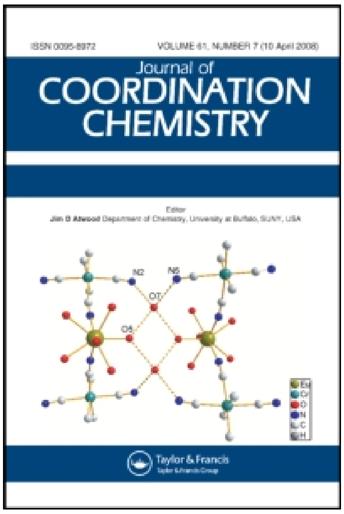

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Template self-assembly of cyano-bridged supramolecular complexes $\{[\mathrm{Cu(en)}_2][\mathrm{KM(CN)}_6]\}$*_n* (M = $\mathrm{Cr}^{\mathrm{III}}$, $\mathrm{Fe}^{\mathrm{III}}$, $\mathrm{Co}^{\mathrm{III}}$)

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TEMPLATE SELF-ASSEMBLY OF CYANO-BRIDGED SUPRAMOLECULAR COMPLEXES $\{[Cu(en)_2][KM(CN)_6]\}_n$ $(M = Cr^{III}, Fe^{III}, Co^{III})$

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Reaction of $K_3[M(CN)_6]$ ($M = Cr^{III}$, Fe^{III}, Co^{III}) with $[Cu(en)_2](ClO_4)_2$ in water gives three cyanide-bridged supramolecular complexes, $\{[Cu(en)_2][KM(CN)_6]\}_n$ [$M = Cr^{III}$ (**1**), Fe^{III} (**2**), Co^{III} (**3**); en = ethylenediamine], which have been characterized by elemental analysis, ICP analysis, IR spectra, TGA-DTA analysis and X-ray diffraction. Complex **1** crystallizes in the monoclinic, space group $C2/c$ with cell dimensions $a = 0.85237(12)$, $b = 1.7014(3)$, $c = 1.2103(2)$ nm, $\beta = 98.70(2)°$ and $Z = 4$, and **2** crystallizes in the same space group with $a = 0.8401(2)$, $b = 1.6844(5)$ Å, $c = 1.1859(2)$ nm, $\beta = 98.98(2)°$ and $Z = 4$. The crystal structures of **1** and **2** reveal a novel three-dimensional porous framework in which $[Cu(en)_2]^{2+}$ acts as a template, $[M(CN)_6]^{3-}$ as a building block and K^+ as a connecting unit.

Keywords: Cyano-bridged complex; Crystal structure; Supramolecule; Template reaction; Self-assembly

INTRODUCTION

Design and synthesis of a framework solid, which is often accessible by self-assembly under exceedingly mild conditions, is of interest because the voids of the porous framework can be designed to selectively trap a particular guest molecular during the formation (crystallization) of the framework [1]. These clathrate supramolecular complexes have many potential applications [2] for technologically useful electronic, optical, electrochemical and catalytic materials. The synthesis and structural characterization of cyanide-bridged framework materials continue to be active areas of investigation [3]. It is well known that the cyanide anion, CN^-, behaves as a bridging ligand at both ends, with carbon and nitrogen atoms between two coordination centers. When a

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cyanometallate $[M(CN)_n]^{m-}$ is linked to another coordination center M′ at the nitrogen atom, the linear M–CN–M′ span has a length of ~0.6 nm. The multidimensional structure formed by the successive –M–CN–M′– linkages produces a void space with the dimensions appropriate to accommodate an oligoatomic molecule. In order to stabilize the crystal structure, a guest molecule or ion is necessary to fill up the void space. The nature (shape, size and charge) of the guest plays a crucial role in determining the structural and geometrical features of cyanide-bridged species. For example, tetrahedral and *pseudo*-tetrahedral guests $CMe_{4-n}Cl_n$ ($n = 0$–4) are accommodated by a cavity of an adamantine-like cage structure in the $Cd(CN)_2$ host, but the large-volume guest Bu^i_2O or $(Pr^iCH_2CH_2)O$ is found in a H-tridymite ($P6_3/mmc$) structure of the same $Cd(CN)_2$ host [4]. In fact, the host structure can be flexible enough to adjust the dimensions of the cavity to suit the guest molecule by changing the degree of puckering of the network and the conformation of the complementary ligand.

Many cyanometallate host–guest supramolecular complexes have linear dicyanoargentate(I) [5], square planar tetracyanonickelate(II) [6] and tetrahedral tetracyanocadmate(II) [7] as the main building blocks, but few hexacyanometallate structures have been reported because suitable complementary ligands were unavailable in these supramolecular complexes. Recently, we have obtained three novel host–guest supramolecular complexes $\{[Cu(en)_2]\ [KM(CN)_6]\}_n$ [M = Cr^{III} (**1**) [8], Fe^{III} (**2**), Co^{III} (**3**)] from hexacyanometallate building blocks [9]. Here, we present details of the syntheses and characterization of these supramolecular complexes.

EXPERIMENTAL

Physical Measurements

Elemental analyses for C, H and N were carried out with a Perkin-Elmer 240C instrument. Metal analyses for Cu, Fe, Cr and Co were made on a Jarrell-Ash 1100 + 2000 inductively coupled plasma atomic emission spectrum apparatus. Infrared spectra from KBr pellets were recorded on a Nicolet FT-IR 170X spectrophotometer in the 4000–400 cm^{-1} region. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out in the temperature range 20–300°C with a heating rate of 5°C/min.

Material

All chemicals used for the synthesis were of reagent grade and used without further purification. $K_3[Cr(CN)_6]$ [10] and $K_3[Co(CN)_6]$ [11] were prepared by literature procedures. $[Cu(en)_2](ClO_4)_2$ was prepared by mixing $Cu(ClO_4)_2 \cdot 6H_2O$ and ethylenediamine in a 1 : 2 mol ratio in water.

Preparation of Complexes 1–3

The preparations of **1**–**3** follow the same procedure. In a typical synthetic procedure, an aqueous solution (10 cm^3) of $[Cu(en)_2](ClO_4)_2$ (1 mmol) was added to an aqueous solution (10 cm^3) of $K_3[M(CN)_6]$ (M = Cr^{III}, Fe^{III} or Co^{III}) (1 mmol) at room temperature.

The resulting solution was filtered and the filtrate was kept in the dark for one week. Purple-red crystals were formed for **1** and **2**, and black crystals were formed for **3**. The crystals were filtered and washed with water three times and dried in the air. **1**, Anal. Calcd. for $C_{10}H_{16}N_{10}CrCuK$(%): C 27.87; H 3.74; N 32.51, Cu 14.74, Cr 12.07. Found: C 27.53, H 4.02, N 31.95; Cu 15.1, Cr 12.6. IR (ν_{CN}): 2124, 2111 cm^{-1}. **2**, Anal. Calcd. for $C_{10}H_{16}N_{10}FeCuK$ (%): C 27.62, H 3.71, N 32.22, Cu 14.62, Fe 12.84. Found: C 27.87, H 3.92, N 32.85, Cu 14.11, Fe 12.6. IR (ν_{CN}): 2121, 2111, 2099 cm^{-1}. **3**, Anal. Calcd. for $C_{10}H_{16}N_{10}CoCuK$ (%): C 27.43, H 3.68, N 31.99, Cu 14.51, Co 13.46. Found: C 27.83, H 3.88, N 31.25, Cu 14.42, Co 12.8. IR (ν_{CN}): 2133, 2121, 2109 cm^{-1}.

X-ray Crystal Analysis

A single crystal of **1** with dimensions of 0.6 × 0.6 ×0.1 mm was stuck to the end of a glass fiber and mounted on a Siemens P4 four-circle diffractometer to perform X-ray diffraction work using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data were collected at 293(2) K using a θ–2θ scan technique to a maximum 2θ value of 60.00°. The data were corrected for Lorentz and polarization effects during data reduction using XSCANS [12]. The structure was solved by the direct method and refined on F^2 by full-matrix least-squares methods using SHELXTL Version 5.0 [13]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions (C–H 0.096 nm and N–H 0.090 nm) and assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U value of the atoms to which they are attached and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure factor calculations. All computations were carried out using the SHELXTL-PC program package. The final cycle of the full-matrix least-squares refinement was based on 2241 observed reflections ($I \geq 2\sigma(I)$) and 108 variable parameters and converged with unweighted and weighted agreement factors of $R_1 = 0.0505$ and $wR_2 = 0.1491$.

A block crystal of **2** with dimensions 0.25 × 0.25× 0.2 mm was selected for lattice parameter determination and collection of intensity data on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The data were collected at 296 K using the ω–2θ scan technique to a maximum 2θ value of 52.00°. The data were corrected for Lorentz polarization effects and empirical absorption. The structure was solved by the Patterson method, followed by Fourier syntheses and refined by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were found from the difference Fourier map and were refined with isotropic thermal parameters. All calculations were performed using the MSC TEXSAN V.2.1 programs. The final cycle of the full-matrix least-squares refinement was based on 1362 observed reflections ($I \geq 3\sigma(I)$) and 107 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.046$ and $R_w = 0.056$.

The crystal parameters and refinement results of **1** and **2** are summarized in Table I. The final position parameters of the non-hydrogen atoms for **1** and **2** with their estimated standard deviations are listed in Tables II and III, respectively. The crystal parameters and refinement results of **3** have been reported in previous papers [14].

TABLE I Crystal data and structure refinement for **1** and **2**

	1 *(M = Cr)*	***2*** *(M = Fe)*
Empirical formula	$C_{10}H_{16}CrCuKN_{10}$	$C_{10}H_{16}FeCuKN_{10}$
Formula weight	430.97	434.79
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$C2/c$
a (nm)	0.85237(12)	0.8401(2)
b (nm)	1.7014(3)	1.6844(5)
c (nm)	1.2103(2)	1.1859(2)
β (°)	98.70(2)	98.98(2)
V (nm^3)	1.7350(5)	1.658(1)
Z	4	4
D_c (Mg/m^3)	1.650	1.74
F(000)	872	880
μ (Mo Kα)(cm^{-1})	21.05	24.26
R^a	0.0505	0.046
R_w (wR_2)	0.1491^b	0.056^c

$^a R = \sum\|F_0 - F_C\|/\sum|F_0|$; $^b wR_2 = [w(F_0^2 - F_C^2)^2/\sum w(F_0^2)^2]^{1/2}$; $^c R_w = [(\sum w(|F_o - F_c|)^2/\sum w|F_o|^2)^{1/2}$.

TABLE II Atomic coordinates and equivalent isotropic displacement parameter ($\times 10^2\,nm^2$) for **1**

Atom	*x*	*y*	*z*	*U(eq)*
Cu(1)	0.5	0.5	1	0.036(1)
Cr(1)	0	0.6173(1)	0.25	0.020(1)
K(1)	0	0.3642(1)	0.25	0.026(1)
N(1)	0.0056(3)	0.6162(2)	0.5171(2)	0.043(1)
N(2)	−0.2858(4)	0.4902(2)	0.2047(3)	0.043(1)
N(3)	−0.2665(3)	0.7508(2)	0.2569(2)	0.057(1)
N(4)	0.3818(3)	0.5876(2)	1.0601(3)	0.050(1)
N(5)	0.6142(3)	0.5860(2)	0.9318(2)	0.042(1)
C(1)	0.0050(3)	0.6165(1)	0.4224(2)	0.028(1)
C(2)	−0.1806(3)	0.5337(1)	0.2247(2)	0.026(1)
C(3)	−0.1724(3)	0.7032(2)	0.2442(2)	0.033(1)
C(4)	0.4215(8)	0.6620(3)	1.0137(6)	0.088(2)
C(5)	0.5648(7)	0.6622(3)	0.9681(5)	0.076(1)

U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE III Atomic coordinates and isotropic thermal parameter B(eq) for **2**

Atom	*x*	*y*	*z*	*B(eq)*
Cu	1/2	1/2	0	2.75(4)
Fe	0	0.38439(5)	3/4	1.28(3)
K	0	0.64030(8)	3/4	1.88(5)
N(1)	0.2746(5)	0.5083(2)	0.7938(4)	3.0(2)
N(2)	−0.0059(5)	0.3834(3)	0.4884(3)	2.9(2)
N(3)	0.2620(5)	0.2566(2)	0.7538(4)	3.7(2)
N(4)	0.6154(5)	0.5854(2)	−0.0703(3)	2.9(2)
N(5)	0.3809(5)	0.5891(3)	0.0591(4)	3.6(2)
C(1)	0.1710(5)	0.4629(2)	0.7741(3)	1.8(2)
C(2)	−0.0056(5)	0.3839(2)	0.5858(4)	1.8(2)
C(3)	0.1655(5)	0.3034(2)	0.7556(4)	2.0(2)
C(11)	0.558(1)	0.6628(4)	−0.0412(7)	6.2(4)
C(12)	0.425(1)	0.6628(4)	0.0138(7)	6.0(4)

RESULTS AND DISCUSSION

Synthesis and Characterization

One-step self-assembly reactions of the complexes **1**–**3** are analogous. According to the microanalyses and TGA-DTA, all three complexes do not have solvent molecules (H_2O) filling the lattice. The single infrared band due to CN at 2128, 2118 and 2129 cm^{-1} in $K_3[Cr(CN)_6]$, $K_3[Fe(CN)_6]$ and $K_3[Co(CN)_6]$, respectively, splits into two bands for **1** (2124 and 2111 cm^{-1}), three bands for **2** (2121, 2111 and 2099 cm^{-1}) and three bands for **3** (2133, 2121 and 2109 cm^{-1}). These spectra are quite different from other cyano-bridged hexacyanometallate complexes; for example, the two-dimensional complex $[Cu(dien)]_3[Fe(CN)_6]_2 \cdot 6H_2O$ [15] shows two strong ν_{CN} bands at 2176 and 2128 cm^{-1}, and the linear Cr–CN–Ni moiety shows sharp ν_{CN} bands about 2150 cm^{-1} [16]. The ν_{CN} modes in **1**–**3** suggest that the coordination modes of cyanide groups are unusual: neither the free non-bridging mode nor the linear bridging to two transition metals (M^{3+} and Cu^{2+}). As shown in the crystal structure, CN coordinates to the potassium ion with σ- and π-coordination.

Four cyano groups of the $[M(CN)_6]^{3-}$ ion donate their bonding electrons to the empty sp^3d^2 hybrid orbitals of the K^+ ions to form four σ bonds which decrease the wavenumber, ν_{CN}. Another two cyano groups of the same $[M(CN)_6]^{3-}$ ion coordinate to K^+ ions sideways. Owing to the poor overlap of the frontier orbitals, the wavenumber of the cyano group is nearly equal to those of terminal ones.

Crystal Structure

X-ray crystallography of $\{[Cu(en)_2][KFe(CN)_6]\}_n$ (**2**) proves that it is isomorphous with **1**. A perspective view of the asymmetric unit with the atom numbering scheme of **2** is shown in Fig. 1. Projections of the molecular entity in the lattice along the *a* and *c* axes are presented in Figs. 2 and 3, respectively. Selected bond distances and angles with their estimated standard deviations for **2** are listed in Table IV together with those of **1**.

The asymmetric unit of $\{[Cu(en)_2][KFe(CN)_6]\}_n$ (**2**) consists of a $[Fe(CN)_6]^{3-}$ ion, a K^+ and a $[Cu(en)_2]^{2+}$ ion (Fig. 1). The Fe^{III} ion is octahedrally coordinated by six cyanide groups with the carbon atoms. The Fe–C bond lengths are 0.1940(4),

TABLE IV Selected bond distances (nm) and bond angles (°) of **1** and **2**

	1 (M = Cr)	*2 (M = Fe)*
M–C(1)	0.2080(2)	0.1940(4)
M–C(2)	0.2085(2)	0.1941(4)
M–C(3)	0.2065(3)	0.1942(3)
Cu–N(4)	0.1996(3)	0.1987(4)
Cu–N(5)	0.2004(3)	0.1991(4)
K–N(1)	0.2846(2)	0.3187(4)
K–N(2)	0.3229(3)	0.2863(4)
K–N(3)	0.2776(3)	0.2804(4)
M–C(1)–N(1)	179.1(2)	176.7(4)
M–C(2)–N(2)	175.4(2)	178.8(4)
M–C(3)–N(3)	176.5(2)	177.0(4)
K–N(1)–C(1)	172.9(3)	85.8(3)
K–N(2)–C(2)	81.3(2)	172.4(4)
K–N(3)–C(3)	178.6(3)	179.7(5)

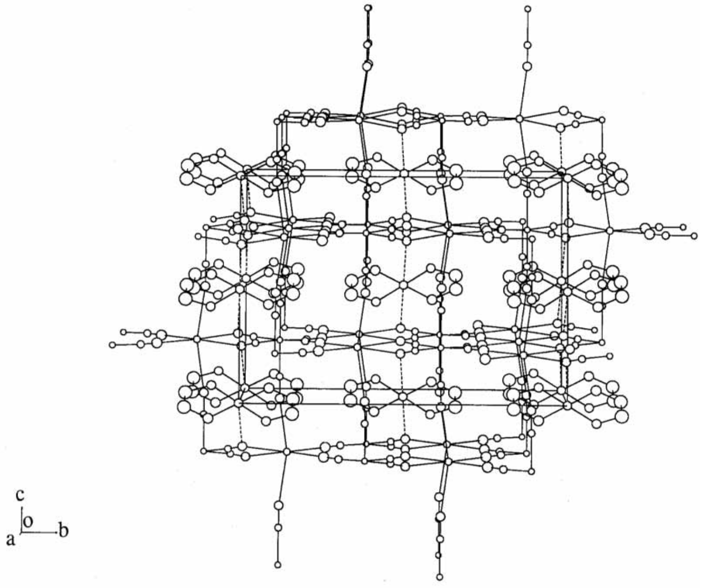

FIGURE 1.

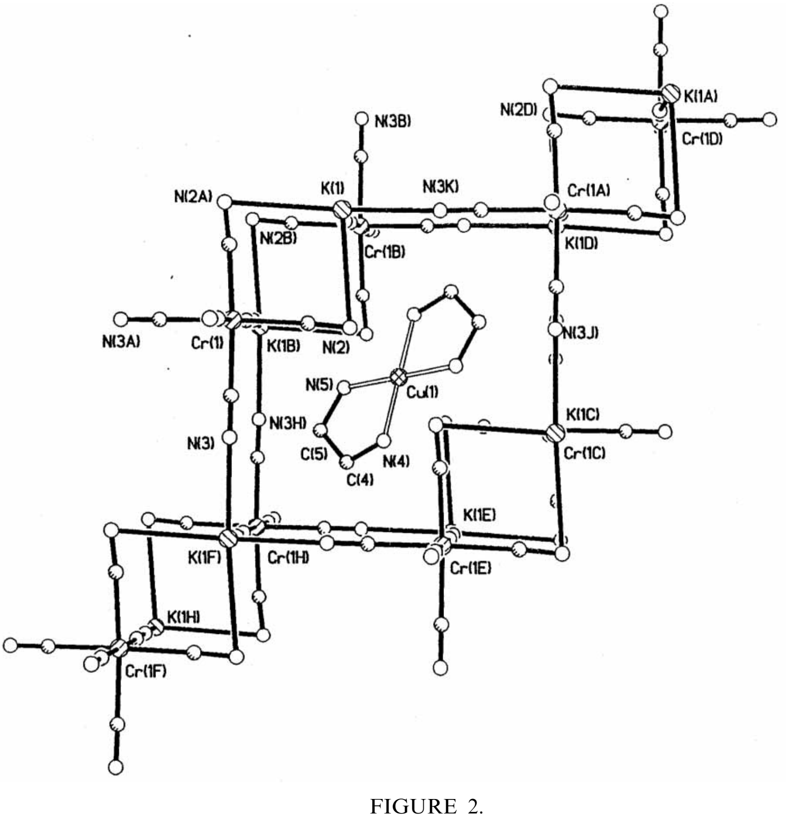

FIGURE 2.

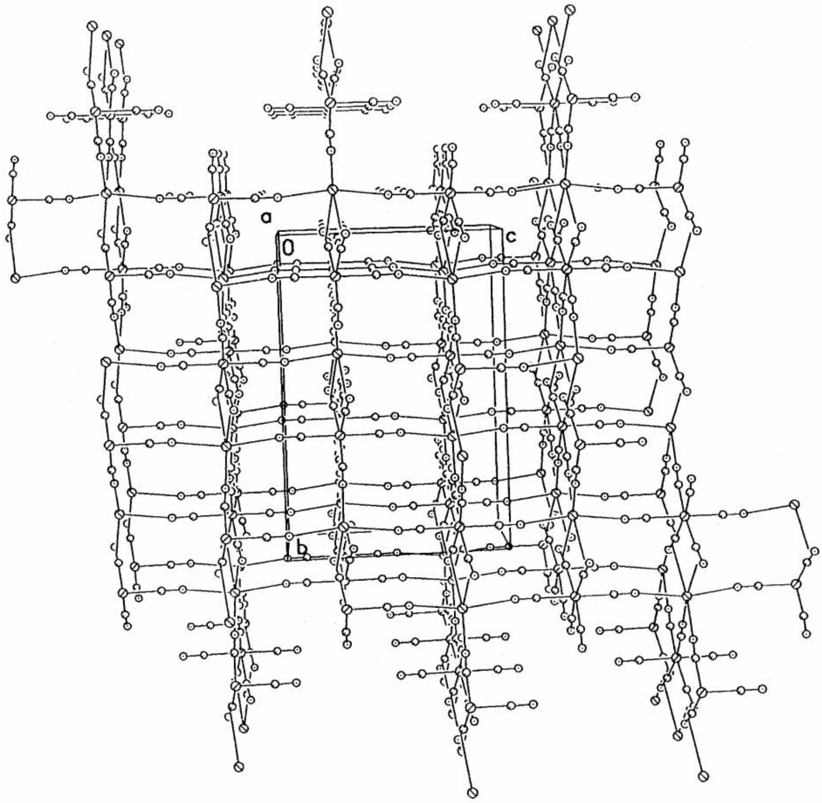

FIGURE 3.

0.1941(4) and 0.1942(4) nm, similar to those of $K_3[Fe(CN)_6]$ (0.1955, 0.1959 and 0.1978 nm) [17]. The potassium cation is unusually coordinated by six cyanide groups, which link Fe^{III} and K^+ ions as bridging ligands. According to the bond lengths (K–N) and bond angles (C–N–K), all cyanide groups can be divided into two groups. One is in the linear Fe–C–N–K spans with N coordinating to the potassium cation. The K–N distances are 0.2863(4) and 0.2804(4) nm and the C–N–K bond angles are 179.7(5) and 172.4(4)°. The other is in the non-linear Fe–C–N–K spans with the CN group side coordinating [18], the K–N distance is 0.3187(4) nm, which is much longer than that of the linear span. The linear Fe–C–N–K span has a length of 0.5–0.6 nm. The successive –Fe–C–N–K– linkages produce a void space with the size and shape to fit a complex cation $[Cu(en)_2]^{2+}$, which is approximately square planar. The Cu–N bond lengths are 0.1987(4) and 0.1991(4) nm, similar to those of $Cu(en)_2X_2$ [19] (X : SCN^-, BF_4^-, ClO_4^-, NO_3^-, Cl^-, Br). Both **1** and **2** have essentially the same molecular and network structures. However, they show a significant difference in the average M–C bond distance, which is longer for Cr–C than for Fe–C. This order is consistent with the decreasing number of dπ electrons at the metal center, suggesting that π-back-donation from the metal to the vacant CN orbital decreases in this order (see Table IV). The crystal cell dimensions and volume of **1** and **2** reflect the M–C distance and increases in the order of $Fe < Cr$. Assembly **3** is an analogue of **1** and **2**, which is proved by IR spectra, elemental analyses and TGA-DTA.

The spontaneous assembly process of $Cu(en)_2(ClO_4)_2$ with $K_3[M(CN)_6]$ is a very specific reaction in one step. The K^+ ions act as connecting blocks linking to $[M(CN)_6]^{3-}$ anions (building block) to form a three-dimensional porous framework structure skeleton $[KM(CN)_6]_\infty^{2-}$ (the host). The $[Cu(en)_2]^{2+}$ ion acts as a template because the structure of the host $[KM(CN)_6]_\infty^{2-}$ is dependent upon the nature (shape, size and charge) of the $[Cu(en)_2]^{2+}$ ion. Moreover, $[Cu(en)_2]^{2+}$ ion acts as the guest matching the special porous channel of the host whose size, shape and charge are just suitable to that of $[Cu(en)_2]^{2+}$. The cavity accommodating the guest $[Cu(en)_2]^{2+}$ is so tight that no bulky substituents can be accommodated. In the self-assembly process of the three complexes, the chemical properties of the $[Cu(en)_2]^{2+}$ ion are important as well as its shape, size and charge. Using $[Ni(en)_2]^{2+}$ (same symmetry) in place of $[Cu(en)_2]^{2+}$ led to different polymer complexes $[Ni(en)_2]_3[Fe(CN)_6]_2 \cdot 2H_2O$ [19].

CONCLUSION

The spontaneous assembly reaction of $[Cu(en)_2](ClO_4)_2$ and $K_3[M(CN)_6]$ in the 1 : 1 mol ratio in aqueous solution formed assemblies of $\{[Cu(en)_2][KM(CN)_6]\}_n$ [M = Cr^{III} (**1**), Fe^{III} (**2**), Co^{III} (**3**)] with a 3D network structure constructed from $[KM(CN)_6]^{2-}$ and $[Cu(en)_2]^{2+}$. The $[Cu(en)_2]^{2+}$ ion acts not only as a template to produce a three-dimensional porous framework structure skeleton $[KM(CN)_6]_\infty^{2-}$ but also as a guest to match the special porous channel in order to stabilize the crystal structure of the host.

Acknowledgement

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Supplementary Data

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137677. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-(0)1223-336033 or Email: teched@chemcrys.cam.ac.uk).

References

[1] (a) C. Janiak, *Angew. Chem. Int. Ed. Engl.* **36**, 1431 (1997); (b) R.H. Baughman and D.S. Galvao, *Nature* **365**, 735 (1993); (c) M. Fujta, Y.J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.* **116**, 1151 (1994); (d) T. Kitazawa, *Chem. Commun.* 891 (1999); (e) Y. Zhao, M. Hong, W. Su, R. Cao, Z. Zhou and A.S.C. Chan, *J. Chem. Soc.*; *Dalton Trans.* 1685 (2000).

[2] (a) D.M.L. Goodgame, D.A. Grachvogel and D.J. Williams, *Angew. Chem. Int. Ed. Engl.* **38**, 153 (1999); (b) H. Gudbjartson, K. Biradha, K.M. Poirier and M.J. Zaworotko, *J. Am. Chem. Soc.* **121**, 2599 (1999); (c) S.S.-Y. Chui, S.M.-F. Lo, J.P.H. Charmant, A.G. Orpen and I.D. Williams, *Science* **283**, 1148 (1999); (d) S.R. Batten and R. Robson, *Angew. Chem. Int. Ed. Engl.* **37**, 1460 (1998); (e) L.R. MacGillivray, R.H. Groeneman and J.L. Atwood, *J. Am. Chem. Soc.* **120**, 2676 (1998).

[3] (a) M. Ohba, N. Usuki, N. Fukita and H. Okawa, *Angew. Chem. Int. Ed. Engl.* **38**, 1795 (1999); (b) H.Z. Kou, S. Gao, B.Q. Ma and D.Z. Liao, *Chem. Commun.* 1309 (2000); (c) G.-C. Guo and T.C.W. Mak, *Angew. Chem. Int. Ed. Engl.* **37**, 3183 (1998); (d) S.W. Zhang, D.G. Fu, W.Y. Sun, Z. Hu, K.B. Yu and W.X. Tang, *Inorg. Chem.* **39**, 1142 (2000); (e) E. Colacio, M. Ghazi, H. Stoeckli-Evans, F. Lloret, J.M. Moreno and C. Perez, *Inorg. Chem.* **40**, 4876 (2001); (f) H.Z. Kou, J.K. Tang, D.Z. Liao, S. Gao, P. Cheng, Z.H. Jiang, S.P. Yan and G.L. Wang, *Inorg. Chem.* **40**, 4839 (2001).

[4] (a) T. Kitazawa, T. Kikuyama, M. Takeda and T. Iwamoto, *J. Chem. Soc.*; *Dalton Trans.* 3715 (1995); (b) T. Kitazawa, S. Nishikiori, R. Kuroda and T. Iwamoto, *J. Chem. Soc.*, *Dalton Trans.* 1029 (1994); (c) T. Kitazawa, *Chem. Commun.* 891 (1999).

[5] (a) G.A. Bowmaker, B.J. Kennedy and J.C. Reid, *Inorg. Chem.* **37**, 3968 (1998); (b) W.F. Yeung, W.T. Wong, J.L. Zuo and T.C. Lau, *J. Chem. Soc.*, *Dalton Trans.* 629 (2000).

[6] (a) A. Ebina, S. Nishikiori and T. Iwamoto, *J. Chem. Soc.*; *Dalton Trans.* 233 (1994); (b) D.W. Knoeppel and S.G. Shore, *Inorg. Chem.* **35**, 1747 (1996); (c) I. Muga, J.M. Gutierrez-Zorrilla, A. Luque, P. Roman and F. Lloret, *Inorg. Chem.* **36**, 743 (1997).

[7] T. Kitazawa, *Chem. Commun.* 891 (1999).

[8] A. Yuan, J. Zou, B. Li, Z. Zha, C. Duan, Y. Liu, Z. Xu and S. Keizer, *Chem. Commun.* 1297 (2000).

[9] R.J. Williams, A.C. Larson and D.T. Cromer, *Acta Crystallogr.* Sect B, **28**, 858 (1972).

[10] W.B. Schaap, R. Krishnamurthy, D.K. Wakefield and W.F. Coleman, In: S. Kirschner (Ed.), Coordination Chemistry (Plenum Press, New York, 1969), p. 177.

[11] J.H. Bigelow, *Inorg. Syn.* **2**, 225 (1946).

[12] *Siemens*, *XSCANS* (*Version* 2.1), Siemens Analytical X-ray Instruments Inc., Madison, USA (1994).

[13] *Siemens*, *SHELXTL* (*Version* 5.0), Siemens Industrial Automation, Inc., Analytical Instrumentation, USA (1995)

[14] (a) B. Li, X. Shen and J. Zou, *J. Acta. Cryst.* **57**, 1242 (2001); (b) B. Li, *J. of Suzhou University* (*Nature Science*), **18**(2) (2002, Apr.).

[15] H.Z. Kou, D.Z. Liao, P. Cheng, Z.H. Jiang and S.P. Yan, *J. Chem. Soc.*, *Dalton Trans.* 1503 (1997).

[16] M. Ohba, N. Usuki, N. Fukita and H. Okawa, *Inorg. Chem.* **37**, 3349 (1998).

[17] (a) M. Ohba, N. Maruono, H. Okawa, T. Enoki and J.-M. Latour, *J. Am. Chem. Soc.* **116**, 11566 (1994); (b) *Inorganica Chimica Acta*, **328**, 185 (2002).

[18] G.C. Guo and T.C.W. Mak, *Angew. Chem. Int. Ed. Engl.* **37**, 3183 (1998).

[19] I.M. Procter, B.J. Hathway and P. Nicholls, *J. Chem. Soc.* (*A*) 1678 (1968)