HFEPR of a Manganese(V) Nitrido Complex with a Novel Tripodal Carbene Ligand

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Introduction

Transition metal nitrido (N^{3-}) complexes are of great interest because of their possible intermediacy in both biological and industrial nitrogen "fixation" (i.e., reduction of dinitrogen (N_2) to ammonia (NH_3)) processes. Biological N_2 reduction is achieved by the enzyme nitrogenase, in which Fe is the likely site of reaction within a complex, multi-metal cluster (FeMoco) [1]. Industrial N_2 reduction occurs via the Haber-Bosch process, which also uses heterogeneous Fe catalysts, but other metals are possible. Catalytic N_2 reduction by small molecules, such as by an Mo(III) complex ($4d^3$, S = 1/2), has been recently achieved as well [2].

The Meyer group in Erlangen have been working actively in this area and have developed a novel, neutral tripodal ligand, which comprises N-heterocyclic carbene (NHC) donors. The ligand is referred to as $TIMEN^R$, where R is a bulky alkyl or aryl protecting group on each NHC; here R = xyl (xylyl, 2,6-dimethylphenyl) [3]. The structure of several Mn complexes of $TIMEN^{xyl}$ has been determined. Our interest here is in the Mn(V) nitrido complex, $[(TIMEN^{xyl})Mn^{V}N](PF_6)_2$ (structure shown in Figure 1), which is prepared by oxidation via NO^+ of $[(TIMEN^{xyl})Mn^{IV}N](PF_6)$. The Mn(IV) ($3d^3$) complex surprisingly has S = 1/2 rather than S = 3/2 and has been investigated by conventional EPR [3]. The Mn(V) ($3d^2$) complex equally surprisingly has an S = 1 spin ground state, as opposed to S = 0, which is typical for nd^2 complexes of this general type. The electronic structure of this Mn(V) nitrido complex is therefore of great interest.

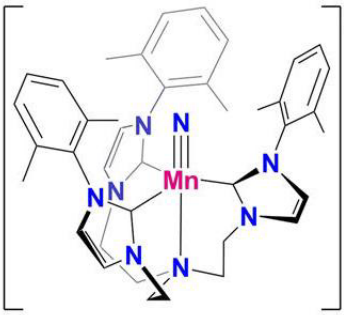

Figure 1. Structure of cation of $[(TIMEN^{xyl})Mn^{V}N](PF_6)_2$

Experimental

The Millimeter and Submillimeter Wave Facility and the 25-T resistive "Keck" magnet at NHMFL were used to measure HFEPR spectra of a 28.7 mg sample of powdered $[(TIMEN^{xyl})MnN](PF_6)_2$. The sample had been loaded into a HFEPR holder (Fisher® polyethylene vial) in Erlangen and was studied without any exposure of this highly air-sensitive complex to atmosphere at NHMFL.

Results and Discussion

The HFEPR spectra of $[(TIMEN^{xyl})MnN](PF_6)_2$ were recorded at multiple frequencies; that at 650 GHz and 4.2 K is shown in Figure 2, together with simulations. These indicate that the sign of axial zero-field splitting (zfs), D, is positive. A slight rhombic zfs, E, is also required, which shows the sensitivity of this parameters as the complex has nearly C_3 symmetry. There may also be two, very slightly different species, which are not distinguished crystallographically.

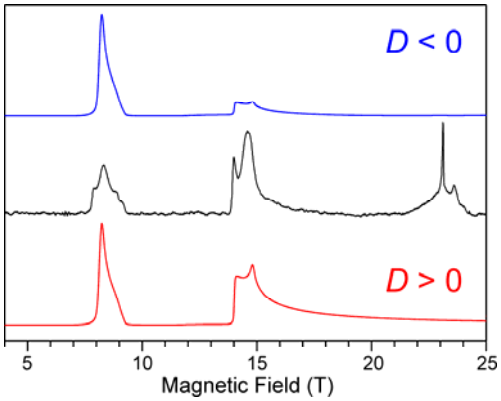

Figure 2. HFEPR spectrum (black trace) recorded at 650 GHz and 4.2 K of powder $[(TIMEN^{xyl})Mn^{V}N](PF_6)_2$. Simulations use S = 1, $|D|$ = 13.32 cm^{-1}, $|E|$ = 0.26 cm^{-1}, g = 2.00, with sign of zfs as indicated, showing the better correspondence with experiment using D > 0.

Conclusions

HFEPR is able to conclusively document the spin triplet ground state of this unusual Mn(V) nitrido complex. The stage is set for computational analysis of the zfs parameters provided.

Acknowledgements

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