

High-Frequency and -Field EPR Spectroscopy of a P-bound V(III)-PCO Complex

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Introduction

Synthetic chemistry within the ligand class formulated as $[XCE]^-$, where X belongs to a Group 16 atom (O, S, Se) and E = a Group 15 atom (N, P, As), has long been centered around the coordination chemistry of the ubiquitous, ambidentate $[OCN]^-$ (cyanate) and $[SCN]^-$ (thiocyanate) ligands [1, 2]. The “hard” Lewis base O or N atom coordinates to “hard” acids, while the “soft” S atom coordinates to “soft” bases. Another in the $[XCE]^-$ series is $[OCP]^-$ (phosphaethynolate ion), which has been only more recently exploited for coordination chemistry [1, 2]. This ligand has been shown to bind via O to “classic” hard acids, such as Sc(III) ($3d^0$), and via P to “classic” soft acids such as W(0) ($5d^6$) [3,4]. The possibility of P-bound complex with a hard acid, i.e., an oxidized, early 3d ion is intriguing. We show that with the proper choice of ancillary ligands, P-coordination by phosphaethynolate ion to V(III) ($3d^2$) is possible, yielding a novel V(III)-PCO complex with a spin triplet ($S = 1$) ground state. The electronic structure of such a complex is of interest for both spectroscopic and computation study.

Experimental

The starting material, $[(nacnac)VCl(OAr)]$ ($nacnac^- = [ArNC(CH_3)_2CH]$; Ar = 2,6-*i*-Pr₂C₆H₃) was treated with 1 equivalent of Na(OCP)(1,4-dioxane)_{2.5} to yield $[(nacnac)V(OAr)(PCO)]$ for which V–P, as opposed to V–O connectivity was unambiguously confirmed by single crystal X-ray diffraction (XRD) studies as shown in **Fig.1**. Microcrystalline $[(nacnac)V(OAr)(PCO)]$ was investigated by HFEPFR spectroscopy using the 17 T SC magnet system in the EMR Facility at NHMFL. A complete multi-frequency study was performed, at several temperatures.

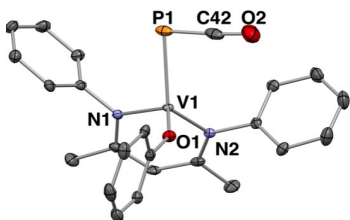


Fig.1 Molecular structure of $[(nacnac)V(OAr)(PCO)]$ from XRD.

Results and Discussion

An unusual aspect of the molecular structure of $[(nacnac)V(OAr)(PCO)]$ is the V–P–C(O) angle, which is $< 90^\circ$: $85.93(5)^\circ$, as opposed to the near linear Sc–O–C(P) angle in the corresponding Sc(III) complex. The correlation of this geometric structure with electronic one requires in part the use of HFEPFR, which readily yielded the following $S = 1$ spin Hamiltonian parameters for the complex: $D = +2.60(1) \text{ cm}^{-1}$, $|E| = 0.346(5) \text{ cm}^{-1}$, $g_x = 1.962(5)$, $g_y = 1.938(5)$, $g_z = 1.953(5)$. A representative spectrum is shown in **Fig.2**, demonstrating the positive sign of D . The zero-field splitting for this complex is in the range for that of other low-coordinate V(III) complexes, but the paucity of corresponding data makes generalizations difficult.

Conclusions

The phosphaethynolate ion, $[OCP]^-$, can coordinate via its “soft” P end to a “hard” transition metal ion, V(III). The resulting complex, $[(nacnac)V(OAr)(PCO)]$, has a spin triplet ground state as shown by HFEPFR. Elucidation of the electronic structure of this complex is in progress by computational methods that make use of the HFEPFR-derived parameters as well as the unusual molecular structure.

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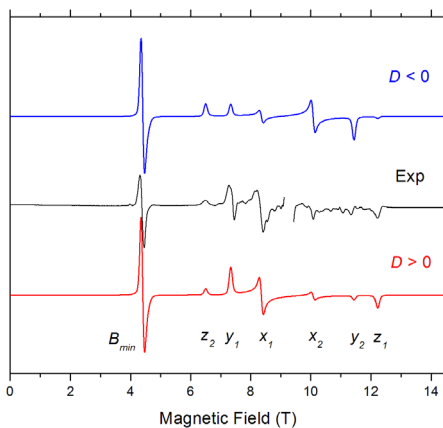


Fig.2 HFEPFR spectrum of $[(nacnac)V(OAr)(PCO)]$ at 10 K and 257 GHz. The black trace is experiment in which the V(IV) impurity signal at $g = 1.98$ was left out; the colored traces are simulations using: $S = 1$, $|D| = 2.62 \text{ cm}^{-1}$, $|E| = 0.36 \text{ cm}^{-1}$, $g_x = 1.96$, $g_y = 1.94$, $g_z = 1.95$. The particular turning points are labelled using standard triplet nomenclature.