

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

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There has been a surge of interest in the use of cyanometalate complexes for the synthesis of magnetic molecules^[1] and solids.^[2] 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 large magnetic anisotropy stemming from spin-orbit coupling, as well as to their diffuse valence d orbitals, which can result in strong magnetic exchange.^[3] Owing to poorly understood reactivity patterns and the preference for low-spin electron configurations, however, there are relatively few examples of simple, paramagnetic building units containing these metals. While $S = 1/2$ complexes, such as $[\text{Nb}(\text{CN})_8]^{4-}$ and $[\text{M}(\text{CN})_8]^{3-}$ ($\text{M} = \text{Mo}, \text{W}$) have been successfully incorporated into high-spin clusters,^[1c,b,4] 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 $[\text{Mo}(\text{CN})_7]^{4-}$ with a $^2E_1''$ ground state has yielded highly anisotropic magnetic solids,^[5] and is predicted to give rise to single-molecule magnets with large relaxation barriers.^[6] Analogous complexes of 5d metal ions should possess still greater anisotropy. This prediction is indeed borne out in the EPR spectrum of $[\text{Re}(\text{CN})_7]^{3-}$, a species which, unfortunately, is highly unstable to reduction.^[7,8] Although the diamagnetic complex $[\text{W}(\text{CN})_7]^{5-}$ has been claimed on the basis of spectroscopic data,^[9] attempts to reproduce these results led only to mixtures containing $[\text{W}(\text{CN})_8]^{4-}$. Herein, we demonstrate the use of a mixed cyanide/carbonyl ligand set^[10] to stabilize two new pentagonal bipyramidal complexes: $[\text{W}(\text{CN})_5(\text{CO})_2]^{3-}$ and $[\text{W}(\text{CN})_5(\text{CO})_2]^{2-}$.

The complex $[\text{W}_2(\text{CO})_3(\text{MeCN})_2]^{11}$ was employed as a convenient, labile source of tungsten(II). Reaction with five equivalents of $(\text{Bu}_4\text{N})\text{CN}$ in toluene readily afforded $(\text{Bu}_4\text{N})_3[\text{W}(\text{CN})_5(\text{CO})_2]$ (**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 $[\text{Cp}_2\text{Fe}]^{0/1+}$, ($\text{Cp} = \text{C}_5\text{H}_5^-$) 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 $[\text{Cp}_2\text{Fe}](\text{PF}_6)$ afforded the one-electron oxidized product $(\text{Bu}_4\text{N})_2[\text{W}(\text{CN})_5(\text{CO})_2]$ (**2**).

X-ray analysis of a single crystal of **1** revealed two molecules of $[\text{W}(\text{CN})_5(\text{CO})_2]^{3-}$ in the asymmetric unit, each adopting a slightly distorted pentagonal bipyramidal geometry (see Figure 1, left).^[12] In both molecules, the two carbonyl

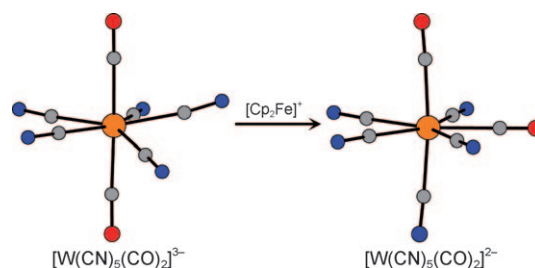


Figure 1. Structures of the pentagonal bipyramidal complexes in **1** (left) and **2** (right). Orange W, gray C, blue N, and red O. In **2**, the complex resides on a twofold rotation axis of the crystal, resulting in disorder of the axial carbonyl and cyanide ligands. Selected mean interatomic distances [Å] and angles [°] for two crystallographically independent molecules in **1**: W–C(O) 1.99(2), W–C(N) 2.17(3), C_{eq}–W–C_{eq} 73(1), C_{ax}–W–C_{ax} 177.5(4), W–C–O 177(1), W–C–N 177(2). Selected interatomic distances [Å] and angles [°] for **2**: W–C_{eq}(O) 2.083(7), mean W–C_{eq}(N) 2.1825(5), W–C_{ax} 2.030(4), mean C_{eq}–W–C_{eq} 72(3), mean C_{ax}–W–C_{ax} 173.9(2), W–C_{eq}–O 180.0, mean W–C_{eq}–N 178.05(5), W–C_{ax}–(O/N) 177.4(3).

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_{ax} distance was found to be approximately 0.2 Å shorter than the mean W–C_{eq} distance, consistent with the stronger π -acceptor ligand occupying the axial sites. Note that this is a significant axial contraction when compared with $[\text{Mo}(\text{CN})_7]^{4-}$ ^[13] and $[\text{Re}(\text{CN})_7]^{3-}$ ^[7] 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

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approximately 8°. Similar deviations from ideal D_{5h} symmetry have been reported for the $[\text{Mo}(\text{CN})_7]^{5-}$ complex in $\text{K}_5[\text{Mo}(\text{CN})_7] \cdot \text{H}_2\text{O}$, 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

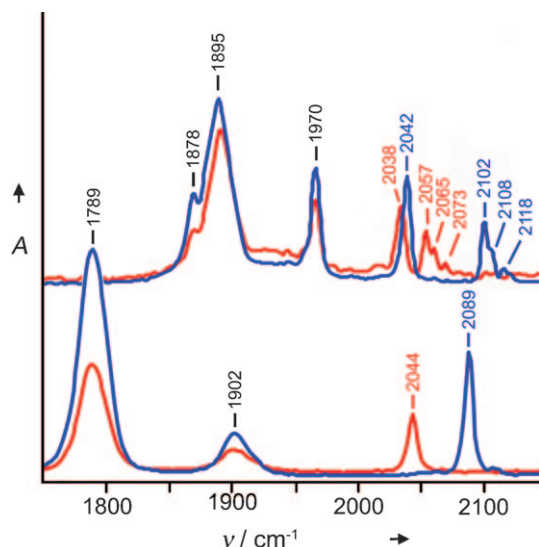


Figure 2. Infrared spectra of single crystals of **1** (lower) and **2** (upper). Red lines correspond to the spectra for complexes with cyanide groups labeled with ^{13}C , while blue lines correspond to spectra of the unlabeled complexes.

analogous compound with ^{13}C -labeled cyanide ligands, $(\text{Bu}_4\text{N})_3[\text{W}(^{13}\text{CN})_5(\text{CO})_2]$, shows the expected isotopic shift in just the highest energy band, which therefore corresponds to a CN stretching mode. Solution spectra collected in CH_2Cl_2 and DMF show qualitatively similar patterns, although the CO stretches shift to higher energy (see Figure S2). The observation of just one CN stretching mode is consistent only with the isomer in which both carbonyl ligands are situated on the axial sites. Note, however, that rigorous D_{5h} symmetry would also allow for just one infrared-active CO stretching mode. The weak CO stretch at 1902 cm^{-1} , which persists in the solution spectrum, could be due to a loss of inversion symmetry at the W center owing to ion-pairing, which could render the symmetric A_1' CO stretch infrared active. Ion-pairing is also consistent with the observed shift in the CO stretches as the polarity of the solvent is changed (see Figure S2). Further consistent with D_{5h} symmetry, we see no mixing of the CO and CN stretches in the spectrum of ^{13}CN -labeled complex. Since any other geometry would generate more infrared active modes (seven bands for both C_{2v} and C_s symmetry), the relative simplicity of the spectrum favors the isomer with two axial CO ligands.

Consistent with D_{5h} symmetry in solution, the ^{13}C NMR spectrum of the ^{13}CN -labeled complex in CDCl_3 exhibits a

single resonance centered at $\delta = 134.5$ ppm with splitting indicative of a ^{183}W – ^{13}C coupling constant of 69.7 Hz (see Figure S4). As expected for a pentagonal bipyramidal complex of tungsten(II) with a low-spin d^4 electron configuration, compound **1** is diamagnetic.

X-ray analysis of a single crystal of **2** revealed a nearly ideal pentagonal bipyramidal arrangement of ligands around the W^{III} center of $[\text{W}(\text{CN})_5(\text{CO})_2]^{2-}$ (see Figure 1, right).^[12] All five equatorial C atoms lie almost exactly within the mean equatorial plane, and the main deviation from the ideal geometry corresponds to a slightly bent $\text{C}_{\text{ax}}\text{--W--C}_{\text{ax}}$ angle of 173.9(2)°. Interestingly, however, an examination of the interatomic distances, together with comparisons of thermal parameters and residual factors from various refinements, suggested 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_{5h} symmetry to a *cis* geometry with C_s 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, upper). On the basis of comparisons with the infrared spectrum of $(\text{Bu}_4\text{N})_2[\text{W}(^{13}\text{CN})_5(\text{CO})_2]$, 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 $[(\text{PY}5\text{Me}_2)\text{Mn}(\text{MeCN})]^{2+}$ ($\text{PY}5\text{Me}_2 = 2,6\text{-bis}(1,1\text{-bis}(2\text{-pyridyl})\text{ethyl})\text{pyridine}$) in acetonitrile afforded the pentanuclear cluster $[(\text{PY}5\text{Me}_2)_4\text{Mn}_4\text{W}(\text{CN})_5(\text{CO})_2]^{6+}$ 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_{2v} 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_{5h} symmetry to afford the C_s symmetry isomer.

The X-band EPR spectrum of **2** in a frozen CH_2Cl_2 solution at 30 K is nearly axial, with $g_x = 1.92$, $g_y = 1.89$, and $g_z = 1.82$ (see Figure S5 in the Supporting Information). It further exhibits hyperfine splitting, attributable to the ^{183}W isotope ($I = 1/2$, 14.3% abundant), with $A_x = 150$ G, $A_y = 20$ G and $A_z = 120$ G. This level of anisotropy is comparable to that observed for $\text{K}_4[\text{Mo}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$ ($g_{\parallel} = 2.10$, $g_{\perp} = 1.97$), wherein $[\text{Mo}(\text{CN})_7]^{4-}$ is suspected to adopt a monocapped trigonal prismatic geometry.^[14,15] It is significantly lower,

however, than would be expected for a pentagonal bipyramidal complex under D_{5h} symmetry,^[16] as observed, for example, in $(\text{Bu}_4\text{N})_3[\text{Re}(\text{CN})_7]$ ($g_{\parallel} = 3.66$, $g_{\perp} = 1.59$).^[7]

Density functional theory (DFT) calculations were carried out to probe the validity of the foregoing conclusions.^[17] Optimization of the structure of $[\text{W}(\text{CN})_5(\text{CO})_2]^{3-}$ revealed the lowest-energy structure to be the isomer with CO ligands on the two axial positions and perfect D_{5h} symmetry. Thus, the distortion away from D_{5h} symmetry observed in the crystal structure of **1** can indeed be attributed to packing effects rather than an electronic effect. The next most stable geometry, just 0.16 eV higher in energy, corresponded to a C_s -symmetry isomer with CO ligands occupying one axial and one equatorial position, and a significantly smaller C(O)-W-C(O) angle of 76.5°. The calculated infrared spectrum for the D_{5h} isomer is in agreement with the two strong stretches in the observed spectrum, exhibiting one CO stretch and one CN stretch, albeit with the peaks approximately 98 cm^{-1} higher in energy. Thus, the intense peaks at 1789 and 2089 cm^{-1} can be assigned to A_2'' and E_1' vibrational modes involving CO and CN stretches, respectively.

Optimization of the structure of $[\text{W}(\text{CN})_5(\text{CO})_2]^{2-}$ confirmed the C_s -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 π backbonding with just one rather than two axial CO ligands. The isomerization of this low-spin d^3 complex can further be viewed as a Jahn–Teller distortion associated with the loss in degeneracy of the pair of e_1'' orbitals to give a fully occupied $1a_1''$ orbital 0.003 eV below a half-occupied $2a_1''$ orbital. This loss of orbital degeneracy may also account for the anisotropy of the g tensor observed by EPR spectroscopy being less than anticipated.

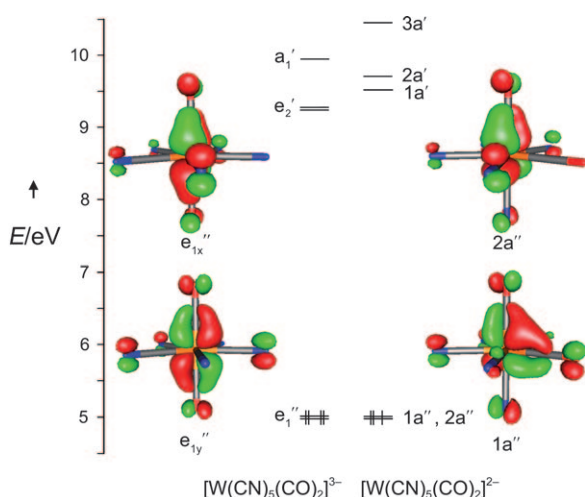


Figure 3. Energy levels and occupied orbitals showing π back-donation from the W center to the axial CO groups of **1** (left) and the one axial and one equatorial CO groups of **2** (right) as calculated using DFT.

These results demonstrate the synthesis of two new pentagonal bipyramidal complexes, $[\text{W}(\text{CN})_5(\text{CO})_2]^{3-}$ and $[\text{W}(\text{CN})_5(\text{CO})_2]^{2-}$, 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 $[\text{W}(\text{CN})_5(\text{CO})_2]^{3-}$ 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.

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