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Further Study of the Reaction of Fe^{2+} with CN^-: Synthesis and Characterization of *cis* and *trans* $[Fe^{II,III}(CN)_4L_2]^{n-}$ Complexes

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An argument can be made that the reaction of Fe^{2+} with CN^- is the oldest reaction in synthetic molecular chemistry. It was one of the steps in the 1704 synthesis of Prussian blue: the reaction of ferrous sulfate with KCN, which was itself generated by the pyrolysis of K_2CO_3 with dried ox blood.[1] Carl Scheele placed this reaction on a more scientific basis in his brilliant 1783 study: "Experiments on the Coloring Principle of Prussian Blue."[2] Considering its 300-year history, it is rather surprising that the reaction has only had very limited use in the synthesis of new compounds.[3] We report that the reactions of Fe^{2+} with CN^- can be used to synthesize a number of very basic but previously unknown Fe−CN compounds.

We recently discovered that $[Fe^{II}(CN)_5(CO)]^{3-}$ (a compound first reported in 1887) and *trans*-$[Fe^{II}(CN)_4(CO)_2]^{2-}$ can be prepared by the simplest possible reaction of aqueous Fe(II) with stoichiometric amounts of NaCN under a CO atmosphere.[4,5] The underdeveloped nature of Fe−CN chemistry is indicated by the fact that *trans*-$[Fe^{II}(CN)_4(CO)_2]^{2-}$ was the first example of a $[Fe(CN)_4L_2]^{n-}$ complex for either Fe(II) or Fe(III) for any type of monodentate ligand. $[Fe^{II,III}(CN)_4(L-L)]^{n-}$, where L−L is a bidentate ligand, such as phen or bipy, are well-known with the first example reported more than 70 years ago.[6] With a few exceptions, there is essentially no coordination chemistry of monomeric $[Fe^{II,III}(CN)_xL_{(6-x)}]^{n-}$ compounds where L are monodentate ligands and the number of CN^- ligands is less than 5. The interest in [Fe(CN)(CO)] compounds as models for the active site of [NiFe] and [FeFe] hydrogenase enzymes has resulted in the recent development of some other monomeric $[Fe^{II}(CO)(CN)]$ compounds with monodentate ligands.[7−12]

The chemistry of $[Fe^{II,III}(CN)_5(L)]^{n-}$ compounds has been extensively developed over the last century for a wide range of ligands.[13,14] The vast majority of these compounds have been obtained by the multistep reaction sequence which starts with the nitric acid oxidation of $[Fe^{II}(CN)_6]^{4-}$ to form the nitroprusside anion ($[Fe(CN)_5(NO)]^{2-}$), followed by a displacement reaction of the NO ligand by NH_3 and finally by the substitution with the ligand L. Using the straightforward reaction of $FeCl_2$ with 5 equiv of CN^- in pyridine, we have synthesized and structurally characterized $[Et_4N]_3[Fe^{II}(CN)_5(py)]$ (**1**) and by subsequent air oxidation $[(n\text{-}Bu)_4N]_2[Fe^{III}(CN)_5(py)]$ (**2**).[15] These anions have been previously studied in detail, but like most $[Fe^{II,III}(CN)_5L]^{3-}$ complexes, they had not been structurally characterized.[16,17] It is likely that this direct synthetic route can be applied to many other $[Fe^{II}(CN)_5L]^{n-}$ compounds.

The reaction of 4 equiv of NaCN with $FeCl_2$ in DMSO solution leads to the isolation of *trans*-$Na_2[Fe(CN)_4(DMSO)_2]$ (**3**) (Figure 1) in good yield.[18] The DMSO ligands are coordinated via S in a *trans* arrangement with the Fe−S distance of 2.2293(4) Å. Although there are many structurally characterized first row transition metal compounds with DMSO as a ligand, only two (both of which are also low spin Fe(II)) have S-bonded DMSO.[19,20] $[Ru(DMSO-S)_2L_4]$ compounds are numerous but with the *cis* isomer almost always more stable than the *trans* isomer.[21] Spectroscopic studies had been previously used to indicate an S-bound DMSO in $[Fe^{II}(CN)_5(DMSO)]^{3-}$.[22,23] The yellow compound is stable in DMSO solution, as there is no change in its solution IR spectrum ($\nu_{CN} = 2074\ cm^{-1}$) over 48 h. ^1H NMR studies of **3** in DMSO-d_6 reveal the complete exchange within minutes of the bound DMSO ligand with solvent; the 3.07 ppm resonance for the CH_3 groups of the bound DMSO rapidly disappears with the appearance of the peak for free DMSO at 2.54 ppm. ^1H and ^{13}C NMR spectra in 80% DMSO/20% DMSO-d_6 show the ^{13}C resonance for the CH_3 groups of the bound DMSO at 48.71 ppm (versus 40.41 ppm for free DMSO) and the ^1H resonance at 3.06 ppm. The observed shifts in the ^1H and ^{13}C resonances for the bound DMSO ligands are consistent with S-bound DMSO coordination. The observation of a single ^{13}C NMR resonance for CN^- at 157.2 ppm supports the *trans* stereochemistry.

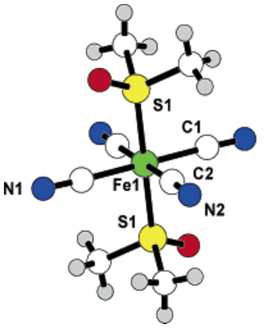

Figure 1. Structure of the centrosymmetric anion of *trans*-$Na_2[Fe^{II}(CN)_4(DMSO)_2]\cdot H_2O$ (**3**). Selected bond distances (Å): Fe1−C1 1.9290(16), Fe1−C2 1.9281(17), Fe−S1 2.2293(4), C1−N1 1.155(2), C2−N2 1.157(2), S1−O1 1.4906(13).

The reaction of $FeCl_2$ in pyridine with 4 equiv of $(Et_4N)CN$ gives red $[Et_4N]_2[Fe^{II}(CN)_4(py)_2]$ (**4**), which was established as the *cis* isomer by X-ray crystallography (Figure 2a).[24] Air oxidation produces the yellow−green *cis*-$[Et_4N][Fe^{III}(CN)_4(py)_2]$ (**5**), which was also structurally characterized.[24] There are only small differences in the Fe−L distances for these two redox pairs. We have chemical and spectroscopic evidence for the *trans* isomers of **4** and **5**, but X-ray quality crystals have not yet been obtained for these compounds. The room temperature ^1H NMR spectrum of **4** in pyridine-d_6 shows no shifted resonances for the coordinated pyridine ligands, indicating that the exchange of the pyridine ligands is fast on the NMR time scale. The ^1H NMR spectrum of **4** at −24 °C in CD_3OD shows shifted resonances for the bound pyridine (compared to those for free pyridine) with the *ortho* H's at 0.344 ppm lower field and the *meta* and *para* protons shifted by 0.298 and 0.175 ppm to higher field. The two equally intense ^{13}C NMR resonances for the CN^- ligands at 180.5 and 174.4 ppm establish that the *cis* stereochemistry of **4** is unchanged in solution. At room temperature in CD_3OD, the resonances for the bound pyridine slowly disappear and are replaced with the resonances for free pyridine. When the solvent is removed and pyridine is added, *cis*-

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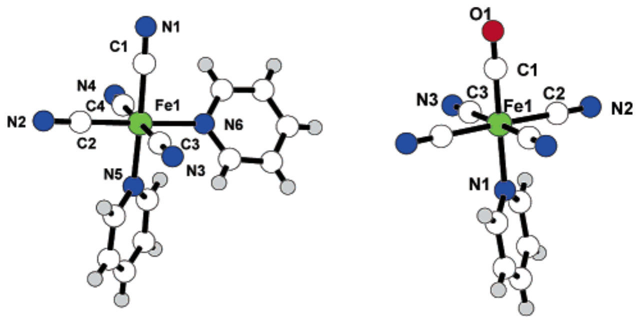

Figure 2. (a) Structure of *cis*-$[\mathrm{Fe^{II}(CN)_4(py)_2}]^{2-}$ (**4**) (the structure of *cis*-$[\mathrm{Fe^{III}(CN)_4(py)_2}]^{1-}$ (**5**) shows a similar orientation of the pyridine rings). Selected bond distances (Å) for **4** with those of **5** in parentheses. Fe1−C1 1.918(4) (1.916(4)), Fe1−C2 1.904(3) (1.916(4)), Fe−C3 1.934(3) (1.954(4)), Fe1−C4 1.931(3) (1.949(4)), Fe1−N5 2.043(3) (2.030(3)), Fe1−N6 2.042(2) (2.044(3). (b) Structure of *trans*-$[\mathrm{Fe^{II}(CN)_4(py)(CO)}]^{2-}$ (**6**). Selected bond distances (Å): Fe1−C1 1.722(6), Fe1−C2 1.931(3), Fe1−C3 1.933(3), Fe1−N1 2.066(3), C1−O1 1.153(5), C2−N2 1.141(4), C3−N3 1.141(4).

$[\mathrm{Et_4N}]_2[\mathrm{Fe^{II}(CN)_4(py)_2}]$ is regenerated, as evident by the color change from the yellow color of the MeOH solution to the red color of the *cis* dipyridine adduct. The combined spectroscopic measurements suggest that the bound pyridines are replaced by MeOH with the $[\mathrm{Fe^{II}(CN)_4(MeOH)_2}]^{2-}$ complex *retaining* the *cis* configuration at the metal center. The paramagnetically shifted resonances for the bound pyridines in the ^{1}H NMR spectrum of **5** in pyridine-d_6 disappear over several hours with the appearance of the unshifted resonances of free pyridine. The exchange of bound pyridine is faster in the Fe(II) low-spin d^6 compound than in the Fi(III) low-spin d^5 compound. The electrochemistry of both **4** and **5** in pyridine establishes that the compounds are related by an $\mathrm{Fe^{3+}/Fe^{2+}}$ redox potential at −0.213 V (vs SCE).

While *trans*-$[\mathrm{Fe^{II}(CN)_4(CO)_2}]^{2-}$ only has limited reactivity,[5] the lability of the non-cyanide ligands of *trans*-$[\mathrm{Fe(CN)_4(DMSO)_2}]^{2-}$ and *cis*-$[\mathrm{Fe^{II}(CN)_4(py)_2}]^{2-}$ makes these compounds useful starting materials for synthesis of other $[\mathrm{Fe(CN)_4L_2}]$ compounds. The room temperature reaction of $[\mathrm{Fe^{II}(CN)_4(DMSO)_2}]^{2-}$ with CO in DMSO solution generates *trans*-$[\mathrm{Fe^{II}(CN)_4(CO)_2}]^{2-}$ together with IR evidence for a monocarbonyl intermediate product. The reaction of *cis*-$[\mathrm{Fe^{II}(CN)_4(py)_2}]^{2-}$ with CO in pyridine generates a monocarbonyl compound which has been structurally characterized as *trans*-$[(n\text{-Bu})_4\mathrm{N}]_2[\mathrm{Fe^{II}(CN)_4(py)(CO)}]$ (**6**) (Figure 2b).[25] Both of these reactions are preformed under mild conditions, which suggests that a wide range of $[\mathrm{Fe(CN)_4LL'}]$ compounds should be accessible. In contrast to the observed behavior of **3**, **4**, and **5**, the ^{1}H and ^{13}C NMR spectra of **6** in $\mathrm{CD_3OD}$ show no evidence for solvent exchange of the bound pyridine at room temperature. The cyclic voltammetry of **6** in pyridine shows an electrochemically reversible oxidation at +0.717 V (vs SCE) which lies between the potentials for **4** and *trans*-$[\mathrm{Fe^{II}(CN)_4(CO)_2}]^{2-}$.[5] The sequential replacements of pyridine by CO result in anodic shifts in the $\mathrm{Fe^{3+}/Fe^{2+}}$ potentials of 0.93 and 0.66 V. As anticipated from our previous observations for $[\mathrm{Fe^{II}(CN)_5(CO)}]^{3-}$,[4] $[\mathrm{Fe^{II}(CN)_4(py)(CO)}]^{2-}$ shows large shifts in its ν_{CO} stretching frequency (2000 cm^{-1} ($\mathrm{H_2O}$); 1943 cm^{-1} (DMSO)) as a function of the hydrogen bonding ability of the solvent. Despite the hydrogen bonding interaction with the CN$^-$ ligands in $\mathrm{H_2O}$, the ν_{CN} (2082 cm^{-1}) is not affected by the solvent change.

The thermodynamic stability and the kinetic inertness of $[\mathrm{Fe^{II}(CN)_6}]^{4-}$ has dominated much of the thinking about the synthesis of Fe(II) cyanide compounds. It is likely that previous workers believed that reactions of Fe(II) with less than 6 equiv of CN$^-$ would, in the absence of chelating ligands, still result in the generation of $[\mathrm{Fe^{II}(CN)_6}]^{4-}$, with the remaining Fe^{2+} ions serving as the cations for a resultant Prussian blue type compound. As we have demonstrated with our work with CO, and now with DMSO and pyridine, such reactivity can be controlled.

Using a very old reaction, we have generated examples of what is likely to become a rich new chapter in the oldest area of transition metal coordination chemistry.[26] The *cis* and *trans*-$[\mathrm{Fe^{II,III}(CN)_4L_2}]$ compounds should be useful building blocks for the synthesis of new Prussian blue type materials and as possible stoichiometric or catalytic reagents.

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Supporting Information Available: The crystallographic parameters and atomic coordinates are available from the cif files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) For **4**: IR (pyridine) ν_{CN} 2048 cm^{-1}; UV−vis in pyridine (λ, nm(ϵ_{M})) 477(7700); ^{1}H NMR ($\mathrm{CD_3OD}$, −24 °C) δ 8.899 (o), 7.698 (p), 7.158 (m); ^{13}C NMR ($\mathrm{CD_3OD}$, −24 °C) δ 158.5(o), 136.7 (p) 124.3 (m), 180.5 (CN), 174.4 (CN). For **5**: IR (pyridine) ν_{CN} 2116 cm^{-1}; UV−vis in pyridine (λ, nm(ϵ_{M})) 426 (680); ^{1}H NMR (pyridine-d_6) δ −7.26 (o), −1.86 (p), +7.15 (m).
(25) For **6**: IR (pyridine) ν_{CO} 2048 cm^{-1}, ν_{CN} 2082 cm^{-1}; UV−vis in pyridine (λ, nm(ϵ_{M})) 327 (391); ^{1}H NMR ($\mathrm{CD_3OD}$) δ 9.27 (o), 7.78 (m), 7.307 (p); ^{13}C NMR ($\mathrm{CD_3OD}$) δ 157.9 (o), 137.7 (p), 124.7 (m), 220.4 (CO) 162.1 (CN).
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