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catena-Poly[[bis(4-aminopyrimidine-κN^1)-copper(II)]-di-μ-dicyanamido-$\kappa^4 N^1$:N^3]

Jozef Kožíšek,[a]* Jesús García Díaz,[b] Marek Fronc[a] and Ingrid Svoboda[c]

[a]Department of Physical Chemistry, Slovak University of Technology, Radlinského 9, SK-812 37 Bratislava, Slovak Republic, [b]Department of Materials, Technological Institute of Morelia, Michoacán, Mexico, and [c]Strukturforschung, FB11 Material- und Geowissenschaften, Technische Universität Darmstadt, Petersenstraße 23, D-64287 Darmstadt, Germany

Correspondence e-mail: kozisek@cvt.stuba.sk

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Key indicators

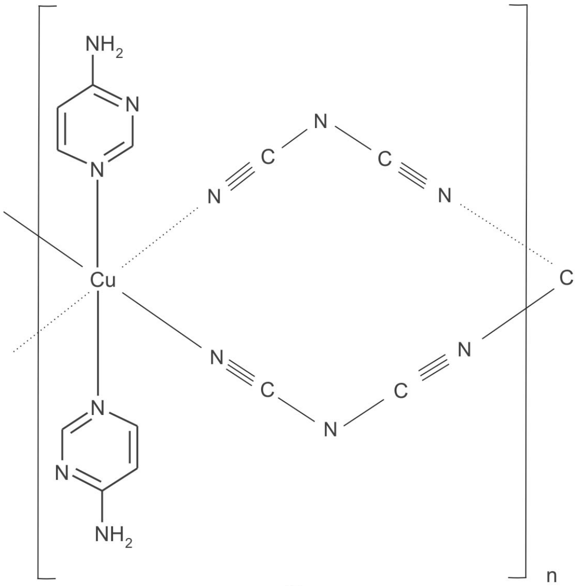
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.025
wR factor = 0.064
Data-to-parameter ratio = 14.8

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

In the title octahedral complex, $[\mathrm{Cu}\{\mathrm{N(CN)_2}\}_2(\mathrm{ampym})_2]_n$ (ampym is 4-aminopyrimidine, $C_4H_5N_3$), the Cu atom is located on an inversion centre and is coordinated in the equatorial plane by two dicyanamide nitrile N atoms and two N atoms from ampym ligands [Cu—N = 1.972 (2) and 2.001 (2) Å, respectively], and in the axial positions by another two dicyanamide nitrile N atoms, at 2.633 (2) Å. Neighbouring Cu atoms are connected *via* double dicyanamide bridges to form a one-dimensional infinite chain.

Comment

In coordination compounds of Cu^{II} and Cu^{I}, the dicyanamide (dca$^-$) anion, $(\mathrm{N(CN)_2})^-$, exhibits a rich variety of bonding modes. It can coordinate either in a monodentate manner (*e.g.* Burčák *et al.*, 2004) or, more typically, in a bidentate manner [two types of binding: mainly through two nitrile N atoms (Potočňák *et al.*, 2002), but also through one amide and one nitrile N atom (Mohamadou *et al.*, 2003)], or even in a tridentate manner in the case of Cu^{I} (Batten *et al.*, 2000).



(I)

4-Aminopyrimidine and derived neutral ligands can also be coordinated either in monodentate mode (*e.g.* Manson *et al.*, 2003) or in bridging mode, as recently reported for $\mathrm{Cu(HCO_2)_2(pyrimidine)}$ (Manson *et al.*, 2005). In the title compound, (I), the bridging mode of dca$^-$ ligands seems to be preferred to the bridging mode of 4-aminopyrimidine.

The geometry around the Cu^{II} ion in (I) is tetrahedrally elongated octahedral (the Cu atom lies on an inversion centre), with the equatorial plane formed by two nitrile N

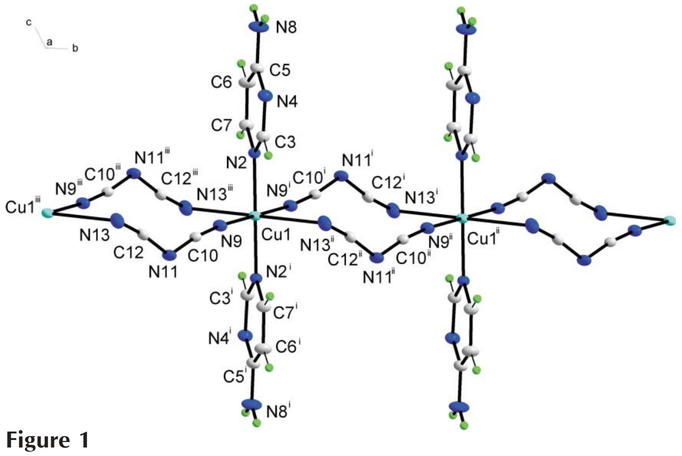


Figure 1
The atom-numbering scheme of the title compound, with displacement ellipsoids at the 50% probability level [symmetry codes: (i) $-x, -y, -z$; (ii) $x, 1 + y, z$; (iii) $-x, -1 - y, -z$].

atoms from dicyanamides and two other N atoms from neutral ligands. Axial positions are occupied by another two nitrile dicyanamide N atoms. Neighbouring Cu atoms are connected *via* double dicyanamide bridges to form a one-dimensional infinite chain in the *b*-axis direction (Fig. 1).

In the Cambridge Structural Database (CSD; Version 5.26; Allen, 2002), there are four crystal structures of the type $[\text{Cu}\{\text{N(CN)}_2\}_2L_2]$ (L = neutral *N*-donor ligand), with the chromophore $[\text{CuN}_6]$, the neighbouring Cu atoms connected *via* double dicyanamide bridges and with an *R* value lower than 0.05. In two of them [CSD refcodes KEQWIM (van Albada *et al.*, 2000) and MEBFEE (Jensen *et al.*, 1999)], there are two dca$^-$ ligands coordinated in the equatorial plane (Cu—N = 1.972 and 1.966 Å) and two others in axial positions (Cu—N = 2.417 and 2.420 Å). Cu—*L* distances are 2.078 and 2.051 Å, respectively. In the present crystal structure, (I), the corresponding distances are Cu1—N9 1.972 (2) Å, Cu1—N13 2.633 (2) Å and Cu1—N2 2.001 (2) Å. In the crystal structure EDALAW (van Albada *et al.*, 2001), the Cu atom lies on a general position with corresponding Cu—N distances 1.983, 1.988, 2.313, 2.967, 2.008 and 2.023 Å, respectively. In the crystal structure PAHWAX (Luo *et al.*, 2004), all dca$^-$ ligands are found in the equatorial plane (Cu—N = 2.003 and 2.005 Å) and the neutral quinoxaline ligand is coordinated in the axial position (Cu—N = 2.479 Å).

The ampym rings in the unit cell of (I) are aligned parallel, approximately perpendicular to the *b* axis, so the distance between these rings is larger than 3.6 Å and does not indicate any π–π interaction. The crystal structure is stabilized by hydrogen bonds (Table 2), which, together with double dicyanamide bridges, form a three-dimensional network (Fig. 2).

Inspection of the interatomic distances (Table 1) shows an extended delocalized π-system N11/C10/N9/Cu1/N2/C3/N4/C5/N8. The bond length N4—C3 [1.320 (2) Å] is clearly shorter than that expected for a single bond (for example, 1.349 Å in imidazole). A similar feature was observed for the free ligand 4-aminopyrimidine (Van Meervelt & Uytterhoeven, 2003), where, *via* hydrogen bonds, two one-dimensional infinite chains are formed along the *b* axis ($\text{N}_{\text{ampym}}\cdots\text{H}_{\text{amine}}$ and $\text{N}_{\text{ampym}}\cdots\text{H}_{\text{amine}}\text{—N}_{\text{amine}}$ separations and angles: 2.100/2.134 Å and 176/174° for two independent molecules).

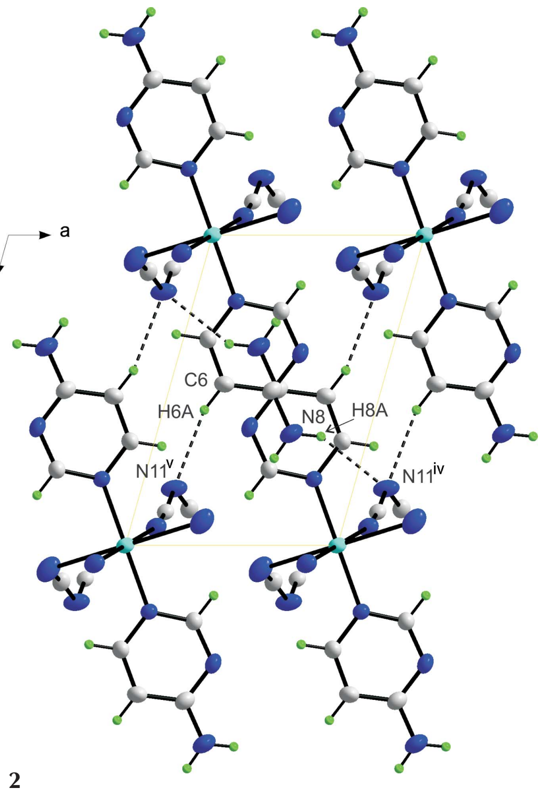


Figure 2
Packing diagram of (I), viewed along the *b* axis. Hydrogen-bond interactions are indicated by dashed lines [symmetry codes: (iv) $1 + x, 1 + y, 1 + z$; (v) $x, 1 + y, 1 + z$].

Experimental

A solution of 2.0 mmol of CuSO_4 in water (3 ml) was mixed with a solution of 4.0 mmol of NaN(CN)_2 in water (10 ml) and with a solution of 4.0 mmol of ampym in ethanol (10 ml). After standing for a few days, blue crystals were isolated (yield: *ca* 10%).

Crystal data

$[\text{Cu(C}_2\text{N}_3)(\text{C}_4\text{H}_5\text{N}_3)]$
$M_r = 385.86$
Triclinic, $P\bar{1}$
$a = 6.260$ (1) Å
$b = 7.248$ (1) Å
$c = 9.451$ (2) Å
$\alpha = 105.29$ (3)°
$\beta = 100.19$ (3)°
$\gamma = 106.27$ (3)°
$V = 382.2$ (1) Å^3
$Z = 1$
$D_x = 1.676$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2020 reflections
$\theta = 3.1$–29.2°
$\mu = 1.45$ mm^{-1}
$T = 293$ (2) K
Block, blue
0.27 × 0.25 × 0.14 mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer
ω scans
Absorption correction: analytical face-indexed (*CrysAlisRED*; Oxford Diffraction, 2003)
$T_{\min} = 0.767$, $T_{\max} = 0.891$
2818 measured reflections
1705 independent reflections
1636 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.024$
$\theta_{\max} = 27.5°$
$h = -8 \rightarrow 8$
$k = -9 \rightarrow 7$
$l = -12 \rightarrow 12$

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.064$
$S = 1.04$
1705 reflections
115 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0264P)^2 + 0.2243P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N2	2.001 (2)	C7—C6	1.352 (3)
Cu1—N9	1.972 (2)	C5—N8	1.334 (3)
Cu1—N13^{iii}	2.633 (2)	C5—C6	1.395 (3)
N2—C3	1.330 (2)	N9—C10	1.143 (2)
N2—C7	1.350 (2)	N11—C10	1.294 (2)
N4—C3	1.320 (2)	N11—C12	1.301 (2)
N4—C5	1.342 (3)	C12—N13	1.146 (2)
N9—Cu1—N2	90.91 (6)	N9—Cu1—N13^{iii}	90.0 (1)
N2—Cu1—N13^{iii}	89.3 (1)		

Symmetry code: (iii) $-x, -1-y, -z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N8—H8$A\cdots$N11^{iv}	0.86	2.378	3.132 (3)	147
C6—H6$A\cdots$N11^{v}	0.93	2.554	3.440 (3)	159

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

H atoms were positioned geometrically and treated as riding atoms, with C—H and N—H distances constrained to 0.93 and 0.86 Å, respectively, and $U_{\rm iso}$(H) values set at $1.2U_{\rm eq}$ of the carrier atom.

Data collection: *CrysAlisCCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlisCCD*; data reduction: *CrysAlisRED* (Oxford Diffraction, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

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References

Albada, G. A. van, Mutikainen, I., Turpeinen, U. & Reedijk, J. (2001). *Acta Cryst.* E**57**, m421–m423.

Albada, G. A. van, Quiroz-Castro, M. E., Mutikainen, I., Turpeinen, U. & Reedijk, J. (2000). *Inorg. Chim. Acta*, **298**, 221–225.

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Batten, S. R., Harris, A. R., Jensen, P., Murray, K. S. & Ziebell, A. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3829–3836.

Brandenburg, K. (1998). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Burčák, M., Potočňák, I., Baran, P. & Jäger, L. (2004). *Acta Cryst.* C**60**, m601–m604.

Jensen, P., Batten, S. R., Fallon, G. D., Hockless, D. C. R., Moubaraki, B., Murray, K. S. & Robson, R. (1999). *J. Solid State Chem.* **145**, 387–393.

Luo, J., Liu, B.-S., Zhou, X.-G., Weng, L.-H., Li, Y.-R. & Wu, H.-X. (2004). *Acta Cryst.* C**60**, m520–m522.

Manson, J. L., Gu, J., Schlueter, J. A. & Wang, H.-H. (2003). *Inorg. Chem.* **42**, 3950–3955.

Manson, J. L., Lancaster, T., Chapon, L. C., Blundell, S. J., Schlueter, J. A., Brooks, M. L., Pratt, F. L., Nygren, C. L. & Qualls, J. S. (2005). *Inorg. Chem.* **44**, 989–995.

Mohamadou, A., van Albada, G. A., Kooijman, H., Wieczorek, B., Spek, A. L. & Reedijk, J. (2003). *New J. Chem.* pp. 983–988.

Oxford Diffraction (2001). *CrysAlisCCD*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

Oxford Diffraction (2003). *CrysAlisRED*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

Potočňák, I., Burčák, M., Massa, W. & Jäger, L. (2002). *Acta Cryst.* C**58**, m523–m528.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Van Meervelt, L. & Uytterhoeven, K. (2003). *Z. Kristallogr. New Cryst. Struct.* **218**, 481–482.

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