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Bis[bis(pyrimidin-2-yl- κ N)amine]- (dicyanamido- κ N¹)(trifluoromethane- sulfonato- κ O)copper(II) ethanol hemisolvate forms a hydrogen-bonded chain

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In the crystal structure of $[\text{Cu}(\text{CF}_3\text{SO}_3)(\text{C}_2\text{N}_3)(\text{C}_8\text{H}_7\text{N}_5)_2] \cdot 0.5\text{C}_2\text{H}_6\text{O}$, the Cu^{II} atom adopts a distorted octahedral geometry, with the basal plane formed by two N atoms of one dipyrimidinylamine ligand, one N atom of the second pyrimidine ligand and a nitrile N atom of the dicyanamide anion [$\text{Cu}-\text{N} = 1.972(2)-2.021(2) \text{ \AA}$]. The apical positions are occupied by an N atom of the second ligand [$\text{Cu}-\text{N} = 2.208(2) \text{ \AA}$], and an O atom of the trifluoromethanesulfonate anion [$\text{Cu}-\text{O} = 2.747(2) \text{ \AA}$] at a semi-coordination distance. Pairs of inversion-related $\text{N}-\text{H} \cdots \text{N}$ hydrogen bonds of the so-called Watson-Crick type, augmented by two $\text{C}-\text{H} \cdots \text{N}$ contacts, link adjacent complexes into an infinite one-dimensional chain running in the [101] direction.

Comment

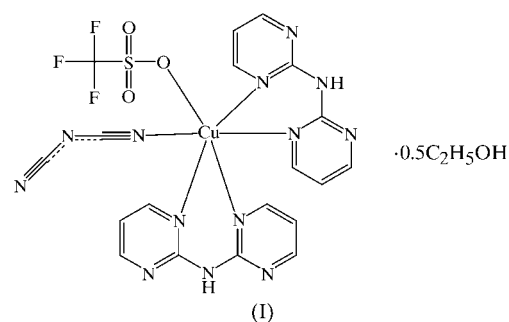
In recent years, the anionic dicyanamide ligand has attracted much interest, in the form of $M^{\text{II}}(\text{dca})_2$ [where M is Ni, Co or Cu, and dca is $\text{N}(\text{CN})_2$], as a new class of molecule-based magnetic materials (Batten *et al.*, 1998; Batten & Murray, 2001; Manson *et al.*, 1999). In the field of crystal engineering, the number of X-ray crystal structures of compounds with the dca anion showing one-, two- and three-dimensional networks has increased enormously in the last few years (*e.g.* Kohout *et al.*, 2000; Vangdal *et al.*, 2002; Mohamadou *et al.*, 2003; Kooijman *et al.*, 2002; Shi *et al.*, 2003).

Dicyanamide itself is an interesting anionic bridging ligand and can act as a monodentate, bidentate or even tridentate ligand (Mroziński *et al.*, 1997; Escuer *et al.*, 2000). Various coordination modes of the dicyanamide ligand and the metal can occur, such as monodentate bonding *via* the nitrile atom,

coordination *via* the amide atom (Marshall *et al.*, 2002; Mohamadou *et al.*, 2003; Shi *et al.*, 2003; Vangdal *et al.*, 2002), and even μ_4 and μ_5 coordination, where nitrile atoms bridge two metal atoms (Chow & Britton, 1975; Shi *et al.*, 2002). However, in most cases, monodentate or bidentate coordination *via* the nitrile N atom is found.

In the field of supramolecular chemistry, not only are direct metal–ligand bonds of interest, but hydrogen bonding is also of great importance (Beatty, 2001; Rodríguez-Martin *et al.*, 2002; Nedelcu *et al.*, 2003; Kutasi *et al.*, 2002; Riggio *et al.*, 2001). One ligand with interesting hydrogen-bonding properties is the recently developed di-2-pyrimidinylamine (abbreviated as dipm). The dipm molecule can both donate and accept hydrogen bonds, and has a more or less linear donor–acceptor array of type *ADA*. This type of array is capable of forming so-called Watson–Crick-type hydrogen bonds (van Albada *et al.*, 2002), as was also shown in the literature for the first generation ligand 2-aminopyrimidine (van Albada, Quiroz-Castro *et al.*, 2000; van Albada, Smeets *et al.*, 2000).

To date, only one X-ray crystal structure determination of a dipm-containing complex has been published, $[\text{Cu}(\text{dipm})(\text{CO}_3)(\text{H}_2\text{O}) \cdot 2\text{H}_2\text{O}]$ (van Albada *et al.*, 2002). In this paper, we present the crystal structure of a new complex of copper with the dipm molecule as ligand, which has the formulation $[\text{Cu}(\text{dca})(\text{dipm})_2(\text{tms})]$, (I), where tms is the trifluoromethylsulfonate anion. An atomic displacement ellipsoid plot of this complex is given in Fig. 1, together with the atomic labelling scheme. Selected geometric parameters are given in Table 1.



The geometry around the Cu^{II} ion in (I) is distorted octahedral, with the basal plane formed by two pyrimidinyl N atoms of one of the coordinating dipm molecules (N111 and N121), one pyrimidinyl N atom of the second coordinating dipm molecule (N211) and a nitrile N atom (N2) of the dca ligand. The $\text{Cu}-\text{N}$ distances are in the range 1.972(2)–2.021(2) \AA . The *trans*-basal angles are 176.41(8)° (N111– Cu –N211) and 165.33(9)° (N2– Cu –N121). The apical positions are occupied by a pyrimidinyl N atom (N221) of the second dipm ligand, at a distance of 2.208(2) \AA , and by an O atom (O1) of the trifluoromethanesulfonate anion at a semi-coordination distance of 2.747(2) \AA .

The dipm molecules in (I) show a significant difference in conformation. The angle between the least-squares planes through the pyrimidine rings is 33.71(12)° in the ligand containing atom N11 and 11.73(13)° in the molecule containing atom N21. In the dipm–copper–carbonate complex

reported previously, the dipm molecule is virtually planar, with a ring–ring angle of $1.80(11)^\circ$.

The lattice of (I) is stabilized by two crystallographically independent hydrogen-bonding systems, both of the so-called Watson–Crick type (Fig. 2). The systems are formed by donation of a hydrogen bond by the amine N atom of a dipm molecule (either N11 or N21) to a non-coordinating pyrimidinyl N atom of an inversion-related dipm molecule (N113 or N213, respectively). Due to the crystallographic inversion symmetry, a hydrogen-bonded ring is formed with unitary graph-set $R_2^2(8)$ (Bernstein *et al.*, 1995). The hydrogen-bonded system involving atom N11 is formed around the inversion centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, while that involving atom N21 is formed around the centre at $(0, \frac{1}{2}, 0)$. Geometric details are given in Table 2.

The hydrogen-bonded systems link the copper complexes into an infinite one-dimensional chain running in the [101] direction. Within each chain, the copper complexes are linked alternately by hydrogen-bonded systems involving atoms N11 or N21 (Fig. 2). This arrangement of hydrogen-bonded dipm molecules may facilitate the formation of two C–H...N contacts adjacent to the N–H...N hydrogen bonds, resulting in the formation of a quadruply hydrogen-bonded array of type *DADA* (a review of quadruply hydrogen-bonded systems is given by Sijbesma & Meijer, 2003). Due to the deviations from planarity of the dipm molecules, the C–H...N contacts are somewhat long, especially that involving C114–H114 (Table 2). However, these contacts may still play a role in the stabilization of the hydrogen-bonded network of (I). The dipm–copper–carbonate complex reported previously displayed a similar hydrogen-bonded structure (van Albada *et al.*, 2002).

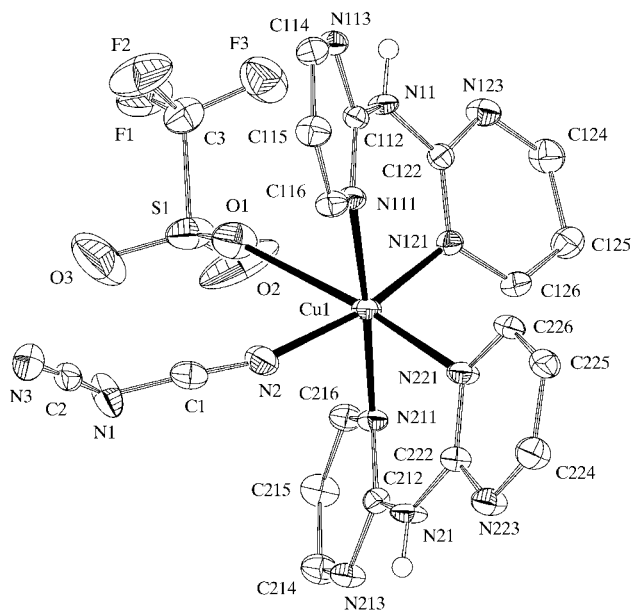


Figure 1

A view of the structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level. H atoms bonded to C atoms have been omitted for clarity.

The non-coordinating nitrile moiety of the dca anion in (I) does not accept any hydrogen bonds. There is a close contact [$2.947(4) \text{ \AA}$, *i.e.* approximately 0.2 \AA less than the sum of the van der Waals radii] between atom N3 of the dca anion and atom C122($1 - x, y - \frac{1}{2}, \frac{1}{2} - z$) of a dipm molecule. Atom N3 also displays a short contact to atom C112 of the same dipm molecule, with a distance of $3.086(3) \text{ \AA}$. Contacts of the type $\text{C}\equiv\text{N}\cdots\text{Csp}^2\text{X}_3$, where $X = \text{C, N, O, P, S}$ or halogen, are not unusual. The July 2003 update of the Cambridge Structural Database (Allen, 2002) contains approximately 150 examples with $\text{N}\cdots\text{C}$ distances in the range $2.8\text{--}3.2 \text{ \AA}$, 23 of which display contact distances shorter than the value observed in the crystal structure of (I).

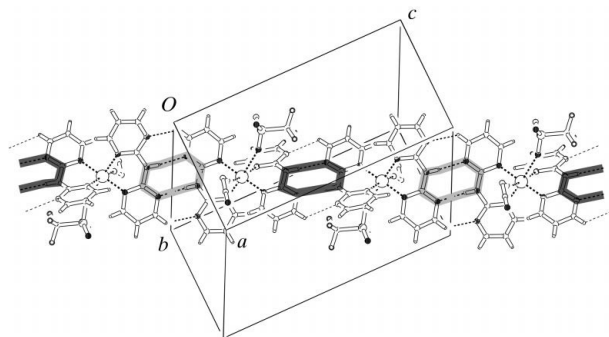


Figure 2

A plot showing a fragment of the hydrogen-bonded network in (I) in the [101] direction. The hydrogen-bonded ring involving atom N11 is highlighted in light grey and that involving atom N21 in dark grey.

The electron paramagnetic resonance (EPR) spectrum for (I), measured as a polycrystalline powder at room temperature and at 77 K, shows an axial $S = \frac{1}{2}$ signal, with $g = 2.06$, a value typical for Cu^{II} and in agreement with a $d_{x^2-y^2}$ ground state.

Experimental

The dipm ligand was synthesized using the method of Yao *et al.* (2000). Metal salts and solvents were commercially available and used without further purification. The title compound was synthesized by mixing equimolar amounts of copper(II) trifluoromethanesulfonate, sodium dicyanamide and di-2-pyrimidylamine in an ethanol–water (1:1) mixture. After standing in air at room temperature for about two weeks, blue–green block-shaped crystals of (I) were formed which were suitable for X-ray structure determination. IR analysis: the characteristic trifluoromethanesulfonate vibrations are observed at $1255, 1246, 1223, 1154$ and 1026 cm^{-1} (van Albada *et al.*, 1997, 1998). The characteristic IR vibrations for the dicyanamide anion are found in the $2400\text{--}2100 \text{ cm}^{-1}$ region (Kohout *et al.*, 2000). The $\nu_s + \nu_{as}(\text{C–N})$ vibration is observed as two weak-to-medium bands at 2361 and 2294 cm^{-1} , and the $\nu(\text{C}\equiv\text{N})$ vibration is observed as two medium-to-strong bands at 2238 and 2167 cm^{-1} . These vibrations occur in the ranges found for other polymeric copper(II) dicyanamide compounds (Kohout *et al.*, 2000; Riggio *et al.*, 2001; van Albada, Quiroz-Castro *et al.*, 2000; van Albada, Smeets *et al.*, 2000).

Crystal data

[Cu(CF ₃ SO ₃)(C ₂ N ₃)(C ₈ H ₇ N ₅) ₂] 0.5C ₂ H ₆ O	$D_x = 1.648 \text{ Mg m}^{-3}$
$M_r = 625.05$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 304 reflections
$a = 9.972(2) \text{ \AA}$	$\theta = 2.0\text{--}25.0^\circ$
$b = 13.751(2) \text{ \AA}$	$\mu = 1.02 \text{ mm}^{-1}$
$c = 18.516(4) \text{ \AA}$	$T = 150 \text{ K}$
$\beta = 97.047(8)^\circ$	Block, blue–green
$V = 2519.8(8) \text{ \AA}^3$	$0.2 \times 0.1 \times 0.1 \text{ mm}$
$Z = 4$	

Data collection

Nonius Kappa CCD area-detector diffractometer	$R_{\text{int}} = 0.119$
φ scans, and ω scans with κ offsets	$\theta_{\text{max}} = 27.4^\circ$
56 102 measured reflections	$h = -12 \rightarrow 12$
5712 independent reflections	$k = -17 \rightarrow 17$
3766 reflections with $I > 2\sigma(I)$	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0468P)^2]$
$R(F) = 0.043$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.104$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.36 \text{ e \AA}^{-3}$
5712 reflections	$\Delta\rho_{\text{min}} = -0.55 \text{ e \AA}^{-3}$
367 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cu1–O1	2.747 (2)	Cu1–N121	2.008 (2)
Cu1–N2	1.972 (2)	Cu1–N211	2.021 (2)
Cu1–N111	2.006 (2)	Cu1–N221	2.208 (2)
O1–Cu1–N2	79.13 (8)	N111–Cu1–N121	88.17 (8)
O1–Cu1–N111	84.62 (7)	N111–Cu1–N211	176.41 (8)
O1–Cu1–N121	86.20 (7)	N111–Cu1–N221	96.99 (8)
O1–Cu1–N211	92.61 (7)	N121–Cu1–N211	93.93 (8)
O1–Cu1–N221	174.31 (7)	N121–Cu1–N221	99.29 (8)
N2–Cu1–N111	90.52 (8)	N211–Cu1–N221	85.56 (8)
N2–Cu1–N121	165.33 (9)	C1–N1–C2	119.9 (3)
N2–Cu1–N211	86.72 (8)	C112–N11–C122	127.4 (2)
N2–Cu1–N221	95.38 (9)	C212–N21–C222	132.0 (2)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
N11–H3 \cdots N113 ⁱ	0.88 (3)	2.10 (3)	2.981 (3)	176 (2)
N21–H5 \cdots N213 ⁱⁱ	0.87 (3)	2.14 (3)	3.001 (3)	174 (3)
C114–H114 \cdots N123 ⁱ	0.95	2.65	3.307 (3)	127
C214–H214 \cdots N223 ⁱⁱ	0.95	2.56	3.276 (3)	132

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

An absorption correction based on multiple measurements of symmetry-related reflections had little influence on R_{int} , $R1$ and the residual density. The correction was therefore not considered necessary and was not applied to the reflection data. The amine H atoms were located in a difference Fourier map and their coordinates

were refined. The other H atoms were placed in calculated positions, riding on their carrier atoms. $U_{\text{iso}}(\text{H})$ values were set at 1.5 or 1.2 times $U_{\text{eq}}(\text{parent atom})$ for amine H atoms and other H atoms, respectively. The unit cell contains two symmetry-related cavities located on the crystallographic inversion centres at $(\frac{1}{2}, 0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, 0)$, filled with disordered solvent, probably ethanol. The volume of each cavity is 81 \AA^3 . Attempts to model an ethanol molecule into the solvent density did not result in an acceptable model. There are no groups lining the cavity which could accept a hydrogen bond from the solvent. The contribution of the disordered solvent to the scattering factors was taken into account with *PLATON/SQUEEZE* (Spek, 2003; van der Sluis & Spek, 1990). A total of 24 e was found in each cavity, corresponding to approximately one ethanol molecule per cavity. Where relevant, the crystal data reported earlier in this paper are given without the contribution of the disordered solvent. Taking into account the presence of one ethanol molecule per cavity, the following values are obtained: $\text{C}_{19}\text{H}_{14}\text{CuF}_3\text{N}_{13}\text{O}_3\text{S}\cdot 0.5\text{C}_2\text{H}_6\text{O}$, $M_r = 648.05$, $\mu = 1.065 \text{ mm}^{-1}$, $F(000) = 1312$ and $D_x = 1.708 \text{ Mg m}^{-3}$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1041). Services for accessing these data are described at the back of the journal.

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