

## Poly[diamminedi- $\mu_3$ -dicyanamido-copper(II)]

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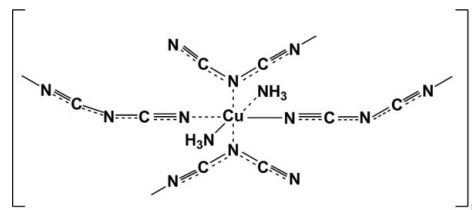
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Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{N}-\text{C}) = 0.002$  Å;  $R$  factor = 0.017;  $wR$  factor = 0.052; data-to-parameter ratio = 15.2.

The asymmetric unit of the title polymeric mononuclear  $\text{Cu}^{\text{II}}$  complex,  $[\text{Cu}(\text{C}_2\text{N}_3)_2(\text{NH}_3)_2]_n$ , contains one half-molecule, the complex being completed through inversion symmetry, with the  $\text{Cu}^{\text{II}}$  atom situated at the centre of symmetry. The coordination polyhedron around  $\text{Cu}^{\text{II}}$  is a Jahn–Teller-distorted  $[\text{CuN}_6]$  octahedron. The terminal N atoms of two dicyanamide ligands and two ammine ligands form an approximate square plane, with  $\text{N}-\text{Cu}-\text{N}$  bite angles of  $89.72(5)$  and  $90.28(5)^\circ$ . The coordination polyhedron is completed in the axial positions by the central amide-type N atoms of two additional dicyanamide ligands, with an elongated  $\text{Cu}-\text{N}$  distance of  $2.548(1)$  Å. In turn, each of the four dicyanamide ligands, acting as bidentate, link the  $\text{Cu}^{\text{II}}$  ions into a two-dimensional polymeric structure parallel to (100). The ammine H atoms are involved in intermolecular hydrogen bonding with the free terminal N atoms of neighbouring dicyanamide ligands, yielding a three-dimensional network.

### Related literature

For bonding modes of the dicyanamide ligand, see: Burčák *et al.* (2004); Yang *et al.* (2004); van Albada *et al.* (2001); Potočník *et al.* (2002); Zhang *et al.* (2004); Mohamadou *et al.* (2003); Batten *et al.* (2000); Kožíšek *et al.* (2007). For magnetic properties of  $[M(\text{dicyanamide})_2]$  compounds, see: Batten & Murray (2003); Kurmoo & Kepert (1998).



### Experimental

#### Crystal data

$[\text{Cu}(\text{C}_2\text{N}_3)_2(\text{NH}_3)_2]$   
 $M_r = 229.72$   
Monoclinic,  $P2_1/c$   
 $a = 7.1310(2)$  Å  
 $b = 9.6301(2)$  Å  
 $c = 7.2162(2)$  Å  
 $\beta = 113.782(3)^\circ$

$V = 453.47(2)$  Å<sup>3</sup>  
 $Z = 2$   
Mo  $K\alpha$  radiation  
 $\mu = 2.38$  mm<sup>-1</sup>  
 $T = 298$  K  
 $0.52 \times 0.32 \times 0.17$  mm

#### Data collection

Oxford Diffraction Gemini R CCD diffractometer  
Absorption correction: analytical [*CrysAlis RED* (Oxford Diffraction, 2010), based on expressions derived by Clark &

Reid (1995)]  
 $T_{\text{min}} = 0.410$ ,  $T_{\text{max}} = 0.682$   
19836 measured reflections  
1126 independent reflections  
1019 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.016$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.017$   
 $wR(F^2) = 0.052$   
 $S = 1.07$   
1126 reflections  
74 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.21$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.25$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{N4}^{\text{i}}$	0.84 (2)	2.43 (2)	3.2555 (18)	165.4 (19)
$\text{N1}-\text{H2}\cdots\text{N4}^{\text{ii}}$	0.89 (2)	2.34 (2)	3.2278 (18)	175.7 (17)
$\text{N1}-\text{H3}\cdots\text{N4}^{\text{iii}}$	0.81 (2)	2.43 (2)	3.2073 (18)	162.1 (19)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2010); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2010); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LR2087).

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## supporting information

*Acta Cryst.* (2012). E68, i89–i90 [doi:10.1107/S1600536812045382]

**Poly[diamminedi- $\mu_3$ -dicyanamido-copper(II)]**

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**S1. Comment**

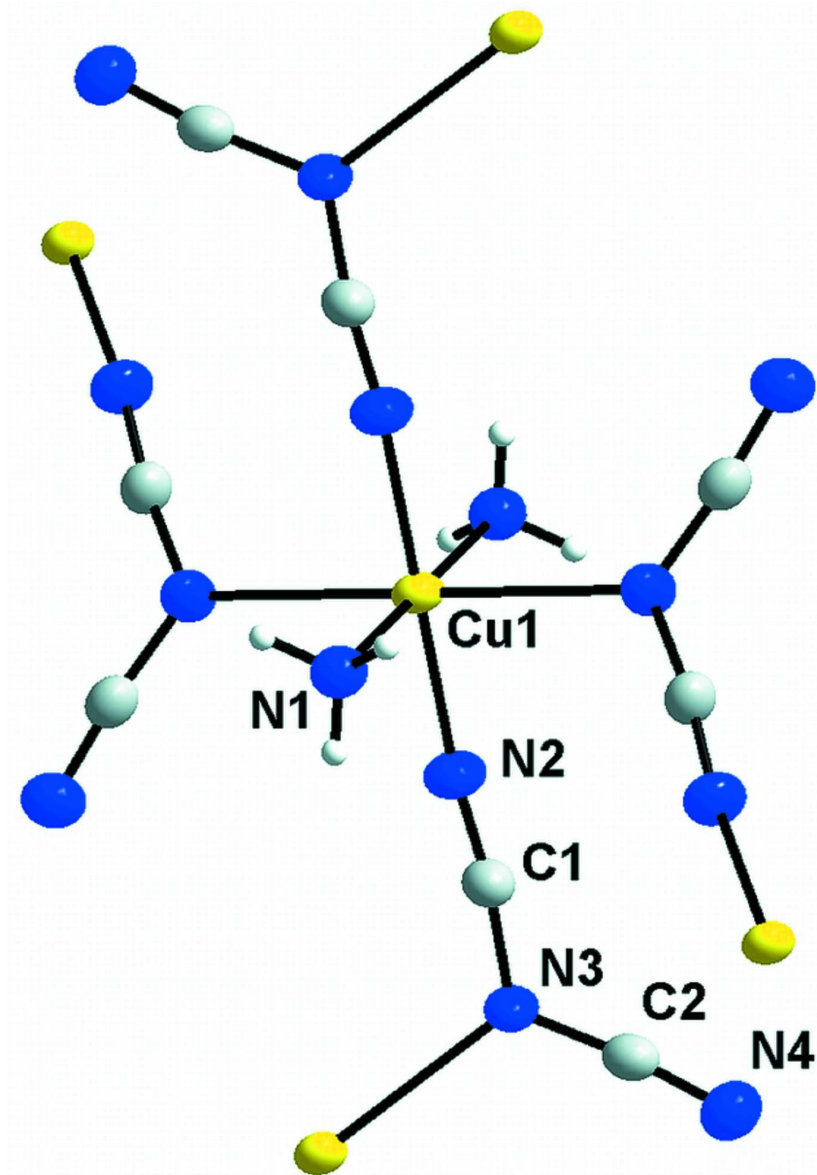
Among the various classes of ligands currently employed for the generation of coordination compounds, dicyanamide (dca) has been attracting a lot of attention, partly due to the discovery of interesting magnetic properties in the  $M(\text{dca})_2$  compounds (Batten & Murray, 2003; Kurmoo & Kepert, 1998). A particular feature of this ligand is the variability in coordination modes it can display and thus it is able to generate one- to three-dimensional networks, as well as molecular and ionic compounds, depending on its metallic centers and its organic coligands. In coordination compounds of copper, the dca anion,  $(\text{N}(\text{CN})_2)$ , exhibits a rich variety of bonding modes. It can coordinate either in a monodentate manner (Burčák *et al.*, 2004; Yang *et al.*, 2004;) or, more typically, in a bidentate manner [two types of binding: mainly through two nitrile N atoms (Albada *et al.*, 2001; Potočňák *et al.*, 2002; Zhang *et al.*, 2004), but also through one amide and one nitrile N atom (Mohamadou *et al.*, 2003), or even in a tridentate manner (Batten *et al.*, 2000; Kožíšek *et al.*, 2007)]. The asymmetric unit of the title compound, (I),  $[\text{Cu}(\text{N}(\text{CN})_2)_2(\text{NH}_3)_2]_n$ , contains one-half of the molecule with the  $\text{Cu}^{\text{II}}$  atom situated at the centre of symmetry and is octahedrally coordinated by two ammino and two bidentate dca ligands, forming a  $\text{CuN}_6$  coordination environment (Fig.1). Two terminal N atoms of two dca units and two ammino ligands forming an approximate square plane with N—Cu—N bite angles of 89.72 (5) and 90.28 (5)°. Coordination polyhedron is completed in axial position by the central amide N atoms of two additional dca ligands with the Cu—N elongated distance of 2.548 (1) Å as a result of the Jahn–Teller effect. The amino H atoms are involved in intermolecular hydrogen bonding with the free terminal N atoms of neighbouring dicyanamide ligands, yielding a three-dimensional network (Fig.2).

**S2. Experimental**

A solution of  $\text{Cu}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$  (2.0 mmol) in water (3 ml) was added to a solution of  $\text{K}[\text{N}(\text{CN})_2]$  (4.0 mmol) in water (10 ml) and mixed with a solution of ammine (4.0 mmol) in water (10 ml). After standing for a few days, blue crystals of (I) were isolated (yield: ca 10%).

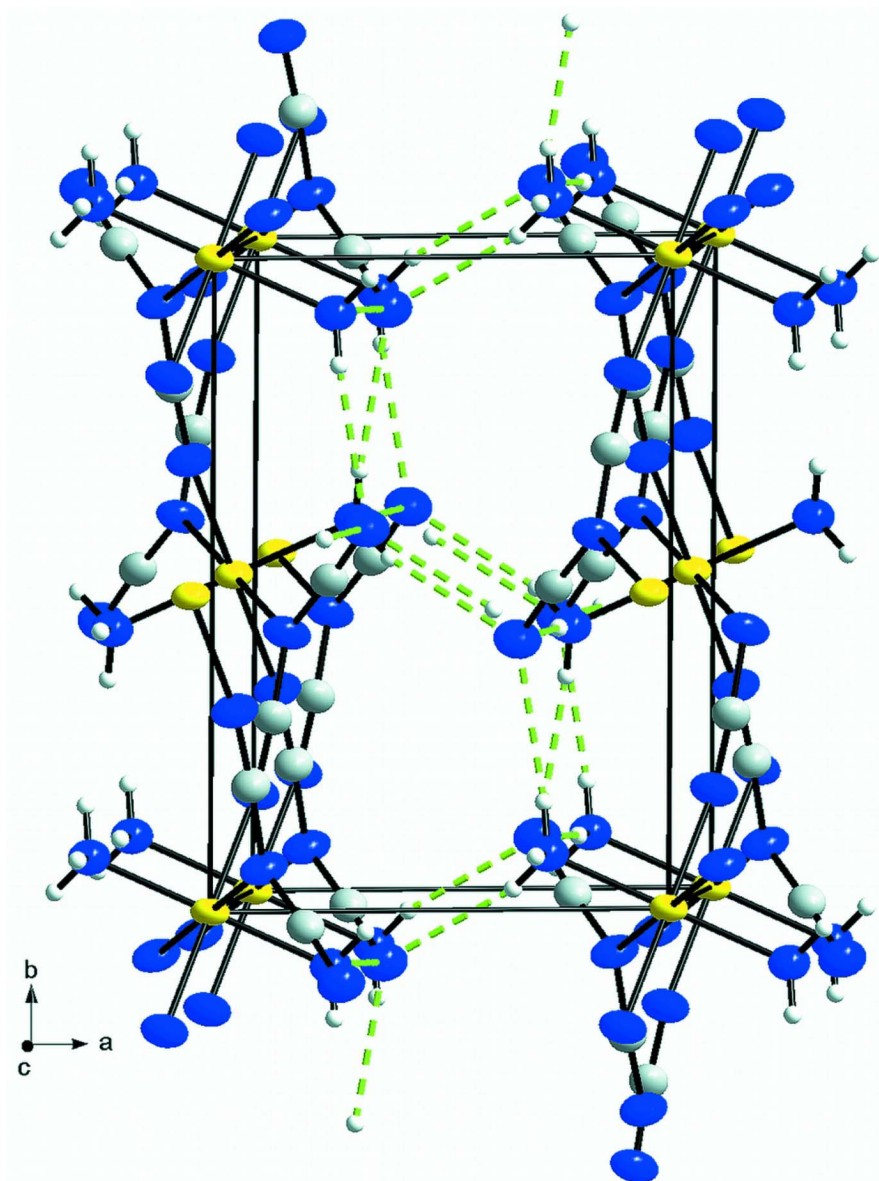
**S3. Refinement**

The ammine H atoms were located in a difference Fourier map and refined with a fixed isotropic displacement parameter.



**Figure 1**

Part of the polymeric structure of (I), with the displacement ellipsoids drawn at the 50% probability level.



**Figure 2**

A packing diagram for (I) showing the hydrogen-bonding network as green dashed lines.

**Poly[diamminedi- $\mu_3$ -dicyanamido-copper(II)]**

*Crystal data*

[Cu(C<sub>2</sub>N<sub>3</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]

$M_r = 229.72$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 7.1310 (2) \text{ \AA}$

$b = 9.6301 (2) \text{ \AA}$

$c = 7.2162 (2) \text{ \AA}$

$\beta = 113.782 (3)^\circ$

$V = 453.47 (2) \text{ \AA}^3$

$Z = 2$

$F(000) = 230$

$D_x = 1.682 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 15460 reflections

$\theta = 3.7\text{--}29.3^\circ$

$\mu = 2.38 \text{ mm}^{-1}$

$T = 298 \text{ K}$

Block, dark blue

$0.52 \times 0.32 \times 0.17 \text{ mm}$

*Data collection*

Oxford Diffraction Gemini R CCD  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 10.4340 pixels mm<sup>-1</sup>

$\omega$  and  $\varphi$  scans

Absorption correction: analytical

[*CrysAlis RED* (Oxford Diffraction, 2010),  
based on expressions derived by Clark & Reid  
(1995)]

$T_{\min} = 0.410$ ,  $T_{\max} = 0.682$

19836 measured reflections

1126 independent reflections

1019 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\max} = 28.3^\circ$ ,  $\theta_{\min} = 3.7^\circ$

$h = -9 \rightarrow 9$

$k = -12 \rightarrow 12$

$l = -9 \rightarrow 9$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.017$

$wR(F^2) = 0.052$

$S = 1.07$

1126 reflections

74 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 atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0314P)^2 + 0.113P]$

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

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

$\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$

*Special details*

**Experimental.** face-indexed (*CrysAlis RED*; Oxford Diffraction, 2010)

Absorption correction: *CrysAlis RED*, Oxford Diffraction Ltd., Version 1.171.32.8 (release 30-07-2007 *CrysAlis171*.NET) (compiled Jul 30 2007, 18:35:48) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* A51, 887-897)

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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  $F^2 > \sigma(F^2)$  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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.12500 (18)	0.20615 (12)	0.40737 (17)	0.0314 (2)
C2	0.2567 (2)	-0.00704 (11)	0.5168 (2)	0.0313 (3)
N1	-0.26849 (18)	0.41648 (13)	0.45514 (19)	0.0362 (2)
H1	-0.351 (3)	0.472 (2)	0.371 (4)	0.054 (6)*
H2	-0.283 (3)	0.417 (2)	0.572 (3)	0.053 (5)*
H3	-0.281 (3)	0.338 (3)	0.410 (3)	0.062 (6)*
N2	0.09027 (19)	0.32110 (12)	0.42058 (18)	0.0416 (3)
N3	0.15107 (18)	0.07772 (11)	0.36879 (16)	0.0389 (3)
N4	0.3460 (2)	-0.09051 (13)	0.63406 (19)	0.0462 (3)
Cu1	0.0000	0.5000	0.5000	0.02839 (10)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0349 (5)	0.0285 (6)	0.0293 (5)	0.0008 (4)	0.0114 (4)	-0.0034 (4)
C2	0.0340 (6)	0.0271 (6)	0.0332 (6)	-0.0019 (4)	0.0140 (5)	-0.0056 (4)
N1	0.0405 (6)	0.0299 (5)	0.0365 (6)	-0.0005 (4)	0.0138 (5)	-0.0001 (5)
N2	0.0518 (7)	0.0276 (5)	0.0431 (6)	0.0054 (5)	0.0168 (5)	-0.0042 (4)
N3	0.0520 (6)	0.0267 (5)	0.0313 (5)	0.0077 (4)	0.0097 (5)	-0.0046 (4)
N4	0.0520 (7)	0.0353 (6)	0.0459 (6)	0.0033 (5)	0.0140 (5)	0.0045 (5)
Cu1	0.03572 (14)	0.01832 (13)	0.03050 (14)	0.00135 (6)	0.01271 (10)	-0.00132 (6)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

C1—N2	1.1466 (17)	N1—H2	0.89 (2)
C1—N3	1.2975 (16)	N1—H3	0.81 (2)
C2—N4	1.1546 (18)	N2—Cu1	2.0021 (11)
C2—N3	1.3135 (17)	Cu1—N1 <sup>i</sup>	1.9793 (12)
N1—Cu1	1.9793 (12)	Cu1—N2 <sup>i</sup>	2.0021 (11)
N1—H1	0.84 (2)		
N2—C1—N3	172.98 (14)	C1—N2—Cu1	163.67 (11)
N4—C2—N3	173.97 (14)	C1—N3—C2	120.18 (11)
Cu1—N1—H1	102.1 (15)	N1 <sup>i</sup> —Cu1—N1	180.00 (7)
Cu1—N1—H2	108.6 (12)	N1 <sup>i</sup> —Cu1—N2	89.72 (5)
H1—N1—H2	111 (2)	N1—Cu1—N2	90.28 (5)
Cu1—N1—H3	112.9 (15)	N1 <sup>i</sup> —Cu1—N2 <sup>i</sup>	90.28 (5)
H1—N1—H3	112 (2)	N1—Cu1—N2 <sup>i</sup>	89.72 (5)
H2—N1—H3	110.2 (19)	N2—Cu1—N2 <sup>i</sup>	180.0
N3—C1—N2—Cu1	124.8 (10)	C1—N2—Cu1—N1 <sup>i</sup>	130.8 (4)
N2—C1—N3—C2	-178.5 (11)	C1—N2—Cu1—N1	-49.2 (4)
N4—C2—N3—C1	179 (100)	C1—N2—Cu1—N2 <sup>i</sup>	24 (100)

Symmetry code: (i)  $-x, -y+1, -z+1$ .Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ N4 <sup>ii</sup>	0.84 (2)	2.43 (2)	3.2555 (18)	165.4 (19)
N1—H2 $\cdots$ N4 <sup>iii</sup>	0.89 (2)	2.34 (2)	3.2278 (18)	175.7 (17)
N1—H3 $\cdots$ N4 <sup>iv</sup>	0.81 (2)	2.43 (2)	3.2073 (18)	162.1 (19)

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