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fac-$[Fe^{II}(CN)_3(CO)_3]^-$ and *cis*-$[Fe^{II}(CN)_4(CO)_2]^{2-}$: New Members of the Class of $[Fe^{II}(CN)_x(CO)_y]$ Compounds

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The reaction of $Fe(CO)_4I_2$ with NaCN or KCN in methanol gives $M[Fe^{II}(CN)_3(CO)_3]$ (M = Na, K), which can be converted to $[Ph_4E][Fe^{II}(CN)_3(CO)_3]$ (E = P, As). The structure of the *fac*-$[Fe^{II}(CN)_3(CO)_3]^-$ (**1**) anion was established by the X-ray crystal structures of K-**1** and $[Ph_4As]$-**1**·H_2O. Compound **1** has also been characterized by IR, Raman, and ^{13}C NMR. The coupling of the CO and CN stretching modes in the vibrational spectra of **1** have been analyzed. The reaction of Na-**1** with NaCN gives Na_2 *cis*-$[Fe^{II}(CN)_4(CO)_2]$ (Na-**2**), which has been structurally characterized as $[Ph_4P][Et_4N]$-**2**. Compounds **1** and **2** are additional members of the series of compounds of general formula $[Fe^{II}(CN)_{(6-x)}(CO)_x]^{(x-4)}$. $[Fe(CN)_x(CO)_y]$ compounds are of interest due to the occurrence of such coordination modes in hydrogenase enzymes.

Carbon monoxide and cyanide are two of the most fundamental ligands in inorganic chemistry. The discovery of [Fe(CN)(CO)] coordination centers in NiFe and Fe-only hydrogenase enzymes[1] has caused us to focus on the series of compounds with the formula $[Fe^{II}(CN)_{(6-x)}(CO)_x]^{(x-4)}$. In addition to their basic interest,[2] these complexes may be useful in the synthesis of realistic analogues for the active sites in these enzymes and as starting materials for the synthesis of extended solid-state structures[3] or supramolecular assemblies.[4] Until recently only two members of this series of compounds were known: $[Fe^{II}(CN)_6]^{4-}$, which was synthesized in the eighteenth century, and $[Fe^{II}(CN)_5(CO)]^{3-}$, which was first reported in the nineteenth century.[5,6] $[Fe^{II}(CO)_6]^{2+}$ was structurally characterized in 1999,[7] and we[8] and others[9] have just reported the synthesis of *trans*-$[Fe^{II}(CN)_4(CO)_2]^{2-}$. Herein we report the synthesis and characterization of two additional members of this series: *fac*-$[Fe^{II}(CN)_3(CO)_3]^{1-}$ (**1**) and *cis*-$[Fe^{II}(CN)_4(CO)_2]^{2-}$ (**2**).

The reactions of *cis*-$Fe(CO)_4I_2$ with 3 equiv of NaCN or KCN in refluxing methanol give $M[Fe^{II}(CN)_3(CO)_3]$ (M = Na, K), which can be converted to $[Ph_4E][Fe^{II}(CN)_3(CO)_3]$ (E = P, As).[10] The facial isomeric structure of the $[Fe^{II}(CN)_3(CO)_3]^-$ anion was established by a combination of structural and spectroscopic studies. The FAB negative ion mass spectrum of Ph_4P-**1** shows the parent anion and sequential loss of the three CO ligands. The ^{13}C NMR spectrum of Ph_4P-**1** in DMSO shows a single resonance for CO at 201.47 ppm and a single resonance for CN at 126.5 ppm.

K-**1** and $[Ph_4As]$-**1**·H_2O were the subjects of X-ray crystallographic investigations.[11,12] In both complexes the $[Fe^{II}(CN)_3(CO)_3]^-$ anions are structurally equivalent with $Fe-C(N)_{av}$ and $Fe-C(O)_{av}$ of 1.925(3) and 1.828(4) Å in

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(10) Preparation of $[Ph_4P]$-*fac*-$[Fe^{II}(CN)_3(CO)_3]$: $Fe(CO)_4I_2$ (0.889 g, 2.11 mmol) and NaCN (0.320 g, 6.53 mmol) were refluxed in 35 mL of MeOH for 20 min. The MeOH was removed, and the residue was washed with CH_3CN. The white powder was dissolved in H_2O, and an aqueous solution of PPh_4Cl (0.80 g) was added. The product crystallized in 60% yield.

(11) Crystal data for $K[Fe(CN)_3(CO)_3]$: rhombohedral space group $R\bar{3}$. $a = b = 6.9564(13)$ Å, $c = 37.063(1)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, volume = 1553.2(6) Å^3, $Z = 6$. Full-matrix least-squares on F^2 with R1 = 0.0328, wR2 = 0.0821 for 509 independent reflections.

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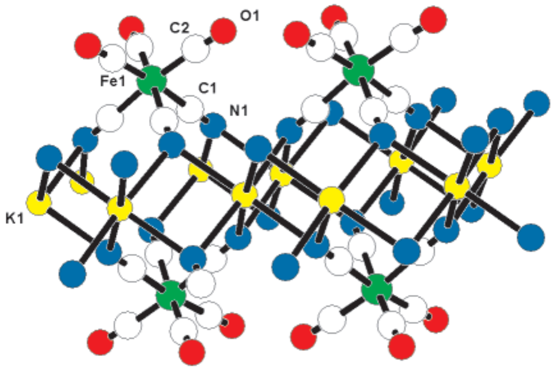

Figure 1. Structural diagram of a fragment of the solid-state structure of $K[Fe^{II}(CN)_3(CO)_3]$. Selected distances (Å) and angles (deg): Fe−C2 1.828(4), Fe−C1 1.925(3), K−N1 2.813(3), N1−C1 1.133(4), C2−O1 1.124(4), C2−Fe−C2′ 96.12(13), C1−Fe−C1′ 87.43(13), C1−Fe−C2 88.34(13), K1−N1−K1′ 90.05(9), K1−N1−C1 130.0(2).

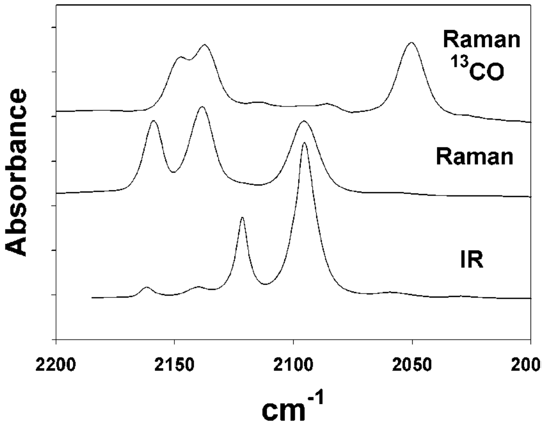

Figure 2. Vibrational spectra of Na-*fac*-$[Fe^{II}(CN)_3(CO)_3]$ in H_2O: (a) IR spectrum; (b) Raman spectrum; (c) Raman spectrum of ^{13}CO-substituted compound.

K-**1** and 1.935(4) and 1.810(9) Å in $[Ph_4As]$-**1**·H_2O. In $[Ph_4As]$-**1**·H_2O, two of the cyano groups are engaged in a hydrogen-bonding interaction with a water molecule. K-**1** crystallized in the rhombohedral space group $R\bar{3}$ with the result that the $[Fe^{II}(CN)_3(CO)_3]^-$ anions have crystallographic C_3 symmetry (Figure 1). The CN^- ligands interact with the K cations and provide structural evidence for the ordering of the CN^- and CO ligands in the anions. The K and the N atoms of the cyano groups are arranged in a 2-dimensional CdI_2 type structure with each K interacting with six μ_2-N atoms in a distorted octahedral arrangement. The $Fe(CO)_3$ groups decorate the top and bottom of the layers with no additional molecules between the layers. These compounds are the first structurally characterized $[M(CN)_3(CO)_3]^{n-}$ complexes, but *fac*-$[Mo(CN)_3(CO)_3]^{3-}$ has been reported.[13] As can be anticipated from the now classic theory of M−CO bonding,[14] there is a direct relationship between the Fe−C(O) distance and the CO stretching frequency (in DMF)[15] in a series of [Fe(CN)(CO)] complexes: $[(PS3)Fe^{II}(CN)(CO)]^-$ (1.71 Å, 1904 cm^{-1});[16] $[Fe^{II}(CN)_5(CO)]^{3-}$ (1.75 Å, 1931 cm^{-1});[6] *trans*-$[Fe(CN)_4(CO)_2]^{2-}$ (1.80 Å, 2029 cm^{-1});[8] and **1** (1.82 Å, 2085 cm^{-1}).

The vibrational spectra of **1** (Figure 2) provide a textbook example of a C_{3v} symmetric complex. The IR spectrum of Na-**1** in H_2O shows two IR-allowed CO stretches at 2096 and 2121 cm^{-1} with the degenerate asymmetric E stretch at lower energy and greater intensity than the A_1 symmetric stretch. The two IR-allowed CN stretches, which occur at 2140 and 2162 cm^{-1}, are markedly reduced in intensity compared to the CO stretches. As predicted by group theory, the Raman transitions are coincident with the IR bands. Since the compound is a light yellow, the intensities of the bands in the Raman spectra are not affected by resonance enhancement. The low intensity of totally symmetric stretching normal modes in the Raman spectra of metal−carbonyl compounds is well precedented.[17]

Isotopic substitution with ^{13}CO (Figure 2) results not only in the expected large shifts of the bands assigned to CO but also significant shifts in the bands assigned as CN stretches.[18] This is an indication of coupling between the (predominately) CO stretching frequencies and the (predominately) CN stretching frequencies of like symmetries. A Cotton−Kraihanzel analysis[19] of the vibrational spectra including data from the ^{13}CO and ^{13}CN labeled species[18] (assuming the interactions of just the CO and CN stretching modes) quantifies the interaction: F_{CO} 18.02 mdyn/Å, F_{CN} 17.42, F_{CO-CO} 0.26, F_{CN-CN}, 0.02, F_{CO-CN} (*cis*) 0.05, F_{CO-CN} (*trans*) 0.19. The observation of CN−CO coupling in **1** results from the relatively small separation in the frequencies of the CO and CN stretching modes.[20,21]

In the $[Fe^{II}(CN)_{(6-x)}(CO)_x]^{(x-4)}$ series, both the CO and CN stretching frequencies are shifted to higher energy with increasing CN^- by CO substitution.[8] The ^{13}C NMR resonances for the CN^- ligands shift to higher frequency as the CO/CN^- ratio increases.[8]

The solvent dependence (H-bonding vs aprotic solvents) of the energy of CO vibrational bands in **1**[22] are smaller than those in *trans*-$[Fe^{II}(CN)_4(CO)_2]^{2-}$ and $[Fe^{II}(CN)_5(CO)]^{3-}$.[6,8] The solvent induces shifts in the CO stretching frequencies,

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(12) Crystal data for $[Ph_4As][Fe(CN)_3(CO)_3]\cdot H_2O$: triclinic space group $P\bar{1}$, $a = 9.1789(10)$ Å, $b = 12.6561(14)$ Å, $c = 13.9666(15)$ Å, $\alpha = 116.693(2)°$, $\beta = 102.184(2)°$, $\gamma = 90.213(2)°$, volume = 1407.9(3) Å^3, $Z = 2$. Full-matrix least-squares on F^2 with R1 = 0.0511, wR2 = 0.1305 for 4047 independent reflections. Selected bond distances (Å) and angles (deg): Fe−C1 1.820(8), Fe1−C2 1.804(8), Fe1−C3 1.805(8), Fe1−C(4) 1.937(7), Fe1−C(5) 1.931(8), Fe1−C6 1.938(8), C2−Fe1−C3 95.2(3), C2−Fe1−C1 94.1(3), C3−Fe1−C1 95.1(3).

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(18) IR spectrum (H_2O) of $Na[Fe(CN)_3(^{13}CO)_3]$: 2138 cm^{-1} (w), 2084 (m), 2048 (s); $Na[Fe(^{13}CN)_3(CO)_3]$ 2147 cm^{-1} (m), 2101 (m) (sh), 2087 (s).

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(22) The IR spectrum of Ph_4P-**1** in DMF (2062 (s), 2108 (s), 2136 (w), 2148 (w) cm^{-1}) shows shifts of 34 cm^{-1} ($E_{(CO)}$) and 13 cm^{-1} ($A_{1(CO)}$) to lower energy compared to those in H_2O.

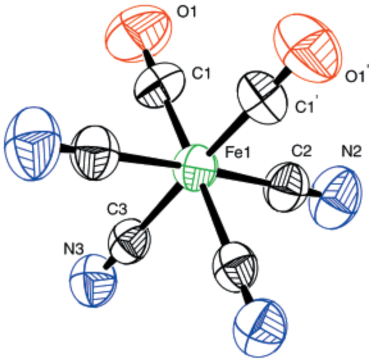

Figure 3. Structural diagram of *cis*-[$Fe^{II}(CN)_4(CO)_2]^{2-}$. Selected distances (Å) and angles (deg): Fe−C1 1.758(6), Fe−C2 1.952(6), Fe−C3 1.935(2), C1−O1 1.145(6), C2−N2 1.117(7), C3−N3 1.126(6), C1−Fe−C1′ 92.5(4), C1−Fe−C2 91.5(2), C1−Fe−C3 88.7(2), C1−Fe−C3′ 178.5(3), C3−Fe−C3′ 90.0(3), C2−Fe−C3 88.7(2).

and the associated shifts in the redox potential (including $[Fe^{II}(CN)_6]^{4-}$) are dependent on the number of CN^- ligands and the associated increase in the negative charge in the $[Fe^{II}(CN)_{(6-x)}(CO)_x]^{(x-4)}$ series.[6,8] The electrochemical studies of **1** show no oxidation or reduction processes from −1.5 to + 2.8 V (vs SCE) in CH_3CN. An extrapolation from our previous observations for $[Fe^{II}(CN)_{(6-x)}(CO)_x]^{(x-4)}$ ($x = 0$, 1, 2) would estimate that the Fe^{3+}/Fe^{2+} couple should be $>+2.4$ V (vs SCE) in aprotic solvents.[8] The CO ligands destabilize oxidative processes while the CN^- ligands destabilize reductive processes.

The reaction of Na-**1** with NaCN in MeOH generated *cis*-$Na_2[Fe^{II}(CN)_4(CO)_2]$, Na_2-**2**, which can also be made directly from the reaction of *cis*-$Fe(CO)_4I_2$ with 4 equiv of NaCN in MeOH. The IR spectrum of **2** in DMF, which is consistent with its C_{2v} structure, shows two equally intense CO stretches at 1967 and 2022 cm^{-1} and two weaker CN stretches at 2080 and 2106 cm^{-1}. The X-ray structure of $[PPh_4][NEt_4]$-**2** confirms the *cis* arrangement of the CO ligands (Figure 3).[23] The *cis*-$[Fe^{II}(CN)_4(CO)_2]^{2-}$ anion has crystallographic C_2 symmetry with the Fe−C(O) distance of 1.758(6) Å and the two independent Fe−C(N) distances of 1.935(5) and 1.952(6) Å. The shorter Fe−C(O) distance in the *cis* vs *trans* isomers (1.758(6) vs 1.800(5) Å) is consistent with the greater π-back-bonding by two *cis* carbonyl groups. This is the first example of a *cis*-$[Fe(CN)_4L_2]^{n-}$ compound with two monodentate ligands. There are only a handful of structurally characterized examples of such compounds for any transition metal.[24] The *cis* isomer is considerably more reactive than the *trans* isomer. Aqueous solutions of **2** decay on the order of minutes into a mixture of products including **1** and $[Fe^{II}(CN)_5(CO)]^{3-}$. As monitored by IR spectroscopy, added NaCN inhibits this reaction.

In the reaction mixtures of $Fe(CO)_4I_2$ with NaCN under the conditions we investigated, there is no indication of the IR bands anticipated for the *mer*-$[Fe(CN)_3(CO)_3]^-$ isomer or those found for the *trans*-$[Fe^{II}(CN)_4(CO)_2]^{2-}$ isomer.[8,9] We have recently reported that *trans*-$[Fe^{II}(CN)_4(CO)_2]^{2-}$ and $[Fe^{II}(CN)_5(CO)]^{3-}$ can be synthesized by the simple reaction of $FeCl_2$ with NaCN in H_2O or MeOH under an atmosphere of CO.[6,8] The characteristic IR bands for neither **1** nor **2** have ever been observed in these reactions. The combined results suggest that the products in both types of reactions are produced under kinetic control.

Although metal−cyanide chemistry is nearly 300 years old, the recent resurgence in this field suggests that it will continue to provide important contributions to basic inorganic chemistry with implications to metalloenzymes and materials chemistry.

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Supporting Information Available: X-ray crystallographic files (CIF) for $K[Fe(CN)_3(CO)_3]$, $[Ph_4As][Fe(CN)_3(CO)_3]\cdot H_2O$, and $[Ph_4P][Et_4N]$-*cis*-$[Fe(CN)_4(CO)_2]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) The crystals were obtained from the reaction of Ph_4P-**1** with Et_4NCN in CH_2Cl_2. Crystal data for $[Ph_4P][Et_4N][Fe(CN)_4(CO)_2]$: monoclinic space group $C2/c$, $a = 11.476(2)$ Å, $b = 29.561(6)$ Å, $c = 11.246(2)$ Å, $\beta = 109.23(3)°$, volume = 3602.2(12) Å^3, $Z = 4$. Full-matrix least-squares on F^2 with R1 = 0.0589, wR2 = 0.1605 for 2609 independent reflections.

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