

Cyano-bridged extended heteronuclear supramolecular architectures with hexacyanocobalt(III) as building blocks

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Received 8 November 2004

Accepted 21 December 2004

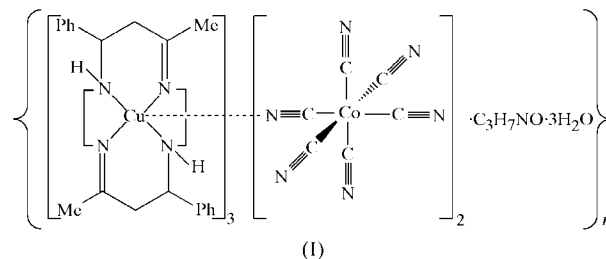
Online 12 February 2005

The cyano-bridged heteronuclear coordination polymer poly[tris[(5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)copper(II)]-hexa- μ -cyano-bis[tricyanocobalt(III)] dimethylformamide solvate trihydrate], $\{[\text{Cu}_3\text{Co}_2(\text{CN})_{12}(\text{C}_{24}\text{H}_{32}\text{N}_4)_3] \cdot \text{C}_3\text{H}_7\text{NO} \cdot 3\text{H}_2\text{O}\}_n$, was synthesized by the assembly reaction of $[\text{CuL}]^{2+}$ (L is 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) and $[\text{Co}(\text{CN})_6]^{3-}$ in a dimethylformamide–water solution. The structure consists of neutral cyano-bridged Cu_3Co_2 units with the unique Co atom in a general position and all three Cu atoms on independent inversion centres. Each $[\text{Co}(\text{CN})_6]^{3-}$ ion connects three Cu^{II} ions *via* three cyano groups to form a novel cyano-bridged two-dimensional stair-shaped-layer structure. The water and dimethylformamide molecules are situated in the inter-fragment spaces.

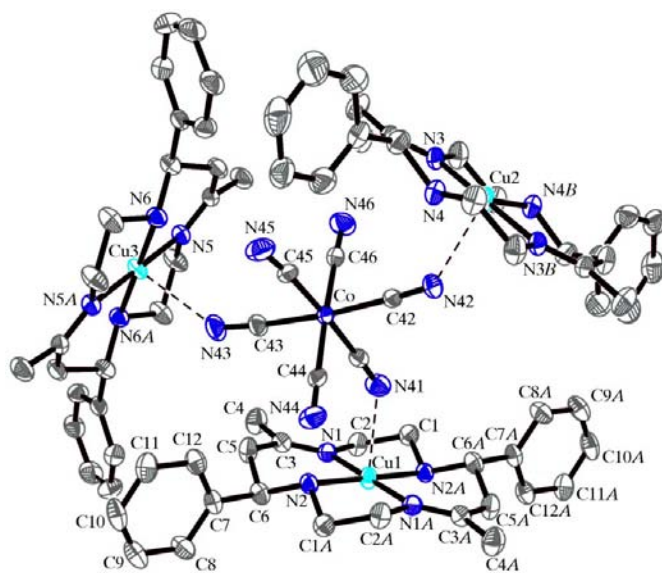
Comment

For many years, chemists have been interested in assembling compounds by connecting building units to give supramolecular structures. Successful recent examples of this process are the cyano-bridged complexes (Misayaka *et al.*, 1998; Re *et al.*, 1998; Fujita *et al.*, 1998; Ohba *et al.*, 1999, 1997) in which a cyanometallate anion serves as the bridging moiety in a multidimensional structure with a second coordination center. When the cyanometallate building block is paramagnetic, molecular-based magnetic materials can be formed, and these have attracted considerable interest. A few high-temperature molecular magnets based on cyanide building blocks have been reported (Gadet *et al.*, 1992; Entley & Girolami, 1995; Mallah *et al.*, 1993). The work of these authors shows that transition metal cyanides are good candidates for a system of

molecule-based magnetic materials. However, the use of $[\text{Co}(\text{CN})_6]^{3-}$ as the bridging moiety in a multidimensional structure has not been reported. We have designed and synthesized a novel coordination polymer, *viz.* $\{(\text{CuL})_3[\text{Co}(\text{CN})_6]_2 \cdot \text{DMF} \cdot 3\text{H}_2\text{O}\}_n$ (L is 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradecane and DMF is dimethylformamide), (I), and its structure is reported here.



Details of the molecular geometry of (I) are given in Table 1 and the asymmetric unit is shown in Fig. 1. The crystal structure consists of a neutral stair-shaped layer network with the stoichiometry $(\text{CuL})_3[\text{Co}(\text{CN})_6]_2$, together with water and DMF solvent molecules. The unique Co atom in a general position and all three Cu atoms on independent inversion centres. Unlike some previously reported cyanometallate complexes (Ferlay *et al.*, 1996; Colacio *et al.*, 1999; Kou *et al.*, 1999) in which three $[\text{Ni}(\text{cyclam})]$ (cyclam is 1,4,8,11-tetraazacyclotetradecane) or $[\text{NiL}]$ (L is 3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane) groups connect three cyanide groups in a *fac* arrangement at an iron(III) or chromium(III) cation, in the title complex, each $[\text{Co}(\text{CN})_6]^{3-}$ unit uses three cyanide groups in a meridional arrangement to


Figure 1

A view showing the arrangement around the $\text{Co}(\text{CN})_6$ moiety in the title compound, shown with 30% probability displacement ellipsoids. H atoms have been omitted and atoms labeled with the suffixes A, B and C are related by the symmetry codes $(1-x, -y, 1-z)$, $(1-x, -y, -z)$ and $(1-x, 1-y, 1-z)$, respectively. The water and DMF molecules have been omitted for clarity.

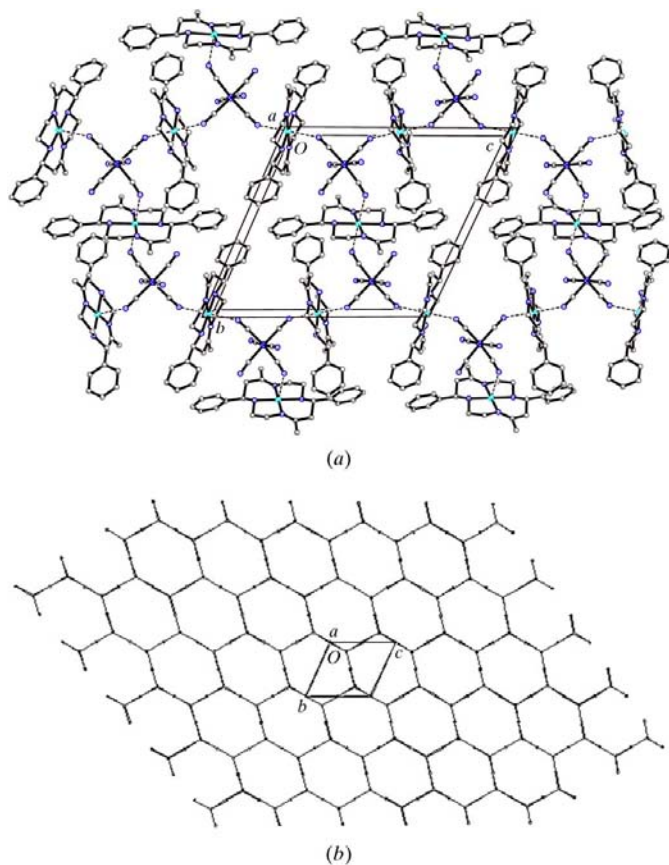


Figure 2
 (a) Projection along the *c* axis, showing the polymeric layer containing Co_6Cu_6 hexagons. (b) The bimetallic hexagonal rings derived from the linkage of six Co^{III} centers and six Cu^{II} centers via 12 cyanide groups.

connect three $[\text{CuL}]^{2+}$ units at the *trans* positions, and this particular local molecular disposition leads to a two-dimensional honeycomb network structure (Fig. 2). This disposition is similar to that of $\{(\text{NiL})_3[\text{Fe}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}\}_n$ (*L* is 3,10-diethyl-1,3,5,8,10,12-hexaazacyclotetradecane; Kou *et al.*, 2000), but this compound has a brick-wall-like structure. The existence of a different structure with the same molecular disposition may be a result of the steric hindrance of the macrocyclic ligands with the benzene groups in the title complex. The distances between adjacent Co and Cu atoms are 5.141 (2) Å for $\text{Co} \cdots \text{Cu}1$, 5.179 (2) Å for $\text{Co} \cdots \text{Cu}2$ and 5.150 (2) Å for $\text{Co} \cdots \text{Cu}3$. Each $[\text{CuL}]^{2+}$ unit is linked to two hexacyanocobalt(III) ions. The coordination environment around the Cu^{II} ion in the $[\text{CuL}]^{2+}$ unit is an elongated octahedron, with short bonds formed by four N atoms from ligand *L* [$\text{Cu}-\text{N} = 1.982$ (4)– 2.037 (4) Å]. The axial coordination sites are occupied by two N atoms from the cyanide group [$\text{Cu}-\text{N} = 2.511$ (5) and 2.553 (5) Å]. The Cu^{II} ion lies at the center of the elongated octahedron. The $\text{Cu}-\text{N}$ distances are similar to those found in $\{[\text{Cu}(\text{cyclam})]_3[\text{Cr}(\text{CN})_6]_2 \cdot 4\text{H}_2\text{O}\}_n$ [cyclam $\text{Cu}-\text{N} = 1.981$ (8)– 2.012 (8) Å and cyano $\text{Cu}-\text{N} = 2.474$ (9)– 2.638 (8) Å; Salah El Fallah *et al.*, 2003). The $\text{Co}-\text{C}$ distances in (I) range from 1.893 (6) to 1.907 (6) Å. As expected, the $\text{Co}-\text{C}-\text{N}$ bond angles vary only over a small

range, 172.9 (6)– 179.8 (7)°, whereas the corresponding $\text{Cu}-\text{N}-\text{C}$ bond angles deviate significantly from linearity [$\text{Cu}1-\text{N}41-\text{C}41 = 135.2$ (5)°, $\text{Cu}2-\text{N}42-\text{C}42 = 139.3$ (5)° and $\text{Cu}3-\text{N}43-\text{C}43 = 138.8$ (5)°].

The structure is further stabilized by several hydrogen-bonding interactions (Table 2).

Experimental

All chemicals were of reagent grade and commercially available from the Beijing Chemical Reagents Company of China. They were used without further purification. The ligand *L* (5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) was synthesized according to the method of Li (1987). To a mixed solution of cyclohexane (150 ml) and ether (300 ml) containing benzoylacetone (32.4 g, 0.2 mol) and ethylenediamine (12 g, 0.2 mol) was added anhydrous K_2CO_3 (41.4 g, 0.3 mol). The solution was stirred and refluxed for 5 h, and then filtered. The filtrate was evaporated and the residue was diffused with ether and refrigerated overnight. The resulting light-yellow solid was filtered off and washed with ether. Recrystallization of the solid from petroleum ether yielded white flaky crystals (yield 55%). *L* (1.9 g, 5 mmol) and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.9 g, 5 mmol) were dissolved in methanol (75 ml), and the solution was stirred and refluxed for 2 h. The red solid that precipitated was filtered off and recrystallized from methanol. Red crystals of $\text{CuL}(\text{ClO}_4)_2$ were obtained. To a solution of $\text{CuL}(\text{ClO}_4)_2$ (0.6 mmol) in DMF/water (30 ml) was added $\text{K}_3[\text{Co}(\text{CN})_6]$ (0.4 mmol) in DMF/water (10 ml). Purple microcrystals precipitated from the resulting purple solution after 10 min, and these were collected by suction filtration, thoroughly washed with water and dried in air. Well shaped purple-brown crystals suitable for X-ray structure analysis were grown at room temperature by the slow diffusion of solutions of $\text{CuL}(\text{ClO}_4)_2$ and $\text{K}_3[\text{Co}(\text{CN})_6]$ in DMF/water in a H-tube. Analysis calculated for $\text{C}_{87}\text{H}_{109}\text{Co}_2\text{Cu}_3\text{N}_{25}\text{O}_4$: C 54.42, H 6.05, N 18.34%; found: C 54.58, H 6.34, N 18.43%.

Crystal data

$[\text{Cu}_3\text{Co}_2(\text{CN})_{12}(\text{C}_{24}\text{H}_{32}\text{N}_4)_3] \cdot$
 $\text{C}_3\text{H}_7\text{NO} \cdot 3\text{H}_2\text{O}$
 $M_r = 1877.47$
 Triclinic, *P1*
 $a = 9.2510$ (3) Å
 $b = 16.4054$ (5) Å
 $c = 17.8005$ (5) Å
 $\alpha = 113.016$ (1)°
 $\beta = 93.684$ (1)°
 $\gamma = 101.966$ (1)°
 $V = 2400.55$ (13) Å³

$Z = 1$
 $D_x = 1.299$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 5807 reflections
 $\theta = 2.3$ – 25.1 °
 $\mu = 1.05$ mm⁻¹
 $T = 293$ (2) K
 Block, purple-brown
 $0.56 \times 0.42 \times 0.26$ mm

Data collection

Siemens SMART CCD diffractometer
 φ and ω scans
 Absorption correction: empirical (using intensity measurements) (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.590$, $T_{\text{max}} = 0.772$
 12 146 measured reflections

8189 independent reflections
 6842 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$
 $\theta_{\text{max}} = 25.0$ °
 $h = -11 \rightarrow 10$
 $k = -19 \rightarrow 17$
 $l = -21 \rightarrow 21$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.076$
 $wR(F^2) = 0.200$
 $S = 1.09$
 8189 reflections
 557 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0864P)^2 + 7.5968P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.10$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.76$ e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Co—C41	1.893 (6)	Cu1—N41	2.553 (5)
Co—C44	1.893 (6)	Cu2—N3	1.987 (4)
Co—C43	1.896 (6)	Cu2—N4	2.012 (5)
Co—C42	1.896 (5)	Cu2—N42	2.511 (5)
Co—C45	1.898 (6)	Cu3—N5	1.982 (4)
Co—C46	1.907 (6)	Cu3—N6	2.037 (4)
Cu1—N1	2.000 (5)	Cu3—N43	2.537 (6)
Cu1—N2	2.011 (4)		
C41—N41—Cu1	135.2 (5)	N43—C43—Co	172.9 (6)
C42—N42—Cu2	139.3 (5)	N44—C44—Co	179.8 (7)
C43—N43—Cu3	138.8 (5)	N45—C45—Co	174.4 (6)
N41—C41—Co	176.7 (5)	N46—C46—Co	178.3 (6)
N42—C42—Co	178.0 (5)		

Table 2
Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N4—H4 <i>D</i> ...O2	0.91	2.47	3.281 (7)	149
N6—H6 <i>B</i> ...N45	0.91	2.51	3.380 (9)	161
O2—H2 <i>D</i> ...N46 ⁱ	0.97	2.24	2.912 (8)	125

Symmetry code: (i) $x + 1, y, z$.

H atoms attached to C atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms [$Csp^3-H = 0.96 \text{ \AA}$, with $U_{iso}(H) = 1.5U_{eq}(C)$]; for H atoms of phenyl, methene ($-CH_2-$) and methine groups, $C-H = 0.93, 0.97$ and 0.98 \AA , respectively, with $U_{iso}(H) = 1.2U_{eq}(C)$; $N-H = 0.91 \text{ \AA}$, with $U_{iso}(H) = 1.2U_{eq}(N)$. H atoms attached to water O atoms were located in difference Fourier maps and constrained to ride on their parent atoms, with $U_{iso}(H)$ values of $1.2U_{eq}(O)$. The DMF molecule was included with an occupancy of 0.5.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

The authors acknowledge the Provincial Natural Science Foundation of Anhui for financial support to FXX (grant No. 29971001). The authors are indebted to Dr Li-Ping Lu for helpful discussions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1035). Services for accessing these data are described at the back of the journal.

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