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Key indicators

Single-crystal X-ray study

 $T = 298$ KMean $\sigma(\text{C}-\text{C}) = 0.006$ Å R factor = 0.048 wR factor = 0.150

Data-to-parameter ratio = 20.2

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Bis(*N*-ethylethylenediamine- κ^2N,N')copper(II)–
hexacyanocobaltate(III)–water (3/2/4): a
two-dimensional ladder structure of a
bimetallic assembly

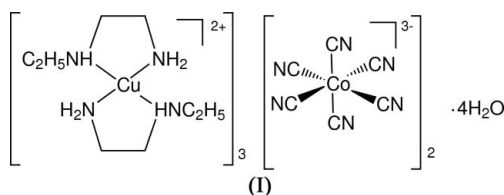
The title compound, poly[[tetracyano-octa- μ -cyano-hexakis(*N*-ethylethylenediamine)tricopper(II)dicobaltate(III)] tetrahydrate], $[\text{Cu}(\text{C}_4\text{H}_{12}\text{N}_2)_2]_3[\text{Co}(\text{CN})_6]_2 \cdot 4\text{H}_2\text{O}$ or $\{[\text{Cu}_3\text{Co}_2(\text{CN})_{12}(\text{C}_4\text{H}_{12}\text{N}_2)_6] \cdot 4\text{H}_2\text{O}\}_n$, was crystallized from an aqueous reaction mixture containing $\text{Cu}(\text{ClO}_4)_2$, *N*-ethylethylenediamine and $\text{K}_3[\text{Co}(\text{CN})_6]$ in a self-assembling process. The polymeric chains are extended through $-\text{Co}^{\text{III}}-\text{CN}-\text{Cu}^{\text{II}}-$ linkages involving four or two cyanide ligands of the centrosymmetric $[\text{Co}(\text{CN})_6]^{3-}$ complex ions, forming a two-dimensional ladder structure. The Cu^{II} atoms, one of which also lies on an inversion centre, have a distorted octahedral coordination geometry, the degree of tetragonal Jahn–Teller distortion being $T = 0.785$ and 0.810 (T is the ratio of mean in-plane $\text{Cu}-\text{N}$ bond lengths to axial $\text{Cu}-\text{N}$ bond lengths). This local Jahn–Teller distortion results from the anisotropic features of this two-dimensional cyano-bridged structure.

Received 23 January 2006

Accepted 6 March 2006

Comment

The design of photofunctional transition-metal complexes such as Fe–Co Prussian blue analogues is one of the challenges in materials science (Sato, 2003; Sato *et al.*, 2003). Recently, Escax *et al.* (2005) elucidated that photo-induced magnetization of Fe–Co Prussian blue analogues caused three-dimensional structural strain, which weakens the ligand field strength of the cyanide ligands. Magneto–structural correlations of cyano-bridged bimetallic assemblies (Ohba & Okawa, 2000; Okawa & Ohba 2002) and the photophysical properties of the $[\text{Co}(\text{CN})_6]^{3-}$ building block (Alexander & Gray 1968; Azumi & McGlynn 2004) have also been investigated. Jahn–Teller switching in response to an applied stress has been proposed in the field of solid-state coordination chemistry (Falvello, 1997). Among the characteristic stereochemistry of copper(II) complexes, the (pseudo) Jahn–Teller effect predicts that only appropriately elongated axial bonds may be effective for thermally accessible distortion, and these systems may be very important for designing photo-controlling materials. We have now prepared and structurally characterized a new two-dimensional cyano-bridged $\text{Cu}^{\text{II}}-\text{Co}^{\text{III}}$ bimetallic assembly, (I), and discuss here the Jahn–Teller distortion of the Cu^{II} sites (Simmons, 1993; Murphy & Hathaway, 2003).



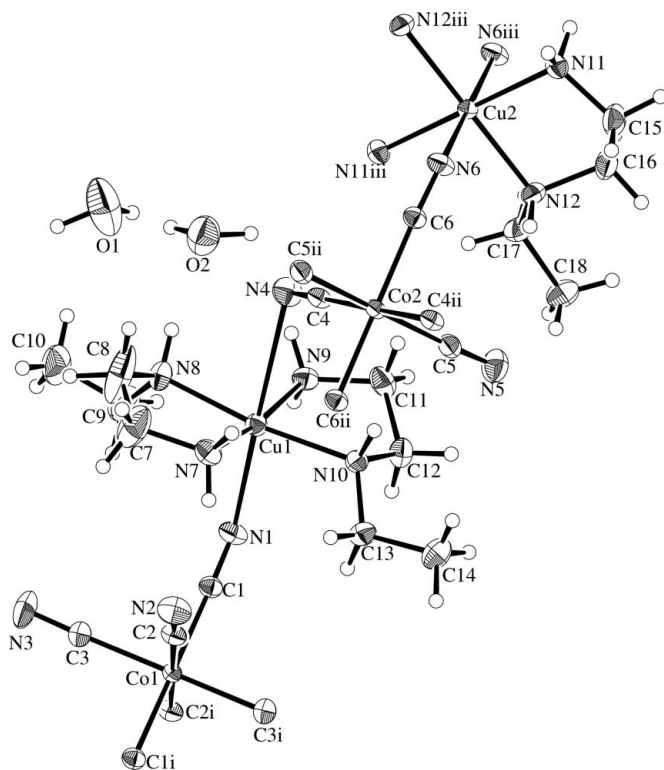


Figure 1

The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (ii) $1 - x, -y, 2 - z$; (iii) $-x, -y, 2 - z$.]

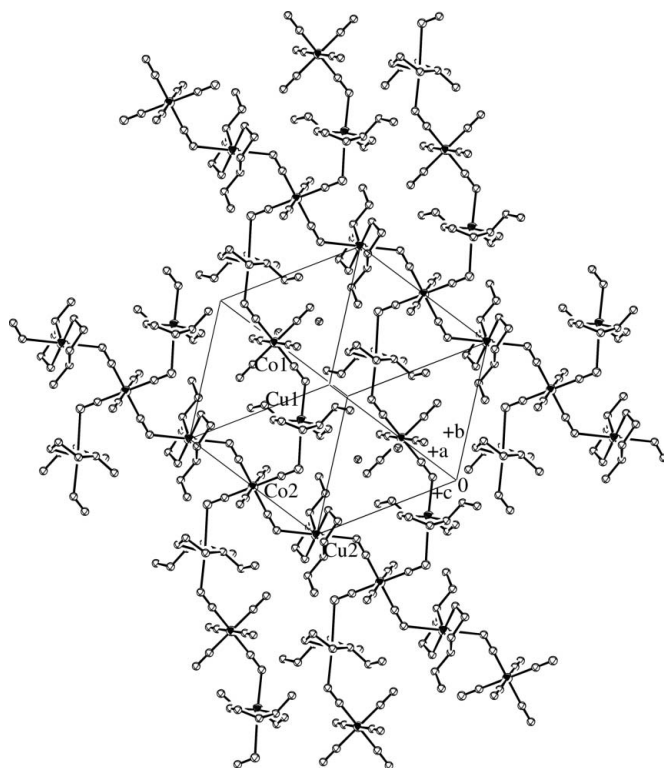


Figure 2

The two-dimensional cyanide-bridged network of (I). H atoms have been omitted for clarity.

The asymmetric unit of (I) consists of one and a half $[\text{Cu}(\text{N-Eten})_2]^{2+}$ cations ($\text{N-Eten} = \text{N-ethylethylenediamine}$), two half $[\text{Co}(\text{CN})_6]^{3-}$ anions, and two water molecules of crystallization (Fig. 1). Atoms Cu2, Co1 and Co2 are located at centre of symmetry. The $[\text{Cu}(\text{N-Eten})_2]^{2+}$ cations are linked to the $[\text{Co}(\text{CN})_6]^{3-}$ anions through cyanide bridges to give a two-dimensional ladder-like structure, the vertical chains of which run along the a axis (Fig. 2). The bond distance ranges include: $\text{Co}-\text{C}$ 1.887 (3)–1.899 (3) Å, $\text{Cu}-\text{N}$ (in-plane) 1.998 (3)–2.070 (3) Å and $\text{C}-\text{N}$ (cyanide) 1.133 (5)–1.157 (4) Å (Table 1). These values are comparable with the analogous cyano-bridged $\text{Cu}^{\text{II}}-\text{Co}^{\text{III}}$ bimetallic assemblies (Ferbinteanu *et al.*, 1999; Mondal *et al.*, 2001; Li *et al.*, 2002; Marvaud *et al.*, 2003; Saha *et al.*, 2004). The axial $\text{Cu}-\text{N}$ bond distances are 2.366 (3)–2.828 (3) Å. There are intermolecular $\text{O}-\text{H}\cdots\text{O}/\text{N}$ and $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds (Table 2), where the acceptor N atoms are those of the cyanide groups.

In the two-dimensional ladder structure, the horizontal bridge (related to Cu1) is more strained than the vertical bridge (related to Cu2, see Fig. 2). The degrees of tetragonal Jahn–Teller distortion of the Cu1 and Cu2 sites are $T = 0.785$ and 0.810, respectively (T is the ratio of mean in-plane $\text{Cu}-\text{X}$ bond lengths to axial $\text{Cu}-\text{X}$ bond lengths; Hathaway & Billing, 1970). The T values for mononuclear $[\text{Cu}(\text{en})_2](\text{ClO}_4)_2$, which shows considerable temperature-induced distortion, are 0.780, 0.785 and 0.791 at 297, 274 and 120 K, respectively (en = ethylenediamine; Akitsu & Einaga, 2004). Therefore, the structural dimensionality of the cyano-bridges in (I) may be ascribed to the anisotropic Jahn–Teller distortion of bimetallic assemblies in the solid state. On the other hand, no significant characteristic in-plane distortion (*e.g.* *cis*- or *trans*- $\text{N}-\text{Cu}-\text{N}$ bond angles) could be observed, notwithstanding the asymmetric introduction of N-ethyl groups.

Experimental

Compound (I) was obtained by slow diffusion of an aqueous solution (30 ml) of $\text{Cu}(\text{ClO}_4)_2$ (0.375 g, 1.00 mmol) and $\text{N-ethylethylenediamine}$ (0.176 g, 2.00 mmol) into an aqueous solution (30 ml) of $\text{K}_3[\text{Co}(\text{CN})_6]$ (0.165 g, 5.00 mmol) at 298 K. The mixed solution was left to stand in the dark for a few days. Blue plate-like single crystals of (I) were obtained (yield 0.224 g). Analysis calculated for $\text{C}_{36}\text{H}_{80}\text{N}_{24}\text{Co}_2\text{Cu}_3\text{O}_4$: C 35.39, H 6.60, N 27.52%; found: C 35.35, H 6.91, N 27.50%. IR (KBr): 2118 cm^{-1} (cyanide). Electronic spectrum (diffuse reflectance): 17500 cm^{-1} ($d-d$ transition of Cu^{II} ion of 2E ground state).

Crystal data

$[\text{Cu}_3\text{Co}_2(\text{CN})_{12}(\text{C}_4\text{H}_{12}\text{N}_2)_6]\cdot 4\text{H}_2\text{O}$
 $M_r = 1221.75$
 Triclinic, $P\bar{1}$
 $a = 9.9783$ (11) Å
 $b = 11.976$ (3) Å
 $c = 12.060$ (2) Å
 $\alpha = 78.131$ (15)°
 $\beta = 82.769$ (11)°
 $\gamma = 88.851$ (12)°
 $V = 1399.1$ (5) Å³

$Z = 1$
 $D_x = 1.450$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 10.1\text{--}14.6^\circ$
 $\mu = 1.76$ mm⁻¹
 $T = 298$ (2) K
 Plate, blue
 $0.60 \times 0.30 \times 0.10$ mm

Data collection

Rigaku AFC-7R diffractometer $R_{\text{int}} = 0.059$
 $\omega/2\theta$ scans $\theta_{\text{max}} = 27.5^\circ$
 Absorption correction: ψ scan $h = -5 \rightarrow 12$
 (North *et al.*, 1968) $k = -15 \rightarrow 15$
 $T_{\text{min}} = 0.398, T_{\text{max}} = 0.839$ $l = -15 \rightarrow 15$
 7176 measured reflections 3 standard reflections
 6418 independent reflections every 150 reflections
 5277 reflections with $I > 2\sigma(I)$ intensity decay: 3.8%

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0966P)^2 + 0.7656P]$
 $R[F^2 > 2\sigma(F^2)] = 0.048$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.150$ $(\Delta/\sigma)_{\text{max}} < 0.001$
 $S = 1.16$ $\Delta\rho_{\text{max}} = 1.58 \text{ e } \text{\AA}^{-3}$
 6418 reflections $\Delta\rho_{\text{min}} = -1.09 \text{ e } \text{\AA}^{-3}$
 317 parameters Extinction correction: *SHELXL97*
 H-atom parameters constrained (Sheldrick, 1997)
 Extinction coefficient: 0.028 (3)

Table 1
 Selected geometric parameters (\AA , $^\circ$).

Cu1—N9	1.998 (3)	Co1—C3	1.899 (3)
Cu1—N7	2.012 (3)	Co2—C6	1.895 (3)
Cu1—N8	2.058 (3)	Co2—C5	1.894 (3)
Cu1—N10	2.070 (3)	Co2—C4	1.896 (3)
Cu1—N1	2.366 (3)	N1—C1	1.157 (4)
Cu1—N4	2.828 (3)	N2—C2	1.153 (4)
Cu2—N11	2.027 (3)	N3—C3	1.133 (5)
Cu2—N12	2.064 (2)	N4—C4	1.143 (4)
Cu2—N6	2.522 (3)	N5—C5	1.153 (4)
Co1—C1	1.887 (3)	N6—C6	1.141 (4)
Co1—C2	1.895 (3)		
N9—Cu1—N7	168.90 (12)	C1 ⁱⁱ —Co1—C2	90.36 (12)
N9—Cu1—N8	92.95 (12)	C1—Co1—C2	89.64 (12)
N7—Cu1—N8	84.29 (12)	C1—Co1—C3	88.58 (13)
N9—Cu1—N10	84.96 (11)	C2—Co1—C3	89.99 (15)
N7—Cu1—N10	96.43 (11)	C1—Co1—C3 ⁱⁱ	91.42 (13)
N8—Cu1—N10	172.71 (11)	C2—Co1—C3 ⁱⁱ	90.01 (15)
N9—Cu1—N1	95.31 (10)	C6—Co2—C5 ⁱⁱⁱ	92.56 (13)
N7—Cu1—N1	95.71 (11)	C6—Co2—C5	87.44 (12)
N8—Cu1—N1	97.37 (12)	C6—Co2—C4 ⁱⁱⁱ	91.05 (11)
N10—Cu1—N1	89.79 (10)	C5—Co2—C4 ⁱⁱⁱ	90.94 (13)
N11—Cu2—N12	84.54 (10)	C6—Co2—C4	88.95 (11)
N11 ⁱ —Cu2—N12	95.46 (10)	C5—Co2—C4	89.06 (13)
Symmetry codes: (i) $-x, -y, -z + 2$; (ii) $-x + 2, -y + 1, -z + 1$; (iii) $-x + 1, -y, -z + 2$.			

Table 2
 Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1A \cdots N3 ^{iv}	0.95	1.97	2.899 (8)	165
O1—H1B \cdots N5 ^v	0.96	2.03	2.979 (6)	174
O2—H2A \cdots N2 ^{iv}	0.95	2.15	3.086 (5)	170
O2—H2B \cdots O1	0.95	1.84	2.792 (6)	176
N7—H7C \cdots N2	0.90	2.36	3.206 (4)	156
N7—H7D \cdots N6 ⁱⁱⁱ	0.90	2.39	3.183 (4)	146
N8—H8C \cdots O2	0.91	2.29	3.146 (4)	157
N9—H9C \cdots N1 ^{vi}	0.90	2.34	3.162 (4)	152
N9—H9D \cdots N4	0.90	2.92	3.204 (4)	100
N11—H11C \cdots N6 ⁱ	0.90	2.99	3.280 (3)	101
N11—H11D \cdots N2 ⁱⁱⁱ	0.90	2.35	3.190 (4)	156

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

H atoms bonded to C and N atoms were placed in calculated positions, with C—H = 0.96–0.97 \AA and N—H = 0.90–0.91 \AA , and included in the final cycles of refinement using riding constraints, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. The water H-atom positions were calculated based on some peaks observed in the difference Fourier map, with O—H = 0.95 \AA and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. The large displacements of atoms C7 and C8, the short C7—C8 distance and the smaller N7—C7—C8—N8 torsion angle than for the other chelate rings suggest positional disorder of these C atoms. The highest peak is located 0.94 \AA from atom Cu1 and the deepest hole 0.80 \AA also from Cu1.

Data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

This work was supported by a Grant-in-Aid for the 21st Century COE programme ‘KEIO Life Conjugate Chemistry’ from the Ministry of Education, Culture, Sports, Science and Technology, the Research Foundation for Opto-Science and Technology, and the Japan and Mizuho Foundation for the Promotion of Science.

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