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Chemistry of $[Fe^{II}(CN)_5(CO)]^{3-}$ New Observations for a 19th Century Compound

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The discovery of $[Fe(CO)_x(CN)_y]$ coordination centers in the active sites of NiFe and Fe-only hydrogenase enzymes[1] has focused attention on compounds of Fe with both CO and CN^- ligands.[2] Understanding the factors that control the vibrational spectra of CO and CN^- ligands in small metal complexes will be useful in interpreting the changes in the vibrational spectra of the various intermediate states of these proteins. The oldest member of this class of molecules is $[Fe^{II}(CN)_5(CO)]^{3-}$, which was first reported 114 years ago,[3] and was sporadically studied during the 20th century.[4] We report new, fundamental aspects of the synthetic, structural, spectroscopic, and redox properties of $[Fe^{II}(CN)_5(CO)]^{3-}$ along with some significant historical implications.

$M_3[Fe(CN)_5(CO)]$ (M = Na, K) was originally synthesized by the reaction of CO with $[Fe^{II}(CN)_6]^{4-}$ at high temperature and pressure[5] and later by ligand displacement reaction of $[Fe^{II}(CN)_5(NH_3)]^{3-}$ complexes by CO.[6] We report that $Na_3[Fe(CN)_5(CO)]$ (**1**) can also be prepared by the reaction of $Fe(CO)_4I_2$ with NaCN. Furthermore, **1** can be prepared by the direct reaction of an aqueous solution of $FeCl_2{\cdot}4H_2O$ with 5 equiv of NaCN under an atmosphere of CO. We recently reported the extension of this new reaction of Fe^{2+}, CO, and NaCN to the preparation of the new compound, *trans*-$[Fe^{II}(CN)_4(CO)_2]^{2-}$.[7,8] To obtain a compound with a wider solubility range, $[Ph_4P]_3[Fe(CN)_5(CO)]$ was obtained by a metathesis reaction of **1** with Ph_4PCl.

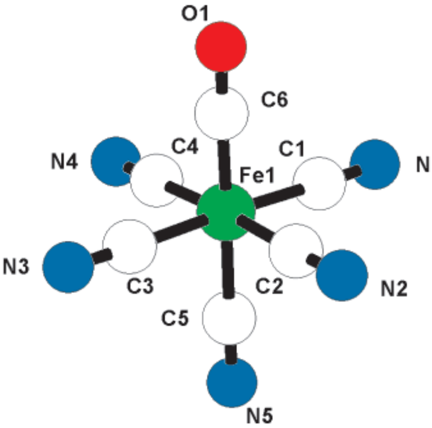

Figure 1. Structure of $[Fe^{II}(CN)_5(CO)]^{3-}$. Selected bond distances and angles: Fe1−C6 1.753(9), Fe1−C1 1.915(12), Fe1−C2 1.909(13), Fe1−C3 1.911(14), Fe1−C4 1.926(14), Fe1−C5 1.903(9).

Crystallization with the $[Co(NH_3)_6]^{3+}$ cation has enabled the first crystal structure determination of the octahedral $[Fe^{II}(CN)_5(CO)]^{3-}$ anion (Figure 1).[9] In the X-ray structure, the CO ligand is crystallographically distinguished from the CN^- ligands. As has been recently seen in other [Fe(CO)(CN)] compounds,[2] the Fe−C(O) (1.753(9) Å) distance is significantly shorter than the Fe−C(N) distances. There is no difference in the Fe−C distances between the 4-*cis*-CN (1.915(7) Å) and the *trans*-CN (1.903(9) Å). The equatorial CN^- ligands are slightly bent away from the CO ligand with the $(O)C{-}Fe{-}C(N)_{ave}$ angle equal to 92.0°. $[Fe(CO)_4(CN)]^{1-}$ and *trans*-$[Fe^{II}(CN)_4(CO)_2]^{2-}$ are the only other compounds of iron with exclusively CO and CN^- ligands.[7,10] Although $[Fe(CN)_5L]$ complexes have been extensively studied[11] for a wide variety of ligands, only a few have been structurally characterized: $[Fe^{III}(CN)_5L]^{2-}$ (L = NH_3, *N*-methylimidazole),[12,13] $[Fe^{II}(CN)_5(SO_3)]$,[5−14] and salts of the nitroprusside anion.

Although the vibrational spectra of $[Fe(CN)_5(CO)]^{3-}$ has been studied in detail in the solid-state, the CO stretching frequency of $[Fe^{II}(CN)_5(CO)]^{3-}$ has never been reported in solution.[15] We observed dramatic solvent induced shifts in the CO stretching frequency (Figure 2). In DMSO solution, **1** shows a strong CO stretching frequency at 1931 cm^{-1} and an equally intense band at 2075 cm^{-1} and a weaker shoulder at 2095 cm^{-1}, which are assigned to CN stretching frequencies. The assignment of these bands was confirmed by spectra of compounds prepared using ^{13}CO and $^{13}CN^-$. In aqueous solution the CO stretching frequency shifts by 70 to 2001 cm^{-1}, while the CN stretching frequencies remain virtually unchanged.

The cyclic voltammograms of $Na_3[Fe(CN)_5(CO)]$ show equally dramatic shifts in the redox potentials as a function of solvent (Figure 3). In H_2O the Fe^{3+}/Fe^{2+} redox couple appears at +0.922

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[8] *trans*-$[Fe^{II}(CN)_4(CO)_2]^{2-}$ is only slowly converted to $[Fe^{II}(CN)_5(CO)]^{3-}$ by reaction with NaCN in boiling H_2O.

[9] Crystal data for $[Co(NH_3)_6][Fe(CN)_5(CO)]{\cdot}3H_2O$ monoclinic C_2 with $a = 11.650(3)$ Å, $b = 10.091(2)$ Å, $c = 15.094(3)$ Å, $\beta = 104.271(5)°$, $V = 1719.7(6)$ Å^3, $Z = 4$. Full-matrix least-squares on F^2 with $R_1 = 0.0583$, $wR_2 = 0.1227$ for 3619 independent reflections.

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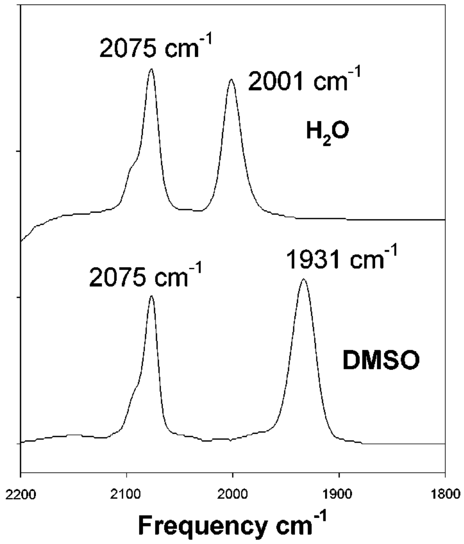

Figure 2. IR spectra of $Na_3[Fe(CN)_5(CO)]$ in H_2O and DMSO.

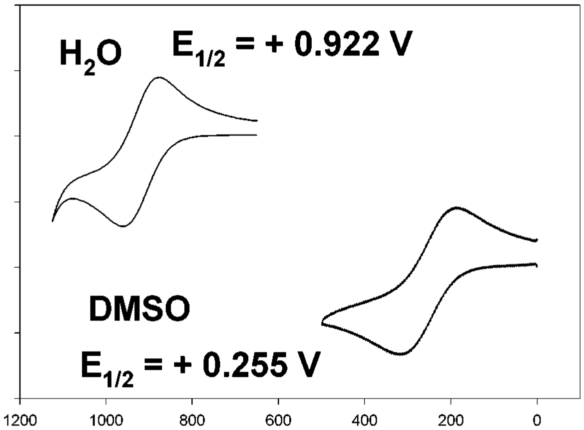

Figure 3. Electrochemical response of $Na_3[Fe(CN)_5(CO)]$ in H_2O and DMSO vs SCE using a Pt electrode with LiCl (H_2O) and (n-Bu_4N)BF_4 (DMSO) as supporting electrolytes.

V (vs SCE), while in DMSO the potential is +0.255 V. The major explanation for the solvent effects on the redox potential and the CO stretching frequency is that the effects result from the increased hydrogen bonding by water compared to DMSO with the CN^- ligands. Support for this analysis comes from the extensive study of the even larger solvent effects on the redox potential of the $Fe(CN)_6]^{3-/4-}$ couple.[16]

There are conflicting reports in the literature as to whether $[Fe^{II}(CN)_5(CO)]^{3-}$ can be oxidized to stable Fe(III) species.[4] Controlled potential electrolysis of $Na_3[Fe^{II}(CN)_5(CO)]$ both in DMSO and in H_2O and $[Ph_4P]_3[Fe(CN)_5(CO)]$[17] in DMF establishes the existence of the oxidized $[Fe^{III}(CN)_5(CO)]^{2-}$ species. CV examination of the solutions after oxidation by 1 e^- shows the equivalent scan of the starting compound. The IR spectra of the electrochemically or chemically (using Cp_2FeBF_4) oxidized $[Ph_4P]_3[Fe(CN)_5(CO)]$ in DMF show a strong band at 2064 cm^{-1}. The assignment of this band as the CO stretching frequencies was confirmed by the corresponding experiment with $[Ph_4P]_3[Fe(CN)_5(^{13}CO)]$ whose isotopically shifted CO stretching frequency shifts from 1875 to 2019 cm^{-1} upon oxidation. This experiment also shows the CN stretch at 2098 cm^{-1}. Oxidation of $Na_3[Fe^{II}(CN)_5(CO)]$, by $Ce(NH_4)_2(NO_3)_6$ in dilute HNO_3 reveals the CO stretching frequency of the $[Fe^{III}(CN)_5(CO)]^{2-}$ species at 2116 cm^{-1}. At room temperature, the Fe(III) species, both in H_2O and nonaqueous solvents, gradually decompose by CO dissociation.

Thus, upon the oxidation of $[Ph_4P]_3[Fe(CN)_5(CO)]$ in DMF, the CO and CN stretching frequencies shift by 145 and 25 cm^{-1}, respectively; these values compare to the 100 and 29 cm^{-1} shifts that we have previously reported for $[Fe^{II,III}(PS3)(CN)(CO)]^{2-/1-}$.[2a] These two sets of compounds are the only examples of nonbiological [Fe(CN)(CO)] complexes which have been spectroscopically characterized in two different electrochemically reversible oxidation states. The redox-induced shifts in the CO and CN stretching frequencies parameters may serve as useful benchmarks for interpreting the IR spectra in the hydrogenase enzymes.

The 1887 report of $K_3[Fe(CN)_5(CO)]$[3] predates the synthesis of $Ni(CO)_4$ (1890)[18] but not the synthesis of $Pt(CO)_2Cl_2$ (1868)[19] which is considered to be the first example of a nonbiological metal−carbonyl compound. There is evidence that $[Fe^{II}(CN)_5(CO)]^{3-}$ was likely generated long before $Pt(CO)_2Cl_2$. The chemical literature of the early 20th century reveals that $[Fe^{II}(CN)_5(CO)]^{3-}$ can be synthesized by heating $K_4Fe(CN)_6$ with concentrated sulfuric acid.[20] Continued, severe heating of $K_4[Fe(CN)_6]$ with concentrated sulfuric acid results in the conversion of all the cyano groups to CO and NH_4^+; we have been able to trace reports of this latter reaction back to at least 1820.[21] In fact, the reaction of the $K_4[Fe(CN)_6]$ with concentrated H_2SO_4 was a convenient laboratory source of CO in the 19th century.[22] Since $K_4[Fe(CN)_6]$ and concentrated sulfuric acid were well known compounds even in the 18th century, it is possible that $[Fe^{II}(CN)_5(CO)]^{3-}$ was generated at least as a transient species even before 1820. In another facet of this chemistry, $[L_xFe{-}CO{-}NH_2]$ species, a likely intermediate in the CN-to-CO transformation, have been implicated as the key intermediate in the biosynthesis of both the Fe−CO and Fe−CN moieties in Fe-only hydrogenase enzymes.[23] Full details of our chemical studies and historical investigations will be published at a later date.

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Supporting Information Available: An X-ray crystallographic file (CIF) for $[Co(NH_3)_6][Fe(CN)_5(CO)]{\cdot}3H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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