

Chemistry

As published in *Angew. Chem. Int. Ed.*, this constitutes the first High Frequency Electron Paramagnetic Resonance (HF EPR) report in the literature on a strongly reduced oxidation state of vanadium, V(II). A broader significance lies in the magnetic characterization of catalytically active complexes of vanadium.

• Published in *Angew. Chem. Int. Ed.*, **49**, 9871–9875 (2010).

HF EPR Studies of a Three-Coordinate Organometallic Vanadium(II) Complex

B. L. Tran, M. Singhal, H. Park, M. Pink, D. J. Mindiola (Indiana University, Chemistry); J. Krzystek, A. Ozarowski (Magnet Lab, FSU); J. Telsler (Roosevelt U., Chemistry); O. P. Lam, K. Meyer (Erlangen U., Germany, Chemistry)

Introduction

Vanadium can access a wide range of oxidation states, many of which are paramagnetic. These include V(IV) ($3d^1$, $S = 1/2$), well-studied by EPR, as well as states with multiple unpaired electrons such as V(III) ($3d^2$, $S = 1$), which has been studied by HF EPR at Magnet Lab¹, and V(II) ($3d^3$, $S = 3/2$), hitherto unstudied by HF EPR. V(II) is best known in vanadocene, Cp_2V ($Cp = \text{cyclopentadiene monoanion}$), but recent synthetic work has led to the preparation of V(II) complexes with a wider variety of ligands, such as nacnac, the β -diketiminato ligand². Mindiola and co-workers have prepared a “masked” three-coordinate vanadium(II) complex, $[(nacnac)V(Ntol_2)]$, where nacnac = $RN=C(CH_3)CH=C(CH_3)NR$ monoanion, with $R = 2,6$ -diisopropylphenyl, and $tol = \text{tolyl}$ ($CH_3C_6H_4$).

Experimental

The Magnet Lab EMR Facility with the superconducting 17-tesla magnet was used to study $[(nacnac)V(Ntol_2)]$ both as a polycrystalline sample and in frozen toluene solution.

Results and Discussion

The structure of $[(nacnac)V(Ntol_2)]$ is shown in Figure 1. In addition to coordination by the two imino N atoms of the nacnac ligand and the amido nitrogen of $[N(tol)_2]^-$, there is an interaction with one of the tolyl rings, which “masks” the V(II) center. This unusual coordination geometry is reflected in the HF EPR spectrum of the complex, both as a solid and in frozen

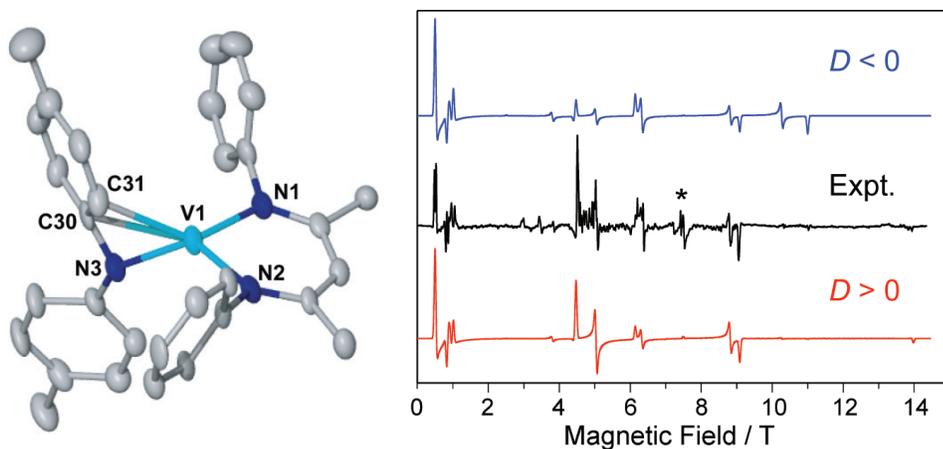


FIGURE 1. Molecular structure of $[(nacnac)V(N(tol)_2)]$. Atoms coordinated to V(II) are labeled.

FIGURE 2. HF EPR spectra of polycrystalline $[(nacnac)V(Ntol_2)]$ recorded at 10 K and 208 GHz (black trace). Simulated traces are given above and below: $S = 3/2$, $|D| = 2.99$, $|E| = 0.11 \text{ cm}^{-1}$, $g_{iso} = 1.98$, $\Delta B_{iso} = 250 \text{ G}$; for the upper (blue) trace, $(D, E) < 0$ was used; for the lower (red) trace, $(D, E) > 0$ was used. The asterisk indicates a minor V(IV) impurity which is not simulated.

toluene solution. A representative spectrum is shown in Figure 2. The pattern is that of a nearly axial spin quartet with axial zero-field splitting, $D = 3.0 \text{ cm}^{-1}$, unusually high for a $3d^3$ (4A_2) system, in particular compared to values reported for typical V(II) coordination complexes³, for which $|D| < \sim 0.2 \text{ cm}^{-1}$.

Conclusions

This study represents the first application of HF EPR to V(II) and is a rare application of this technique to an organometallic complex. It is hoped that the observation of a large magnitude zero-field splitting for V(II) in this case will stimulate computational investigations as well as spectroscopic studies on related d^3 complexes. These include “true” three-coordi-

nate V(II) complexes (recently prepared in the Mindiola group) since this will allow us to understand the effect of the “masking” arene moiety in the electronic structure of these low-valent metal ions.

Acknowledgements

This work was supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Science, Office of Science, U.S. Department of Energy (No. DE-FG02-07ER15893).

REFERENCES

- Ye, S., et al., *Inorg. Chem.*, **49**, 977-988 (2010).
- Bourget-Merle, L. et al., *Chem. Rev.*, **102**, 3031-3065 (2002).
- Jacobsen, C.J.H. et al., *Inorg. Chem.*, **32**, 1216-1221 (1993).