Supplementary Material (ESI) for Chemical Communications


# Playing with isostructurality: from tectons to molecular alloys and composite crystals

Pierre Dechambenoit, Sylvie Ferlay*, Nathalie Kyritsakas and Mir Wais Hosseini*

*Laboratoire de Chimie de Coordination Organique, UMR CNRS 7140, Université de Strasbourg, Institut Le Bel, 4, rue Blaise Pascal, F-67000, Strasbourg, France. E-mail: hosseini@chimie.u-strasbg.fr, ferlay@chimie.u-strasbg.fr*

*Table ESM1. Crystallographic Parameters for the reported crystals, recorded at 173 K.(previously published see ref 14)*

| **Formula** | (**1**-2H$^+$)$_3$[Cr(CN)$_6$]$^{3-}{}_2$ . 7 H$_2$O<br>$A_3X_2$ | (**2**-2H$^+$)$_3$[Cr(CN)$_6$]$^{3-}{}_2$ . 8 H$_2$O<br>$B_3X_2$ | (**1**-2H$^+$)$_3$[Fe(CN)$_6$]$^{3-}{}_2$ . 8 H$_2$O<br>$B_3Y_2$ | (**1**-2H$^+$)$_3$[Co(CN)$_6$]$^{3-}{}_2$ . 8 H$_2$O<br>$B_3Z_2$ |
|---|---|---|---|---|
| **Molecular weight** | 1275.37 | 1389.39 | 1397.09 | 1403.25 |
| **Crystal system** | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| **Space group** | P2(1)/n | P2(1)/n | P2(1)/n | P2(1)/n |
| **a(Å)** | 7.1142(4) | 7.1190(2) | 7.0978(5) | 7.1180(10) |
| **b(Å)** | 21.4319(13) | 22.3250(6) | 22.2254(16) | 22.252(4) |
| **c(Å)** | 20.9403(13) | 21.0110(6) | 20.6357(12) | 20.508(4) |
| **α(deg)** | 90 | 90 | 90 | 90 |
| **β(deg)** | 91.702(2) | 92.8190(17) | 92.363(3) | 92.239(6) |
| **γ(deg)** | 90 | 90 | 90 | 90 |
| **V(Å$^3$)** | 3191.4(3) | 3335.27(16) | 3252.5(4) | 3245.8(10) |
| **Z** | 2 | 2 | 2 | 2 |
| **Colour** | colourless | colourless | yellow | colourless |

*Table ESM2. Crystallographic Parameters for molecular alloys reported (recorded at 173 K).*

| **Formula** | [**2**-2H$^+$]$_3$[Cr(CN)$_6$]$^{3-}$[Fe(CN)$_6$]$^{3-}$ 8 H$_2$O<br>$B_3XY$ | [**2**-2H$^+$]$_3$[Co(CN)$_6$]$^{3-}$[Fe(CN)$_6$]$^{3-}$ 8 H$_2$O<br>$B_3YZ$ | [**2**-2H$^+$]$_3$[Fe$_{1/3}$Co$_{1/3}$Cr$_{1/3}$ (CN)$_6$]$^{3-}{}_2$ 8 H$_2$O<br>$B_3(X_{2/3}Y_{2/3}Z_{2/3}$ |
|---|---|---|---|
| **Crystal system** | Monoclinic | Monoclinic | Monoclinic |
| **Space group** | P2(1)/n | P2(1)/n | P2(1)/n |
| **a(Å)** | 7.095(6) | 7.101(9) | 7.097(11) |
| **b(Å)** | 22.220(19) | 22.22(3) | 22.19(3) |
| **c(Å)** | 20.798(19) | 20.57(3) | 20.66(3) |
| **α(deg)** | 90 | 90 | 90 |
| **β(deg)** | 92.67(3) | 92.14(2) | 92.53(4) |
| **γ(deg)** | 90 | 90 | 90 |
| **V(Å$^3$)** | 3275(7) | 3243(13) | 3252(15) |
| **Colour** | yellow | yellow | yellow |

# ESM Experimental part

Thermogravimetric (TGA) Studies.

TGA measurements have been performed on Pyris 6 TGA Lab System (Perkin-Elmer), using a $N_2$ flow of 20 ml/mn and a heat rate of 10°C/ mn.

**Preparation of crystalline solid solutions $[2\text{-}2H^+]_3[Fe(CN)_6]^{3-}[Co(CN)_6]^{3-}\cdot 8H_2O$ and $[2\text{-}2H^+]_3[Fe(CN)_6]^{3-}[Cr(CN)_6]^{3-}\cdot 8H_2O$ ($B_3YZ$ and $B_3XY$ see text)**

5 mg (0.015 mmol) of $K_3Fe(CN)_6\cdot 2H_2O$ and 5 mg (0.015 mmol) of $K_3Co(CN)_6\cdot 2H_2O$ or $K_3Cr(CN)_6\cdot 2H_2O$ are dissolved in 5 ml of distilled water. 5 ml of an aqueous solution containing 17 mg (0.44 mmol) of **2**-2HCl were added. After two days, 16 mg of yellow crystals were obtained by filtration and air drying.

IR : 2126 and 2115 $cm^{-1}$ for $B_3YZ$, corresponding to the elongation mode for C≡N in $Co(CN)_6$ and $Fe(CN)_6$ respectively; 2129 and 2115 $cm^{-1}$ for $B_3XY$, corresponding to the elongation mode for C≡N in Cr(CN)6 and $Fe(CN)_6$ respectively.

**Preparation of solid solutions $[2\text{-}2H^+]_3[Cr(CN)_6]^{3-}{}_{2/3}[Fe(CN)_6]^{3-}{}_{2/3}[Co(CN)_6]^{3-}{}_{2/3}\cdot 8H_2O$ ($B_3X_{0.66}Y_{0.66}Z_{0.66}$)**

3.3 mg (0.01 mmol) of $K_3Fe(CN)_6\cdot 2H_2O$, 3.3 mg (0.01 mmol) of $K_3Co(CN)_6\cdot 2H_2O$ and 3.3 mg (0.01 mmol) of $K_3Cr(CN)_6\cdot 2H_2O$ are dissolved in 5 ml of distilled water. 5 ml of an aqueous solution containing 17 mg (0.44 mmol) of 2-2HCl were added. After one day, 14 mg of yellow crystals were obtained by filtration and air drying.

IR : 2125 and 2114 $cm^{-1}$

**Preparation of solid solutions $[1\text{-}2H^+]_{3y}[2\text{-}2H^+]_{3(1-y)}[Cr(CN)_6]^{3-}{}_2\cdot nH_2O$ ($A_{3y}$ $B_{3(1-y)}X_2$)**

For y~0.25: 100 mg (0.307 mmol) of $K_3Cr(CN)_6\cdot 2H_2O$ are dissolved in 60 ml of distilled water. 60 ml of an aqueous solution containing 42 mg (0.110 mmol) of **2**-2HCl (B) and 128 mg (0.330 mmol) of **1**-2HCl (A) were added. After two days, 151 mg of colourless crystals were obtained by filtration and air drying.

For y~0.5: 100 mg (0.307 mmol) of $K_3Cr(CN)_6\cdot 2H_2O$ are dissolved in 60 ml of distilled water. 60 ml of an aqueous solution containing 85 mg (0.222 mmol) of **2**-2HCl (B) and 85 mg (0.219 mmol) of **1**-2HCl (A) were added. After two days, 168 mg of colourless crystals were obtained by filtration and air drying.

For y~0.75: 100 mg (0.307 mmol) of $K_3Cr(CN)_6\cdot 2H_2O$ are dissolved in 60 ml of distilled water. 60 ml of an aqueous solution containing 128 mg (0.334 mmol) of **2**-2HCl (B) and 42 mg (0.108 mmol) of **1**-2HCl (A) were added. After two days, 167 mg of colourless crystals were obtained by filtration and air drying.

**Preparation of "crystals of crystals" with $[2\text{-}2H^+]_3[Co(CN)_6^{3-}]_2\cdot 8H_2O$ and $[2\text{-}2H^+]_3[Fe(CN)_6]^{3-}{}_2\cdot 8\ H_2O$: ($B_3Y_2$) and ($B_3Z_2$)**

A yellow single crystal (size 1x1x0.5 mm) of ($B_3Y_2$) was glued on a cupper wire and then immersed into an aqueous solution (15 mL) containing 6 mg of $K_3Co(CN)_6\cdot 2H_2O$ and 10 mg of **2**-2HCl (B). After one day, the growth of colourless crystalline layer ($B_3Z_2$) on the surface of the yellow seed crystal was observed. Conversely, the same procedure was repeated starting with a colourless crystal of ($B_3Z_2$) as seed and an aqueous solution containing 6 mg of $K_3Fe(CN)_6\cdot 2H_2O$ and 10 mg of **2**-2HCl (B). Again the growth of a yellow layer of ($B_3Y_2$) surrounding the colourless seed crystals was observed.

**Preparation of composite crystals with $[1\text{-}2H^+]_3[Cr(CN)_6^{3-}]_2{\cdot}7H_2O$ and $[2\text{-}2H^+]_3[Fe(CN)_6]^{3-}{}_2{\cdot}8\ H_2O$: $(B_3Y_2)$ and $(A_3X_2)$**

The same procedure as mentioned above was used starting from a yellow seed single crystal of $(B_3Y_2)$ or a colourless seed single crystal of $(A_3X_2)$ immersed into 15 ml of an aqueous solution containing 5 mg of $K_3Cr(CN)_6{\cdot}2H_2O$ and 9 mg of **1**-2HCl (A), or 5 mg of $K_3Fe(CN)_6{\cdot}2H_2O$ and 9 mg of **2**-2HCl (B) respectively. Composite single crystals were obtained after one or two days.

**Preparation of composite crystals with $[1\text{-}2H^+]_3[Cr(CN)_6]^{3-}{}_2{\cdot}7H_2O$ and $[2\text{-}2H^+]_3[Fe(CN)_6]^{3-}$ $[Co(CN)_6]^{3-}{\cdot}8H_2O$ and $[2\text{-}2H^+]_3[Fe(CN)_6]^{3-}[Cr(CN)_6]^{3-}{\cdot}8H_2O$: $(B_3YZ)$ or $(B_3XY)$ and $(A_3X_2)$.**

A yellow single crystal of the solid solution of $(B_3XY)$ or $(B_3YZ)$ was glued on a cupper wire and then immersed into an 15 ml of an aqueous solution containing 6 mg of $K_3Cr(CN)_6{\cdot}2H_2O$ and 10 mg of **1**-2HCl (A). After one day, a 3-D epitaxial growth of colourless crystalline layer $(A_3X_2)$ on the surface of the yellow seed crystals was observed.

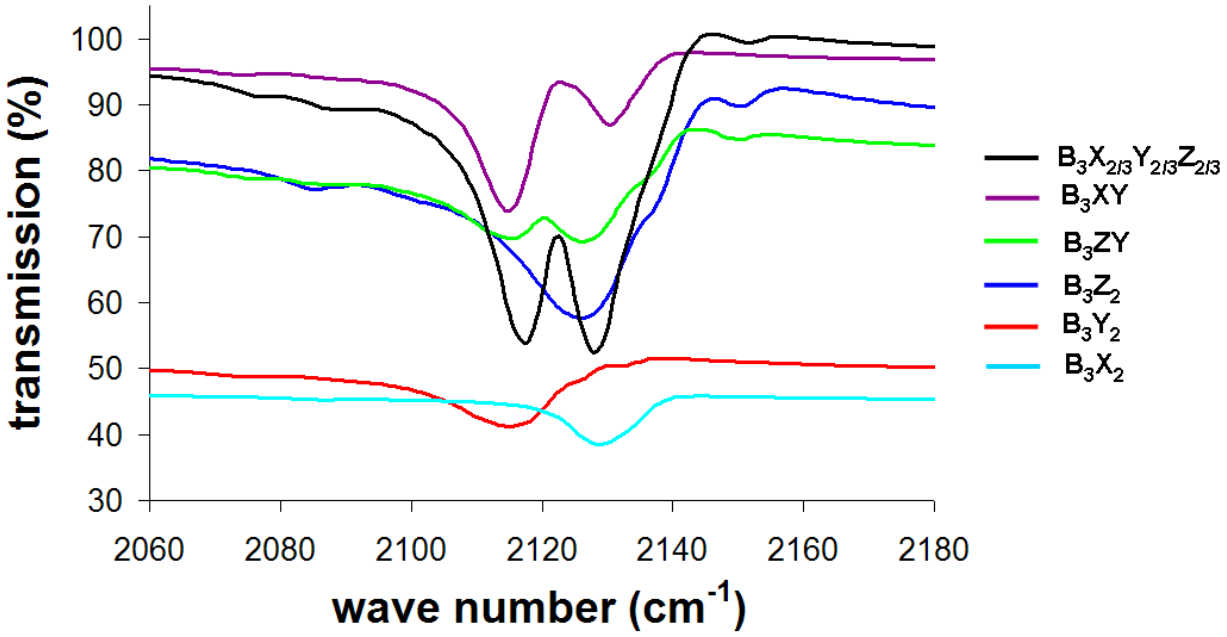


***Figure S1***: Portions of the IR spectra (2060 – 2180 $cm^{-1}$) for binary ($(B_3YZ)$, $(B_3XY)$) and ternary ($B_3X_{2/3}Y_{2/3}Z_{2/3}$) molecular alloys.

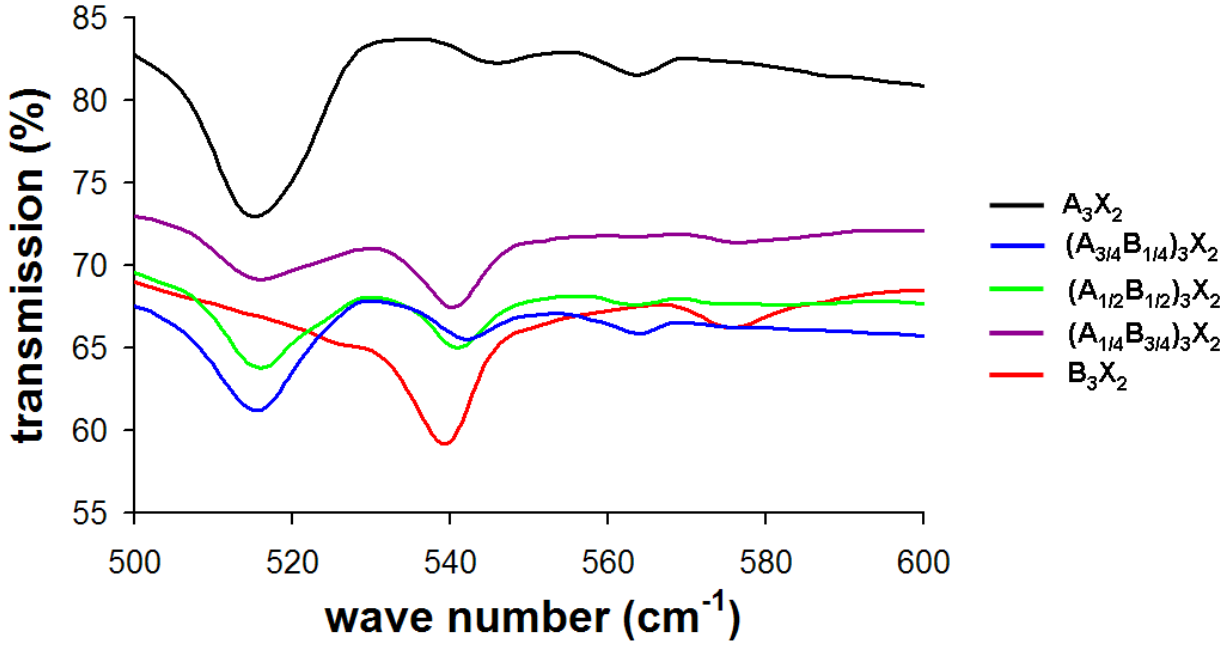


***Figure S2***: Portions of the IR spectra (500 – 600 $cm^{-1}$) for binary ($A_{3y}$ $B_{3(1-y)}X_2$) molecular alloys.