

catena-Poly[tri- μ -cyano-1,10-phenanthroline- κ^2N,N' -tricopper(I)]Ju-Tao Liu^a and Seik Weng Ng^{b*}^aCollege of Life Science, Dalian Nationalities University, Dalian 116600, People's Republic of China, and ^bDepartment of Chemistry, University of Malaya, Kuala Lumpur 50603, Malaysia

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Key indicatorsSingle-crystal X-ray study
 $T = 295$ K
Mean $\sigma(\text{C}-\text{C}) = 0.008$ Å
Disorder in main residue
 R factor = 0.060
 wR factor = 0.171
Data-to-parameter ratio = 16.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

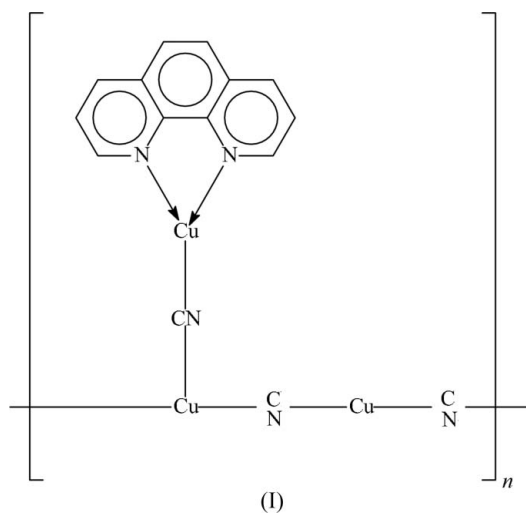
The crystal structure of the centrosymmetric title compound, fully described by the name catena-poly[[[1,10-phenanthroline- κ^2N,N']cupriocyno]copper(I)- μ -cyano-[[[1,10-phenanthroline- κ^2N,N']cupriocyno]copper(I)- μ -cyano-copper(I)- μ -cyano-copper(II)- μ -cyano], $[\text{Cu}_3(\text{CN})_3(\text{C}_{12}\text{H}_8\text{N}_2)]_n$, consists of $(\text{Cu}-\text{CN})_n$ polymeric chains in which two consecutive Cu atoms in every contiguous set of four each carry a pendant (phenanthroline)coppercyano unit. The Cu atoms with pendant groups are three-coordinate, as are the phenanthroline-chelated Cu atoms; the other independent Cu atom that comprises the backbone is two-coordinate. Two adjacent chains are linked by a $\text{Cu}\cdots\text{Cu}$ interaction [$2.941(1)$ Å] into a ribbon. All cyano groups are disordered with no distinction between C and N atoms.

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Comment

Copper(I) cyanide forms, with 1,10-phenanthroline, adducts of varying stoichiometries. The 1:1 copper(I) cyanide–1,10-phenanthroline adduct that crystallizes in the trigonal crystal system is orange in colour (Dyason *et al.*, 1985), whereas that belonging to the orthorhombic crystal system is red (Mao *et al.*, 2005). A monoclinic 3:2 adduct is also red in colour (Yu *et al.*, 2003), as is the monoclinic 3:1 adduct (Chestnut *et al.*, 2001). These linear polymeric adducts have one cyano group bridging two Cu atoms, and the coordination number is 2 for the atoms that merely comprise the backbone of the chain, and 3 for those that also bear a pendant heterocycle-chelated unit.



The present brown 3:1 adduct, (I), features a linear $(\text{Cu}-\text{CN})_n$ polymeric chain in which two consecutive Cu atoms in

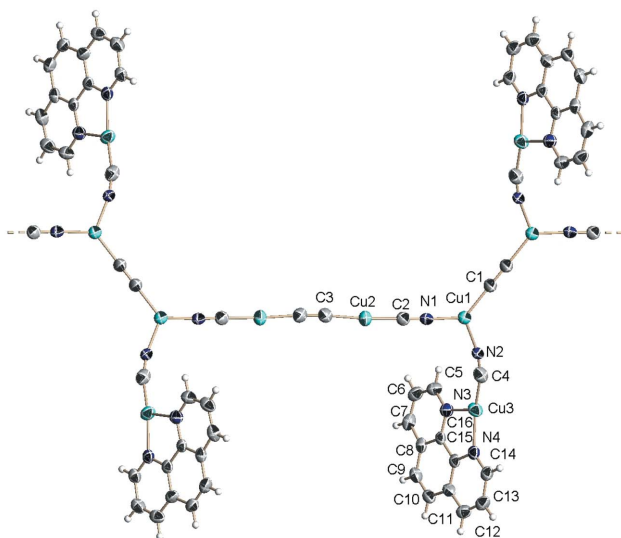


Figure 1
Part of the polymeric structure of the title compound, showing the Cu coordination environment. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary radii. The cyanide groups are disordered. The CN group with the C1 atom lies at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and the CN group with the C3 atom lies at $(\frac{3}{2}, y, \frac{1}{4})$; the carbon atoms are disordered with respect to nitrogen atoms.

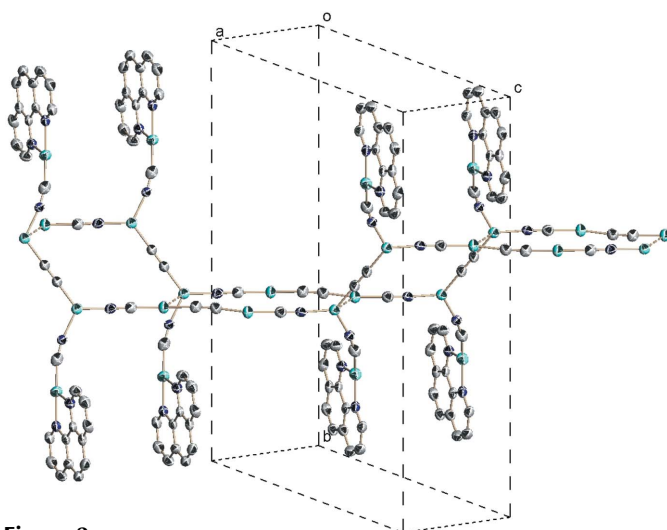


Figure 2
Part of the ribbon structure that arises from the Cu...Cu interactions (shown as dashed lines). H atoms have been omitted.

every contiguous set of four are each cyano-bridged to a pendant (phenanthroline)copper unit (Fig. 1). The other part of the chain is almost linear. Interestingly, two chains are positioned in such a way that copper-copper interactions $[\text{Cu1} \cdots \text{Cu1}(-1 + x, y, z) = 2.941(1) \text{ \AA}]$ give rise to the formation of fused rings; the sides are made up of these interactions (Fig. 2).

Experimental

Potassium hexacyanoferrate(III) (66 mg, 0.2 mmol), copper(II) chloride dihydrate (34 mg, 0.2 mmol) and 1,10-phenanthroline

(36 mg, 0.2 mmol) in water (15 ml) were placed in a Teflon-lined stainless steel Parr bomb. The bomb was heated at 403 K for 36 h. The bomb was then cooled to room temperature over a period of 24 h. Brown crystals of the title compound were isolated in about 40% yield.

Crystal data

$[\text{Cu}_3(\text{CN})_3(\text{C}_{12}\text{H}_8\text{N}_2)]$
 $M_r = 448.88$
 Monoclinic, $C2/c$
 $a = 6.790(1) \text{ \AA}$
 $b = 24.642(5) \text{ \AA}$
 $c = 18.136(4) \text{ \AA}$
 $\beta = 99.43(3)^\circ$
 $V = 2993.5(10) \text{ \AA}^3$

$Z = 8$
 $D_x = 1.992 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 4.23 \text{ mm}^{-1}$
 $T = 295(2) \text{ K}$
 Block, brown
 $0.22 \times 0.18 \times 0.16 \text{ mm}$

Data collection

Rigaku R-Axis RAPID IP
 diffractometer
 ω scans
 Absorption correction: multi-scan
 (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.441, T_{\max} = 0.551$
 (expected range = 0.407–0.508)

14429 measured reflections
 3430 independent reflections
 2232 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.111$
 $\theta_{\max} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.060$
 $wR(F^2) = 0.171$
 $S = 1.02$
 3430 reflections
 208 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0785P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.67 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.85 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

Cu1—C1	1.895 (5)	Cu2—C3	1.846 (5)
Cu1—N1	1.913 (6)	Cu3—C4	1.864 (6)
Cu1—N2	1.935 (5)	Cu3—N3	2.081 (5)
Cu2—C2	1.852 (6)	Cu3—N4	1.989 (5)
C1—Cu1—N1	126.0 (2)	N3—Cu3—N4	82.8 (2)
C1—Cu1—N2	117.7 (2)	C2—N1—Cu1	176.2 (5)
N1—Cu1—N2	116.2 (2)	C4—N2—Cu1	167.5 (4)
C2—Cu2—C3	166.5 (2)	C5—N3—C16	118.3 (5)
C4—Cu3—N3	118.7 (2)	C5—N3—Cu3	131.8 (4)
C4—Cu3—N4	156.1 (2)		

The C and N atoms of the four independent cyanide units are disordered with an occupancy factor of 0.5, the C and N atoms sharing the same positions and displacement parameters. H atoms were positioned geometrically ($\text{C—H} = 0.93 \text{ \AA}$) and were included in the refinement in the riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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