*′,*N*′-tetraacetate). These ligands have exclusively light atom donors, N and O, in contrast to the heavy atoms donors P and S in PS3. As a result, the electronic structure is expected to be better described by a $3d^2$ ligand-field basis set. This is in contrast to the V(III) complexes with the PS3 ligands, which have extensive contribution of ligand-centered spin. These aminocarboxylate complexes of V(III) are of biological interest in their own right, as they are found in ascidian (sea squirt) blood cells.[2]

## Experimental

The NHMFL Mm- and Sub-mm Wave Facility with the resistive ("Keck") 25-T magnet, and the EMR Facility with the superconducting 17-T magnet were used to study polycrystalline samples of $[V(nta)(H_2O)_3]$, $Na[V(trdta)]\cdot 3H_2O$, and $Na[V(edta)(H_2O)]\cdot 3H_2O$, as well as the same complexes in frozen aqueous solution.

## Results and Discussion

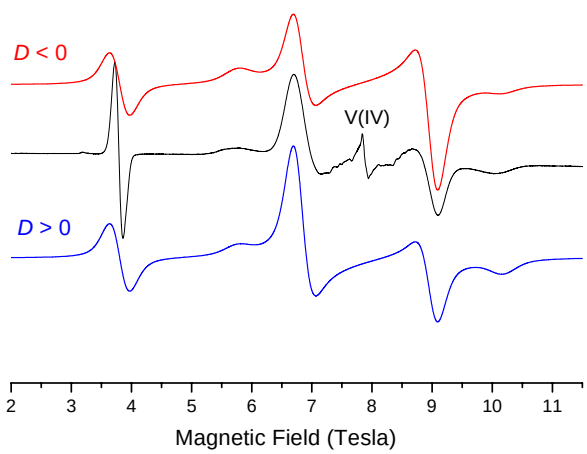


**Figure 1.** HFEPR spectrum of aqueous $[V(edta)(H_2O)]^-$ at 208 GHz and 20 K. Black trace: experiment; colored traces: simulations using the parameters: $S = 1$, $|D| = 2.01\ cm^{-1}$; $E = 0$, $g_{iso} = 1.95$; red: $D < 0$; blue: $D > 0$.

High-frequency and -field EPR (HFEPR) spectroscopy was performed on a series of aminocarboxylate complexes of V(III). As expected, the ground spin state is a non-Kramers triplet. Spectra were recorded not only for solid samples, as in previous studies of non-Kramers ions, but also for frozen aqueous solutions, as shown in Fig. 1. As also indicated in Fig. 1, full spin Hamiltonian parameters were extracted for these complexes.

## Conclusions

The ability of HFEPR to determine spin Hamiltonian parameters for the non-Kramers ion V(III) has been further demonstrated. These data, in combination with crystallographic[2] and solution optical (UV-Vis-NIR) spectroscopic data[3] will provide a complete picture of the electronic structure of this interesting ion in complexes with biologically relevant ligands. Equally important, from a methodological point of view, is the ability to record HFEPR spectra in frozen aqueous solution for an unstable non-Kramers spin triplet transition metal ion.

## Acknowledgements

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## References

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