

High-Field EPR Studies on V(IV) and V(III) Complexes of Schiff Bases and Diaminebis(aryloxides)

Janas, Z. (Wroclaw U., Poland, Chemistry); Ozarowski, A. (NHMFL)

Introduction

The chemistry of vanadium complexes with tetradentate ONNO ligands like Schiff bases (salens) and diaminebis-(aryloxides) (salans) is of wide interest to chemists in the context of their relevance to bioinorganic chemistry, molecular magnetism, catalysis and prospective therapeutic applications [1]. In this work, several mono- and binuclear complexes of V(IV) as well as mononuclear complexes of V(III) were synthesized and studied by magnetic methods and EPR.

Experimental

HFEPR spectra were recorded on the 15/17 T SC magnet and transmission instrument of the EMR facility. Magnetic susceptibility measurements were performed at the Wroclaw University.

Results and Discussion

The binuclear V(IV) systems proved to be difficult subjects for HFEPR owing to very small zero-field splitting accompanied by the “g-strain”, as well as strong antiferromagnetic coupling.

Two mononuclear V(III) complexes were studied at high frequencies. Both exhibited spectra of spin $S=1$ state with large positive parameters of spin Hamiltonian [1], $D = 5.02 \text{ cm}^{-1}$ and $E = 1.52 \text{ cm}^{-1}$.

$$\hat{H} = \mu_B \mathbf{B} \{g\} \hat{S} + D \left\{ \hat{S}_z^2 - \frac{1}{3} S(S+1) \right\} + E (\hat{S}_x^2 - \hat{S}_y^2) \quad [1]$$

Compound **2** differs from **1** in **Fig.1** by the substituent in the benzene ring. **1** has two slightly different molecules in its crystal cell, opposite to **2**. Two different spectra are resolved in HFEPR of **1** (**Fig.2**), whose D parameters differ by 0.53 cm^{-1} .

Conclusions

The integer-spin $S = 1$ electronic configuration d^2 of the V(III) ion gives rise to large zero-field splitting which can only be studied by HFEPR. Two slightly different molecules present in the crystal lattice of **1** could be distinguished. There are features in the spectra indicating weak intermolecular interactions. This research is ongoing. Theoretical calculations of the spin Hamiltonian parameters are being currently performed

Acknowledgements

The National High Magnetic Field Laboratory is supported by the National Science Foundation through NSF/DMR-1157490/1644779 and the State of Florida.

ZJ acknowledges financial support by the Wroclaw University.

References

[1] Kober, E., *et al.*, *Inorg. Chem.*, **175**, 10888–10898 (2016).

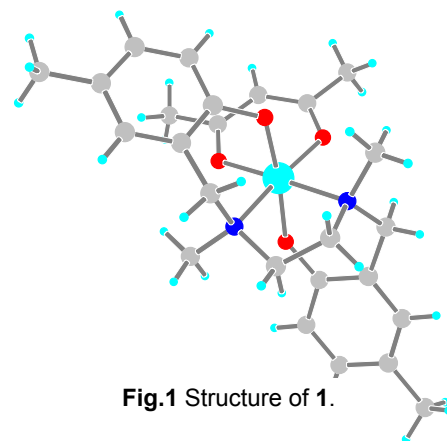


Fig.1 Structure of **1**.

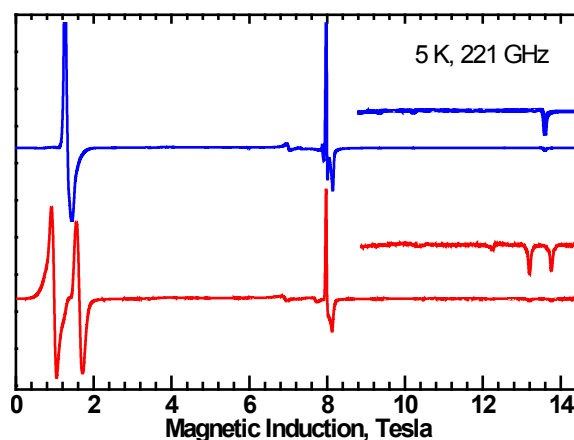


Fig.2 HFEPR spectra of **1** (bottom) and **2** (top).