

Poly[diethylammonium [tetra- μ_2 -cyanido- κ^8 C:N-tricuprate(I)]], a two-dimensional network solid

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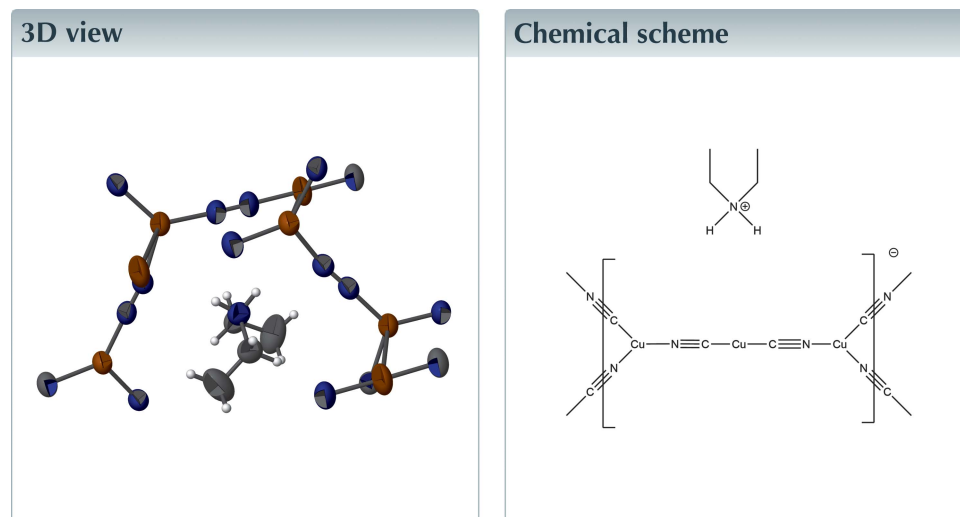
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Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $(C_4H_{12}N)[Cu_3(CN)_4]_n$, crystallizes as a CuCN network solid, with diethylammonium cations sandwiched between planar CuCN sheets comprised of trigonal planar and digonally coordinated Cu^I atoms bridged by linear CN groups to form 24-membered rings. The digonally coordinated Cu^I atoms and the diethylammonium cations lie on separate crystallographic twofold rotation axes. One of the two independent CN groups has a 50:50 disordered orientation, while the other has one orientation favored due to a $N-H \cdots NC$ hydrogen bond between the diethylammonium cation and the anionic CuCN framework. These hydrogen bonds link the sheets together into a three-dimensional network.



Structure description

There has been continuing interest in the synthesis and structures of CuCN network solids containing protonated nitrogen bases, with at least 40 such structures listed in the CSD (Groom *et al.*, 2016). For instance, a recent paper reports optical memory effects for two tetramethylammonium CuCN structures (Nicholas *et al.*, 2019) while Grifasi *et al.* (2016) is one of several papers reporting on the interesting topologies and photoluminescence of many CuCN networks. The present compound was prepared as part of our own ongoing structural studies in this area.

Of the two independent Cu atoms, Cu1 is linearly coordinated to two CN groups and lies on the crystallographic twofold rotation axis $[0, y, 0]$, while trigonally coordinated Cu2 is in a general position, Fig. 1. Each of the two independent CN groups bridges two copper(I) atoms to build a two-dimensional CuCN network perpendicular to the a axis. Four such sheets cross the unit cell, as shown in the packing diagram, Fig. 2. The network is made up of 24-membered rings, which are almost planar, with an r.m.s. deviation from the 24-atom plane of 0.128 (5) Å, where the e.s.d. given is the average of the 24 individual

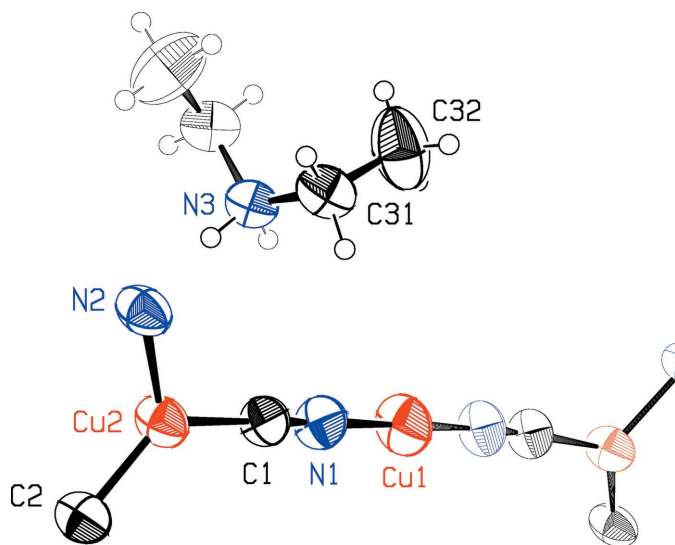


Figure 1
The asymmetric unit of the title compound is emboldened. Different crystallographic twofold axes pass through Cu1 and N3. Displacement ellipsoids are drawn at the 50% probability level, while H atoms are depicted as arbitrary spheres. Cu atoms are colored red, N atoms blue, and C and H atoms black.

e.s.d.'s. Most such networks in the literature are honeycomb structures made up of 18-membered hexagonal rings, although a network similar to that described here was reported by Ferlay *et al.* (2013). The three-coordinated Cu2 atom has a geometry far from ideal trigonal planar, with C/N–Cu–C/N angles of 114.7 (3), 116.4 (2), and 128.3 (3)° and bond lengths Cu–C/N ranging from 1.889 (8) to 1.960 (7) Å.

The ammonium cation lies on the crystallographic twofold axis $[0, y, \frac{1}{2}]$ and assumes a *gauche* conformation, with the torsion angle C32–C31–N3–C31 $(-x, y, 1 - z) = -62.1 (6)^\circ$. Each cation forms two N–H···N hydrogen bonds to N2 of the bridging C2≡N2 group of two adjacent sheets, which ties adjacent sheets into a three-dimensional network, as shown in Fig. 2. Table 1 gives details of the single independent hydrogen bond, while the lower part of Fig. 2 reveals that the hydrogen bonds in the crystal point along the $[102]$ direction.

Synthesis and crystallization

A mixture of 0.359 g (4.01 mmol) of CuCN and 0.330 g of NaCN (6.73 mmol) with 25 ml of H₂O was stirred and the light remaining precipitate was filtered off. 1.55 g (21.2 mmol) of diethylamine dissolved in 10 ml of H₂O were added, and the stirred mixture was left open to air. Crystals began to form after one week and were harvested as conglomerates of thick, yellow–green plates several weeks later. The intent had been to prepare a mixed-valence compound similar to those prepared from bidentate amines (Corfield & Michalski, 2014; Corfield & Sabatino, 2017) and to use the fivefold excess of base to stabilize any Cu^{II} formed by air-oxidation. However, no crystalline mixed-valence compounds containing the base were obtained in this and similar preparations with diethylamine. The IR spectrum, obtained with a Thermo Scientific

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N3–H3···N2	0.89 (1)	2.44 (4)	3.230 (6)	149 (6)

Nicolet iS50 FT–IR instrument, showed strong stretching bands at 2111 cm^{−1} and 2136 cm^{−1} for CN, and at 3118 cm^{−1} and 3186 cm^{−1} for N–H. The N–H frequencies for the protonated base may be compared with the band at 3281 cm^{−1} (*w*) found for the free base diethylamine.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Towards the end of the refinements, each of the two CN groups was refined as a superposition of NC and CN groups, whose occupancies were varied. For C1≡N1, the occupancy factor refined to close to 50%, so this occupancy was fixed at 50%, while the occupancy for C2≡N2 favors one orientation over the other by 78 (8)%. This preferred orientation is doubtless due to the hydrogen-bonding interactions with the cation discussed above. The Flack *x* factor (Parsons *et al.*, 2013) is 0.096 (25), which implies

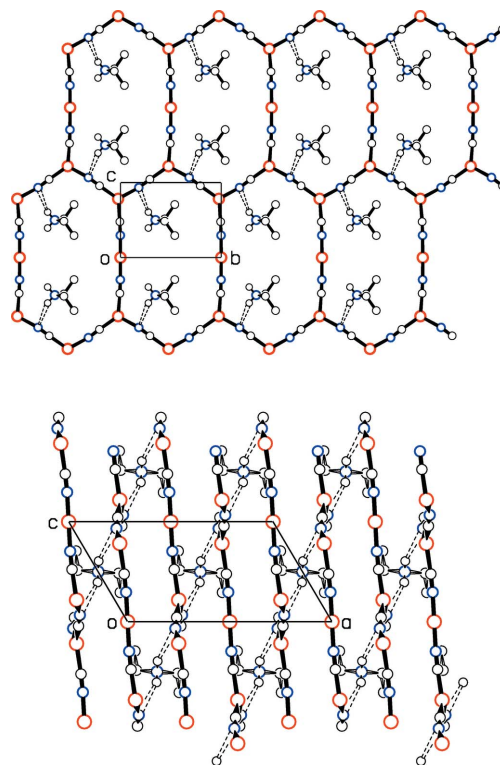


Figure 2
Top: View along the *a* axis of one sheet. Hydrogen bonds from cations above and below the sheet are shown. Bottom: Projection down the *b* axis, showing the sheets stacked perpendicular to the *a* axis, and the hydrogen bonds linking the sheets together. (Scale is slightly larger than in the top diagram.) The chains of hydrogen bonds along the $[102]$ direction are evident. Cu atoms are colored red, N atoms blue, and C and NH atoms black. H atoms of the C₂H₅ group are not shown, and only one orientation for each of the disordered CN groups is drawn.

Table 2
Experimental details.

Crystal data	
Chemical formula	(C ₄ H ₁₂ N)[Cu ₃ (CN) ₄]
<i>M_r</i>	368.85
Crystal system, space group	Monoclinic, C2
Temperature (K)	302
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.6825 (8), 8.3355 (5), 7.2205 (5)
β (°)	120.444 (3)
<i>V</i> (Å ³)	658.07 (8)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	4.78
Crystal size (mm)	0.15 × 0.13 × 0.08
Data collection	
Diffractometer	Enraf–Nonius KappaCCD
Absorption correction	Multi-scan (Otwinowski & Minor, 1997)
<i>T</i> _{min} , <i>T</i> _{max}	0.51, 0.68
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	2500, 1487, 1191
<i>R</i> _{int}	0.039
(sin θ / λ) _{max} (Å ⁻¹)	0.648
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.031, 0.069, 1.04
No. of reflections	1487
No. of parameters	82
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.22, -0.29
Absolute structure	Twinning involves reflection, so the Flack parameter of 0.13 (5) implies the presence of a small amount of the inverted form
Absolute structure parameter	0.13 (5)

Computer programs: *KappaCCD Server Software* (Nonius, 1997), *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997), *SHELXS97* (Sheldrick, 2008), *SHELXL2017/1* (Sheldrick, 2015), *ORTEP3* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 2012) and *pubCIF* (Westrip, 2010).

that the crystal exhibits minor twinning about the (010) plane; more pronounced twinning was seen in a different crystal not used in this work. The final refinement uses the *SHELXL* BASF and TWIN commands, with no noticeable changes in the structure.

Acknowledgements

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References

- Burnett, M. N. & Johnson, C. K. (1996). *ORTEP3*. Report ORNL6895. Oak Ridge National Laboratory, Tennessee, USA.
- Corfield, P. W. R. & Michalski, J. F. (2014). *Acta Cryst.* **E70**, m76–m77.
- Corfield, P. W. R. & Sabatino, A. (2017). *Acta Cryst.* **E73**, 141–146.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Ferlay, S., Dechambenoit, P., Kyritsakas, N. & Hosseini, M. W. (2013). *Dalton Trans.* **42**, 11661–11671.
- Grifasi, F., Priola, E., Chierotti, M. R., Diana, E., Garino, C. & Gobetto, R. (2016). *Eur. J. Inorg. Chem.* pp. 2975–2983.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Nicholas, A. D., Bullard, R. M., Wheaton, A. M., Streep, M., Nicholas, V. A., Pike, R. D. & Patterson, H. H. (2019). *Materials*, **12**, 1211–1229.
- Nonius (1997). *KappaCCD Server Software*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* **B69**, 249–259.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

full crystallographic data

IUCrData (2020). 5, x200968 [https://doi.org/10.1107/S2414314620009682]

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Crystal data

(C₄H₁₂N)[Cu₃(CN)₄]

$M_r = 368.85$

Monoclinic, *C*2

Hall symbol: C 2y

$a = 12.6825$ (8) Å

$b = 8.3355$ (5) Å

$c = 7.2205$ (5) Å

$\beta = 120.444$ (3)°

$V = 658.07$ (8) Å³

$Z = 2$

$F(000) = 364$

$D_x = 1.861$ Mg m⁻³

$D_m = 1.84$ (1) Mg m⁻³

D_m measured by flotation in

CCl₄/dibromoethane mixtures

Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å

Cell parameters from 791 reflections

$\theta = 3.3$ – 27.4 °

$\mu = 4.78$ mm⁻¹

$T = 302$ K

Irregular block, pale green

$0.15 \times 0.13 \times 0.08$ mm

Data collection

Enraf–Nonius KappaCCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 9 pixels mm⁻¹

combination of ω and φ scans

Absorption correction: multi-scan
(Otwinowski & Minor, 1997)

$T_{\min} = 0.51$, $T_{\max} = 0.68$

2500 measured reflections

1487 independent reflections

1191 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

$\theta_{\max} = 27.4$ °, $\theta_{\min} = 3.3$ °

$h = -16 \rightarrow 16$

$k = -10 \rightarrow 10$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.069$

$S = 1.04$

1487 reflections

82 parameters

2 restraints

Primary atom site location: heavy-atom method

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.021P)^2 + 0.730P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.22$ e Å⁻³

$\Delta\rho_{\min} = -0.29$ e Å⁻³

Extinction correction: SHELXL-2017/1

(Sheldrick 2015),

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.015 (3)

Absolute structure: Twinning involves

reflection, so the Flack parameter of 0.13 (5)

implies the presence of a small amount of the

inverted form

Absolute structure parameter: 0.13 (5)

Special details

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

Refinement. Hydrogen atoms on the C atoms were constrained, with C—H distances of 0.97 Å for the methylene group and 0.96 Å for the methyl group. The N—H atom was refined, with a restraint on the N—H bond length but not on the temperature factor.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cu1	0.000000	0.0002 (2)	0.000000	0.0860 (6)	
Cu2	0.18717 (6)	−0.02348 (14)	0.78258 (9)	0.0636 (3)	
C1	0.1211 (4)	−0.0060 (10)	0.4775 (7)	0.0605 (12)	0.5
N1A	0.1211 (4)	−0.0060 (10)	0.4775 (7)	0.0605 (12)	0.5
N1	0.0777 (4)	−0.0015 (11)	0.2956 (8)	0.0683 (16)	0.5
C1A	0.0777 (4)	−0.0015 (11)	0.2956 (8)	0.0683 (16)	0.5
C2A	0.2142 (6)	0.1819 (7)	0.9323 (10)	0.066 (2)	0.22 (8)
N2	0.2142 (6)	0.1819 (7)	0.9323 (10)	0.066 (2)	0.78 (8)
N2A	0.2525 (7)	0.2919 (8)	1.0428 (11)	0.064 (2)	0.22 (8)
C2	0.2525 (7)	0.2919 (8)	1.0428 (11)	0.064 (2)	0.78 (8)
N3	0.000000	0.3473 (8)	0.500000	0.0606 (17)	
H3	0.033 (6)	0.277 (6)	0.606 (8)	0.09 (2)*	
C31	0.0968 (5)	0.4390 (8)	0.4846 (11)	0.071 (2)	
H31A	0.140222	0.506523	0.610650	0.106*	
H31B	0.155145	0.363683	0.484731	0.106*	
C32	0.0488 (8)	0.5391 (14)	0.2931 (14)	0.118 (4)	
H32A	0.115278	0.590203	0.288774	0.177*	
H32B	−0.004388	0.619311	0.297044	0.177*	
H32C	0.003720	0.473602	0.167536	0.177*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0970 (8)	0.0960 (16)	0.0395 (5)	0.000	0.0158 (5)	0.000
Cu2	0.0685 (4)	0.0588 (4)	0.0457 (3)	0.0009 (4)	0.0157 (3)	0.0021 (4)
C1	0.057 (2)	0.068 (3)	0.047 (2)	0.007 (3)	0.0188 (19)	0.003 (3)
N1A	0.057 (2)	0.068 (3)	0.047 (2)	0.007 (3)	0.0188 (19)	0.003 (3)
N1	0.065 (3)	0.081 (5)	0.045 (2)	0.008 (3)	0.017 (2)	−0.001 (3)
C1A	0.065 (3)	0.081 (5)	0.045 (2)	0.008 (3)	0.017 (2)	−0.001 (3)
C2A	0.079 (4)	0.051 (4)	0.050 (3)	0.000 (3)	0.020 (3)	0.002 (3)
N2	0.079 (4)	0.051 (4)	0.050 (3)	0.000 (3)	0.020 (3)	0.002 (3)
N2A	0.074 (4)	0.053 (4)	0.047 (4)	0.004 (3)	0.016 (3)	0.007 (3)
C2	0.074 (4)	0.053 (4)	0.047 (4)	0.004 (3)	0.016 (3)	0.007 (3)
N3	0.056 (4)	0.056 (4)	0.062 (4)	0.000	0.023 (3)	0.000
C31	0.054 (3)	0.067 (6)	0.077 (4)	0.001 (3)	0.023 (3)	0.006 (3)
C32	0.089 (5)	0.158 (12)	0.097 (6)	0.007 (6)	0.040 (5)	0.049 (6)

Geometric parameters (Å, °)

Cu1—N1 ⁱ	1.842 (5)	N3—C31 ⁱⁱⁱ	1.497 (7)
Cu1—N1	1.842 (5)	N3—H3	0.885 (14)
Cu2—N2A ⁱⁱ	1.889 (7)	C31—C32	1.457 (10)
Cu2—C1	1.925 (4)	C31—H31A	0.9700
Cu2—N2	1.960 (7)	C31—H31B	0.9700
C1—N1	1.139 (6)	C32—H32A	0.9600
N2—C2	1.149 (7)	C32—H32B	0.9600
N3—C31	1.497 (7)	C32—H32C	0.9600
N1 ⁱ —Cu1—N1	179.1 (6)	C32—C31—H31A	108.9
N2A ⁱⁱ —Cu2—C1	128.3 (3)	N3—C31—H31A	108.9
N2A ⁱⁱ —Cu2—N2	116.4 (2)	C32—C31—H31B	108.9
C1—Cu2—N2	114.7 (3)	N3—C31—H31B	108.9
N1—C1—Cu2	176.5 (6)	H31A—C31—H31B	107.7
C1—N1—Cu1	176.8 (6)	C31—C32—H32A	109.5
C2—N2—Cu2	167.0 (6)	C31—C32—H32B	109.5
N2—C2—Cu2 ^{iv}	178.3 (5)	H32A—C32—H32B	109.5
C31—N3—C31 ⁱⁱⁱ	118.6 (7)	C31—C32—H32C	109.5
C31—N3—H3	111 (5)	H32A—C32—H32C	109.5
C31 ⁱⁱⁱ —N3—H3	109 (5)	H32B—C32—H32C	109.5
C32—C31—N3	113.5 (5)		

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N3—H3 \cdots N2	0.89 (1)	2.44 (4)	3.230 (6)	149 (6)