Molecular tectonics: crystal engineering of mixed valence Fe(II)/Fe(III) solid solutions

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Based on isostructurality between crystals formed upon combining the dicationic tecton **2** with either $M_3Fe^{III}(CN)_6$ or $M_4Fe^{II}(CN)_6$ ($M = Na, K, Rb$ and Cs), a rare example of H bonded mixed valence Fe(II)-Fe(III) solid solution ($((Cs_2)_2-[Fe^{II}(CN)_6]_{0.83}(2_3-[Fe^{III}(CN)_6]_{0.17}))$) and curious necklace-like composite crystals were generated.

The construction of molecular crystals by design still remains elusive.¹ However, by considering crystals as periodic networks resulting from mutual interconnection of tectons² through specific recognition events,³ one may control some of the recognition processes and thus the connectivity between the building blocks.⁴ Engineering crystals based on networks⁵ and containing the same metal center with two different oxidation states (mixed valence system) is a real challenge. Indeed, only scarce examples of hydrogen-bonded networks involving mixed valence system have been reported.⁶ Here, we report on the tuning of crystals parameters and the engineering of a solid solution based on H-bonded networks containing the mixed valence Fe(II)/Fe(III) hexacyanometallate system.

Polycyanometallates are attractive entities because they can display interesting physical properties such as magnetism and photomagnetism.⁷ Considering these species as anionic tectons, the formation of molecular networks based on a combination of rather directional H-bonding⁸ with less directional but more energetic charge/charge electrostatic interactions⁹ was envisaged. Thus, cationic tectons such as compounds **1** and **2** (Fig. 1) capable of interacting with $[M^{III}(CN)_6]^{3-}$ ($M = Co, Fe$ and Cr) through a dihapto mode of H-bonding were designed.¹⁰ As expected, the combination of **1**¹¹ or **2**¹² with $[M^{III}(CN)_6]^{3-}$ leads to the formation of 2D neutral honeycomb type H-bonded networks with a 3/2 cation/anion stoichiometry (Fig. 1a, type A). On the other hand, the combination of **1** with $[M^{II}(CN)_6]^{4-}$ ($M = Fe$ and Ru) leads again to the formation of neutral 2D H-bonded networks however with a different connectivity resulting from the 2/1 cation/anion stoichiometry (Fig. 1b, type B).^{10a} Much to our surprise, for the combination of **2** with $K_4[M^{II}(CN)_6]^{4-}$ ($M = Fe$ and Ru), instead of observing the expected network shown in Fig. 1b, the honeycomb H-bonded architecture with the cation/anion ratio of 3/2 ($K_2_2_3-[M^{II}(CN)_6]_2$) (Fig. 1a) was obtained and characterized by X ray diffraction on single crystals[‡] and on powder for $M = Fe$ (see fig X in ESI). However, structures of ($1_3-[M^{III}(CN)_6]_2$)

and ($K_2_2_3-[M^{II}(CN)_6]_2$) differ by their compositions since in the case of $[M^{II}(CN)_6]^{4-}$ anions, the crystal contains also K^+ cations (O_h geometry, surrounded by six cyanides with K-N distance varying between 2.96(2) and 3.18(2) Å for $M = Fe$) located between two consecutive anionic 2-D H-bonded networks (Fig. 3b) leading thus to a 3-D network.

Figure 1: Schematic representations of neutral 2-D H-bonded networks formed by combining dicationic tectons **1** or **2** with $[M^{III}(CN)_6]^{3-}$ ($M = Cr, Fe$ or Co) (a, Type A) or **1** with $[M^{II}(CN)_6]^{4-}$ ($M = Fe$ or Ru) (b, Type B).

Owing to the connector role played by K^+ cation, the distance (7.18Å) along the c axis between two consecutive Fe centers belonging to two consecutive layers is shorter than the one of 8.61Å observed for the isostructural $2_3-[Fe^{III}(CN)_6]_2$.¹²

Since crystals of $2_3-[Fe^{III}(CN)_6]_2$ and $K_2_2_3-[Fe^{II}(CN)_6]_2$ are isostructural,[‡] we thought that it might be possible to generate solid solutions¹³ containing both iron oxidation states II and III. The combination of an equimolar ratio of $K_4Fe^{II}(CN)_6$ and $K_3Fe^{III}(CN)_6$ with **2** do not form a solid solution but rather leads to segregated rod-like orange crystals of $K_2_2_3-[Fe^{II}(CN)_6]_2$ and yellowish plate-like crystals of $2_3-[Fe^{II}(CN)_6]_2$ (Fig. 2a). Surprisingly, but not systematically, necklace-like assemblies of crystals, resulting from the growth of several yellow crystallites of $2_3-[Fe^{II}(CN)_6]_2$ on rod-like orange crystals of $K_2_2_3-[Fe^{II}(CN)_6]_2$ are observed (Fig. 2b). This type of composite crystals probably results from an epitaxial growth¹⁴ of $2_3-[Fe^{III}(CN)_6]_2$ on $K_2_2_3-[Fe^{II}(CN)_6]_2$.

Figure 2: Two different views (in the (001) plane and along the c axis) of portions of $X_2[23-[Fe^{II}(CN)_6]_2$ ($X = Na$ (a), K (b), Rb (c) and Cs (d)). H atoms not involved in H-bonds are omitted for clarity.

The observed segregation phenomenon is probably due to the fact that the two isostructural crystals are not perfectly isometric. Indeed, $a = b$ and c (related to the distance between two consecutive planes) parameters for $23-[Fe^{III}(CN)_6]_2$ (17.9242(4) and 8.6140(4) respectively) are rather different than those observed for $K_2[23-[Fe^{II}(CN)_6]_2$.^{12‡} Consequently, by substituting K^+ connecting cations by other alkali cations, one may modulate the distance between $Fe(II)$ centers belonging to consecutive layers and thus the c parameter.

In a systematic study, $X_4Fe^{II}(CN)_6$ ($X = NH_4^+$, Li^+ , Na^+ , Rb^+ and Cs^+) salts have been combined with **2**. For both NH_4^+ and Li^+ a neutral 2-D network of the type B ($23-[Fe^{II}(CN)_6]_2 \cdot 6H_2O$) is obtained (see Table TS1 and short description of the structure in ESI). Interestingly for the other three cations (Na^+ , Rb^+ and Cs^+), crystals of general formula $X_2[23-[Fe^{II}(CN)_6]_2$ have been obtained[‡] (see experimental part in ESI). As shown in figure 3, these crystals are isostructural to $K_2[23-[Fe^{II}(CN)_6]_2$ and the alkali cations occupy the same sites as K^+ cations.

Table 1. Cell parameters (Å), volume (Å³) for $X_2[23-[Fe^{II}(CN)_6]_2$ ($X = Na^+$, K^+ , Rb^+ and Cs^+) networks and for $23-[Fe^{II}(CN)_6]_2$.¹²

	Na	K	Rb	Cs	$23-[Fe^{II}(CN)_6]_2$
$a=b$	19.1776(8)	19.0191(3)	18.9482(8)	18.0456(6)	17.9242(4)
c	6.9473(6)	7.1810(3)	7.3664(6)	8.3728(5)	8.6140(4)
V	2212.8(2)	2249.55(11)	2290.5(2)	2361.26(18)	2396.71(13)

As expected, the increase in the c parameter from 6.9473(6) Å for Na^+ to 8.3728(5) Å for Cs^+ is accompanied by a less pronounced decrease of a , b parameters. However, most significant changes in $a = b$ and c parameters are observed for the substitution of K^+ by Cs^+ (Fig. 3). As given in table 1, the volume of the cell is constantly enhanced by increasing the radii of the inserted cation. It is worth noting that for Cs^+ , the obtained metrics are the closest ones to those observed for $23-[Fe^{II}(CN)_6]_2$.¹²

Figure 3 : Plots of the variation of the cell parameters (i) and cell volume (ii) for $X_2[23-[Fe^{II}(CN)_6]_2$ ($X = Na, K, Rb$ and Cs) (■). The same parameters for $23-[Fe^{II}(CN)_6]_2$ (●) and the mixed-valence solid solution ($Cs_2[23-[Fe^{II}(CN)_6]_2]_{0.83}[23-[Fe^{III}(CN)_6]_2]_{0.17}$) (●) are also given for sake of comparison.

The generation of solid solutions based on simultaneous presence of $Fe(II)$ and $Fe(III)$ centers was attempted by combining an equimolar mixture of $X_4Fe^{II}(CN)_6$ and $X_3Fe^{III}(CN)_6$ ($X = Na, Rb$) with compound **2**. In the case of Na^+ , only segregation (yellowish and orange crystals) and no necklace-type crystals (Fig. 4b) were observed. This is in agreement with the hypothesis made above on the difference in unit cell metrics. For Rb^+ , the same type of segregation was obtained, however with systematic formation of necklace-like crystalline assemblies. For Cs^+ , the formation of pure $Cs_2[23-[Fe^{II}(CN)_6]_2$ could only be achieved under reductive conditions (presence of hydrazine). Indeed, starting with $Cs_4Fe^{II}(CN)_6$ and **2**, the presence of O_2 causes the spontaneous oxidation of $Fe(II)$ to $Fe(III)$. However, in solvent saturated with Argon, the process produced one type of yellow-orange crystals, i.e. no segregation nor formation of necklace-type crystals have been observed (Fig. 4c).

Figure 4: Segregation between orange crystals of $K_2[23-[Fe^{II}(CN)_6]_2$ and pale yellow crystals of $23-[Fe^{III}(CN)_6]_2$ (a), necklace-like crystals observed upon combining **2** with an equimolar mixture of $K_4Fe^{II}(CN)_6$ and $K_3Fe^{III}(CN)_6$ (b) and solid solution ($Cs_2[23-[Fe^{II}(CN)_6]_2]_{0.83}[23-[Fe^{III}(CN)_6]_2]_{0.17}$) (c).

The XRD analysis[‡] revealed the formation of the desired mixed-valence $Fe(II)/Fe(III)$ solid solution with 83/17 ratio ($(Cs_2[23-[Fe^{II}(CN)_6]_2]_{0.83}[23-[Fe^{III}(CN)_6]_2]_{0.17})$). The latter was, determined by considering the occupation ratio of Cs^+ cations. The presence of both oxidation states was confirmed by IR spectroscopy (Fig. 5) which revealed the presence of signatures of both species ($\nu_{C\equiv N}$ at 2032 cm^{-1} for $Cs_2[23-[Fe^{II}(CN)_6]_2$ and 2111 cm^{-1} for $23-[Fe^{III}(CN)_6]_2$).

Figure 5: IR spectrum, in the 1940–2160 cm^{−1} region (right), of Cs₂23-[Fe^{II}(CN)₆]₂ (red), 23-[Fe^{III}(CN)₆]₂ (blue) and of the mixed valence solid solution (Cs₂23-[Fe^{II}(CN)₆]₂)_{0.83}(23-[Fe^{III}(CN)₆]₂)_{0.17} (black).

Conclusions

The combination of the dicationic tecton **2** with either M₃Fe^{III}(CN)₆ or M₄Fe^{II}(CN)₆ (M = Na, K, Rb and Cs) leads to the formation of isostructural crystals of formula 23-[Fe^{III}(CN)₆]₂ and M₂23-[Fe(CN)₆]₂ respectively. Whereas a mixture of X₃Fe^{III}(CN)₆ and X₄Fe^{II}(CN)₆ (X = Na, K or Rb) leads to segregation or epitaxial growth, Cs₄Fe^{II}(CN)₆ generates a rare example of H bonded mixed valence Fe(II)-Fe(III) solid solution. The latter may be regarded as a crystalline material composed of Fe^{II}(CN)₆^{4−} doped with 17% of Fe^{III}(CN)₆^{3−}. Applying the same strategy, we are currently investigating the formation of other mixed valence solid solutions with different metal centres and different ratio.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Crystallographic data for 22-[Fe^{II}(CN)₆]₆•6H₂O and short structural description as well as experimental details.

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‡ 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-Kα (λ = 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).¹⁵

K₂23-[Fe(CN)₆]₂, M = 1740.10, Trigonal, a = b = 19.0191(3) Å, c = 7.1810(3) Å, α = β = 90°, γ = 120° U = 2249.55(11) Å³, Space group P-3, Z = 1, μ = 0.474 mm^{−1}, Refs measured : 15227, Independent Refls : 3334, Final R indices [I>2σ(I)]: R1 = 0.0472, wR2 = 0.1127, R indices (all data): R1 = 0.0886, wR2 = 0.1270, GOF = 1.012;

K₂23-[Ru(CN)₆]₂, M = 915.27, Trigonal, a = b = 19.2156(9) Å, c = 7.1461(6) Å, α = β = 90°, γ = 120° U = 2285.1(2) Å³, Space group P-3, Z = 2, μ = 0.480 mm^{−1}, Refs measured : 10016, Independent Refls : 3526, Final R indices [I>2σ(I)]: R1 = 0.0573, wR2 = 0.1392, R indices (all data): R1 = 0.0836, wR2 = 0.1525, GOF = 1.027;

Na₂23-[Fe(CN)₆]₂, M = 1707.88, Trigonal, a = b = 19.1776(8) Å, c = 6.9473(6) Å, α = β = 90°, γ = 120° U = 2212.8(2) Å³, Space group P-3, Z = 1, μ = 0.398 mm^{−1}, Refs measured : 10800, Independent Refls : 3379, Final R indices [I>2σ(I)]: R1 = 0.0452, wR2 = 0.1066, R indices (all data): R1 = 0.0780, wR2 = 0.1207, GOF = 1.073;

Rb₂23-[Fe(CN)₆]₂, M = 1832.84, Trigonal, a = b = 18.9482(8) Å, c = 7.3664(6) Å, α = β = 90°, γ = 120° U = 2290.5(2) Å³, Space group P-3, Z = 1, μ = 1.431 mm^{−1}, Refs measured : 10885, Independent Refls : 3508, Final R indices [I>2σ(I)]: R1 = 0.0864, wR2 = 0.2178, R indices (all data): R1 = 0.1768, wR2 = 0.2851, GOF = 1.012;

Cs₂23-[Fe(CN)₆]₂, M = 1927.72, Trigonal, a = b = 18.0456(6) Å, c = 8.3728(5) Å, α = β = 90°, γ = 120° U = 2361.26(18) Å³, Space group P-3, Z = 1, μ = 1.356 mm^{−1}, Refs measured : 12284, Independent Refls : 4624, Final R indices [I>2σ(I)]: R1 = 0.0637, wR2 = 0.1324, R indices (all data): R1 = 0.1000, wR2 = 0.1524, GOF = 1.091;

(Cs₂23-[Fe^{II}(CN)₆]₂)_{0.83}(23-[Fe^{III}(CN)₆]₂)_{0.17}, M = 1857.36, Trigonal, a = b = 18.0505(4) Å, c = 8.4055(4) Å, α = β = 90°, γ = 120° U = 2371.77(14) Å³, Space group P-3, Z = 1, μ = 0.986 mm^{−1}, Refs measured : 17497, Independent Refls : 4538, Final R indices [I>2σ(I)]: R1 = 0.0698, wR2 = 0.2152, R indices (all data): R1 = 0.951, wR2 = 0.2346, GOF = 1.245.

- a) J. Maddox, *Nature*, 1988, **335**, 201; b) A. Gavezzotti, *Acc. Chem. Res.*, 1994, **27**, 309; c) J. D. Dunitz, *Chem. Comm.*, 2003, 545.
- a) M. Simard, D. Su, J. D. Wuest, *J. Am. Chem. Soc.*, 1991, **113**, 4696; b) S. Mann, *Nature*, 1993, **365**, 499; c) M. W. Hosseini, *Acc. Chem. Res.*, 2005, **38**, 313.
- J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH, Weinheim, 1995.
- a) M. W. Hosseini, *Chem. Commun.*, 2005, 582; b) J. D. Wuest, *Chem. Commun.*, 2005, 5830.
- M. W. Hosseini, *CrystEngComm*, 2004, **6**, 318.
- a) T. K. Maji, D. Ghoshal, E. Zangrando, J. Ribas, N. R. Chaudhuri, *CrystEngComm*, 2004, 623; b) C. T. Brewer, G. Brewer, R. J. Butcher, E. E. Carpenter, A. M. Schmiedekamp, C. Viragh, *Dalton*, 2007, 295.
- a) W. Kaneko, S. Kitagawa, M. Ohba, *J. Am. Chem. Soc.*, 2007, **129**, 248; b) J. M. Herrera, A. Bachschmidt, F. Villain, A. Bleuzen, V. Marvaud, W. Wernsdorfer, M. Verdaguer, *Phil. Trans. R. Soc., A: Mathematical, Physical & Engineering Sciences*, 2008, **366**, 127.
- a) C. B. Aakeröy, K. R. Seddon, *Chem. Soc. Rev.* 1993, **22**, 397; b) S. Subramanian, M. J. Zaworotko, *Coord. Chem. Rev.* 1994, **137**, 357; c) J. C. MacDonald, G. M. Whitesides, *Chem. Rev.* 1994, **94**, 2383; d) G. R. Desiraju *Angew. Chem. Int. Ed. Engl.* 1995, **34**, 2311.
- a) K. T. Holman, A. M. Pivovar, J. A. Swift, M. D. Ward, *Acc. Chem. Res.*, 2001, **34**, 107; b) M. W. Hosseini, *Coord. Chem. Rev.* 2003, **240**, 157.
- a) S. Ferlay, V. Bulach, O. Félix, M. W. Hosseini, J.-M. Planeix, N. Kyritsakas, *CrystEngComm* 2002, **4**, 447; b) S. Ferlay, O. Félix, M. W. Hosseini, J.-M. Planeix, N. Kyritsakas, *Chem. Commun.* 2002, 702.
- P. Dechambenoit, S. Ferlay, N. Kyritsakas, M. W. Hosseini, *J. Am. Chem. Soc.*, 2008, **130**, 17106.
- P. Dechambenoit, S. Ferlay, M. W. Hosseini, J.-M. Planeix, N. Kyritsakas, *New. J. Chem.*, 2006, **30**, 1403.
- a) A. I. Kitaigorodsky *Organic Chemical Crystallography*, Consultants Bureau, New York, 1961, page 234; b) D. Braga, G. Cozzani, D. Paolucci, F. Grepioni, *Chem. Commun.*, 2001, 803; c) P. Dechambenoit, S. Ferlay, M. W. Hosseini, J.-M. Planeix, N. Kyritsakas *Chem. Commun.*, 2009, 1559.
- a) J. C. MacDonald, P. C. Dorrestein, M. M. Pilley, M. M. Foote, J. L. Lundburg, R. W. Henning, A. J. Schultz, J. L. Manson, *J. Am. Chem. Soc.* 2000, **122**, 11692; b) J. C. Noveron, M. S. Lah, R. E. A. Del Sesto, M. Arif, J. S. Miller, P. J. Stang, *J. Am. Chem. Soc.* 2002,

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- 124, 6613; c) B. K. Olmsted, S. Ferlay, P. Dechambenoit, M. W. Hosseini, M. D. Ward, *Cryst. Gr. & Des.*, 2009, **6**, 2841.
- 15 G. M. Sheldrick, Programs for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1996.
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