metal-organic compounds

A three-dimensional framework complex, poly[[bis(ethylenediamine)copper(II)] [potassium hexacyanocobalt(III)]]

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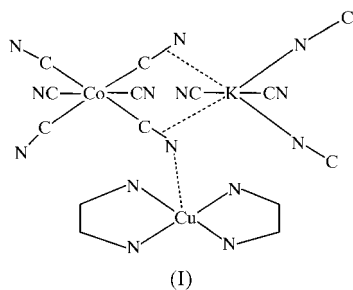Correspondence e-mail: liuhb1970@yahoo.com.cn

The crystal structure of the title compound, $\{[Cu(en)_2][KCo(CN)_6]\}_n$ (en is ethylenediamine, $C_2H_8N_2$), reveals a novel three-dimensional porous framework in which $[Cu(en)_2]^{2+}$ acts as a template and K^+ as a connecting unit. The Cu atom lies on an inversion centre and the Co and K atoms are on twofold axes.

Comment

The design and synthesis of well characterized molecular-based magnets remains a challenge (Kou *et al.*, 2000). It is well known that hexacyanometallate ions, $[M(CN)_6]^{3-}$, acting as good building blocks, play an important role in realising bimetallic assemblies. Although a series of bimetallic assemblies derived from a hexacyanometallate ion and a four-coordinate bis(diamine)–metal complex have been synthesized (Ohba *et al.*, 1994; Fukita *et al.*, 1998; Zhang *et al.*, 2000), the most commonly employed building blocks are $[Fe(CN)_6]^{3-}$, $[Cr(CN)_6]^{3-}$ and $[Co(CN)_6]^{3-}$ (Ferbinteanu *et al.*, 1999). We have previously reported the three-dimensional

(I)

porous framework complex $\{[Cu(en)_2][KCr(CN)_6]\}_n$ (Yuan *et al.*, 2000), and we report here the crystal structure of the title complex, $\{[Cu(en)_2][KCo(CN)_6]\}_n$, (I).

The structure of (I) is shown in Figs. 1, 2 and 3. The Co^{3+} ion is coordinated by six C atoms of the cyano groups, forming a slightly distorted octahedral geometry, and the Co—C bond lengths are 1.9001 (19), 1.9004 (19) and 1.9056 (18) Å, which are similar to the values found in $K_3[Co(CN)_6]$ [1.876 (11),

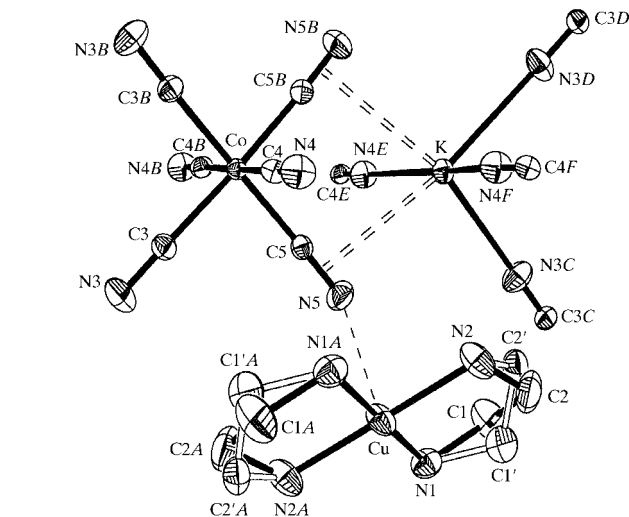**Figure 1**
The coordination geometry of the K^+, Co^{3+} and $[Cu(en)_2]^{2+}$ ions of (I), with displacement ellipsoids at the 30% probability level. H atoms have been omitted for clarity.

1.896 (11) and 1.916 (11) Å; Vannerberg, 1972] and less than the Cr—C bond lengths in $\{[Cu(en)_2][KCr(CN)_6]\}_n$ [2.065 (3), 2.080 (2) and 2.085 (2) Å]. The C3—Co—C4, C4—Co—C5 and C5—Co—C3 bond angles are 92.71 (8), 87.95 (7) and 89.05 (8)°, respectively. The K^+ cation is unusually coordinated by six cyano groups of neighbouring cyanometallates, which act as bridging ligands to link the Co^{3+} and K^+ ions.
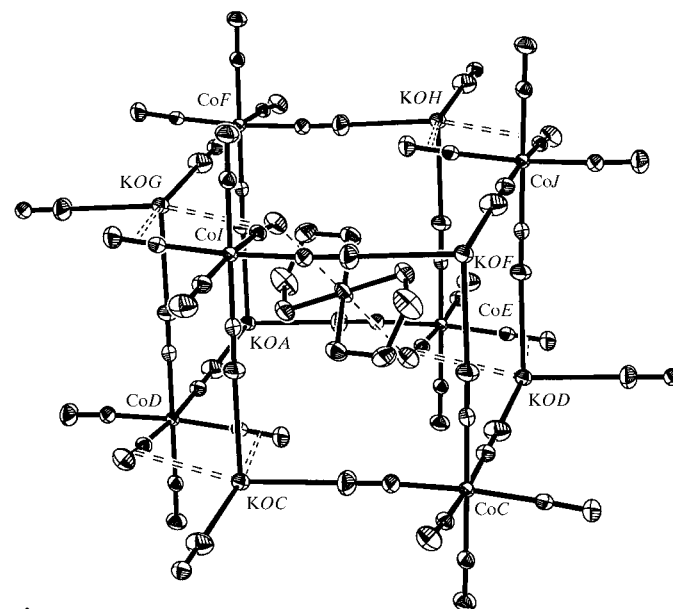

Figure 2
A view of (I) parallel to the *b* axis.

All the cyano groups in (I) can be divided into two groups according to the K···N distances and C—N···K angles. One group has a linear Co—C—N—K linkage, using the σ electrons of the N atom coordinating to the K$^+$ cation, the K···N distances of which are 2.8158 (18) and 2.8746 (16) Å; the C—N···K angles are 179.28 (17) and 172.46 (17)°. The other group is with a non-linear Co—C—N—K linkage, using the π electrons of the CN group coordinating to the K$^+$ cation (Guo & Mak, 1998). Here, the K···N and K···C distances are 3.183 (2) and 3.326 (2) Å, respectively; the K···N distance is much longer than that of the above linear span. The C—N···K and N—C···K angles are 86.88 (14) and 72.85 (13)°, respectively.
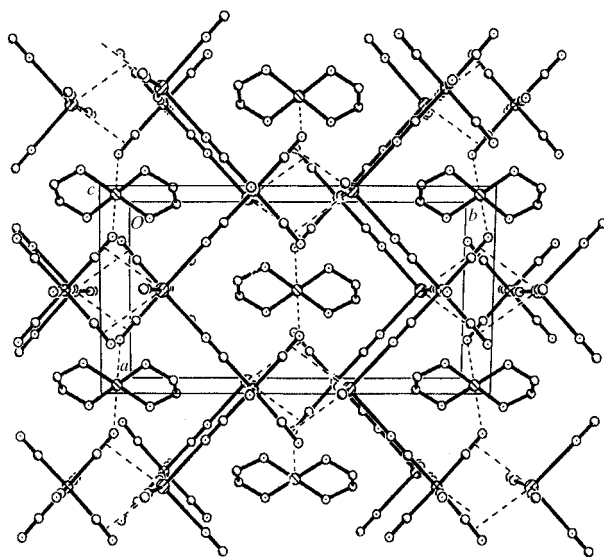

Figure 3
The unit-cell contents for (I).

The three-dimensional framework of (I) is composed of two kinds of linkage, CN—Co—CN—K and Co—CN—K—CN, with σ- and π-coordination forming a distorted cube-like void space, as shown in Fig. 2, with sides of about 9.0 × 8.9 Å. There are two small squares in both the upper and lower planes of the cube, which are composed of KOC, CoD and two CN with a π-coordination mode. Three other squares are as follows: KOD, CoE and two CN; KOG, CoF and two CN; and KOH, CoJ and two CN (atom labels as in Fig. 2). The sides of the square are about 3.2 × 3.1 Å. The complex [Cu(en)$_2$]$^{2+}$ ions occupy the centre of the cube with two positions of occupancies 0.54 and 0.46.

The Cu—N bond lengths within [Cu(en)$_2$]$^{2+}$ are 1.9929 (18) and 1.9895 (19) Å, which are similar to those found in [Cu(en)$_2X_2$] (where X is NCS$^-$, BF$_4^-$, ClO$_4^-$, NO$_3^-$, Cl$^-$ or Br$^-$; Procter et al., 1968). The distance between Cu and the nearest cyano N atom is 2.891 (4) Å. The Cu^{2+} ion is coordinated by four N atoms from two en ligands and by two cyano N atoms, forming an elongated octahedral geometry.

Experimental

Caution! Perchlorate salts are potentially explosive and should be handled in small quantities. Ethylenediamine (en; 2 mmol) was added to an aqueous solution (20 ml) of Cu(ClO$_4$)$_2$·6H$_2$O (1 mmol) with stirring. The colour of the solution turned to blue–violet. After stirring for 20 min, the solution was mixed with an aqueous solution (20 ml) of K$_3$[Co(CN)$_6$] (1 mmol). The resulting solution was filtered and the filtrate was left for one week in the dark at room temperature. Violet–red crystals of {[Cu(en)$_2$][KCo(CN)$_6$]}$_n$, (I), suitable for X-ray diffraction analysis, were obtained. The product is stable under ambient conditions and is insoluble in most common inorganic and organic solvents. Analysis, found: C 27.14, H 3.58, N 31.32%; calculated for C$_{10}$H$_{16}$CoCuKN$_{10}$: C 27.43, H 3.68, N 32.00%.

Crystal data

[Cu(C$_2$H$_8$N$_2$)$_2$][KCo(CN)$_6$]	D_x = 1.764 Mg m^{-3}
M_r = 437.90	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 26
a = 8.391 (2) Å	reflections
b = 16.866 (3) Å	θ = 3.0–17.5°
c = 11.791 (2) Å	μ = 2.56 mm^{-1}
β = 98.91 (2)°	T = 295 (2) K
V = 1648.6 (6) Å^3	Block, violet–red
Z = 4	0.44 × 0.41 × 0.20 mm

Data collection

Siemens $P4$ diffractometer	R_{int} = 0.013
ω scans	θ_{max} = 27°
Absorption correction: ψ scan	h = 0 → 10
(North et al., 1968)	k = −1 → 21
T_{min} = 0.333, T_{max} = 0.599	l = −15 → 14
2172 measured reflections	3 standard reflections
1797 independent reflections	every 97 reflections
1606 reflections with $I > 2\sigma(I)$	intensity decay: 3.6%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0355P)^2$
$R(F)$ = 0.024	$+ 0.0854P]$
$wR(F^2)$ = 0.062	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.05	$(\Delta/\sigma)_{max}$ = 0.001
1797 reflections	$\Delta\rho_{max}$ = 0.43 e Å^{-3}
127 parameters	$\Delta\rho_{min}$ = −0.28 e Å^{-3}
H-atom parameters constrained	Extinction correction: SHELXL97
	(Sheldrick, 1997)
	Extinction coefficient: 0.0044 (3)

Table 1
Selected geometric parameters (Å, °).

Cu—N2^i	1.9895 (19)	Co—C4^{ii}	1.9056 (18)
Cu—N2	1.9895 (19)	K···N3^{iii}	2.8158 (18)
Cu—N1	1.9928 (18)	K···N3^{iv}	2.8158 (18)
Cu—N1^i	1.9928 (18)	K···N4^v	2.8746 (16)
Co—C5^{ii}	1.9001 (19)	K···N4^{vi}	2.8746 (16)
Co—C5	1.9001 (19)	K···N5^{ii}	3.183 (2)
Co—C3	1.9004 (19)	K···N5	3.183 (2)
Co—C3^{ii}	1.9004 (19)	K···C5	3.326 (2)
Co—C4	1.9056 (18)	K···C5^{ii}	3.326 (2)
N2^i—Cu—N1^i	84.90 (9)	C3—Co—C4	92.71 (8)
N2—Cu—N1^i	95.10 (9)	C3^{ii}—Co—C4	86.58 (8)
C5^{ii}—Co—C5	92.21 (11)	C4—Co—C4^{ii}	179.00 (11)
C5^{ii}—Co—C3	174.44 (7)	N3—C3—Co	176.75 (18)
C5—Co—C3	89.05 (8)	N4—C4—Co	179.06 (18)
C3—Co—C3^{ii}	90.20 (12)	N5—C5—Co	176.10 (17)
C5—Co—C4	87.95 (7)		

Symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, y, -\frac{1}{2}-z$; (iii) $-\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z$; (iv) $x-\frac{1}{2}, \frac{1}{2}+y, z$; (v) $x-\frac{1}{2}, \frac{1}{2}+y, z$; (v) $x, -y, z-\frac{1}{2}$; (vi) $1-x, -y, -z$.

H atoms were treated as riding, with C—H = 0.97 Å and N—H = 0.90 Å, and with U_{iso}(H) equal to 1.2 times U_{eq} of the parent atom.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1474). Services for accessing these data are described at the back of the journal.

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