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Poly[tetraamminecopper(II) bis[tris(μ_2-cyanido-κ^2*C*,*N*)dicuprate(I)]]: a unique Cu^I–Cu^{II} mixed-valence complex containing anionic cuprous cyanide layers and $[Cu(NH_3)_4]^{2+}$ cations

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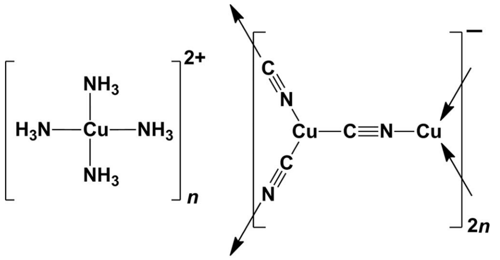
The title compound, $\{[Cu(NH_3)_4][Cu(CN)_3]_2\}_n$, features a Cu^I–Cu^{II} mixed-valence CuCN framework based on $\{[Cu_2(CN)_3]^-\}_n$ anionic layers and $[Cu(NH_3)_4]^{2+}$ cations. The asymmetric unit contains two different Cu^I ions and one Cu^{II} ion which lies on a centre of inversion. Each Cu^I ion is coordinated to three cyanide ligands with a distorted trigonal–planar geometry, while the Cu^{II} ion is ligated by four ammine ligands, with a distorted square-planar coordination geometry. The interlinkage between Cu^I ions and cyanide bridges produces a honeycomb-like $\{[Cu_2(CN)_3]^-\}_n$ anionic layer containing 18-membered planar $[Cu(CN)]_6$ metallocycles. A $[Cu(NH_3)_4]^{2+}$ cation fills each metallocyclic cavity within pairs of exactly superimposed $\{[Cu_2(CN)_3]^-\}_n$ anionic layers, but there are no cations between the layers of adjacent pairs, which are offset. Pairs of N—H$\cdots$N hydrogen-bonding interactions link the N—H groups of the ammine ligands to the N atoms of cyanide ligands.

Comment

Cuprous cyanide (CuCN) has attracted much attention in chemistry and in industry for its applications in electroplating, metal abstraction, ceramic superconductor preparation and as a potential catalyst in organic synthesis (Fehlhammer & Fritz, 1993; Lancashire, 1987; Ondono-Castillo *et al.*, 1995). In particular, metal–organic frameworks (MOFs) based on CuCN have been widely developed in crystal engineering because of the strong binding ability of the cyanide anion towards the Cu^I ion. It has been found that a single cyanide anion can bridge two, three or even four Cu^I ions, and that one Cu^I ion can be coordinated by two, three or four cyanide anions, giving rise to linear $Cu(CN)_2$ (Hibble & Chippindale, 2005), trigonal $Cu(CN)_3$ (Pretsch *et al.*, 2004; Pretsch & Hartl, 2004) and tetrahedral $Cu(CN)_4$ geometries (Qin *et al.*, 2011; Zhang *et al.*, 2011), respectively, which results in a remarkable diversity of structures of CuCN frameworks, such as chain, layer and three-dimensional patterns (Hou *et al.*, 2010; Pretsch & Hartl, 2004; Su *et al.*, 2011). Much research interest has been focused on the construction of CuCN–ammine complexes with abundant structural diversity, some of which exhibit excellent luminescent properties in the visible region (Ley *et al.*, 2010; Pike *et al.*, 2007; Tronic *et al.*, 2007; Xia *et al.*, 2010). However, there has been relatively little work carried out on Cu^I–Cu^{II} mixed-valence cyanide systems because of the high resistance to oxidation of Cu^I ions in the presence of cyanide anions (Colacio *et al.*, 2002; Song *et al.*, 2006), which leads to difficulties in the preparation of Cu^I–Cu^{II} mixed-valence complexes. To obtain a Cu^I–Cu^{II} mixed-valence cyanide framework, we reacted a mixture of CuCN and 3,5-diethyl-4-(pyridin-4-yl)pyrazole in aqueous ammonia media, because the Cu^{II} ion is more stable than the Cu^I ion in aqueous ammonia. As expected, partial oxidation of Cu^I to Cu^{II} occurred, and a new Cu^I–Cu^{II} mixed-valence cyanide framework, $\{[Cu(NH_3)_4][Cu_2(CN)_3]_2\}_n$, (I), was successfully synthesized.



(I)

The structure of (I) consists of a honeycomb-like $\{[Cu_2(CN)_3]^-\}_n$ anionic layer and a $[Cu(NH_3)_4]^{2+}$ cation, as shown in Fig. 1. The asymmetric unit contains three Cu ions, with that of the cation lying on a centre of inversion, three cyanide ligands and two ammine ligands. Atoms Cu1 and Cu2 are monovalent and display distorted trigonal–planar geometries through the coordination of three cyanide ligands *via*

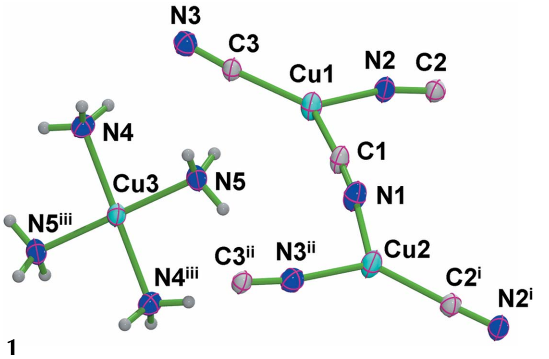


Figure 1
The coordination geometry of the Cu ions of (I), with displacement ellipsoids drawn at the 30% probability level and with the H atoms shown as spheres of arbitrary radius. [Symmetry codes: (i) $x - 1, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $x - 1, -y + \frac{3}{2}, z - \frac{1}{2}$; (iii) $-x + 1, -y + 2, -z$.]

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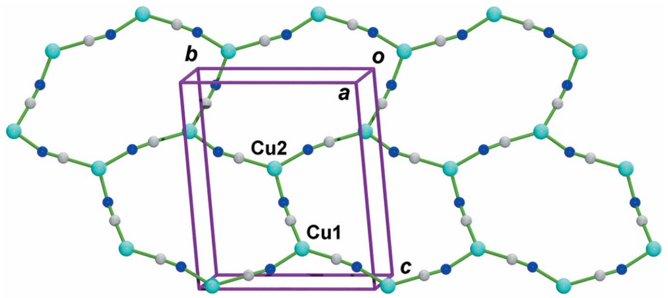

Figure 2
A view of the honeycomb-like $\{[Cu_2(CN)_3]^-\}_n$ anionic layer in the title compound.

two C and one N atom and *via* one C and two N atoms, respectively. The C/N—Cu—N/C bond angles are in the ranges 107.69 (14)–132.12 (14) and 106.52 (13)–130.57 (13)° around Cu1 and Cu2, respectively. The Cu—C distances [in the range 1.897 (3)–1.907 (3) Å for Cu1 and Cu2] are slightly shorter than the Cu—N distances [1.949 (3)–1.992 (3) Å] and are in reasonable agreement with those found in other CuCN frameworks (Pretsch *et al.*, 2004; Yun *et al.*, 2004). In contrast to the Cu1 and Cu2 atoms, the Cu3 atom is divalent and involved in the $[Cu(NH_3)_4]^{2+}$ counter-cation, in which the Cu^{II} ion lies on an inversion centre and is ligated by four ammine ligands to give a distorted square-planar geometry, with Cu—N distances of 2.008 (3) and 2.028 (3) Å.

In complex (I), each cyanide anion bridges two Cu^I ions, and each Cu^I ion links three cyanide ligands to form a honeycomb-like $\{[Cu_2(CN)_3]^-\}_n$ anionic layer, as shown in Fig. 2. The layer contains 18-atom $\{Cu(CN)\}_6$ rings, with the longest Cu···Cu separation being 11.596 (3) Å, which is longer than that of 9.97 Å in the recently reported guanidinium cyanocuprate $\{[C(NH_2)_3][Cu_2(CN)_3]\}_n$ framework (Lin *et al.*, 2008). In the crystal packing, two adjacent layers are eclipsed to form a pair of superimposed anionic layers, while the adjacent pairs are offset along the *c* axis. It is interesting that the two superimposed layers generate a hexagonal cavity with large enough window sizes (6.05 × 3.58 Å, excluding van der Walls radii of the atoms) so that the $[Cu(NH_3)_4]^{2+}$ cation is adducted to form a Cu^I–Cu^{II} mixed bilayer system, which is further stabilized by an N4—H4*A*···N3 hydrogen-bonding interaction (Table 1) between an ammine ligand and a cyanide anion (Fig. 3). However, no $[Cu(NH_3)_4]^{2+}$ cation is deposited between the two offset layers because their staggered stack leads to a decrease in the hexagonal window sizes. A similar $\{[Cu_2(CN)_3]^-\}_n$ layer has been observed in some CuCN–ammine complexes; however, the difference is that the hexagonal cavities are filled by di- and tetraammonium cations, forming different adducts to that in (I) (Colacio *et al.*, 2002; Pretsch *et al.*, 2004).

A Cu^I–Cu^{II} mixed-valence cyanide framework based on a $\{[Cu_2(CN)_3]^-\}_n$ anionic layer has only previously been observed in the $\{[Cu(pn)_2][Cu_2(CN)_3]_2\}_n$ framework (pn is propane-1,3-diamine; Benmansour *et al.*, 2009); however, in this structure, the layers stack in a superimposed fashion to form infinite hexagonal channels, resulting in the $[Cu(pn)_2]^{2+}$ cations being arranged in line along the channels, which contrasts with complex (I).

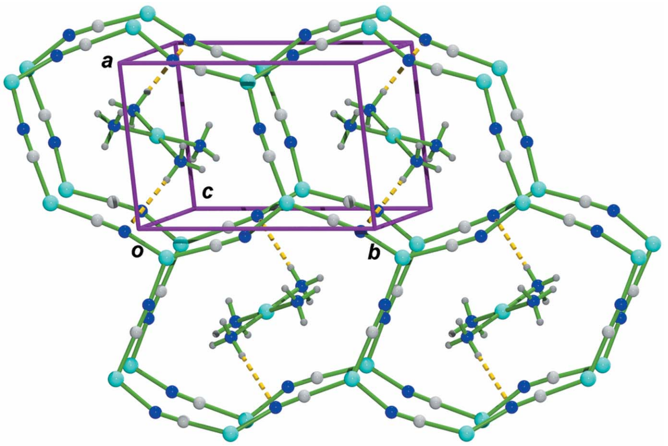

Figure 3
The stacking along the *c* axis, showing the adduction between the two superimposed $\{[Cu_2(CN)_3]^-\}_n$ layers and $[Cu(NH_3)_4]^{2+}$ cations through N—H···N hydrogen-bonding interactions (shown as dashed lines).

It should be noted that the presence of 3,5-diethyl-4-(pyridin-4-yl)pyrazole is essential for the generation of complex (I) because in its absence only a blue solution was obtained under the same reaction conditions; therefore, 3,5-diethyl-4-(pyridin-4-yl)pyrazole appears to act as a directing or templating agent during the generation of complex (I), although the mechanism for its involvement is presently not clear.

Experimental

A mixture of CuCN (0.036 g, 0.4 mmol), 3,5-diethyl-4-(pyridin-4-yl)pyrazole, ethanol (8 ml) and aqueous ammonia (25%, 1 ml) was sealed in a 15 ml Teflon-lined stainless steel container, which was heated to 413 K and held at that temperature for 72 h. After cooling to room temperature at a rate of 0.1 K min^{-1}, purple block-shaped crystals of the title compound were obtained in 55% yield (yield 0.020 g, based on CuCN). Analysis calculated for $C_6H_{12}Cu_5N_{10}$: C 13.30, H 2.23, N 25.84%; found: C 13.34, H 2.18, N 25.87%.

Crystal data

$[Cu(NH_3)_4][Cu(CN)_3]_2$
$M_r = 541.96$
Monoclinic, $P2_1/c$
$a = 7.6501$ (9) Å
$b = 8.9083$ (10) Å
$c = 13.2509$ (12) Å
$\beta = 123.086$ (5)°
$V = 756.61$ (14) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 6.92$ mm^{-1}
$T = 295$ K
0.19 × 0.17 × 0.11 mm

Data collection

Bruker SMART area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) $T_{min} = 0.353$, $T_{max} = 0.517$
3397 measured reflections
1479 independent reflections
1261 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.094$
$S = 1.06$
1479 reflections
97 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.75$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N4—H4$A\cdots$N3	0.89	2.61	3.498 (5)	178

H atoms on N atoms were placed at calculated positions (N—H = 0.89 Å) and refined as riding, with $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(N).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: WQ3010). Services for accessing these data are described at the back of the journal.

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