

catena-Poly[[[4-amino-3,5-bis(pyridin-2-yl)-4*H*-1,2,4-triazole- κ^2 N¹,N⁵](dicyanamido- κ N)copper(II)]- μ_2 -dicyanamido- κ^2 N:N']]: coordination polymer chains linked into a bilayer by hydrogen bonds and π - π stacking interactions

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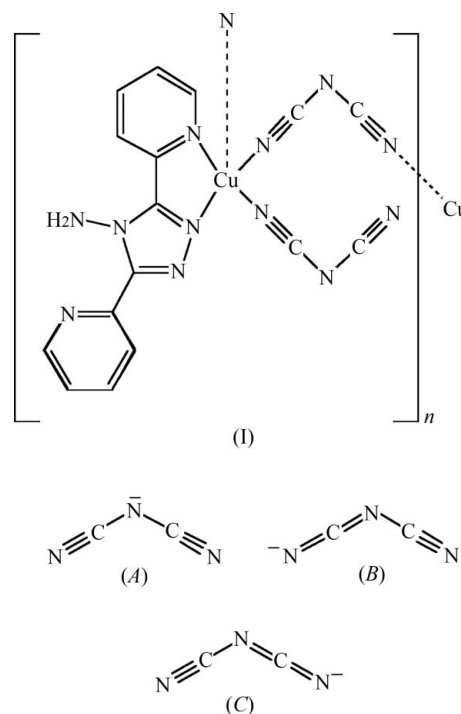
In the title compound, [Cu(C₂N₃)₂(C₁₂H₁₀N₆)_n or [Cu(dca)₂(abpt)]_n, where abpt is 4-amino-3,5-bis(pyridin-2-yl)-4*H*-1,2,4-triazole and dca is the dicyanamide anion, the Cu^{II} centre is five-coordinate with an approximately square-pyramidal geometry. One of the two dicyanamide ligands is a terminal ligand, but the other one acts as a $\mu_{1,5}$ -bridging ligand between pairs of Cu^{II} centres, so generating a one-dimensional coordination polymer. A combination of N—H...N and C—H...N hydrogen bonds, augmented by π - π stacking interactions, links the coordination polymer chains into a bilayer structure. Comparisons are made with some related Cu^{II} complexes containing dca ligands and heteroaromatic co-ligands.

Keywords: crystal structure; one-dimensional coordination polymer; square-pyramidal Cu^{II}; dicyanamide; hydrogen bonding; 4-amino-3,5-bis(pyridin-2-yl)-4*H*-1,2,4-triazole; polynitrile ligands.

1. Introduction

Polynitrile ligands are of great interest as they can lead to a rich variety of supramolecular architectures (Setifi *et al.*, 2009, 2014; Benmansour *et al.*, 2010, 2012). One such ligand is the dicyanamide (dca) anion, [N(CN)₂]⁻, which can coordinate to metal centres in a wide variety of ways, using either the central

N atom as a ligating atom or one or both of the terminal N atoms, or various combinations of these three N atoms. In addition, each terminal N atom can coordinate to either one metal centre or two. Overall, eight different modes of coordination have been identified and the number of different metal centres to which a single dca ligand can coordinate ranges from one to five, leading to the formation of coordination polymers which may be one-, two- or three-dimensional (Batten & Murray, 2003). We have therefore found it of interest to explore the effect of chelating co-ligands on the architectures of Cu^{II} complexes containing dca ligands, and we report here the synthesis and structure of *catena*-poly[[[4-amino-3,5-bis(pyridin-2-yl)-4*H*-1,2,4-triazole- κ^2 N¹,N⁵](dicyanamido- κ N)copper(II)]- μ_2 -dicyanamido- κ^2 N:N']], (I) (Fig. 1).



2. Experimental

2.1. Synthesis and crystallization

Copper(II) nitrate dihydrate (0.25 mmol, 60 mg) and 4-amino-3,5-bis(pyridin-2-yl)-4*H*-1,2,4-triazole (0.25 mmol, 59 mg) were dissolved in water (10 ml), producing a blue solution. A solution of sodium dicyanamide (0.5 mmol, 44 mg) in water (5 ml) was then added with stirring. The resulting solution was filtered and the filtrate set aside to crystallize at ambient temperature and in the presence of air. After 10 d, the resulting blue crystals of (I) were collected by filtration, washed with water and dried in air (yield 85%).

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. C-bound H atoms were treated as riding in geometrically idealized positions, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The H atoms bonded to primary amine atom N41 were permitted to ride at the

Table 1

Experimental details.

Crystal data	
Chemical formula	[Cu(C ₂ N ₃) ₂ (C ₁₂ H ₁₀ N ₆)]
<i>M_r</i>	433.91
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.5946 (5), 8.4284 (5), 14.1106 (8)
α , β , γ (°)	96.668 (4), 101.019 (5), 102.962 (4)
<i>V</i> (Å ³)	851.96 (9)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	1.32
Crystal size (mm)	0.25 × 0.22 × 0.22
Data collection	
Diffractometer	Agilent Xcalibur diffractometer
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 2003)
<i>T_{min}</i> , <i>T_{max}</i>	0.694, 0.749
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	13231, 6097, 4835
<i>R_{int}</i>	0.048
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.756
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.049, 0.101, 1.06
No. of reflections	6097
No. of parameters	262
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.44, -0.59

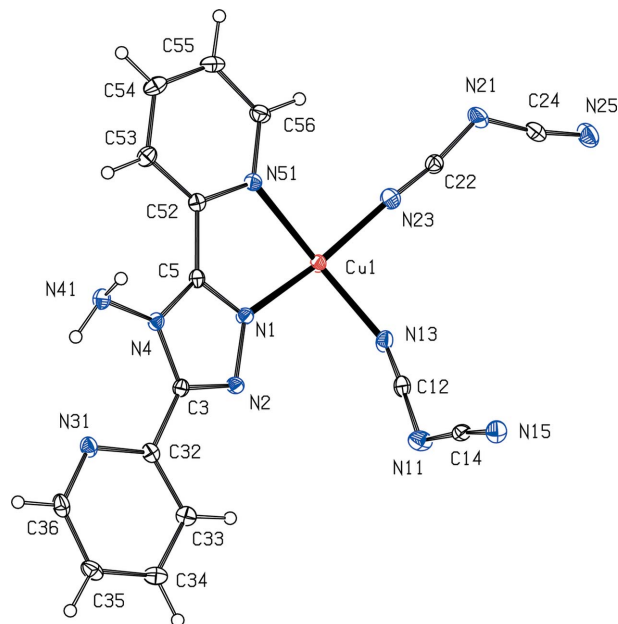
Computer programs: *CrysAlis PRO* (Agilent, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

positions located in a difference map, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$, giving the N–H distances shown in Table 3. Reflection 001, which had been attenuated by the beam stop, was omitted from the final refinements.

3. Results and discussion

In the title compound, (I), the 4-amino-3,5-bis(pyridin-2-yl)-4*H*-1,2,4-triazole ligand coordinates to the Cu^{II} centre *via* triazole atom N1 and pyridine atom N51 (Fig. 1), and the two independent dicyanamide (dca) ligands are coordinated *via* atoms N13 and N23. In addition, atom N15 at (*x*, *y*, *z*) coordinates to the Cu^{II} centre at (*x* – 1, *y*, *z*), so completing the square-pyramidal coordination at the Cu^{II} centre (Fig. 2) and generating a one-dimensional coordination polymer running parallel to the [100] direction (Fig. 3), along which the Cu···Cu distance is 7.5946 (5) Å. The behaviour of the two dca ligands thus differs, in that the anion containing atom N11 acts as a bridging ligand between a pair of Cu^{II} centres related by translation, whereas the anion containing atom N21 exhibits no bridging action. Of the five independent Cu–N distances (Table 2), the apical distance Cu1–N15ⁱ [symmetry code: (i) *x* + 1, *y*, *z*] is longer than the remainder, and it is significantly longer than the two basal Cu–N distances (Cu1–N13 and Cu1–N23) which involve the dca ligands.

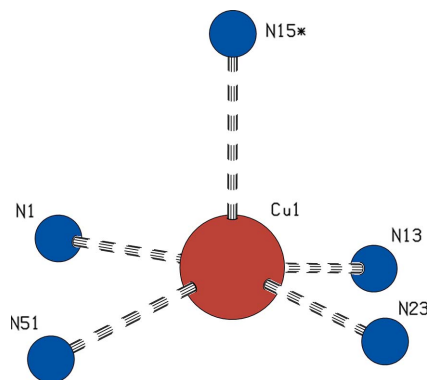
Addison *et al.* (1984) have introduced a simple parameter, denoted τ , which can be used to assess five-coordinate geometries which are intermediate between the idealized trigonal bipyramidal and square-pyramidal forms. For a trigonal bipyramidal geometry, where the bond angles conform exactly to *D*_{3h} ($\bar{6}m2$) symmetry, the value of τ is 1.00, and for a


Figure 1

The selected asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

square-pyramidal geometry, where the bond angles conform exactly to *C*_{4v} (*4mm*) symmetry, the value of τ is 0.00. In compound (I), the value of τ is 0.249, indicating a coordination geometry which approximates much more closely to square-pyramidal than trigonal bipyramidal (Fig. 2). For mutually *cis* pairs of ligand atoms, the bond angles at the Cu^{II} centre (Table 2, and Figs. 1 and 2) range from 78.77 (7) to 94.20 (8)° within the basal ligand group (atoms N1, N51, N13 and N23), and from 95.15 (7) to 105.20 (8)° for the angles between apical atom N15ⁱ and the basal atoms.

Within the triazole ring, the four independent N–C distances (Table 2) span a rather small range, *ca* 0.06 Å, despite the fact that the N1–C5 and N2–C3 bonds are formally double bonds, whereas the N4–C3 and N4–C5 bonds are formally single bonds; these observations point to a considerable degree of aromatic delocalization within this


Figure 2

Part of the crystal structure of (I), showing the square-pyramidal coordination at atom Cu1. The atom marked with an asterisk (*) is at the symmetry position (*x* + 1, *y*, *z*).

Table 2
 Selected geometric parameters (Å, °).

Cu1—N1	1.9727 (16)	N4—N41	1.421 (2)
Cu1—N13	1.9737 (18)	N11—C12	1.297 (3)
Cu1—N23	1.9447 (18)	C12—N13	1.157 (3)
Cu1—N51	2.0912 (17)	N11—C14	1.301 (3)
Cu1—N15 ⁱ	2.1534 (19)	C14—N15	1.155 (3)
N1—N2	1.364 (2)	N21—C22	1.288 (3)
N2—C3	1.317 (2)	C22—N23	1.151 (3)
C3—N4	1.377 (3)	N21—C24	1.315 (3)
N4—C5	1.347 (2)	C24—N25	1.147 (3)
C5—N1	1.316 (2)		
N1—Cu1—N51	78.77 (7)	C12—N11—C14	119.6 (2)
N1—Cu1—N13	89.47 (7)	N11—C12—N13	175.4 (3)
N13—Cu1—N23	94.20 (8)	N11—C14—N15	173.7 (2)
N23—Cu1—N51	92.58 (7)	C22—N21—C24	124.3 (2)
N1—Cu1—N23	167.27 (8)	N21—C22—N23	171.4 (2)
N13—Cu1—N51	152.33 (7)	N21—C24—N25	171.1 (3)
N1—Cu1—N15 ⁱ	95.15 (7)	C12—N13—Cu1	147.64 (17)
N13—Cu1—N15 ⁱ	105.20 (8)	C14—N15—Cu1 ⁱⁱ	164.63 (18)
N23—Cu1—N15 ⁱ	95.64 (8)	C22—N23—Cu1	174.51 (19)
N51—Cu1—N15 ⁱ	100.77 (7)		
N2—C3—C32—N31	−168.69 (18)	N1—C5—C52—N51	−5.0 (3)

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

ring. Amine atom N4 is markedly pyramidal, with a sum of bond angles of 317.8°, but despite this, atom N41 does not act as a hydrogen-bond acceptor. The non-H atoms of the bis(pyridinyl)triazole ligand are fairly close to being coplanar; the dihedral angles between the planes of the triazole ring and the pyridine rings containing atoms N31 and N51 are 9.72 (11) and 6.38 (11)°, respectively, while the dihedral angle between the planes of the two pyridine rings is only 3.53 (11)°.

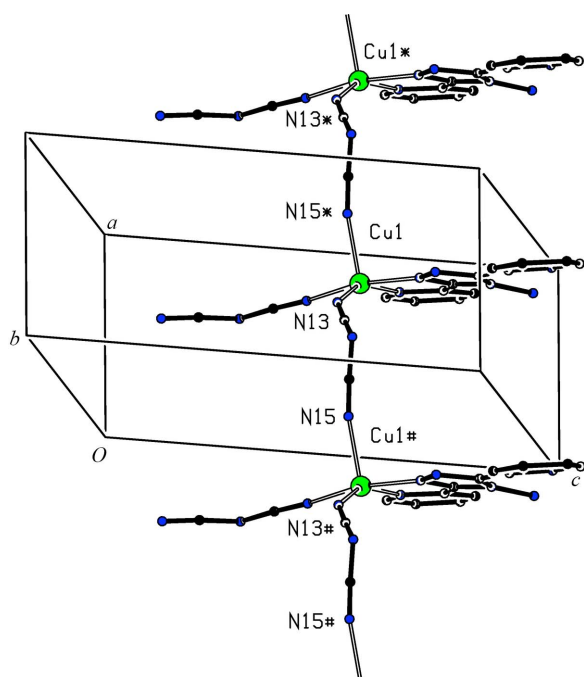

Figure 3
 Part of the crystal structure of compound (I), showing the formation of a coordination polymer chain along [100]. For the sake of clarity, H atoms have all been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x + 1, y, z)$ and $(x - 1, y, z)$, respectively.

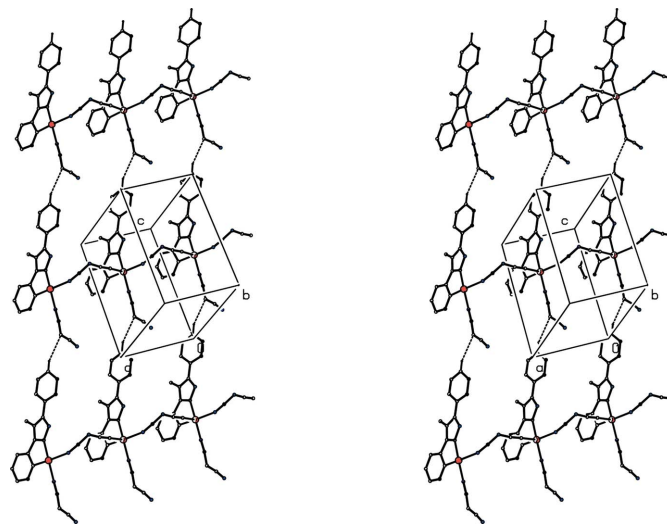
Table 3
 Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N41—H41A \cdots N25 ⁱⁱⁱ	0.89	2.26	3.067 (3)	151
N41—H41B \cdots N31	0.91	2.08	2.834 (2)	139
C35—H35 \cdots N21 ^{iv}	0.95	2.61	3.499 (3)	155
C54—H54 \cdots N2 ^v	0.95	2.61	3.260 (3)	126

 Symmetry codes: (iii) $-x + 1, -y, -z + 1$; (iv) $x, y + 1, z + 1$; (v) $x, y - 1, z$.

In the bridging dca ligand, the N11—C12 and N11—C14 distances are identical within experimental uncertainty (Table 2), but in the terminal ligand the corresponding distances are significantly different. This indicates that for the terminal ligand, in addition to any contribution from the symmetrical form (A), there are unequal contributions from the two canonical forms (B) and (C) (see Scheme), such that the anionic terminus is bonded to the Cu^{II} centre. On the other hand, the bridging ligand has equal contributions from the two forms (B) and (C).

There is a short intramolecular N—H \cdots N interaction (Table 3) which may be associated with the near coplanarity of the rings containing atoms N1 and N31. The coordination polymer chains are linked into bilayers by a combination of N—H \cdots N and C—H \cdots N hydrogen bonds, and it is convenient to consider the C—H \cdots N hydrogen bond first, although this is probably the weaker of the two. The C—H \cdots N hydrogen bond, which has atom N21 as the acceptor, links the coordination polymer chains related by translation along the [011] direction *via* a $C(12)$ (Bernstein *et al.*, 1995) motif to form a sheet lying parallel to (01 $\bar{1}$) and built from a single type of 36-membered ring (Fig. 3). Inversion-related pairs of these sheets are linked into bilayers by an intermolecular N—H \cdots N hydrogen bond in an $R_2^2(22)$ motif (Fig. 4). It may be worth noting that, in both of these hydrogen bonds, the acceptor N


Figure 4
 A stereoview of part of the crystal structure of (I), showing the sheet parallel to (01 $\bar{1}$) formed from the linking of coordination polymer chains by C—H \cdots N hydrogen bonds. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

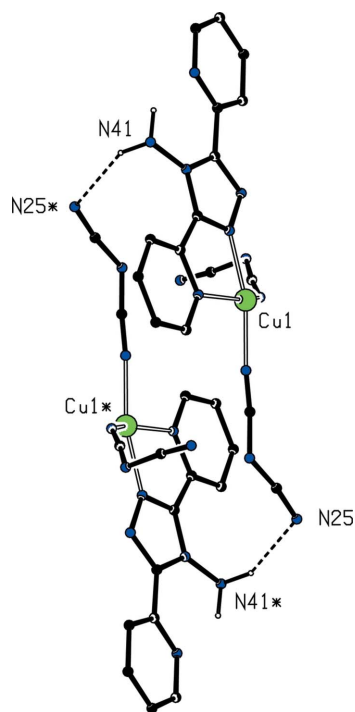


Figure 5

Part of the crystal structure of (I), showing the formation of the centrosymmetric $R_2^2(22)$ motif which links the $(01\bar{1})$ sheets into a bilayer. For the sake of clarity, the unit-cell outline and H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(-x + 1, -y, -z + 1)$.

atom lies in the terminal dca ligand. There is a second short intermolecular C—H...N contact present, this time involving triazole atom N2, but the C—H...N angle is only 126° (Table 3), so this contact cannot be regarded as structurally significant (Wood *et al.*, 2009).

The hydrogen-bonded bilayer is reinforced by two π – π stacking interactions, both of which involve pairs of rings, one in each component sheet of the bilayer. The N31/C32–C36 pyridine rings at (x, y, z) and $(-x + 1, -y + 1, -z + 2)$ are strictly parallel, with an interplanar separation of 3.278 Å; the ring-centroid separation is 3.5326 (13) Å, corresponding to a ring-centroid offset of 1.318 Å. The planes of the triazole ring at (x, y, z) and the N31/C32–C36 pyridine ring at $(-x + 2, -y + 1, -z + 2)$ make a dihedral angle of 9.71° , and the shortest perpendicular distance from the centroid of one ring to the plane of the other is *ca* 3.17 Å. The ring-centroid separation is 3.6130 (13) Å, corresponding to a ring-centroid offset of *ca* 1.73 Å, indicative of only a rather weak interaction.

It is of interest briefly to compare the structure of (I) reported here with those of some related Cu^{II} compounds also containing dca ligands, where fairly minor changes in the constitution of the nonbridging heteroaromatic co-ligands lead to quite wide variations in the nature of the supramolecular assembly. Thus, in $[\text{Cu}(\text{dca})_2(\text{Hambi})]$, (II), where Hambi represents 2-(aminomethyl)benzimidazole, the Cu^{II} cation lies on a centre of inversion in the space group $P\bar{1}$ (He *et al.*, 2003). The bidentate Hambi ligands occupy the equa-

torial sites in an axially elongated (4+2) coordination polyhedron, and the apical sites are occupied by dca ligands coordinated *via* the central N atoms, as opposed to the terminal N atoms which are involved in (I). There is no further coordination to Cu^{II} , so the aggregation can be regarded as finite or zero-dimensional. Finite zero-dimensional aggregation is also observed in $[\text{Cu}(\text{bpca})(\text{dca})(\text{H}_2\text{O})]$, (III), where bpca represents bis(pyridin-2-ylcarbonyl)amidate (Vangdal *et al.*, 2002). Here, inversion-related pairs of Cu^{II} centres are linked by inversion-related pairs of bidentate dca ligands coordinated *via* the central N atom and one of the terminal atoms, so forming a dimeric unit containing an eight-membered ring structure.

In the complex $[\text{Cu}(\text{dca})_2(2,2'\text{-bipyridyl})]$, (IV) (Potočňák *et al.*, 2002; Vangdal *et al.*, 2002), the two dca ligands adopt different coordination modes, one acting as a bidentate bridging ligand while the other is monodentate. Only the terminal N atoms of the dca ligands are involved in metal coordination, as found in (I), but this differs from the bridging action found in (III). A one-dimensional coordination polymer thus results in (IV), analogous to that in (I), but whereas the Cu^{II} centres along the polymer chain in (I) are related by translation, those in (IV) are related by a glide plane: the Cu...Cu distances along the chain in (IV) were reported as 8.212 (1) (Potočňák *et al.*, 2002) and 8.1999 (8) Å (Vangdal *et al.*, 2002), slightly longer than the corresponding distance of 7.5946 (5) Å in (I). Chains similar to those in (I) are observed in $[\text{Cu}(\text{dca})_2(5,5'\text{-dimethyl-2,2'-bipyridyl})]$, (V) (Kooijman *et al.*, 2002), with a Cu...Cu distance between Cu centres related by translation along the chain of 7.5297 (10) Å, and in $[\text{Cu}(\text{dca})_2(\text{dpa})]$, (VI) (dpa is 2,2-dipyridinylamine; Carranza *et al.*, 2002), with an intrachain Cu...Cu distance of 7.689 (2) Å.

A more complex one-dimensional coordination polymer is present in $[\text{Cu}(\text{dca})_2(2,2'\text{-bipyrimidyl})]$, (VII) (Vangdal *et al.*, 2002), the composition of which differs from that of (IV) only in the number of N atoms in the heteroaromatic rings. In (VII), the 2,2'-bipyrimidyl ligand, which lies across a centre of inversion in the space group $P2_1/c$, acts as a bis-bidentate ligand towards two inversion-related Cu^{II} centres; as in compounds (I) and (IV)–(VI), the dca ligands coordinate only *via* the terminal N atoms, where one is monodentate and the other bidentate. The bidentate dca ligand links two Cu^{II} centres related by translation, and the combination of translation and inversion generates a molecular ladder structure in the form of a chain of centrosymmetric edge-fused 20-membered rings. The shortest Cu...Cu distance along the ladder is 7.555 (2) Å, while the distance between two Cu^{II} centres sharing a common 2,2'-bipyrimidyl ligand is 5.5673 (4) Å. In $[\text{Cu}(\text{dca})_2(2\text{-aminopyridine})_2]$, (VIII) (van Albada *et al.*, 2000), both dca ligands are bidentate, coordinating *via* the terminal N atoms and producing a chain of spiro-fused 12-membered rings with an intrachain Cu...Cu distance of 7.570 Å (no s.u. value was given).

The constitution of $[\text{Cu}(\text{dca})_2(1,10\text{-phen})]$, (IX) (1,10-phen is 1,10-phenanthroline; Wang *et al.*, 2000; Luo, Hong, Weng *et al.*, 2002), differs from that of (IV) only in the presence of an additional ring in the heteroaromatic ligand. However, the

resulting coordination polymer is now two-dimensional, forming a sheet containing equal numbers of 12- and 36-membered rings, in which both dca ligands are bidentate, again using only the terminal N atoms. The six-coordination of the Cu^{II} centre is very distorted, with axial Cu–N distances of 2.287 (4) and 2.821 (4) Å. The two shortest Cu···Cu distances within the sheet are 7.3002 (7) and 7.7079 (4) Å (Wang *et al.*, 2000). It may be noted here that the structure of the cadmium analogue of (IX), [Cd(dca)₂(1,10-phen)], has also been reported (Luo, Hong, Cao *et al.*, 2002), and this compound appears to be isostructural with the Cu analogue, with axially elongated (4+2) coordination at the Cd atom. This striking and rather unexpected similarity was not noted in the almost simultaneous reports (Luo, Hong, Weng *et al.*, 2002; Luo, Hong, Cao *et al.*, 2002) on these structures.

The dca ligand contains only five atoms but, despite this simplicity, four distinct modes of coordination to Cu^{II} can be identified in compounds (I)–(IX): (a) monodentate coordination *via* the central N atom (μ_3 -coordination) (Batten & Murray, 2003); (b) monodentate coordination *via* one of the terminal N atoms (μ_1 -coordination); (c) bidentate coordination *via* the central N atom and one of the terminal N atoms ($\mu_{1,3}$ -coordination); (d) bidentate coordination *via* the two terminal N atoms ($\mu_{1,5}$ -coordination). Mode (a) is the sole form observed in the mononuclear compound (II), and mode (c) is the sole form observed in the binuclear compound (III) and in the chain polymer (VII). Modes (b) and (d) occur together in compounds (I) and (IV)–(VIII), each of which forms a one-dimensional coordination polymer, while mode (d) is the sole form observed in (IX), where the coordination polymer is two-dimensional. Accordingly, dca appears to be a versatile ligand, as indicated by both the various coordination modes available, either singly or in combination, and the wide variety of coordination architectures which can result.

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supplementary materials

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catena-Poly[[[4-amino-3,5-bis(pyridin-2-yl)-4H-1,2,4-triazole- κ^2N^1,N^5](dicyanamido- κN)copper(II)]- μ_2 -dicyanamido- $\kappa^2N:N'$]: coordination polymer chains linked into a bilayer by hydrogen bonds and π - π stacking interactions

Zouaoui Setifi, Fatima Setifi, Mohamed Saadi, Djamil-Azzeddine Rouag and Christopher Glidewell

Computing details

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO* (Agilent, 2013); data reduction: *CrysAlis PRO* (Agilent, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

catena-Poly[[[4-amino-3,5-bis(pyridin-2-yl)-4H-1,2,4-triazole- κ^2N^1,N^5](dicyanamido- κN)copper(II)]- μ_2 -dicyanamido- $\kappa^2N:N'$]

Crystal data

[Cu(C₂N₃)₂(C₁₂H₁₀N₆)]

$M_r = 433.91$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 7.5946$ (5) Å

$b = 8.4284$ (5) Å

$c = 14.1106$ (8) Å

$\alpha = 96.668$ (4)°

$\beta = 101.019$ (5)°

$\gamma = 102.962$ (4)°

$V = 851.96$ (9) Å³

$Z = 2$

$F(000) = 438$

$D_x = 1.691$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 6098 reflections

$\theta = 2.5$ – 32.5 °

$\mu = 1.32$ mm⁻¹

$T = 150$ K

Block, blue

$0.25 \times 0.22 \times 0.22$ mm

Data collection

Agilent Xcalibur

diffractometer

Graphite monochromator

ω scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 2003)

$T_{\min} = 0.694$, $T_{\max} = 0.749$

13231 measured reflections

6097 independent reflections

4835 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.048$

$\theta_{\max} = 32.5$ °, $\theta_{\min} = 2.5$ °

$h = -11 \rightarrow 11$

$k = -12 \rightarrow 12$

$l = -21 \rightarrow 20$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.101$
 $S = 1.06$
 6097 reflections
 262 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
 $w = 1/[\sigma^2(F_o^2) + (0.0355P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.59 \text{ e } \text{\AA}^{-3}$

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.75026 (3)	0.22702 (3)	0.601776 (17)	0.01768 (8)
N1	0.7736 (2)	0.2875 (2)	0.74376 (12)	0.0170 (3)
N2	0.7463 (2)	0.4178 (2)	0.80088 (12)	0.0183 (3)
C3	0.7618 (3)	0.3802 (2)	0.88962 (14)	0.0172 (4)
N4	0.7979 (2)	0.2274 (2)	0.89006 (11)	0.0167 (3)
C5	0.8072 (3)	0.1757 (2)	0.79761 (14)	0.0163 (4)
N11	0.3537 (3)	0.5046 (2)	0.63214 (14)	0.0287 (4)
C12	0.4691 (3)	0.4291 (3)	0.60224 (15)	0.0206 (4)
N13	0.5809 (2)	0.3718 (2)	0.57711 (12)	0.0239 (4)
C14	0.1779 (3)	0.4303 (3)	0.61239 (14)	0.0208 (4)
N15	0.0202 (3)	0.3759 (2)	0.60091 (13)	0.0267 (4)
N21	0.6398 (3)	-0.0063 (2)	0.29552 (14)	0.0325 (5)
C22	0.6667 (3)	0.0704 (3)	0.38353 (15)	0.0216 (4)
N23	0.6942 (3)	0.1209 (2)	0.46577 (13)	0.0287 (4)
C24	0.5993 (3)	0.0588 (3)	0.21636 (16)	0.0249 (5)
N25	0.5623 (3)	0.0958 (3)	0.14076 (14)	0.0345 (5)
N31	0.8001 (2)	0.4446 (2)	1.06232 (12)	0.0219 (4)
C32	0.7492 (3)	0.4897 (2)	0.97524 (14)	0.0177 (4)
C33	0.6868 (3)	0.6302 (3)	0.96337 (15)	0.0215 (4)
H33	0.6522	0.6576	0.9002	0.026*
C34	0.6767 (3)	0.7294 (3)	1.04667 (16)	0.0257 (5)
H34	0.6362	0.8275	1.0418	0.031*
C35	0.7263 (3)	0.6835 (3)	1.13709 (16)	0.0260 (5)
H35	0.7199	0.7490	1.1953	0.031*
C36	0.7850 (3)	0.5410 (3)	1.14086 (15)	0.0251 (5)
H36	0.8168	0.5093	1.2030	0.030*
N41	0.8140 (3)	0.1338 (2)	0.96739 (12)	0.0232 (4)
H41A	0.7058	0.0592	0.9580	0.028*
H41B	0.8217	0.2051	1.0224	0.028*
N51	0.8200 (2)	0.0212 (2)	0.65314 (12)	0.0190 (3)
C52	0.8430 (3)	0.0252 (2)	0.75076 (14)	0.0177 (4)
C53	0.8977 (3)	-0.0954 (3)	0.79808 (16)	0.0232 (4)
H53	0.9144	-0.0875	0.8671	0.028*
C54	0.9277 (3)	-0.2290 (3)	0.74188 (18)	0.0274 (5)
H54	0.9657	-0.3147	0.7720	0.033*

C55	0.9019 (3)	-0.2361 (3)	0.64206 (17)	0.0277 (5)
H55	0.9201	-0.3274	0.6024	0.033*
C56	0.8493 (3)	-0.1087 (3)	0.60037 (16)	0.0239 (4)
H56	0.8332	-0.1137	0.5316	0.029*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01992 (13)	0.02354 (14)	0.01221 (12)	0.01002 (10)	0.00448 (9)	0.00316 (9)
N1	0.0205 (8)	0.0179 (8)	0.0148 (8)	0.0081 (7)	0.0053 (6)	0.0031 (6)
N2	0.0236 (9)	0.0183 (8)	0.0153 (8)	0.0077 (7)	0.0068 (7)	0.0027 (7)
C3	0.0161 (9)	0.0194 (9)	0.0171 (9)	0.0050 (7)	0.0046 (7)	0.0042 (8)
N4	0.0203 (8)	0.0176 (8)	0.0139 (7)	0.0061 (7)	0.0047 (6)	0.0051 (6)
C5	0.0163 (9)	0.0186 (9)	0.0147 (9)	0.0046 (7)	0.0044 (7)	0.0034 (7)
N31	0.0218 (9)	0.0280 (9)	0.0156 (8)	0.0081 (7)	0.0028 (7)	0.0013 (7)
C32	0.0162 (9)	0.0208 (10)	0.0153 (9)	0.0029 (8)	0.0051 (7)	0.0015 (8)
C33	0.0240 (10)	0.0213 (10)	0.0209 (10)	0.0055 (8)	0.0089 (8)	0.0037 (8)
C34	0.0284 (11)	0.0204 (10)	0.0290 (11)	0.0047 (9)	0.0121 (9)	0.0002 (9)
C35	0.0257 (11)	0.0283 (11)	0.0224 (10)	0.0054 (9)	0.0082 (9)	-0.0046 (9)
C36	0.0247 (11)	0.0352 (12)	0.0149 (9)	0.0089 (9)	0.0031 (8)	0.0015 (9)
N41	0.0317 (10)	0.0251 (9)	0.0157 (8)	0.0097 (8)	0.0062 (7)	0.0093 (7)
N51	0.0201 (8)	0.0201 (8)	0.0177 (8)	0.0073 (7)	0.0049 (7)	0.0016 (7)
C52	0.0161 (9)	0.0186 (9)	0.0196 (9)	0.0048 (7)	0.0058 (7)	0.0038 (8)
C53	0.0251 (11)	0.0238 (10)	0.0247 (11)	0.0083 (9)	0.0085 (9)	0.0105 (9)
C54	0.0305 (12)	0.0190 (10)	0.0376 (13)	0.0100 (9)	0.0123 (10)	0.0099 (9)
C55	0.0297 (12)	0.0196 (10)	0.0344 (12)	0.0084 (9)	0.0090 (10)	-0.0008 (9)
C56	0.0268 (11)	0.0228 (10)	0.0223 (10)	0.0085 (9)	0.0062 (9)	-0.0011 (9)
N11	0.0234 (10)	0.0299 (10)	0.0340 (11)	0.0084 (8)	0.0121 (8)	-0.0026 (9)
C12	0.0198 (10)	0.0250 (10)	0.0174 (9)	0.0052 (8)	0.0044 (8)	0.0058 (8)
N13	0.0243 (9)	0.0339 (10)	0.0176 (8)	0.0143 (8)	0.0042 (7)	0.0074 (8)
C14	0.0284 (11)	0.0257 (11)	0.0139 (9)	0.0140 (9)	0.0092 (8)	0.0044 (8)
N15	0.0240 (10)	0.0350 (11)	0.0248 (9)	0.0108 (8)	0.0098 (8)	0.0059 (8)
N21	0.0501 (13)	0.0296 (11)	0.0158 (9)	0.0115 (10)	0.0033 (8)	-0.0008 (8)
C22	0.0221 (10)	0.0218 (10)	0.0213 (10)	0.0069 (8)	0.0042 (8)	0.0039 (8)
N23	0.0382 (11)	0.0317 (10)	0.0190 (9)	0.0146 (9)	0.0058 (8)	0.0046 (8)
C24	0.0242 (11)	0.0238 (11)	0.0219 (11)	0.0016 (9)	0.0051 (9)	-0.0057 (9)
N25	0.0428 (12)	0.0361 (12)	0.0212 (10)	0.0064 (10)	0.0044 (9)	0.0026 (9)

Geometric parameters (\AA , $^\circ$)

Cu1—N1	1.9727 (16)	C36—H36	0.9500
Cu1—N13	1.9737 (18)	N41—H41A	0.8918
Cu1—N23	1.9447 (18)	N41—H41B	0.9089
Cu1—N51	2.0912 (17)	N51—C56	1.336 (3)
Cu1—N15 ⁱ	2.1534 (19)	N51—C52	1.350 (2)
N1—N2	1.364 (2)	C52—C53	1.376 (3)
N2—C3	1.317 (2)	C53—C54	1.388 (3)
C3—N4	1.377 (3)	C53—H53	0.9500
N4—C5	1.347 (2)	C54—C55	1.377 (3)
C5—N1	1.316 (2)	C54—H54	0.9500

N4—N41	1.421 (2)	C55—C56	1.381 (3)
C3—C32	1.464 (3)	C55—H55	0.9500
C5—C52	1.465 (3)	C56—H56	0.9500
N31—C36	1.335 (3)	N11—C12	1.297 (3)
N31—C32	1.340 (3)	C12—N13	1.157 (3)
C32—C33	1.386 (3)	N11—C14	1.301 (3)
C33—C34	1.386 (3)	C14—N15	1.155 (3)
C33—H33	0.9500	N15—Cu1 ⁱⁱ	2.1534 (19)
C34—C35	1.384 (3)	N21—C22	1.288 (3)
C34—H34	0.9500	C22—N23	1.151 (3)
C35—C36	1.374 (3)	N21—C24	1.315 (3)
C35—H35	0.9500	C24—N25	1.147 (3)
N1—Cu1—N51	78.77 (7)	C34—C35—H35	120.7
N1—Cu1—N13	89.47 (7)	N31—C36—C35	123.9 (2)
N13—Cu1—N23	94.20 (8)	N31—C36—H36	118.0
N23—Cu1—N51	92.58 (7)	C35—C36—H36	118.0
N1—Cu1—N23	167.27 (8)	N4—N41—H41A	106.8
N13—Cu1—N51	152.33 (7)	N4—N41—H41B	105.2
N1—Cu1—N15 ⁱ	95.15 (7)	H41A—N41—H41B	105.8
N13—Cu1—N15 ⁱ	105.20 (8)	C56—N51—C52	117.69 (18)
N23—Cu1—N15 ⁱ	95.64 (8)	C56—N51—Cu1	126.98 (14)
N51—Cu1—N15 ⁱ	100.77 (7)	C52—N51—Cu1	115.29 (13)
C5—N1—N2	109.55 (16)	N51—C52—C53	123.38 (19)
C5—N1—Cu1	116.22 (13)	N51—C52—C5	110.82 (17)
N2—N1—Cu1	133.94 (13)	C53—C52—C5	125.77 (19)
C3—N2—N1	105.99 (16)	C52—C53—C54	117.9 (2)
N2—C3—N4	110.10 (17)	C52—C53—H53	121.0
N2—C3—C32	124.22 (18)	C54—C53—H53	121.0
N4—C3—C32	125.63 (18)	C55—C54—C53	119.3 (2)
C5—N4—C3	105.43 (16)	C55—C54—H54	120.3
C5—N4—N41	124.93 (16)	C53—C54—H54	120.3
C3—N4—N41	129.57 (16)	C54—C55—C56	119.2 (2)
N1—C5—N4	108.89 (17)	C54—C55—H55	120.4
N1—C5—C52	118.64 (17)	C56—C55—H55	120.4
N4—C5—C52	132.45 (18)	N51—C56—C55	122.5 (2)
C36—N31—C32	116.81 (19)	N51—C56—H56	118.7
N31—C32—C33	123.82 (18)	C55—C56—H56	118.7
N31—C32—C3	116.13 (18)	C12—N11—C14	119.6 (2)
C33—C32—C3	120.04 (18)	N11—C12—N13	175.4 (3)
C34—C33—C32	117.8 (2)	N11—C14—N15	173.7 (2)
C34—C33—H33	121.1	C22—N21—C24	124.3 (2)
C32—C33—H33	121.1	N21—C22—N23	171.4 (2)
C35—C34—C33	119.1 (2)	N21—C24—N25	171.1 (3)
C35—C34—H34	120.4	C12—N13—Cu1	147.64 (17)
C33—C34—H34	120.4	C14—N15—Cu1 ⁱⁱ	164.63 (18)
C36—C35—C34	118.5 (2)	C22—N23—Cu1	174.51 (19)
C36—C35—H35	120.7		

N23—Cu1—N1—C5	44.0 (4)	C32—C33—C34—C35	-0.8 (3)
N13—Cu1—N1—C5	150.98 (15)	C33—C34—C35—C36	0.4 (3)
N51—Cu1—N1—C5	-3.82 (14)	C32—N31—C36—C35	-1.9 (3)
N15 ⁱ —Cu1—N1—C5	-103.81 (15)	C34—C35—C36—N31	1.1 (3)
N23—Cu1—N1—N2	-128.9 (3)	N23—Cu1—N51—C56	12.70 (19)
N13—Cu1—N1—N2	-21.96 (18)	N1—Cu1—N51—C56	-176.71 (19)
N51—Cu1—N1—N2	-176.76 (19)	N13—Cu1—N51—C56	116.8 (2)
N15 ⁱ —Cu1—N1—N2	83.25 (18)	N15 ⁱ —Cu1—N51—C56	-83.54 (18)
C5—N1—N2—C3	-0.9 (2)	N23—Cu1—N51—C52	-169.56 (15)
Cu1—N1—N2—C3	172.42 (15)	N1—Cu1—N51—C52	1.02 (14)
N1—N2—C3—N4	-0.2 (2)	N13—Cu1—N51—C52	-65.5 (2)
N1—N2—C3—C32	177.54 (17)	N15 ⁱ —Cu1—N51—C52	94.20 (15)
N2—C3—N4—C5	1.2 (2)	C56—N51—C52—C53	1.2 (3)
C32—C3—N4—C5	-176.55 (18)	Cu1—N51—C52—C53	-176.76 (16)
N2—C3—N4—N41	-175.82 (18)	C56—N51—C52—C5	179.54 (18)
C32—C3—N4—N41	6.5 (3)	Cu1—N51—C52—C5	1.6 (2)
N2—N1—C5—N4	1.6 (2)	N1—C5—C52—N51	-5.0 (3)
Cu1—N1—C5—N4	-172.98 (12)	N4—C5—C52—N51	173.8 (2)
N2—N1—C5—C52	-179.29 (16)	N1—C5—C52—C53	173.32 (19)
Cu1—N1—C5—C52	6.1 (2)	N4—C5—C52—C53	-7.9 (4)
C3—N4—C5—N1	-1.7 (2)	N51—C52—C53—C54	-1.1 (3)
N41—N4—C5—N1	175.48 (17)	C5—C52—C53—C54	-179.15 (19)
C3—N4—C5—C52	179.4 (2)	C52—C53—C54—C55	0.0 (3)
N41—N4—C5—C52	-3.4 (3)	C53—C54—C55—C56	0.9 (3)
C36—N31—C32—C33	1.4 (3)	C52—N51—C56—C55	-0.2 (3)
C36—N31—C32—C3	-178.40 (18)	Cu1—N51—C56—C55	177.45 (16)
N2—C3—C32—N31	-168.69 (18)	C54—C55—C56—N51	-0.8 (3)
N4—C3—C32—N31	8.7 (3)	N23—Cu1—N13—C12	136.6 (3)
N2—C3—C32—C33	11.5 (3)	N1—Cu1—N13—C12	-31.2 (3)
N4—C3—C32—C33	-171.04 (19)	N51—Cu1—N13—C12	32.9 (4)
N31—C32—C33—C34	0.0 (3)	N15 ⁱ —Cu1—N13—C12	-126.4 (3)
C3—C32—C33—C34	179.72 (18)		

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N41—H41A \cdots N25 ⁱⁱⁱ	0.89	2.26	3.067 (3)	151
N41—H41B \cdots N31	0.91	2.08	2.834 (2)	139
C35—H35 \cdots N21 ^{iv}	0.95	2.61	3.499 (3)	155
C54—H54 \cdots N2 ^v	0.95	2.61	3.260 (3)	126

Symmetry codes: (iii) $-x+1, -y, -z+1$; (iv) $x, y+1, z+1$; (v) $x, y-1, z$.