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catena-Poly[[μ-cyano-[1,3-bis(tetramethylguanidino)propane]dicopper(I)]-μ-cyano]

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Key indicators

Single-crystal X-ray study
T = 133 K
Mean σ(C–C) = 0.005 Å
R factor = 0.039
wR factor = 0.078
Data-to-parameter ratio = 18.7

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

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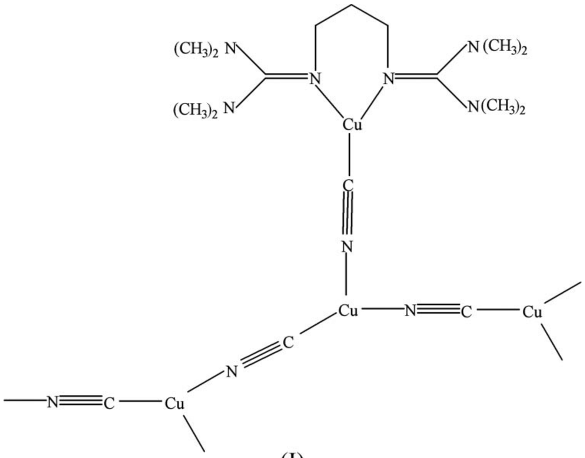
The structure of the title compound, *catena*-poly[[μ-cyano-1:2C:N-[1,3-bis(tetramethylguanidino)propane-1κ^2N,N']dicopper(I)]-μ-cyano-2:1$'C$:N], $[Cu_2(CN)_2(C_{13}H_{30}N_4)]_n$, shows one-dimensional zigzag $\{Cu(CN)\}_\infty$ chains with copper centres trigonally coordinated either by a chelating guanidine and a cyano ligand or by three cyano ligands.

Comment

The development of polyfunctional nitrogen-donor ligands which are able to stabilize unusually high metal oxidation states is a very important objective in coordination and bioinorganic chemistry. Therefore, we have extended our interests towards guanidyl-type systems. The first derivative in this series, 1,3-bis(tetramethylguanidino)propane (btmgp), and its participation in copper, iron and nickel coordination, was investigated (Harmjanz, 1997; Waden, 1999; Pohl *et al.*, 2000; Schneider, 2000; Herres, 2002). The resulting complexes are stabilized by co-ligands, such as halide or chalcogenolato ions. In an attempt to control the reactivity of these complexes towards oxygen, the halide ions in [Cu(btmgp)I] (Pohl *et al.*, 2000) were replaced by cyanide ions which are able to use both the N as well as the C atom as soft donor functions. If both functionalities act simultaneously, not only chain structures but also two-dimensional networks are stabilized (Stocker *et al.*, 1999; Chesnut *et al.*, 1999). This behaviour was also expected to occur in complexes which contain the btmgp ligand.



(I)

The structure of the title compound $[\{Cu(btmgp)CN\}_n\text{-}\{CuCN\}_n]$, (I) (Fig. 1), is an extension of the one-dimensional chain present in CuCN (Heller & Sheldrick, 2001). The Cu atoms within the $\{CuCN\}_n$ backbone complete their coordi-

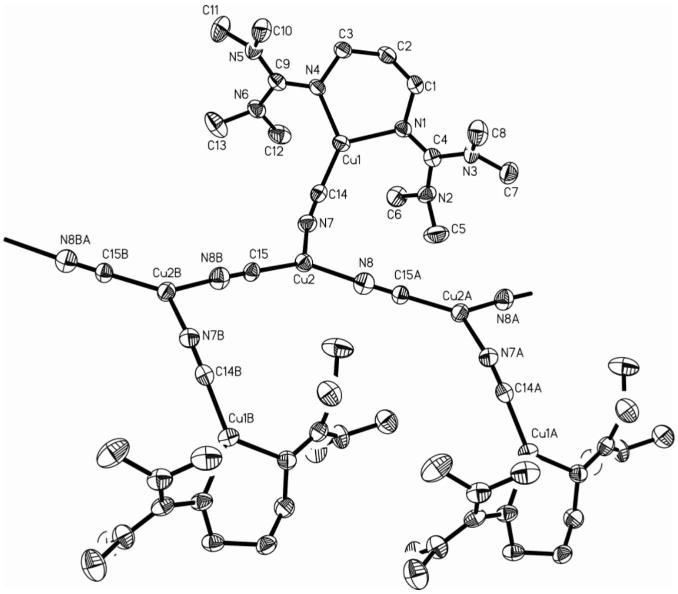


Figure 1
Part of the polymeric structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. [Symmetry codes: $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.]

nation spheres by binding a cyanide ion as a third ligand each. The resulting structure reflects the architecture of the $[Cu(CN)_2]^-$ sublattice observed in $M[Cu(CN)_2]$ (Kappenstein & Hugel, 1977; Cromer, 1957; Asplund *et al.*, 1983) and acts as a polydentate metallocyano ligand towards {Cubtmgp} fragments which are immobilized by binding to the C atoms of the cyanide groups branching off the $\{CuCN\}_n$ chain. As a consequence, we observe two different Cu atoms with trigonal-planar ligand fields, one of which (Cu1) is defined by two guanidine N atoms and one cyano C atom, and the other (Cu2) by two cyano N atoms and one C atom of a third cyano ligand. Cu1 lies 0.123 (1) Å above the N1/N4/C14 plane and Cu2 lies 0.053 (1) Å above the N7/N8/C15 plane. The sums of the angles at the Cu atoms are 358.7 and 359.8° for Cu1 and Cu2, respectively. The Cu2 atoms within the endless zigzag chains along [010] form C15—Cu2—N8 angles of 130.2 (1)°. The {Cu1(btmgp)} moieties provide the usual chair conformation and form side chains attached to Cu2 centres through cyano group C14≡N7. The angles N8—Cu2—N7 and C15—Cu2—N7 are 105.5 (1) and 124.1 (1)°, respectively. Main and side chains show similar C—N [average 1.150 (4) Å], Cu—C [average 1.871 (4) Å] and Cu—N(cyano) [average 1.965 (3) Å] distances. Cu—N(guanidine) bonds are slightly longer, with an average of 2.009 (3) Å. Somewhat similar packing and coordination patterns are known from Cambridge Structural Database refcode SUYGUO (Allen, 2002; Chesnut *et al.*, 2001), displaying, however, disordered cyano groups. The overall geometry of the guanidine ligand compares well with that of related compounds (Herres *et al.*, 2004, 2005) and needs no further discussion. The shortest nonbonding intermolecular interaction is C5—H···N8($-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$), with an H···N distance of 2.8 (1) Å.

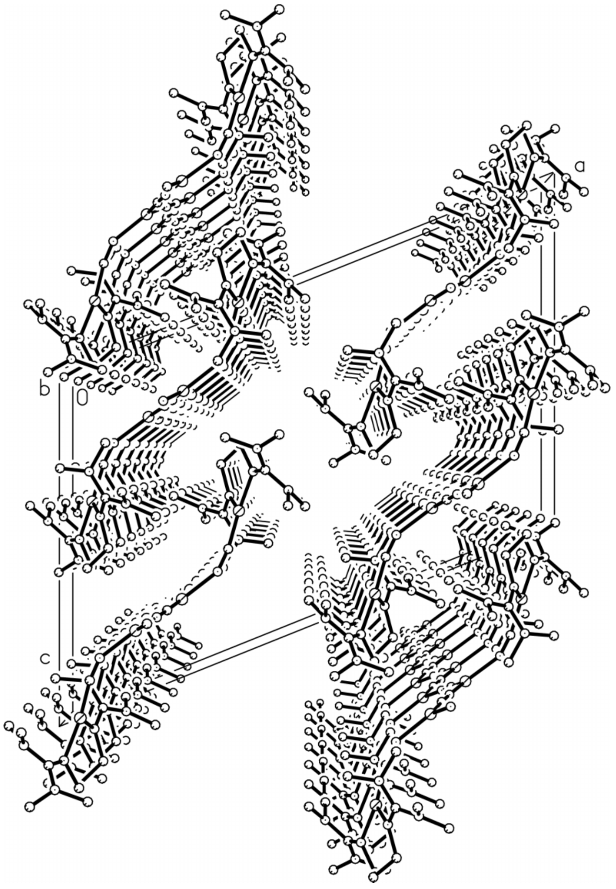


Figure 2
The crystal packing, viewed along [010]. H atoms have been omitted.

Experimental

Btmgp (288 mg, 1.06 mmol) was added dropwise to a suspension of CuCN (90 mg, 1 mmol) in tetrahydrofuran (10 ml). The reaction mixture was refluxed for 2 h. An off-white solid formed. Very slow cooling to room temperature of the solution yielded colourless blocks suitable for X-ray diffraction. Analysis calculated for $C_{15}Cu_2H_{30}N_8$: C 40,08, H 6,73, N 24,93%; found: C 40,09, H 6,74, N 24,32%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.58 (*m*, 2H, Hβ), 2.79 (*s*, 12H, CH_3), 2.91 (*s*, 12H, CH_3), 3.24 (*m*, 4H, Hα); ^{13}C NMR (70 MHz, CD_3CN): δ 33.8 (Cβ), 39.1 (CH_3), 39.5 (CH_3), 51.7 (Cα), 164.5 [$(Me_2N)_2$–C—N], 219.6 (cyanide–C). IR (KBr, ν, cm^{-1}): 2953 [*w*, ν(CH)], 2934 [*w*, ν(CH)], 2910 [*m*, ν(CH)], 2893 [*m*, ν(CH)], 2788 (*w*), 2123 (*s*, cyanide), 2104 (*s*, cyanide), 1560 [*vs*, ν(C=N)], 1508 [*s*, ν(C=N)], 1473 [*m*, δ(CH)], 1454 [*m*, δ(CH)], 1419 (*m*), 1385 [*vs*, ν(C=N)], 1356 (*m*), 1238 (*m*), 1151 (*m*), 1138 (*m*), 1113 (*w*), 1092 (*m*), 1073 (*w*), 1059 (*m*), 1030 (*m*), 985 (*w*), 949 (*m*), 914 (*m*), 769 (*m*), 758 (*w*).

Crystal data

$C_{15}H_{30}Cu_2N_8$
$M_r = 449.55$
Monoclinic, $C2/c$
$a = 27.158$ (2) Å
$b = 9.0145$ (7) Å
$c = 18.1825$ (15) Å
$\beta = 111.918$ (2)°
$V = 4129.6$ (6) Å^3
$Z = 8$

$D_x = 1.446$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1900 reflections
$\theta = 2.4$–23.0°
$\mu = 2.07$ mm^{-1}
$T = 133$ (2) K
Block, colourless
0.18 × 0.15 × 0.10 mm

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Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{\min} = 0.655$, $T_{\max} = 0.810$
11 785 measured reflections
4216 independent reflections
2627 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.047$
$\theta_{\max} = 26.4°$
$h = -29 \rightarrow 33$
$k = -11 \rightarrow 11$
$l = -19 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.078$
$S = 0.84$
4216 reflections
226 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0241P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.56$ e Å^{-3}
$\Delta\rho_{\min} = -0.31$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—C14	1.866 (4)	Cu2—N7	1.986 (3)
Cu1—N4	1.995 (3)	N1—C4	1.302 (4)
Cu1—N1	2.023 (3)	N4—C9	1.308 (4)
Cu2—C15	1.875 (4)	N7—C14	1.150 (4)
Cu2—N8	1.944 (3)	N8—C15$^{\text{i}}$	1.151 (4)
C14—Cu1—N4	134.25 (13)	N8—Cu2—N7	105.51 (12)
C14—Cu1—N1	125.42 (13)	C14—N7—Cu2	152.3 (3)
N4—Cu1—N1	99.09 (12)	C15$^{\text{i}}$—N8—Cu2	175.2 (3)
C15—Cu2—N8	130.15 (13)	N7—C14—Cu1	171.0 (3)
C15—Cu2—N7	124.11 (13)	N8$^{\text{ii}}$—C15—Cu2	177.3 (3)

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

H atoms were located in difference Fourier maps and placed at idealized positions, riding on their attached C atoms (C—H = 0.98 and 0.99 Å), with isotropic displacement parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$. Methyl groups were allowed to rotate but not to tip.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2002); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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