

An unusual three-dimensional porous framework complex $\{[\text{Cu}(\text{en})_2][\text{KCr}(\text{CN})_6]\}_\infty$ (en = ethylenediamine) from a template self-assembly reaction

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The crystal structure of $\{[\text{Cu}(\text{en})_2][\text{KCr}(\text{CN})_6]\}_\infty$ reveals a novel three-dimensional porous framework in which $[\text{Cu}(\text{en})_2]^{2+}$ acts as a template and K^+ as a connecting unit.

For years, chemists have devoted their efforts and have dreamt about the ability to assemble compounds, by using building units and connecting units in similar way that a bricklayer would erect a building. With the development of crystallography and synthesis chemistry, the assembly of polymer compounds¹ on the basis of simply adding building units and connecting them, is now achievable. Recently, a successful example of this process was construction of cyano bridged complexes² in which the cyanometallate anion behaves as the bridging moiety to build a multidimensional structure with a second coordination center and the resulting complexes demonstrated unique properties. These complexes are usually composed of a cyanometallate $[\text{M}(\text{CN})_n]^{m-}$ (building unit), and a guest molecule and/or a complementary ligand. In general, the choice of the cyanometallate is limited, since the geometry of the complexes are restricted to, e.g. linear as in $[\text{Ag}(\text{CN})_2]^-$,^{2a} trigonal as in $[\text{Cu}(\text{CN})_3]^{2-}$,³ tetrahedral as in, $[\text{Cd}(\text{CN})_4]^{2-}$,⁴ square planar as in $[\text{Ni}(\text{CN})_4]^{2-}$,⁵ and octahedral $[\text{M}(\text{CN})_6]^{3-}$.^{2b,c} The second coordination center, however, can be almost any metal ion in the Periodic Table. Usually, the transition metal ion is selected because of the existence of a σ - π feedback bond between the selected metal ion and the cyano group which enables production of more stable complexes. The guest ion is often associated with organic molecules or other ions,^{4,5} such as H_2O , unidentate aliphatic amines, ambidentate α,ω -diaminoalkanes, aromatic amines, pyrazine or piperazine. These compounds are necessary to fill up the void space so stabilizing the crystal structure.

We have recently prepared and structurally characterized a new polymeric supramolecular compound $\{[\text{Cu}(\text{en})_2][\text{KCr}(\text{CN})_6]\}_n$ **1** (en = ethylenediamine) through a one-step self-assembly reaction of the complex $[\text{Cu}(\text{en})_2](\text{ClO}_4)_2$ and $\text{KCr}(\text{CN})_6$ in aqueous solution. The compound assembles itself *via* hexacyanochromium $[\text{Cr}(\text{CN})_6]^{3-}$ as the building unit, and potassium cations as the connecting units. The copper(II) complex $[\text{Cu}(\text{en})_2]^{2+}$ acts as the template/guest molecule. This is also a novel example where the potassium ion acts as a connecting unit to form a three-dimensional porous framework with the $[\text{Cr}(\text{CN})_6]^{3-}$ ion. It is uncommon that the complex ion $[\text{Cu}(\text{en})_2]^{2+}$ acts both as a special template, whose size, shape and charge match that of the cavity in the host lattice, and as a guest which stabilizes the crystal lattice. In fact, without $[\text{Cu}(\text{en})_2]^{2+}$, $\text{K}_3[\text{Cr}(\text{CN})_6]$ cannot form a three dimensional porous structure.

The IR spectra of complex **1** shows two sharp ν_{CN} bands at 2124 and 2111 cm^{-1} which are at lower wavenumber than that of the bridging cyano group (2150 cm^{-1} for the linear Cr–CN–Ni moiety^{2c}) or a non-bridging cyano group (2128 cm^{-1} for the complex $\text{K}_3[\text{Cr}(\text{CN})_6]$) and indicates that these two cyano groups are neither linear bridging linked to two transition metals (Cr^{3+} , Cu^{2+}), nor non-bridging. Indeed the cyano group coordinates to potassium ions, as has been established by crystallography.

The asymmetric unit of **1** consists of a $[\text{Cr}(\text{CN})_6]^{3-}$ ion, a K^+ and a $[\text{Cu}(\text{en})_2]^{2+}$ ion and the structure is shown in Fig. 1. The geometry of the Cr^{3+} ion is octahedral with coordination of six carbon atoms of the cyano groups. The Cr–C bond lengths are 2.065(3), 2.080(2) and 2.085(2) Å, similar to values found in $\text{K}_3[\text{Cr}(\text{CN})_6]$ (2.057, 2.075, 2.100 Å)⁷ and $\text{PPh}_4[\text{Ni}(\text{pn})_2][\text{Cr}(\text{CN})_6]\cdot\text{H}_2\text{O}$ (pn = 1,3-propanediamine) (2.062, 2.083 and 2.087 Å).^{2c} The six nitrogen atoms of the cyano groups coordinate to a potassium cation. According to the bond lengths (K–N) and bond angles (C–N–K) the six cyano groups can be divided into two groups. The first group is found in linear Cr–C–N–K chains, with K–N distances of 2.846 and 2.766 Å, and C–N–K bond angles of 172.3 and 178.6°. The

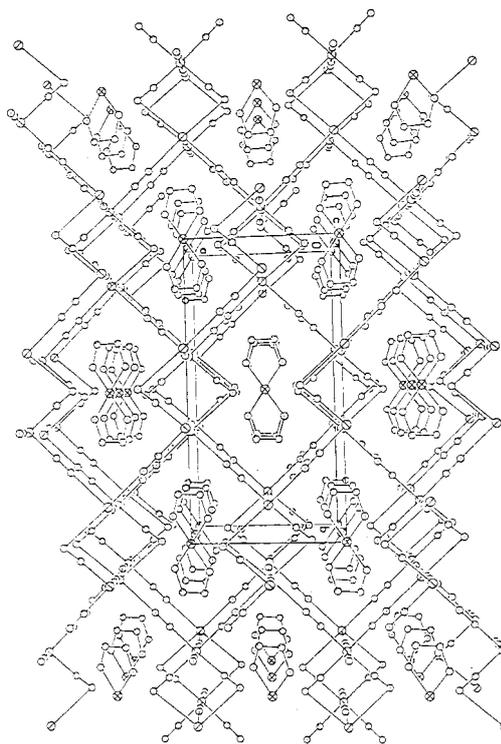


Fig. 1 Projection of the 3-D network structure of **1** in which the $[\text{Cu}(\text{en})_2]^{2+}$ cations act as templates.

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second group comprises non-linear Cr–C–N–K chains with the CN group coordinating sideways,⁸ with K–N distance of 3.229 Å, much longer than the linear bond distance. IR spectroscopy provides additional evidence with two ν_{CN} bands being observed with the intensity of the low wavenumber band at 2111 cm^{-1} being more intense than that of the high wavenumber band at 2124 cm^{-1} . The first band is due to the four σ bonded cyano groups linearly attached to a potassium cation while the second band results from the two cyano groups bonded sideways to potassium cations. This assignment is consistent with the molecular structure, in which four cyano groups donate their σ bonding electrons to the empty d^2sp^3 hybrid orbitals of the K^+ ions to form four σ -bonds which decreases the wavenumber, ν_{CN} . Another two cyano groups, which are part of the same hexacyanochromium ion, coordinate to K^+ ions sideways,⁸ which owing to the orientation of the frontier orbitals, leads to poorer overlap. Consequently, the wavenumber of the cyano group is higher for the sideways coordination mode than for a linear σ bond.

The spontaneous assembly process of $\text{Cu}(\text{en})_2(\text{ClO}_4)_2$ and $\text{K}_3[\text{Cr}(\text{CN})_6]$ is a very specific one-step reaction. The $[\text{Cu}(\text{en})_2]^{2+}$ ion acts both as a template and a guest while the structure of the host $\{[\text{KCr}(\text{CN})_6]^{2-}\}_\infty$ is dependant upon the shape, size and charge of the guest ion. The cavity is very tight, and use of bulkier substituents $\{[\text{Cu}(\text{nmen})_2]^{2+}, [\text{Cu}(\text{dmen})_2]^{2+}, [\text{Cu}(\text{tmen})_2]^{2+}, [\text{Cu}(\text{pn})_2]^{2+}; \text{nmen} = N\text{-methyleneethylenediamine}, \text{dmen} = N,N\text{-dimethyleneethylenediamine}, \text{tmen} = \text{tetramethyleneethylenediamine}\}$, led to different types of complexes. In the self-assembly process of **1**, other than its shape, size and charge, the chemical properties of the $[\text{Cu}(\text{en})_2]^{2+}$ ion is another important factor. Using $[\text{Ni}(\text{en})_2]^{2+}$ (same symmetry) in place of $[\text{Cu}(\text{en})_2]^{2+}$ ion, led to a different polymer complex $\{[\text{Ni}(\text{en})_2]_3[\text{Cr}(\text{CN})_6]\}_\infty$.

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Notes and references

1 K. Biradha, D. Dennis, V. A. MacKinnon, C. Seward and M. J. Zaworotko, in *Current Challenges on Large Scale Supramolecular*

Assemblies, NATO Advanced Research Workshop, ed. G. Tsoucaris, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1999, pp. 115–132; B. F. Abrahams, S. R. Batten, M. J. Grannas, H. Hamit, B. F. Hoskins and R. Robson, *Angew. Chem., Int. Ed.*, 1999, **38**, 1475; P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638.

- 2 (a) G. A. Bowmaker, B. J. Kennedy and J. C. Reid, *Inorg. Chem.*, 1998, **37**, 3968; (b) M. Ohba, N. Usuki, N. Fukita and H. Okawa, *Angew. Chem., Int. Ed.*, 1999, **38**, 1795; (c) M. Ohba, N. Usuki, N. Fukita and H. Okawa, *Inorg. Chem.*, 1998, **37**, 3349.
- 3 D. J. Chesnut and J. Zubieta, *Chem. Commun.*, 1998, 1707.
- 4 T. Iwamoto, *Supramolecular Chemistry in Cyanometallate Systems*, in *Comprehensive Supramolecular Chemistry*, ed. D. D. MacNicol, F. Toda and R. Bishop, Pergamon, Oxford, 1996, vol. 6, ch. 19, pp. 643–690; T. Kitazawa, *Chem. Commun.*, 1999, 891.
- 5 D. W. Knoeppel and S. G. Shore, *Inorg. Chem.*, 1996, **35**, 1747; I. Muga, J. M. Gutierrez-Zorrilla, A. Luque, P. Roman and F. Lloret, *Inorg. Chem.*, 1997, **36**, 743.
- 6 L. H. Jones, *Inorg. Chem.*, 1963, **2**, 777.
- 7 S. Jagner, E. Ljungstrom and N.-G. Vannerberg, *Acta. Chem. Scand., Ser. A*, 1974, **28**, 623.
- 8 G.-C. Guo and T. C. W. Mak, *Angew. Chem., Int. Ed.*, 1998, **37**, 3183.
- 9 X-Ray crystallographic structure determination of **1**: all data were measured on a Siemens P4 four-circle diffractometer with monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) using the θ - 2θ scan mode. The data were corrected for Lorentz and polarization effects during data reduction using XSCANS. The structure was solved by the direct method and refined on F^2 by full-matrix least-squares methods using SHELXTL Version 5.0. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions (C–H 0.96 Å, N–H 0.90 Å) assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U 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 on a PC-586 computer using the SHELXTL-PC program package. Analytical anomalous dispersion corrections were incorporated. *Crystal data*: $\text{C}_{10}\text{H}_{16}\text{CrCuKN}_{10}$, $M = 430.97$, monoclinic, space group $C2/c$, $a = 8.5237(12)$, $b = 17.014(3)$, $c = 12.103(2)$ Å, $\beta = 98.70(2)^\circ$, $V = 1735.0(5)$ Å³, $Z = 4$, $D_c = 1.650$ g cm^{-3} , $4.70 < \theta < 60.00^\circ$, crystal size $0.6 \times 0.6 \times 0.1$ mm; 2540 unique reflections and 108 variables converged to $R1 = 0.0505$, $wR2 = 0.1492$. CCDC 182/1670. See <http://www.rsc.org/suppdata/cc/b0/b002913k/> for crystallographic files in .cif format.