

Two-dimensional materials based on $trans$ -[Fe^{II}(CN)₄(CO)₂]²⁻ building blocks; first structural evidence for a hydrated metal carbonyl ligation

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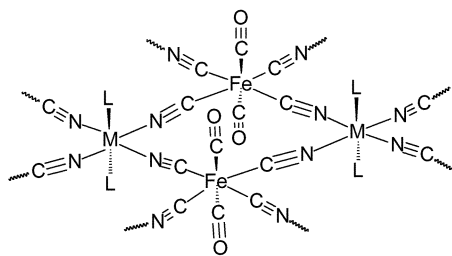
Received (in Columbia, MO, USA) 9th January 2002, Accepted 18th June 2002

First published as an Advance Article on the web 16th July 2002

Analogue to the Hofmann-type clathrates have been characterized using $trans$ -[Fe^{II}(CN)₄(CO)₂]²⁻ as the building blocks.

Square planar [M(CN)₄]²⁻ (M = Ni, Pd, Pt) have been extensively used as building blocks for the synthesis of extended cyanobridged metal structures.¹ In particular, the Hofmann-type clathrates (M'L₂M(CN)₄), which were first prepared by Hofmann² in 1897 and extensively studied by Iwamoto and others,³ show 2D structures with a wide variety of small molecules intercalated between the layers. We report the synthesis and characterization of a series of 2-dimensional structures related to the Hofmann-type clathrates based on reaction of transition metal divalent cations with the $trans$ -[Fe^{II}(CN)₄(CO)₂]²⁻ building block (Scheme 1). We⁴ and the Rauchfuss group⁵ have recently characterized the $trans$ -[Fe^{II}(CN)₄(CO)₂]²⁻ anion (**1**) which is the first example of a $trans$ -[Fe(CN)₄L₂] complex.

The single crystals of these compounds were grown by combining solutions of Na₂(DMF)₄**1** with a variety of divalent cations using agar gels. [M^{II}(DMF)₂Fe^{II}(CN)₄(CO)₂]·H₂O (M = Co (**2**), Fe (**3**)) produced isomorphous structures with colourless crystals for Fe(II) and pink crystals for Co(II) (Fig. 1).[†] Two crystallographically unique octahedral $trans$ -[Fe(CN)₄(CO)₂] units have crystallographic C_{2h} symmetry with the [Fe(CO)₂] groups in the crystallographic mirror plane while the octahedral $trans$ -[M(NC)₄(DMF)₂] units have a plane of symmetry. The two-dimensional sheets (Scheme 1) have the basic square [M₂M'₂(CN)₄] structural motif that is found in two- and three-dimensional Prussian blue type structures.⁶ The two-dimensional sheets have a significant wave in the structure such that the adjacent $trans$ -[Fe(CO)₂] units are not parallel with respect to one another but make an angle of 60° with each other. The deviation in planarity is associated with the divergence of C–N–Co angles from 180° (159.1(4) and 170.4(4)°). The Fe–C–N angles are nearly linear (177.1(4) and 178.3(4)°). The metal–ligand distances in the [M(NC)₄(DMF)₂] units, which are similar those in [M(H₂O)₂Ni(CN)₄] compounds,⁷ support their assignment as high-spin Fe(II) and Co(II). The spin state assignments are consistent with the previous establishment of N bound cyano groups having a comparable ligand field as NH₃.⁸ Certain [Fe^{II}L₂(Ni(CN)₄] compounds display evidence of high spin/low spin equilibria.⁹ The metrical parameters of the $trans$ -[Fe(CN)₄(CO)₂] units are very similar to those in Na₂(DMF)₄**1** and [Ph₄P]₂**1**.^{4,5}



Scheme 1

The reaction of CoCl₂ with Na₂(DMF)₄**1** gives pink crystals of [Co^{II}(H₂O)₂Fe^{II}(CN)₄(CO)₂]·8H₂O (**4**) which display a similar two-dimensional structure (Fig. 2).[†] Both the $trans$ -[Fe^{II}(CN)₄(CO)₂] and $trans$ -[Co^{II}(NC)₄(H₂O)₂] centers have crystallographic 2/m (C_{2h}) symmetry with both the C₂ axis and the mirror plane bisecting L–M–L angles. The layer has a less pronounced undulation, which reflects the C–N–Co angle of 165.0(5)°. A double layer of water molecules separates the Fe(CN)Co layers. The H₂O bound to Co and the 8 interstitial water molecules create a H-bonded network that is shown in Fig. 2. The water molecules are arranged in 4-, 5-, and 6-membered rings with O–O distances of 2.78–2.89 Å. Water molecules have been observed to separate the layers in [M(H₂O)₂Ni(CN)₄]·4H₂O (M = Cd, Co, Fe) but in that case the water layer is only one molecule thick.^{10,11} Interstitial water networks and clusters have attracted recent structural and spectroscopic interest.¹²

There is a feature in this structure, which has not been found in the more than 25000 previously reported crystal structures of metal carbonyl compounds.¹³ The Fe(CO) groups are projected into the water layer and are entirely 'solvated' by water molecules. The O of the CO is surrounded by six H₂O molecules at van der Waals distances of 3.116(9), 3.220(9) and 3.376(9) Å. However, none of these H₂O molecules are serving

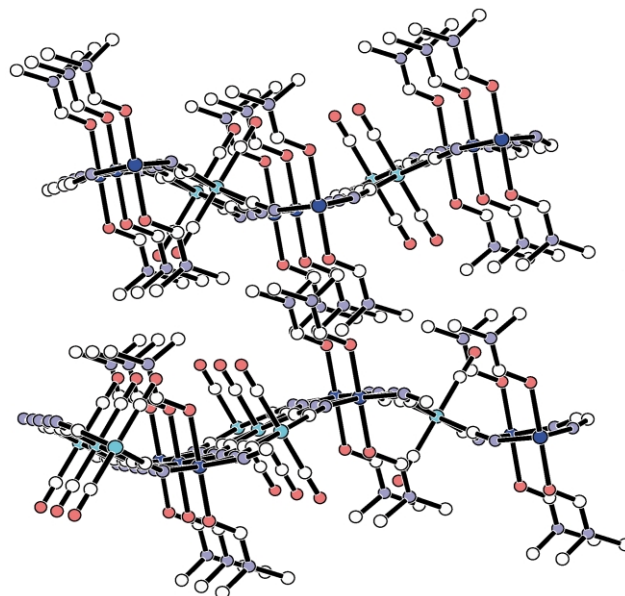


Fig. 1 A fragment of the solid-state structure of [Co^{II}(DMF)₂Fe^{II}(CN)₄(CO)₂]·H₂O **2** (the H₂O, which is omitted, is involved in hydrogen bonding interactions with the CH and C=O of adjacent DMF molecules). Selected bond distances (Å): Fe1–C1 1.819(8), Fe1–C3 1.936(5), Fe2–C2 1.810(8), Fe2–C4 1.917(4), Co1–N3 2.093(4), Co1–N4 2.096(3), Co1–O3 2.177(5), Co1–O4 2.108(5), O1–C1 1.126(9), C2–O2 1.124(8), C3–N3, 1.144(5), C4–N4 1.147(5). Selected bond distances (Å) for isomorphous [Fe^{II}(DMF)₂(Fe^{II}(CN)₄(CO)₂]·H₂O **3**: Fe1–C1 1.820(5), Fe1–C3 1.930(3), Fe2–C2 1.811(5), Fe2–C4 1.924(3), Fe3–N3 2.136(3), Fe3–N4 2.141(2), Fe3–O4 2.114(3), C1–O1 1.117(6), C4–N4 1.147(3), C3–N3 1.151(4).

as hydrogen bond donors to the O of the CO group. Although the H atoms of the water molecules have not been located in the crystal structure, an examination of the network of the H₂O molecules reveals that the H₂O nearest neighbours to the CO are fully involved in H-bonding with other H₂O molecules *i.e.* each of the H₂O has four H₂O nearest neighbours. This structure provides structural evidence of the observation that terminal M–CO ligands do not readily serve as H-bonding acceptors. There are only a small number of examples of metal carbonyl compounds in which hydrogen bonding to the CO have been structurally confirmed.¹⁴ Hydrogen bonding in molecular metal–carbonyl compounds is found in electron rich metal complexes and in the case of μ_2 and μ_3 -CO ligands.¹⁴ The difference in the tendency of M–CN and M–CO ligands to serve as hydrogen bonding acceptors provides the means by which CN and CO ligands have been differentiated in the protein structures of the hydrogenase enzymes.¹⁵ Hydrogen bonding to CO has been suggested in certain heme protein CO adducts.¹⁶

The bonding of the M²⁺ cations to each of the cyano group reduces the electron donating properties of the CN⁻ groups such that there is reduced electron density at the iron centers. As a result, the CO stretching frequency observed in the IR spectra of **2–4** (2084 cm⁻¹ in **4**) are shifted to higher energy compared to that of Na₂(DMF)₄**1** (2025 cm⁻¹) whose solid-state structure has Na⁺ cations interacting with the NC groups.⁴ The CN stretching frequency is shifted to higher energy, (2142 cm⁻¹ in **4** vs. 2115 cm⁻¹ in **1**) which is typical for bridging M^{II}(CN)M^{II} groups.¹⁷ There is no change in the CO stretching frequency of **4** when the interstitial water molecules are removed by dehydration. Additional studies of extended structures based on the *trans*-[Fe^{II}(CN)₄(CO)₂]²⁻ building block are in progress.

We thank the National Institutes of Health for support (GM 58000).

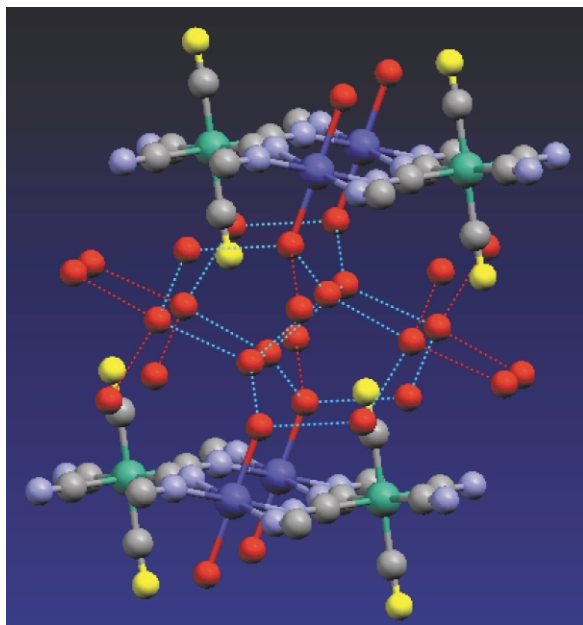


Fig. 2 A fragment of the solid-state structure of [Co^{II}(H₂O)₂Fe^{II}(CN)₄(CO)₂]_n·8H₂O **4** showing the network on hydrogen bonded water molecules with the O atoms shown in red and the carbonyl oxygen atoms shown in yellow. Selected bond distances (Å): Fe1–C2 1.794(11), Fe1–C1 1.937(6), Co1–N1 2.086(3), Co1–O2 2.143(6), C2–O1 1.147(11), C1–N1 1.135(8).

Notes and references

† *Crystal data*: for [Co^{II}(DMF)₂Fe^{II}(CN)₄(CO)₂]_n·H₂O **2**: C₁₂H₁₆CoFeN₆O₅, *M* = 439.09, monoclinic, space group *I2/m*, *a* = 13.4386(17), *b* = 7.4128(10), *c* = 19.479(3) Å, β = 97.153(3)°, *U* = 1925.4(4) Å³, *Z* = 4, μ = 1.647 mm⁻¹, 4446 reflections collected, 1506 independent reflections (*I* > 2 σ (*I*)), *R*₁ = 0.0437 (0.0647), *wR*₂ = 0.1012 (0.1110) (all data), GOF (on *F*²) = 0.969. For [Fe^{II}(DMF)₂Fe^{II}(CN)₄(CO)₂]_n·H₂O **3**: C₁₂H₁₆Fe₂N₆O₅, *M* = 436.01, monoclinic, space group *I2/m*, *a* = 13.4721(10), *b* = 7.4905(6), *c* = 19.5630(15) Å, β = 97.754(2)°, *U* = 1956.1(3) Å³, *Z* = 4, μ = 1.647 mm⁻¹, 4446 reflections collected, 1506 independent reflections (*I* > 2 σ (*I*)), *R*₁ = 0.0313 (0.0419), *wR*₂ = 0.0789(0.0848) (all data), GOF (on *F*²) = 1.037. For [Co^{II}(H₂O)₂-Fe^{II}(CN)₄(CO)₂]_n·8H₂O **4**, C₆H₂₀CoFeN₄O₁₂, *M* = 455.02, monoclinic, space group *P2/m*, *a* = 6.971(2), *b* = 7.467(2), *c* = 9.267(3) Å, β = 100.377(5)°. *U* = 474.4(3) Å³, *Z* = 1, μ = 1.682 mm⁻¹, 2183 reflections collected, 755 independent reflections (*I* > 2 σ (*I*)) *R*₁ = 0.0544(0.0759), *wR*₂ = 0.1392(0.1532)(all data), GOF (on *F*²) 1.060. CCDC reference numbers 177591–177593. See <http://www.rsc.org/suppdata/cc/b2/b200337f/> for crystallographic data in CIF or other electronic format.

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