Synthesis and Redox-Induced Structural Isomerization of the Pentagonal Bipyramidal Complexes \([W(CN)_5(CO)_2]^3-\) and \([W(CN)_5(CO)_2]^2-\)**

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There has been a surge of interest in the use of cyanometallate complexes for the synthesis of magnetic molecules and solids. The variation of the metal electron configuration and coordination geometry enables adjustment of magnetic properties, such as the spin ground state, magnetic anisotropy, and the strength of the exchange coupling. Second- and third-row transition-metal ions are of particular interest, owing to a variety of reactivity patterns and the preference for low-spin configurations, however, there are relatively few examples of simple, paramagnetic building units containing these metals. While S = 1/2 complexes, such as \([Nb(CN)_8]^4-\) and \([M(CN)_7]^3-\) (M = Mo, W) have been successfully incorporated into high-spin clusters, the symmetric ligand arrangement and lack of orbital angular momentum have typically led to only a small overall magnetic anisotropy. In contrast, use of the pentagonal bipyramidal species \([Mo(CN)_5]^2+\) with a \(2E_1\) ground state has yielded highly anisotropic magnetic solids, and is predicted to give rise to single-molecule magnets with large relaxation barriers. Analogous complexes of 5d metal ions should possess still greater anisotropy. This prediction is indeed borne out in the EPR spectrum of \([Re(CN)_7]^3-\), a species which, unfortunately, is highly unstable to reduction. Although the diamagnetic complex \([W(CN)_5]^2-\) has been claimed on the basis of spectroscopic data, attempts to reproduce these results led only to mixtures containing \([W(CN)_5]^+\). Herein, we demonstrate the use of a mixed cyanide/carbonyl ligand set to stabilize two new pentagonal bipyramidal complexes: \([W(CN)_5(CO)]^2-\) and \([W(CN)_5(CO)]^3-\).

The complex \([WI_2(CO)_3(MeCN)]\) was employed as a convenient, labile source of tungsten(II). Reaction with five equivalents of \((Bu_4N)CN\) in toluene readily afforded \((Bu_4N)_2[W(CN)_5(CO)_2]\) (1). Compound 1 is soluble in polar organic solvents, such as chloroform, dichloromethane, and acetonitrile. A cyclic voltammogram of 1 in dichloromethane revealed successive oxidation waves at \(-0.91, -0.25,\) and \(-0.04\) V versus \([Cp_2Fe]\) with the first wave exhibiting partial reversibility (see Figure S3 in the Supporting Information). Accordingly, reaction of 1 with slightly more than one equivalent of \([Cp_2Fe][(PF_6)_2]\) afforded the one-electron oxidized product \((Bu_4N)_2[W(CN)_5(CO)_2]\) (2).

X-ray analysis of a single crystal of 1 revealed two molecules of \([W(CN)_5(CO)_2]^3-\) in the asymmetric unit, each adopting a slightly distorted pentagonal bipyramidal geometry (see Figure 1, left). In both molecules, the two carbonyl groups were tentatively assigned to the axial sites on the basis of comparisons of thermal ellipsoids, W–C and W–O/N distances, and refinement residual factors. The mean W–C eq distance was found to be approximately 0.2 Å shorter than the mean W–C eq distance, consistent with the stronger σ-acceptor ligand occupying the axial sites. Note that this is a significant axial contraction when compared with \([Mo(CN)_7]^3-\) and \([Re(CN)_7]^3-\) which show no differences between the axial and equatorial bonds within experimental error. For each molecule, the distortion away from a perfect pentagonal bipyramidal coordination of the \(W^{II}\) center occurs amongst the cyanide ligands, one of which (the rightmost in Figure 1) is raised above the mean equatorial plane by approximately 10°, and one of which (the foremost) is pushed below the plane by approximately 17°.
approximately 8°. Similar deviations from ideal $D_{3h}$ symmetry have been reported for the $[\text{Mo(CN)}_6]^3-$ complex in K$_3[\text{Mo(CN)}_6] \cdot \text{H}_2\text{O}$, and were attributed to crystal packing effects.\[14\]

Spectroscopic characterization was performed to confirm the assignment of carbonyl and cyanide ligand positions in the crystal structure. The infrared spectrum of a single crystal of 1 displays three peaks in the CO/CN stretching region: two intense bands centered at 2089 and 1789 cm$^{-1}$ and a weaker band at 1902 cm$^{-1}$ (see Figure 2). The spectrum of the analogous compound with $^{13}$C-labeled cyanide ligands, (Bu$_4$N)$_3[\text{W(}^{13}\text{CN})_5(\text{CO})_2]$, shows the expected isotopic shift in just the highest energy band, which therefore corresponds to a CN stretching mode. Solution spectra collected in CH$_2$Cl$_2$ in just the highest energy band, which therefore corresponds to a CN stretching mode. The solution spectrum, could be due to a loss of inversion symmetry. The weak CO stretch at 1902 cm$^{-1}$, with approximately 8°, suggests that one carbonyl ligand has moved from an axial site to an equatorial site. Thus, oxidation of the complex appears to induce an isomerization from a trans geometry with approximate $D_{3h}$ symmetry to a cis geometry with $C_2v$ symmetry.

The properties of 2 are indeed consistent with a less-symmetric molecule. Consistent with $C_s$ symmetry, the infrared spectrum exhibits seven peaks in the CO/CN stretching region (see Figure 2). On the basis of comparisons with the infrared spectrum of (Bu$_4$N)$_3[\text{W(}^{13}\text{CN})_5(\text{CO})_2]$, the three lowest-energy peaks can be assigned as CO stretches, while the three highest energy peaks clearly correspond to CN stretches. The band at intermediate energy shifts from 2042 to 2038 cm$^{-1}$, suggesting a CO stretching mode admixed with some slight CN stretching character. The solution spectra are similar, although the band at intermediate energy is now split into two peaks that maintain the CO/CN mixed character. As for 1, all stretches with CO character shift to higher frequency in more polar solvents, suggestive of ion-pairing (see Figure S2). This situation complicates assignment of the geometry of the complex. However, we can also utilize the ability of the cyanide ligand to bridge metal centers to attempt to distinguish the two types of ligands. Reaction of 2 with [(PY$_5$Me$_2$)$_2\text{Mn(}^{15}\text{MeCN})_2^2$]Cl$_2$ (PY$_5$Me$_2$ = 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine) in acetonitrile afforded the pentanuclear cluster [(PY$_5$Me$_2$)$_2\text{Mn}_2\text{W(}^{15}\text{MeCN})_2^4\text{]}_2$ depicted in Figure S7 of the Supporting Information. In this cluster four of the equatorial ligands bridge to the Mn$^{II}$ centers, fixing these as cyanide groups. This situation eliminates both isomers with $C_{6v}$ symmetry, and again suggests $C_s$ symmetry. Note that, since pentagonal bipyramidal complexes can be dynamic in solution, we still cannot conclusively rule out the possibility of other lower symmetry isomers. Taken together, however, the results strongly support an oxidation-induced structural isomerization away from $D_{3h}$ symmetry to afford the $C_s$ symmetry isomer.

The X-band EPR spectrum of 2 in a frozen CH$_2$Cl$_2$ solution at 30 K is nearly axial, with $g_a = 1.92$, $g_c = 1.89$, and $g_e = 1.82$ (see Figure S5 in the Supporting Information). It further exhibits hyperfine splitting, attributable to the $^{183}\text{W}$ isotope ($I = 1/2$, 14.3% abundant), with $A_a = 150$ G, $A_c = 20$ G and $A_e = 120$ G. This level of anisotropy is comparable to that observed for $K_3[\text{Mo(CN)}_6]^3\text{]}_2\text{H}_2\text{O}$ ($g_c = 2.10$, $g_a = 1.97$), wherein [Mo(CN)$_6$]$^{3-}$ is suspected to adopt a monocapped trigonal prismatic geometry.\[14,15\] It is significantly lower,
anticipated. The isomerization of this low-spin $d^3$ complex can further be viewed as a Jahn–Teller distortion associated with the loss in energy. Thus, the intense peaks at 1789 and 2089 cm$^{-1}$ can be assigned to A'$_2$ and E', vibrational modes involving CO and CN stretches, respectively.

Optimization of the structure of [W(CN)$_5$(CO)$_2$]$^{2+}$ confirmed the C$_5$-symmetry isomer observed in 2 to be lowest in energy. The D$_{5h}$ isomer, the next most stable structure, was calculated to be just 0.15 eV higher in energy. Unfortunately, reliable vibrational frequencies could not readily be obtained from this open-shell calculation. As evident from the HOMO depictions in Figure 3, the driving force for the oxidation-induced ligand isomerization can be traced to a preference for the less-electron-rich W$^{III}$ center to engage in extensive back-donation from the W center to the axial CO groups of 2.

These results demonstrate the synthesis of two new pentagonal bipyramidal complexes, [W(CN)$_5$(CO)$_2$]$^{3+}$ and [W(CN)$_5$(CO)$_2$]$_2$$^{3+}$, with structures related through a remarkable oxidation-induced ligand isomerization. Future efforts will focus on the incorporation of these species into new magnetic and photomagnetic compounds. In particular, we will attempt to oxidize [W(CN)$_5$(CO)$_2$]$^{3+}$ after incorporating it into a high-nuclearity cluster. Given the small calculated energy difference between isomers and appropriate steric constraints within a cluster, it is envisioned that the $D_{5h}$ structure will be preserved, thereby enabling access to a very substantial magnetic anisotropy.

Keywords: carbonyl ligands · cyanides · isomerization · oxidation · tungsten

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Figure 3. Energy levels and occupied orbitals showing π back-donation from the W center to the axial CO groups of 1 (left) and the one axial and one equatorial CO groups of 2 (right) as calculated using DFT.


[12] See Tables S1 and S2 in the Supporting Information for crystal data and structure refinement details. CCDC 672441 and 672442 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.


[17] DFT calculations were performed using Jaguar, version 6.5, Schrödinger, LLC, New York, NY, 2005, with a spin restricted formalism. Complex geometries were taken from the crystal structures of 1 and 2, and were then optimized using the LACVP functional. Effective core potentials were employed for W (LanL2DZ) while C, N, and O atoms were described with the 6-31G basis set.