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catena-Poly[[diacetonitrilecopper(I)]- μ -dicyanamido]

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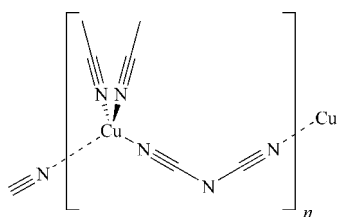
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.032; wR factor = 0.066; data-to-parameter ratio = 13.5.

The crystal structure of the title compound, $[\text{Cu}(\text{C}_2\text{N}_3)(\text{C}_2\text{H}_3\text{N}_2)]_n$, features zigzag chains along the a axis that consist of alternating $[\text{Cu}(\text{MeCN})_2]$ and dicyanamido units, the latter acting as bidentate ligands *via* both terminal N atoms. The Cu atom shows a slightly distorted tetrahedral coordination sphere. The anionic and neutral ligands lie on different mirror planes (perpendicular to the b and a axis, respectively), while the Cu atom is situated on their intersection. The asymmetric unit comprises one fourth of the formula unit.

Related literature

For ionic liquids (ILs) with dicyanamido anions, see: MacFarlane *et al.* (2001). For copper-based ILs, see: Stricker *et al.* (2010). For solvent-free $[\text{Cu}(\text{dicyanamido})]$ and its mono-adduct with acetonitrile, see: Bessler *et al.* (2000); Batten *et al.* (2000).



Experimental

Crystal data

 $[\text{Cu}(\text{C}_2\text{N}_3)(\text{C}_2\text{H}_3\text{N}_2)]$ $M_r = 211.71$ Orthorhombic, $Pmmn$ $a = 7.5222$ (5) Å $b = 10.5307$ (11) Å $c = 5.5378$ (4) Å $V = 438.67$ (6) Å³ $Z = 2$ Mo $K\alpha$ radiation $\mu = 2.44$ mm⁻¹ $T = 100$ K $0.45 \times 0.27 \times 0.12$ mm

Data collection

Stoe IPDS 2 diffractometer

Absorption correction: multi-scan (Blessing, 1995)

 $T_{\min} = 0.375$, $T_{\max} = 0.783$

4132 measured reflections

528 independent reflections

510 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.097$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.032$ $wR(F^2) = 0.066$ $S = 1.13$

528 reflections

39 parameters

H-atom parameters constrained

 $\Delta\rho_{\max} = 0.89$ e Å⁻³ $\Delta\rho_{\min} = -1.05$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—N2	1.974 (2)	N1—C1	1.312 (3)
Cu1—N3	2.021 (2)	N2—C1	1.155 (3)
N2 ⁱ —Cu1—N2	110.34 (11)	C1 ⁱⁱ —N1—C1	117.0 (3)
N2—Cu1—N3	111.79 (4)	C1—N2—Cu1	172.85 (18)
N3 ⁱ —Cu1—N3	98.91 (11)	N2—C1—N1	176.2 (2)

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

Data collection: *X-Area* (Stoe & Cie, 2001); cell refinement: *X-Area*; data reduction: *X-Area*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2007); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Routine data collection was performed by the XRD service department (Dr K. Harms, G. Geiseler and R. Riedel) of the Chemistry Department, Philipps-University, and is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HP2020).

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supporting information

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catena-Poly[[diacetonitrilecopper(I)]- μ -dicyanamido]**Benjamin Oelkers, Marion Stricker and Jörg Sundermeyer****S1. Comment**

Salts with dicyanamide (DCA) as anion have gained some interest recently because of their use as ionic liquids (ILs) with low viscosities (MacFarlane *et al.*, 2001). During our ongoing investigations on copper-containing ILs (Stricker *et al.*, 2010), we found that upon heating a mixture of Cu(DCA) and [BMIM](DCA) ([BMIM]⁺ = 1-*n*-butyl-3-methylimidazolium) in acetonitrile the title compound [Cu(DCA)(MeCN)₂]_∞ is formed instead of the expected product [BMIM][Cu(DCA)₂]. It is interesting to note that slightly different conditions ([Cu(MeCN)₄]ClO₄, (Ph₃P=N=PPh₃)(DCA), acetonitrile/acetone, ambient temperature) lead to the monoadduct [Cu(DCA)(MeCN)]_∞ (Batten *et al.*, 2000), while solvent-free copper(I)-dicyanamide results from reduction of an aqueous solution of Na(DCA) and CuSO₄ with NaHSO₃ (Bessler *et al.*, 2000).

The crystal structure of the title compound features zigzag chains along the *a* axis that consist of alternating [Cu(MeCN)₂] and dicyanamide units. The latter act as bidentate ligands *via* both terminal nitrogen atoms, the copper atoms show a slightly distorted tetrahedral coordination sphere (Fig. 1). The anionic and neutral ligands lie on different mirror planes (perpendicular to the *b* and *a* axis, respectively) while the metal is situated on their intersection. The asymmetric unit comprises one fourth of the formula unit.

The comparison of the title compound [Cu(DCA)(MeCN)₂]_∞ and the monoadduct [Cu(DCA)(MeCN)]_∞ (Batten *et al.*, 2000) shows similarities in terms of bond lengths and angles. In fact, both structures can locally be related to each other by formally breaking the copper-imide bonds of the latter and replacing them with acetonitrile ligands. The obtained structural motif is then very similar to the one-dimensional polymer building up the title compound (Fig. 2). Thus a partial depolymerization of [Cu(DCA)(MeCN)]_∞ formally leads to the reported structure of [Cu(DCA)(MeCN)₂]_∞ without additional bond breaking.

S2. Experimental

To a mixture of Cu(DCA) (68 mg, 0.52 mmol) and [BMIM](DCA) (108 mg, 0.53 mmol; [BMIM]⁺ = 1-*n*-butyl-3-methylimidazolium) acetonitrile (60 ml) was added. Although the mixture was heated to 80 °C for 4.5 h, some amorphous solid remained. Upon slow cooling to room temperature colourless crystals of the title compound formed.

S3. Refinement

Hydrogen atoms of the methyl groups were placed on idealized positions and refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.5 \times U_{\text{eq}}(\text{C})$ and C–H bond lengths of 0.98 Å.

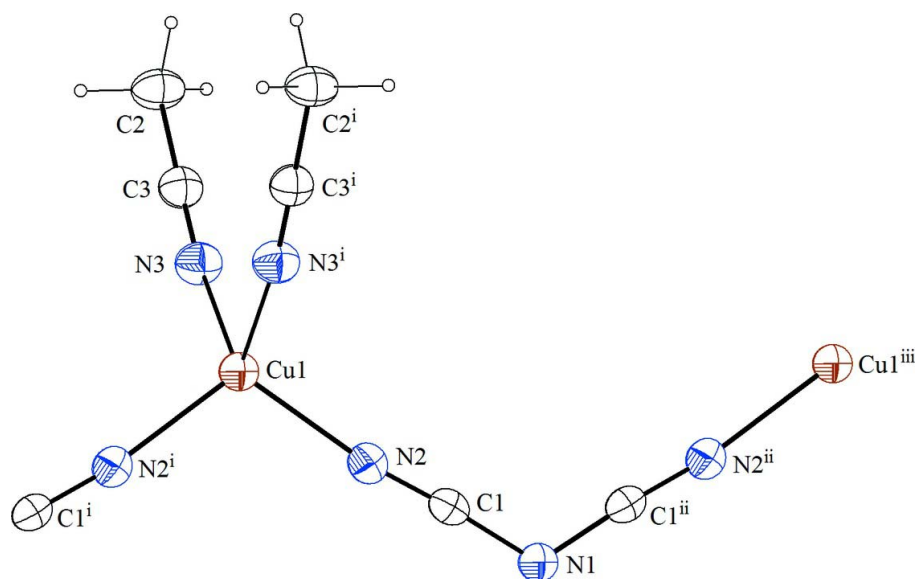


Figure 1

Molecular structure of the title compound. Displacement ellipsoids are shown for 50% probability. Symmetry codes: (i) $3/2-x, 3/2-y, z$; (ii) $1/2-x, 3/2-y, z$; (iii) $-1+x, y, x$.

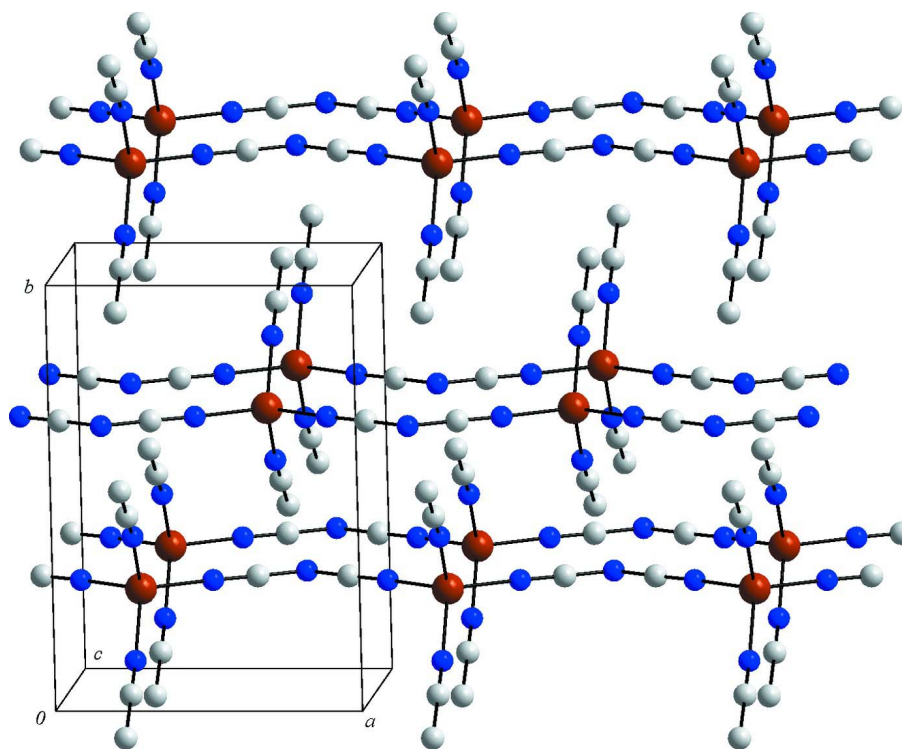


Figure 2

Packing diagram of the title compound, view along $[1\ 1\ 10]$.

catena-Poly[[diacetonitrilecopper(I)]- μ -dicyanamido]*Crystal data*[Cu(C₂N₃)(C₂H₃N)₂] $M_r = 211.71$ Orthorhombic, *Pmmn*

Hall symbol: -P 2ab 2a

 $a = 7.5222$ (5) Å $b = 10.5307$ (11) Å $c = 5.5378$ (4) Å $V = 438.67$ (6) Å³ $Z = 2$ $F(000) = 212$ $D_x = 1.603$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9024 reflections

 $\theta = 1.9$ – 27.1° $\mu = 2.44$ mm⁻¹ $T = 100$ K

Prism, colourless

 $0.45 \times 0.27 \times 0.12$ mm*Data collection*

Stoe IPDS 2

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 6.67 pixels mm⁻¹

rotation method scans

Absorption correction: multi-scan

(Blessing, 1995)

 $T_{\min} = 0.375$, $T_{\max} = 0.783$

4132 measured reflections

528 independent reflections

510 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.097$ $\theta_{\max} = 26.7^\circ$, $\theta_{\min} = 3.3^\circ$ $h = -8$ → 9 $k = -13$ → 13 $l = -7$ → 6 *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.032$ $wR(F^2) = 0.066$ $S = 1.13$

528 reflections

39 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 0.0839P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.89$ e Å⁻³ $\Delta\rho_{\min} = -1.05$ e Å⁻³*Special details*

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger. The methyl group was modelled using AFIX 133 as a riding group with idealized geometry. As the most favourable conformation was found to be symmetric with respect to a mirror plane, two protons with half occupancy were generated at symmetry-related positions. These two symmetry-dependent protons were combined by eliminating one of them, setting the other one to full occupancy and finally changing the AFIX code to 03 in order to retain the idealized geometry.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.7500	0.7500	0.37747 (6)	0.02393 (18)

N1	0.2500	0.7500	0.8017 (5)	0.0267 (5)
N2	0.5346 (3)	0.7500	0.5810 (3)	0.0270 (4)
N3	0.7500	0.8958 (2)	0.1402 (3)	0.0299 (4)
C1	0.3987 (3)	0.7500	0.6779 (4)	0.0226 (4)
C2	0.7500	1.0397 (2)	-0.2413 (4)	0.0318 (5)
H2A	0.7500	0.9863	-0.3861	0.048*
H2B	0.8562	1.0937	-0.2407	0.048*
C3	0.7500	0.95947 (19)	-0.0270 (4)	0.0267 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0242 (3)	0.0252 (2)	0.0224 (3)	0.000	0.000	0.000
N1	0.0233 (12)	0.0342 (13)	0.0224 (12)	0.000	0.000	0.000
N2	0.0241 (9)	0.0312 (9)	0.0256 (8)	0.000	-0.0021 (7)	0.000
N3	0.0348 (11)	0.0268 (10)	0.0281 (11)	0.000	0.000	0.0007 (7)
C1	0.0258 (10)	0.0214 (8)	0.0205 (9)	0.000	-0.0044 (8)	0.000
C2	0.0463 (13)	0.0246 (10)	0.0245 (11)	0.000	0.000	0.0028 (9)
C3	0.0307 (10)	0.0235 (10)	0.0261 (11)	0.000	0.000	-0.0014 (9)

Geometric parameters (Å, °)

Cu1—N2 ⁱ	1.974 (2)	N2—C1	1.155 (3)
Cu1—N2	1.974 (2)	N3—C3	1.143 (3)
Cu1—N3 ⁱ	2.021 (2)	C3—C2	1.457 (3)
Cu1—N3	2.021 (2)	C2—H2A	0.9800
N1—C1 ⁱⁱ	1.312 (3)	C2—H2B	0.9800
N1—C1	1.312 (3)		
N2 ⁱ —Cu1—N2	110.34 (11)	C1—N2—Cu1	172.85 (18)
N2 ⁱ —Cu1—N3 ⁱ	111.79 (4)	C3—N3—Cu1	166.44 (18)
N2—Cu1—N3 ⁱ	111.79 (4)	N2—C1—N1	176.2 (2)
N2 ⁱ —Cu1—N3	111.79 (4)	C3—C2—H2A	109.5
N2—Cu1—N3	111.79 (4)	C3—C2—H2B	109.5
N3 ⁱ —Cu1—N3	98.91 (11)	H2A—C2—H2B	109.6
C1 ⁱⁱ —N1—C1	117.0 (3)	N3—C3—C2	179.6 (2)
N2 ⁱ —Cu1—N3—C3	117.87 (5)	N3 ⁱ —Cu1—N3—C3	0.000 (4)
N2—Cu1—N3—C3	-117.87 (5)		

Symmetry codes: (i) $-x+3/2, -y+3/2, z$; (ii) $-x+1/2, -y+3/2, z$.