

Crystallographic table :

Table TS1. Crystallographic Parameters of $2_2\text{-[Fe}^{\text{II}}(\text{CN})_6]\cdot 6\text{H}_2\text{O}$ recorded at 173 K.

Formula	$\text{C}_{58}\text{H}_{100}\text{FeN}_{14}\text{O}_6$
Molecular weight	1145.37
Crystal system	Triclinic
Space group	P-1
a(Å)	11.1100(8)
b(Å)	17.7957(11)
c(Å)	18.0780(13)
α (deg)	70.187(3)
β (deg)	83.944(3)
γ (deg)	80.834(3)
V(Å ³)	3314.6(4)
Z	2
Color	orange
Crystal dim (mm)	0.08 x 0.06 x 0.05
Dcalc (gcm ⁻³)	1.148
F(000)	1240
μ (mm ⁻¹)	0.283
Wavelength (Å)	0.71073
Number of data meas.	30641
Number of data with I > 2 σ (I)	15294
R	0.0839
Rw	0.2242
GOF	1.012
Largest peak in final difference (eÅ ⁻³)	1.327 and -1.137

Description of structure of $2_2\text{-[Fe}^{\text{II}}(\text{CN})_6]\cdot 6\text{H}_2\text{O}$

The combination of **2** and $\text{Li}_4\text{Fe}^{\text{II}}(\text{CN})_6$ or $(\text{NH}_4)_4\text{Fe}^{\text{II}}(\text{CN})_6$ leads to the formation of identical 2D network with anion/cation ratio of 1/2 ($2_2\text{-[Fe}^{\text{II}}(\text{CN})_6]$). The structure, analogous to the one previously described** for ($1_2\text{-[Fe}^{\text{II}}(\text{CN})_6]$), may be regarded as anionic 1D arrays (dihapto mode of H-bonding between the dications **2** and the four cyanide groups occupying the basal plane of the $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ octahedron) interconnected by cationic units **2** through H-bonds in a monhapto mode, *i.e.* one out of the two NH groups located on the same face of the tecton **2** is participating in H-bonding. The N-N distances (amidinium-cyano) are 2.84Å and 2.85Å for the basal plane and 2.80Å and 2.94Å for the two CN groups in the apical positions of the $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ octahedron (figure S1a). The observation of short and long distances is probably due to steric hindrance owing to the presence of the propyl groups located on the tecton **2**. The crystal contains 6 water molecules. The latter are located within the networks and form trimeric units with O-O distances varying between 2.77 and 3.10Å. (Figure S1b)

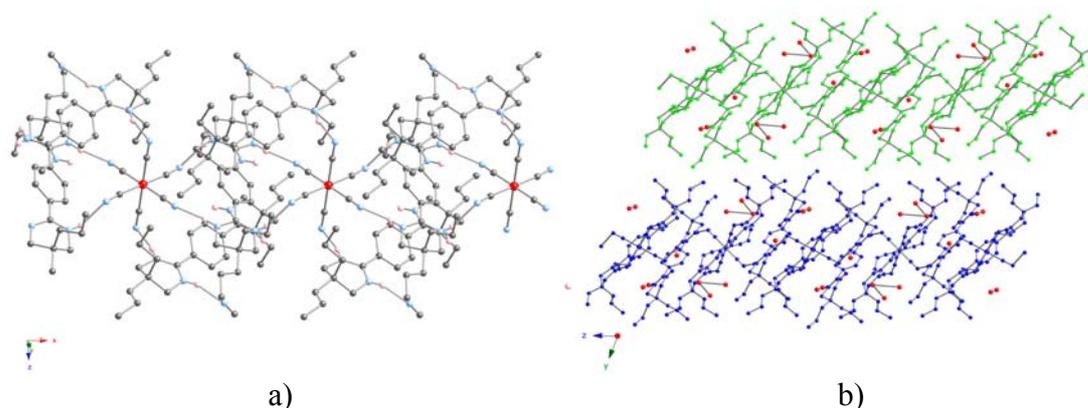


Figure S1. Two different views of a portion of the structure of $(2_2\text{-[Fe}^{\text{II}}(\text{CN})_6]_2)$ in the 010 plane (a) and the packing along y direction (b). H atoms not involved in H-bonds are omitted for clarity.

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Experimental Section

Single-Crystal Studies

Data were collected at 173(2) K on a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using graphite-monochromated Mo-K α ($\lambda = 0.71073$) radiation. For all structures, diffraction data were corrected for absorption. The structures were solved using SHELXS-97 and refined by full matrix least-squares on F² using SHELXL-97. The hydrogen atoms were introduced at calculated positions and not refined (riding model).¹

Powder diffraction studies (PXRD)

Diagrams were collected on a Bruker D8 diffractometer using monochromatic Cu-K α radiation with a scanning range between 3.8 and 30° using a scan step size of 2°/mn.

Infra-red Studies

IR spectra have been recorded on a Perkin Elmer Spectrometer RX1.

Synthesis

The synthesis of **2-Cl**₂ has been already described.²

Preparation of X₂2₃-[Fe^{II}(CN)₆]₂ (X = Na, K, Rb and Cs)

Na₄Fe(CN)₆, K₄Fe(CN)₆ and (NH₄)₄Fe(CN)₆ used were commercially available. All the other three salts X₄Fe(CN)₆ (X = Li, Rb or Cs) have been prepared by reacting (NH₄)₄Fe(CN)₆ with X₂CO₃ (X = Li, Rb or Cs).

Preparation of K₂2₃-[M^{II}(CN)₆]₂ (M = Fe or Ru)

In a 4 mm diameter crystallization tube equipped with a stopper, upon slow diffusion at room temperature, through a layer of MeOH (0.5 ml), of a solution of **2-Cl**₂ (4 mg) in MeOH (0.25 ml) into an aqueous solution (0.25 ml) of K₄Fe(CN)₆ (4 mg), orange crystalline rods of K₂2₃-[Fe^{II}(CN)₆]₂ were obtained after few days.

It is worth noting that, in contrast with the other alkali cations, in the case of K⁺ the spontaneous oxidation (Fe(II)-Fe(III)) occurs very slowly and thus the crystallization process did not require degassed solvents or the presence of reducing agents.

The orange crystals were characterized by X-ray diffraction (see crystallographic footnote) on single crystal and by IR ($\nu_{\text{C}\equiv\text{N}} = 2032 \text{ cm}^{-1}$). The purity of the phase was checked by PXRD (Fig. S2) which revealed the presence of a single set of peaks perfectly matching the simulated diffractogram.

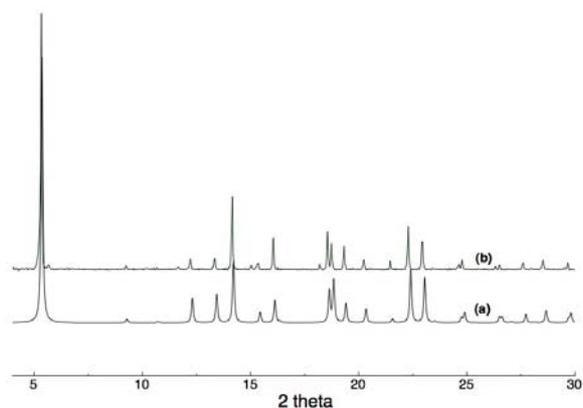


Figure S2: Comparison of the simulated (a) and recorded (b) PXRD patterns for powdered K₂2₃-[Fe^{II}(CN)₆]₂.

Preparation of Na₂2₃-[Fe^{II}(CN)₆]₂

In a 4 mm diameter crystallisation tube, a solution of **2-Cl**₂ (5 mg) in degassed MeOH (0.25 ml) was first layered with degassed MeOH (0.5 ml) and then a degassed aqueous solution (0.25 ml) of Na₄Fe^{II}(CN)₆ (5 mg) was carefully added. After one week, a mixture of orange

[1] G. M. Sheldrick, *Programs for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, **1996**.

[2] P. Dechambenoit, S. Ferlay, M. W. Hosseini, J-M. Planeix, N. Kyritsakas *New. J. Chem.*, **2006**, *30*, 1403-1410.

crystalline rods of $\text{Na}_2\mathbf{2}_3\text{-[Fe}^{\text{II}}(\text{CN})_6\text{]}_2$ and some yellow crystals of $\mathbf{2}_3\text{-[Fe}^{\text{III}}(\text{CN})_6\text{]}_2$ resulting from spontaneous oxidation of Fe^{II} to Fe^{III} by oxygen, were obtained. The orange crystals of $\text{Na}_2\mathbf{2}_3\text{-[Fe}^{\text{II}}(\text{CN})_6\text{]}_2$ were characterized by X-ray diffraction on single crystal (see crystallographic footnote) and by IR ($\nu_{\text{C}\equiv\text{N}}$ at 2032 cm^{-1}).

Preparation of $\text{Rb}_2\mathbf{2}_3\text{-[Fe}^{\text{II}}(\text{CN})_6\text{]}_2$

In a 4 mm diameter crystallisation tube, a solution of $\mathbf{2}\text{-Cl}_2$ (3.75 mg) in MeOH (0.25 ml) was first layered with MeOH (0.5 ml) and then an aqueous solution (0.25 ml) of $\text{Rb}_4\text{Fe}^{\text{II}}(\text{CN})_6$ (3.75 mg) was carefully added. After one week, in addition to orange crystalline rods of $\text{Rb}_2\mathbf{2}_3\text{-[Fe}^{\text{II}}(\text{CN})_6\text{]}_2$ and few yellow crystals of $\mathbf{2}_3\text{-[Fe}^{\text{III}}(\text{CN})_6\text{]}_2$, resulting from the spontaneous oxidation of Fe^{II} to Fe^{III} by oxygen, and few necklace-type crystals (see figure 4b and text for explanation in the manuscript) were obtained. The orange crystals of $\text{Rb}_2\mathbf{2}_3\text{-[Fe}^{\text{II}}(\text{CN})_6\text{]}_2$ were characterized by X-ray diffraction on single crystal (see crystallographic footnote) and by IR ($\nu_{\text{C}\equiv\text{N}} = 2032\text{ cm}^{-1}$).

The use of degassed solvents or a drop of hydrazine as reducing agent affords mainly the $\text{Rb}_2\mathbf{2}_3\text{-[Fe}^{\text{II}}(\text{CN})_6\text{]}_2$ as orange crystals.

Preparation of $\text{Cs}_2\mathbf{2}_3\text{-[Fe}^{\text{II}}(\text{CN})_6\text{]}_2$

In a 4 mm diameter crystallisation tube, a solution of $\mathbf{2}\text{-Cl}_2$ (3.75 mg) in MeOH (0.25 ml) was first layered with MeOH (0.5 ml) and then an aqueous solution (0.25 ml) of $\text{Cs}_4\text{Fe}^{\text{II}}(\text{CN})_6$ (3.75 mg) and a drop of hydrazine were added carefully. After one week, orange yellow crystals of $\text{Cs}_2\mathbf{2}_3\text{-[Fe}^{\text{II}}(\text{CN})_6\text{]}_2$ were obtained and characterised by X-ray diffraction on single crystal (see crystallographic footnote) and by IR ($\nu_{\text{C}\equiv\text{N}} = 2032\text{ cm}^{-1}$).

Formation of solid solutions based an equimolar mixture of $\text{X}_4\text{Fe}^{\text{II}}(\text{CN})_6$ and $\text{X}_3\text{Fe}^{\text{III}}(\text{CN})_6$ (X = Na, K and Rb) with compound $\mathbf{2}$.

Potassium salt: In a 4 mm diameter crystallisation tube, a solution of $\mathbf{2}\text{-Cl}_2$ (4 mg) in MeOH (0.5 ml) was first layered with MeOH (1 ml) and then an aqueous solution (1 ml) of a mixture of $\text{K}_4\text{Fe}^{\text{II}}(\text{CN})_6$ (2 mg) and $\text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6$ (2 mg) was added carefully. After several days, mainly two types of crystals corresponding to $\mathbf{2}_3\text{-[Fe}^{\text{III}}(\text{CN})_6\text{]}_2$ (yellow) and $\text{K}_2\mathbf{2}_3\text{-[Fe}^{\text{II}}(\text{CN})_6\text{]}_2$ (orange) were obtained. However, although not systematically, in some trials necklace-type crystals have been observed as well (see figure 4 in the manuscript).

Sodium salt: The same procedure was used in the case of $\text{Na}_4\text{Fe}^{\text{II}}(\text{CN})_6$ and $\text{Na}_3\text{Fe}^{\text{III}}(\text{CN})_6$ mixture. However the sodium salt, no necklace-type crystals were observed (see figure 4b).

Rubidium salt: In a 4 mm diameter crystallisation tube, a solution of $\mathbf{2}\text{-Cl}_2$ (4 mg) in MeOH (0.5 ml) was first layered with MeOH (1 ml) and then an aqueous solution (1 ml) of a mixture of $\text{Rb}_4\text{Fe}^{\text{II}}(\text{CN})_6$ (1.8 mg) and $\text{Rb}_3\text{Fe}^{\text{III}}(\text{CN})_6$ (1.8 mg) was added carefully. After several days, in addition to the two types of crystals corresponding to $\mathbf{2}_3\text{-[Fe}^{\text{III}}(\text{CN})_6\text{]}_2$ (yellow) and $\text{K}_2\mathbf{2}_3\text{-[Fe}^{\text{II}}(\text{CN})_6\text{]}_2$ (orange), necklace-type crystals were obtained systematically (see figure 4 in the manuscript).

Caesium salt: Preparation of $(\text{Cs}_2\mathbf{2}_3\text{-[Fe}^{\text{II}}(\text{CN})_6\text{]}_2)_{0.83}(\mathbf{2}_3\text{-[Fe}^{\text{III}}(\text{CN})_6\text{]}_2)_{0.17}$

In a 4 mm diameter crystallisation tube, a solution of $\mathbf{2}\text{-Cl}_2$ (3.75 mg) in non degassed MeOH (0.25 ml) was first layered with non degassed MeOH (0.5 ml) and then a non degassed aqueous solution (0.25 ml) of $\text{Cs}_4\text{Fe}^{\text{II}}(\text{CN})_6$ (3.75 mg) was added carefully. After one week, only yellow-orange crystals, displaying the same type of morphology, of the solid solution containing both Fe^{II} and Fe^{III} were obtained and studied X-ray diffraction on single crystal (see crystallographic footnote) and by IR (see Figure 5 in the manuscript). The formula $(\text{Cs}_2\mathbf{2}_3\text{-[Fe}^{\text{II}}(\text{CN})_6\text{]}_2)_{0.83}(\mathbf{2}_3\text{-[Fe}^{\text{III}}(\text{CN})_6\text{]}_2)_{0.17}$ was deduced from the structural refinement.