

Dicaesium pentacyanotricuprate(I), $\text{Cs}_2\text{Cu}_3(\text{CN})_5$

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Key indicators

Single-crystal X-ray study
 $T = 150 \text{ K}$
 Mean $\sigma(\text{N}-\text{C}) = 0.004 \text{ \AA}$
 Disorder in main residue
 R factor = 0.017
 wR factor = 0.020
 Data-to-parameter ratio = 15.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

$\text{Cs}_2\text{Cu}_3(\text{CN})_5$ has a layered structure consisting of $[\text{Cu}_3(\text{CN})_5]^{2-}$ sheets stacked in an *ABAB* fashion along the *c* axis, with Cs^+ cations lying between the sheets. The sheets are generated by linking $-(\text{CuCN})-$ chains, in which the $\text{C}\equiv\text{N}$ groups are ordered, *via* $[\text{Cu}(\text{CN})_3]^{2-}$ units. The two bridging cyanide groups of each $[\text{Cu}(\text{CN})_3]^{2-}$ unit show partial 'head-to-tail' disorder of C and N, whilst the third $\text{C}\equiv\text{N}$ group is terminal and ordered with C bonded to Cu.

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Comment

Copper(I) cyanide frameworks, like those of other transition-metal cyanides, can be viewed as constructed from $M(\text{CN})_x$ structural building blocks. For copper(I), a range of potential building blocks are known, including simple species, such as linear $[\text{Cu}(\text{CN})_2]^-$, trigonal $[\text{Cu}(\text{CN})_3]^{2-}$ and tetrahedral $[\text{Cu}(\text{CN})_4]^{3-}$ units, and larger fragments, such as $-(\text{CuCN})-$ chains. These units have well defined geometries and can be assembled to form new solids by combining with themselves, in association with charge-balancing species where necessary, or with other complex metal ions or organic species, *e.g.* Lewis bases such as amines, to generate one-, two- and three-dimensional frameworks.

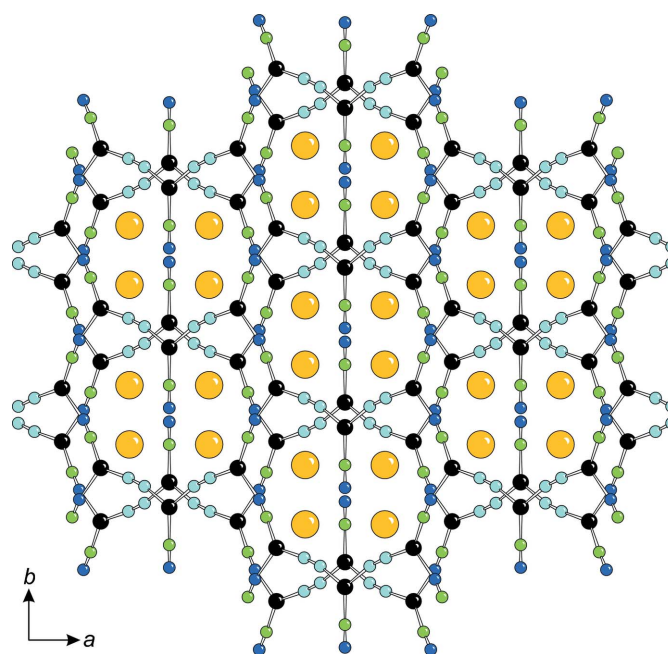


Figure 1

A projection of the crystal structure along the *c* axis, showing layers stacked as *ABAB* with Cs^+ cations between the layers. Key: Cu atoms are black, Cs orange, C green, N blue and Z (C or N of a disordered cyanide group) cyan.

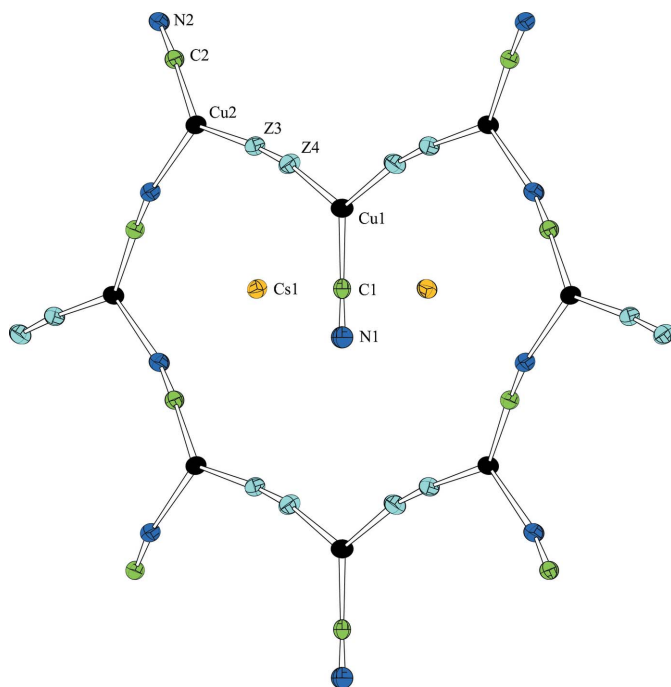


Figure 2

A $(\text{Cu}(\text{CN})_8)$ ring from the $[\text{Cu}_3(\text{CN})_5]^{2-}$ layer, showing the approximately trigonal-planar coordination of atoms Cu1 and Cu2. The terminal cyanide group C1 \equiv N1 points into the centre of the ring. Key as given for Fig. 1. Displacement ellipsoids are drawn at the 50% probability level.

The present work is a continuation of our investigations of copper(I) cyanide materials prepared in the presence of alkali-metal cations (Chippindale *et al.*, 2004; Pohl *et al.*, 2006). $\text{Cs}_2\text{Cu}_3(\text{CN})_5$ reported here has the same layer structure as $\text{K}_2\text{Cu}_3(\text{CN})_5$, prepared previously in acetonitrile under solvothermal conditions (Pohl *et al.*, 2006).

The layer structure of $\text{Cs}_2\text{Cu}_3(\text{CN})_5$ can be described in terms of $-(\text{Cu}_2\text{CN})-$ chains running along the *b* axis and linked through bridging $[\text{Cu}_1(\text{CN})_3]^{2-}$ units to generate a network of $(\text{CuCN})_8$ rings within the layers. The layers stack in an *ABAB* fashion along the *c* axis (Fig. 1). Cs^+ cations lie between the layers bonded to 12 cyanide groups, with Cs—C/N distances in the range 3.11 (2)–3.58 (3) Å.

There are two crystallographically distinct Cu atoms, both of which have approximately trigonal-planar coordination (Fig. 2). Atom Cu1, on a special position of site symmetry 2, is bonded to two equivalent bridging cyanide groups, Z3 \equiv Z4, through the Z4 ends of the groups. The Z3 \equiv Z4 unit shows partial ‘head-to-tail’ disorder, as determined by refinement, with Z3 having occupancy 0.78 (4) for C3 and 0.22 (4) for N3 and Z4 having occupancy 0.22 (4) for C4 and 0.78 (4) for N4. The coordination around Cu1 is completed by a third cyanide group, C1 \equiv N1, bonded as a terminal group to Cu1 through C1. Atom Cu2, sited on a general position, bonds directly to C2, N2 and Z3 and is also approximately trigonal planar, although the geometry around Cu2 is less regular than that found for Cu1. The refinement of site occupancies for the cyanide group C2 \equiv N2 indicates that the C and N atoms are fully ordered. The greater deviation from linearity of the

Cu2—N2 \equiv C2 angle compared with the Cu2—C2 \equiv N2 angle in Cu2—C2 \equiv N2—Cu2ⁱⁱⁱ (symmetry code as in Table 1) confirms this assignment: strong π – π interactions between a metal and the C end of a cyanide usually result in a smaller deviation from linearity of the *M*—C—N angle than the *M'*—N—C angle (Vahrenkamp *et al.*, 1997).

Experimental

Crystals of $\text{Cs}_2\text{Cu}_3(\text{CN})_5$ were prepared at 293 K. KCN (1.30 g, 20.0 mmol), CuCN (0.46 g, 5.1 mmol) and CsNO_3 (1.94 g, 10.0 mmol) were dissolved in deionized water (15 ml) to form a colourless solution. On addition of 1 M H_2SO_4 (7.4 ml), a white precipitate formed immediately. This was subsequently identified as $\text{Cs}_2\text{Cu}_3(\text{CN})_5$ using powder X-ray diffraction. The precipitate was allowed to stand in the solution at room temperature, and after three weeks colourless rectangular blocks of $\text{Cs}_2\text{Cu}_3(\text{CN})_5$ had grown. The crystals were filtered off, washed with water and allowed to dry in the air. A powder X-ray diffraction pattern of the ground crystals confirmed that the product was monophasic. IR data (Nujol mull): $\nu(\text{C}\equiv\text{N})$ 2140 (*m*), 2104 (*s*), 2098 (*s*) cm^{-1} .

Crystal data

$\text{Cs}_2\text{Cu}_3(\text{CN})_5$
 $M_r = 586.54$
 Monoclinic, $C2/c$
 $a = 17.8156$ (9) Å
 $b = 8.0962$ (15) Å
 $c = 8.3890$ (8) Å
 $\beta = 91.771$ (8)°
 $V = 1209.4$ (3) Å³

$Z = 4$
 $D_x = 3.221$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 11.13$ mm⁻¹
 $T = 150$ K
 Block, colourless
 0.24 × 0.12 × 0.08 mm

Data collection

Oxford Gemini S Ultra diffractometer
 $\omega/2\theta$ scans
 Absorption correction: multi-scan (*ABSPACK*; Oxford Diffraction, 2006)
 $T_{\min} = 0.21$, $T_{\max} = 0.41$

9301 measured reflections
 1343 independent reflections
 1123 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.021$
 $\theta_{\max} = 28.5^\circ$

Refinement

Refinement on F
 $R[F^2 > 2\sigma(F^2)] = 0.017$
 $wR(F^2) = 0.020$
 $S = 1.08$
 1123 reflections
 71 parameters

Modified Chebyshev polynomial (Watkin, 1994; Prince, 1982) with coefficients: 16.0, -11.9, 11.5, 1.63
 $(\Delta/\sigma)_{\max} = 0.003$
 $\Delta\rho_{\max} = 0.88$ e Å⁻³
 $\Delta\rho_{\min} = -0.70$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Z denotes a disordered cyanide group.

| | | | |
|--------------------------|-------------|---------------------------|-----------|
| Cu1—C1 | 1.915 (4) | Cu2—Z3 | 1.916 (3) |
| Cu1—Z4 | 1.951 (3) | N1—C1 | 1.151 (6) |
| Cu2—C2 | 1.912 (3) | N2—C2 | 1.145 (4) |
| Cu2—N2 ⁱ | 2.016 (3) | Z3—Z4 | 1.156 (4) |
| Z4 ⁱⁱ —Cu1—Z4 | 114.60 (16) | Cu2 ⁱⁱⁱ —N2—C2 | 160.7 (3) |
| Z4—Cu1—C1 | 122.70 (8) | Cu2—Z3—Z4 | 173.8 (3) |
| N2 ⁱ —Cu2—Z3 | 111.60 (11) | Cu1—Z4—Z3 | 168.7 (3) |
| N2 ⁱ —Cu2—C2 | 110.50 (12) | N1—C1—Cu1 | 180 |
| C2—Cu2—Z3 | 137.26 (12) | N2—C2—Cu2 | 176.7 (3) |

Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 1, y, -z + \frac{1}{2}$; (iii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.

The orientations of the three distinct C≡N groups were investigated as follows. Each C≡N was modelled as $Z_x \equiv Z_y$ with starting values for the occupancies of both Z_x and Z_y set to (0.5 C + 0.5 N). The site occupancies were then refined subject to the constraints that the total occupancy for each site was 1.00 and the displacement parameters of C and N on the same site were equal. Cyanide groups C1≡N1 and C2≡N2 were found to be fully ordered and the occupancies of these groups were fixed in subsequent refinements. The occupancies in the remaining bridging Z3≡Z4 group have refined values for Z3 of 0.78 (4) for C3 and 0.22 (4) for N3, and for Z4 of 0.22 (4) for C4 and 0.78 (4) for N4.

Data collection: *CrysAlisPro*, (Oxford Diffraction, 2006); cell refinement: *CrysAlisPro*; data reduction: *CrysAlisPro*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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