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Further Study of the Reaction of Fe^{2+} with CN^- : Synthesis and Characterization of *cis* and *trans* $[\text{Fe}^{\text{II,III}}(\text{CN})_4\text{L}_2]^{n-}$ Complexes

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Abstract

The reaction of Fe^{2+} with CN^- , which was first performed in 1704, has been used to synthesize a new series of basic $[\text{Fe}^{\text{II,III}}(\text{CN})_4\text{L}_2]^{n-}$ complexes where L is a monodentate ligand. *Trans*- $\text{Na}_2[\text{Fe}^{\text{II}}(\text{CN})_4(\text{DMSO})_2]$ and *cis*- $[\text{NET}_4]_2[\text{Fe}^{\text{II}}(\text{CN})_4(\text{pyridine})_2]$ are synthesized by the direct reaction of FeCl_2 with 4 equiv of CN^- in DMSO or pyridine. Air oxidation of the latter compound gives *cis*- $[\text{NET}_4][\text{Fe}^{\text{III}}(\text{CN})_4(\text{pyridine})_2]$. The non-cyanide ligands in these complexes undergo facile ligand exchange reactions with solvent. Reaction of *cis*- $[\text{NET}_4]_2[\text{Fe}^{\text{III}}(\text{CN})_4(\text{pyridine})_2]$ with CO at RT gives *trans*- $[\text{NET}_4]_2[\text{Fe}^{\text{II}}(\text{CN})_4(\text{pyridine})(\text{CO})]$.

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 the 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 on “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 $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{CO})]^{3-}$ (a compound first reported in 1887) and *trans*- $[\text{Fe}^{\text{II}}(\text{CN})_4(\text{CO})_2]^{2-}$ 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*- $[\text{Fe}^{\text{II}}(\text{CN})_4(\text{CO})_2]^{2-}$ was the first example of a $[\text{Fe}(\text{CN})_4\text{L}_2]^{n-}$ complex for either Fe(II) or Fe(III) for any type of monodentate ligand. $[\text{Fe}^{\text{II,III}}(\text{CN})_4\text{L}]^{n-}$, where 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 $[\text{Fe}^{\text{II,III}}(\text{CN})_x\text{L}_{(6-x)}]^{n-}$ 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 compounds has resulted in the recent development of some other monomeric [Fe^{II}(CO)(CN)] compounds with monodentate ligands.^{7,8,9,10,11,12}

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 NH₃ and finally the substitution with the ligand L. Using the straight forward reaction of FeCl₂ with 5 equiv of CN⁻ in pyridine, we have synthesized and structurally characterized [Et₄N]₃[Fe^{II}(CN)₅(py)] (**1**) and by subsequent air oxidation [(*n*-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 the direct synthetic route can be applied to many other [Fe^{II}(CN)₅L]ⁿ⁻ compounds.

The reaction of 4 equiv of NaCN with FeCl₂ in DMSO solution leads to the isolation of *trans*-Na₂[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)₂L₄] 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 (ν_{CN} = 2074 cm⁻¹) over 48 hours. ¹H NMR studies of **3** in d⁶-DMSO reveal the complete exchange within minutes of the bound DMSO ligand with solvent; the 3.07 ppm resonance for the CH₃ groups of the bound DMSO rapidly disappears with the appearance of the peak for free DMSO at 2.54 ppm. ¹H and ¹³C NMR spectra in 80% DMSO/20% d⁶ DMSO show the ¹³C resonance for the CH₃ groups of the bound DMSO at 48.71 ppm (vs 40.41 ppm for free DMSO) and the ¹H resonance at 3.06 ppm. The observed shifts in the ¹H and ¹³C resonances for the bound DMSO ligands are consistent with S-bound DMSO coordination. The observation of a single ¹³C NMR resonance for CN⁻ at 157.2 ppm supports the *trans* stereochemistry.

The reaction of FeCl₂ in pyridine with 4 equiv. of (Et₄N)CN gives red [Et₄N]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*-[Et₄N][Fe^{III}(CN)₄(py)₂] (**5**) which was also structurally characterized.²⁴ There are only small changes 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 d⁶-pyridine 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 CD₃OD, 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 ¹³C 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 CD₃OD, 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*-[Et₄N]₂[Fe^{II}(CN)₄(py)₂] is regenerated as evident by the color change from yellow color of the MeOH solution to the red color of the *cis* dipyridine adduct. The combined spectroscopic measurements suggests that the bound pyridines are replaced by MeOH with the [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 ^1H NMR spectrum of **5** in d^6 pyridine disappear over several hours with the appearance of the unshifted resonances of free pyridine. The exchange of bound pyridine is faster in the low spin d^6 compound than in the low spin d^5 compound. The electrochemistry of both **4** and **5** in pyridine establishes that the compounds are related by a $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox potential at -0.213 volts (vs. SCE).

While *trans*- $[\text{Fe}^{\text{II}}(\text{CN})_4(\text{CO})_2]^{2-}$ only has limited reactivity,⁵ the lability of the non-cyanide ligands of *trans*- $[\text{Fe}(\text{CN})_4(\text{DMSO})_2]^{2-}$ and *cis*- $[\text{Fe}^{\text{II}}(\text{CN})_4(\text{py})_2]^{2-}$ makes these compounds useful starting materials for synthesis of other $[\text{Fe}(\text{CN})_4\text{L}_2]$ compounds. The room temperature reaction of $[\text{Fe}^{\text{II}}(\text{CN})_4(\text{DMSO})_2]^{2-}$ with CO in DMSO solution generates *trans*- $[\text{Fe}^{\text{II}}(\text{CN})_4(\text{CO})_2]^{2-}$ together with IR evidence for a mono carbonyl intermediate product. The reaction of *cis*- $[\text{Fe}^{\text{II}}(\text{CN})_4(\text{py})_2]^{2-}$ with CO in pyridine generates a mono carbonyl compound which has been structurally characterized as *trans*- $[(n\text{-Bu})_4\text{N}]_2[\text{Fe}^{\text{II}}(\text{CN})_4(\text{py})(\text{CO})]$ (**6**) (Figure 2b).²⁵ Both of these reactions are preformed under mild conditions which suggests that a wide range of $[\text{Fe}(\text{CN})_4\text{LL}']$ compounds should be accessible. In contrast to the observed behavior of **3**, **4** and **5**, the ^1H and ^{13}C NMR spectra of **6** in 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*- $[\text{Fe}^{\text{II}}(\text{CN})_4(\text{CO})_2]^{2-}$.⁵ The sequential replacements of pyridine by CO, results in anodic shifts in the $\text{Fe}^{3+}/\text{Fe}^{2+}$ potentials of 0.93 and 0.66 V. As anticipated from our previous observations for $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{CO})]^{3-}$,⁴ $[\text{Fe}^{\text{II}}(\text{CN})_4(\text{py})(\text{CO})]^{2-}$ shows large shifts in its ν_{CO} stretching frequency (2000 cm^{-1} (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 H_2O , the ν_{CN} (2082 cm^{-1}) is not affected by the solvent change.

The thermodynamic stability and the kinetic inertness of $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ 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 six equivalents of CN^- would, in the absence of chelating ligands, still result in the generation $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ with the remaining Fe^{2+} ions serving as the cations for resultant Prussian blue type network solids. 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 *Cis* and *trans*- $[\text{Fe}^{\text{II,III}}(\text{CN})_4\text{L}_2]$ compounds should be useful building blocks for the synthesis of new Prussian blue type materials and as possible stoichiometric or catalytic reagents.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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15. Selected bond distances (Å) and angles (°) for **1** (with analogous parameters for **2** in parentheses) Fe1–C1 1.880(5) (1.911(4)), Fe1–C2 1.930(3) (1.935(4)), Fe1–C3 1.930(3) (1.944(4)), Fe1–N4 2.039(4) (2.041(3)), C1–Fe1–N4 179.30(18) (177.80(14)).
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24. For **4**: IR (pyridine) ν_{CN} 2048 cm^{−1}; UV-vis in pyridine (λ , nm(εM)) 477(7700); ¹H NMR (CD₃OD, −24°C) 8.899 ppm (o), 7.698 ppm(p), 7.158 ppm (m); ¹³C NMR (CD₃OD, −24°C) 158.5(o), 136.7 (p) 124.3 (m), 180.5 (CN), 174.4ppm (CN). For **5**: IR (pyridine) ν_{CN} 2116 cm^{−1}; UV-vis in pyridine (λ , nm(εM)) 426 (680); ¹H NMR (d⁶-pyridine) −7.26 (o), −1.86 (p), +7.15 (m).
25. For **6**: IR (pyridine) ν_{CO} 2048cm^{−1}, ν_{CN} 2082 cm^{−1}; UV-vis in pyridine (λ , nm(εM)) 327 (391); ¹H NMR (CD₃OD) 9.27 ppm (o), 7.78 (m), 7.307(p); ¹³C NMR (CD₃OD) 157.9 (o), 137.7 (p), 124.7 (m), 220.4 (CO) 162.1 (CN).
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Figure 1.

Structure of the centrosymmetric anion of *trans*-Na₂[Fe^{II}(CN)₄](DMSO)₂·H₂O. 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).

Figure 2.

(a). Structure of *cis*-[Fe^{II}(CN)₄(py)₂]²⁻ (**4**) (the structure of *cis*-[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 parenthesis. Fe1-C1 1.918(4) (1.916(4)), Fe1-C2 1.904(3) (1.916(4)), Fe1-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*-[Fe^{II}(CN)₄(py)(CO)]²⁻. 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).