Low-dimensional compounds containing cyano groups. II. catena-Poly[[(2,2'-bipyridine-$\kappa^2 N{:}N'$)(dicyanamido-κN)copper(II)]-μ-dicyanamido-$\kappa^2 N{:}N'$]

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The crystal structure of the title compound, [Cu-$(C_2N_3)_2(C_{10}H_8N_2)]_n$, is formed by neutral zigzag chains of the [–NC–N–CN–Cu{(bpy)N(CN)$_2$}–NC–N–CN–] type running along the c axis (bpy is 2,2'-bipyridine). The Cu atoms in the chains are pentacoordinated in the form of a distorted tetragonal pyramid, with a CuN_5 chromophore. The coordination sites are occupied by two N atoms of one bpy molecule in the basal plane [Cu–N 2.018 (4) and 2.025 (2) Å] and by three terminal N atoms of two dicyanamide ligands. One of the dicyanamide ligands is coordinated in a monodentate fashion through a nitrile N atom in the basal plane [Cu–N 1.963 (4) Å]. The second acts as an end-to-end bridging ligand to a neighbouring Cu atom and is coordinated by one nitrile N atom in the basal plane [Cu–N 2.001 (2) Å], while the second nitrile N atom occupies the apical position [Cu–N 2.159 (2) Å] and originates from the bridge connecting another Cu atom. The shortest intrachain Cu···Cu distance is 8.212 (1) Å, as a consequence of the large bridging ligand, whereas the minimum interchain distance between Cu atoms is only 5.77 (7) Å, because of the interdigitation of the chains.

Comment

The dicyanamide (dca) anion, $[N(CN)_2]^-$, can coordinate to a central metal atom either in a monodentate manner, through a nitrile or amide N atom, or in a bidentate, tridentate or even tetradentate manner, with the participation of two or three donor N atoms. Nevertheless, monodentate coordination of dca through the amide N atom is rather improbable and, to date, no crystal structure of such a compound is known (Kohout et al., 2000). On the other hand, the structures of several molecular and ionic compounds with dca coordinated

in a monodentate manner through the nitrile N atom have been reported. These compounds contain either six-coordinated central atoms and are of the general formula [ML_4(dca)$_2$], e.g. [Ni(4Meim)$_4$(dca)$_2$] (4Meim is 4-methyl-imidazole; Kožíšek et al., 1996), [Cu(phen)$_2$(dca)$_2$] (phen is 1,10-phenanthroline; Potočňák et al., 1995) and [Cu(NITp-Py)$_2$(H$_2$O)$_2$(dca)$_2$] (NITpPy is the nitronyl nitroxide radical; Dasna et al., 2001), or five-coordinated central atoms and are of the general formula [ML_4(dca)]X, e.g. [Cu(phen)$_2$(dca)]-[C(CN)$_3$] (Potočňák et al., 1996), [Cu(bpy)$_2$(dca)][C(CN)$_3$] (bpy is 2,2'-bipyridine; Potočňák, Dunaj-Jurčo, Mikloš & Jäger, 2001) and [Cu(bpy)$_2$(dca)]BF$_4$ (Potočňák, Dunaj-Jurčo, Mikloš et al., 2001), in which L may be four monodentate or two bidentate ligands and X is a monoanion.

(I)
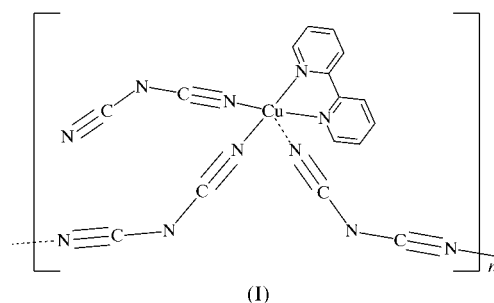
As a consequence of the possible bridging function of dca, there has been unusual interest in this ligand during recent years, especially in connection with the preparation of magnetic materials. Among them, weak ferromagnets of the general formula α-[M(dca)$_2$], with a three-dimensional rutile-type structure, have attracted much attention because of the ability of dca to act as a molecular-based magnet precursor, with several transition metal ions octahedrally coordinated by tridentate dca ligands (Batten et al., 1998; Jensen, Batten, Fallon, Hockless et al., 1999; Jensen, Batten, Fallon,
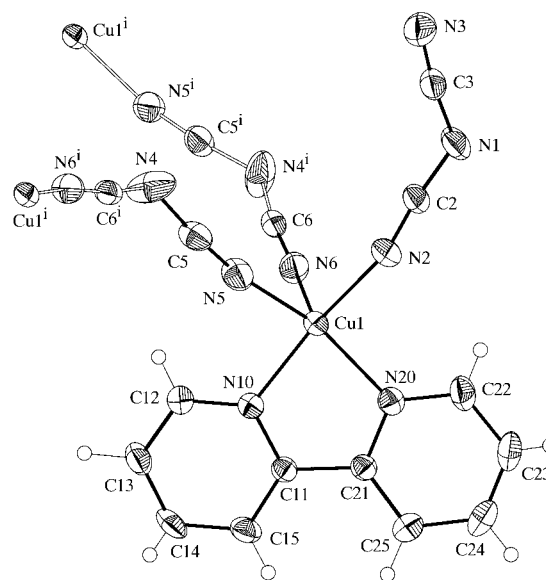

Figure 1
The structure of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry code: (i) x, $-y$, $z - \frac{1}{2}$].

metal-organic compounds

Moubaraki *et al.*, 1999; Kurmoo & Kepert, 1998; Manson *et al.*, 1998). If the two dca ligands are tetrahedrally coordinated only through the nitrile N atoms, β-isomers of these compounds occur in the form of sheet-like structures (Jensen, Batten, Fallon, Hockless *et al.*, 1999; Jensen, Batten, Fallon, Moubaraki *et al.*, 1999).

When two coordination sites of hexacoordinated metallic centres are occupied by additional blocking ligands, the dca acts as a bidentate bridging ligand coordinated through the nitrile N atoms, and the resulting compounds contain [ML_2(dca)$_2$] units (L is one bidentate or two monodentate ligands; Manson *et al.*, 1999; Escuer *et al.*, 2000; van Albada *et al.*, 2000; Jäger *et al.*, 2001; Dasna *et al.*, 2001; Sun *et al.*, 2001). All these compounds are one-dimensional and contain chains in which two metallic centres are connected by a pair of dca ligands, forming double bridges. Moreover, if the ligands L can serve as additional bridges between the central atoms, the above chains are connected by these ligands, giving a two-dimensional sheet (Jensen, Batten, Fallon, Hockless *et al.*, 1999; Jensen, Batten, Fallon, Moubaraki *et al.*, 1999; Jensen *et al.*, 2001).

The [ML_2(dca)$_2$] units are also present in another type of one-dimensional structure. This type was previously observed in [M(bpym)(dca)$_2$]·H$_2$O (M is Mn, Fe or Co, and bpym is 2,2'-bipyrimidine; Marshall *et al.*, 2000) and is formed by chains in which two hexacoordinated metallic centres are connected by only one bridging dca, while the second remains monodentate. The one-dimensional structure of the title complex, [Cu(bpy)(dca)$_2$], (I), which we present herein as part of our study of low-dimensional magnetic materials (Černák *et al.*, 2001), is of this last type, but it contains five-coordinated central atoms and is similar to the very recently published structures of [Cu(dmbpy)(dca)$_2$] (dmbpy is 5,5'-dimethyl-2,2'-

bipyridine; Kooijman *et al.*, 2002) and [Cu(phen)(dca)$_2$] (Luo *et al.*, 2002).

The structure of (I) (Fig. 1) is formed by neutral zigzag chains of the [–NC–N–CN–Cu{(bpy)N(CN)$_2$}–NC–N–CN–] type running along the c axis. The coordination sites of the Cu atoms in the chains are occupied by two N atoms of one bpy molecule [Cu1—N10 2.018 (4) Å and Cu1—N20 2.025 (2) Å] and three nitrile N atoms of two dicyanamide ligands. The shortest bond around the Cu atom is to the monodentate dca ligand, with a Cu1—N2 distance of 1.963 (4) Å. The second dca acts as an end-to-end bridging ligand to a neighbouring Cu atom and is coordinated by one nitrile N atom (N5) at a distance of 2.001 (2) Å, while the second nitrile N atom (N6), originating from the bridge connecting another Cu atom, is coordinated at the longest distance, at 2.159 (2) Å.

The chromophore of (I) is thus CuN$_5$ and the coordination polyhedron adopts the shape of a distorted tetragonal pyramid. Atoms N10 and N20 of the bpy molecule, atom N2 of the monodentate dca ligand and atom N5 of the bridging dca ligand occupy the basal plane, while atom N6 from the second end of the bridging dca ligand is coordinated apically. Relatively small deviations of the bond angles around the Cu atom from the corresponding values for an ideal tetragonal pyramid indicate that the degree of distortion is not dramatic. This is confirmed by the value of the τ parameter (Addison *et al.*, 1984), which is 31.3 (the τ parameter is 100 for an ideal trigonal bipyramid and 0 for an ideal tetragonal pyramid).

As the angle between the two planar pyridine rings of the bpy molecule, originating from possible free rotation of the pyridine rings around their common single C—C bond, is only 5.0 (1)°, the whole bpy molecule is almost planar [the largest deviation of atoms from the mean plane is 0.112 (4) Å for atom C23]. Bond distances and angles within the bpy molecule are normal for aromatic heterocycles (Anderson, 1973) and range from 1.327 (4) to 1.401 (4) Å, while the single C—C bond distance is 1.486 (3) Å. The angles within the individual pyridine rings of the bpy molecule range from 118.0 (3) to 121.7 (2)°, while the angles involving the two pyridine rings lie in a somewhat larger range.

There are two independent dca ligands in the structure of (I). Although they differ in ligation, the values of the corresponding bond distances and angles are similar (Table 1). Inspection of the bond lengths shows that none of the three possible canonical formulae (Golub *et al.*, 1986) properly describes the bonding mode of the dicyanamide. Both the N$_{nitrile}$≡C and N$_{amide}$═C distances are close to N≡C triple (1.15 Å) and N═C double bonds (1.27 Å), respectively. The N$_{amide}$—C≡N$_{nitrile}$ angles are almost linear, while the values of the C—N$_{amide}$—C angles are somewhat larger than 120°. Both dca ligands are perfectly planar, the largest deviation of atoms from the mean plane being 0.009 (3) Å (for C5), and their bonding mode to the Cu atom (C≡N$_{nitrile}$—Cu) can be considered angular.

A similar one-dimensional structure, with one bridging and one terminal dca ligand, has been observed in [M(bpym)-(dca)$_2$]·H$_2$O (M is Mn, Fe or Co; Marshall *et al.*, 2000). The complex consists of interdigitated zigzag chains, in which two
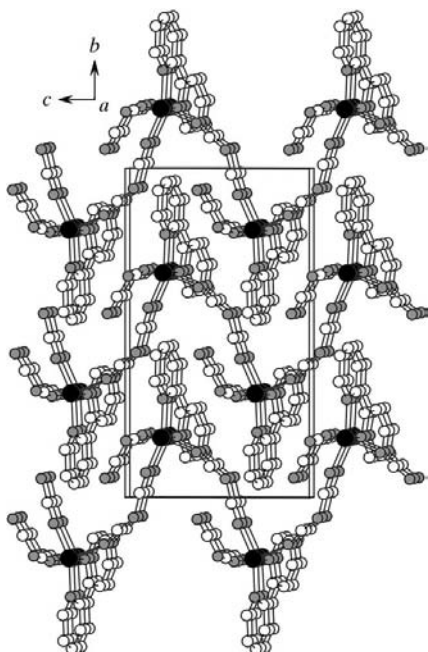

Figure 2
The stacking of the chains of (I) viewed down the a axis. H atoms have been omitted for clarity.

hexacoordinated metallic centres are connected by one bridging dca ligand. Because of the interdigitation of the chains, the nearest interchain $M \cdots M$ distances are about 2 Å shorter than the nearest intrachain $M \cdots M$ distances, which range from 8.630 (Fe) to 8.983 Å (Mn). Similarly, the shortest intrachain Cu1$\cdots$Cu1 distance in (I) is 8.212 (1) Å, as a consequence of the large bridging ligand, and, because of the interdigitation of the chains (Fig. 2), the minimum interchain distance between Cu atoms is 5.77 (7) Å.

Experimental

Crystals of (I) were prepared by mixing a 0.1 M aqueous solution of Cu(BF₄)₂ (5 ml) with a 0.1 M ethanol solution of bpy (10 ml). To the resulting blue solution, a 0.1 M aqueous ethanol solution of KN(CN)₂ (6 ml) was added (all solutions were warmed before mixing). A mixture of blue crystals of [Cu(bpy)₂(dca)]BF₄ [for the structure, see Potočňák, Dunaj-Jurčo, Mikloš *et al.* (2001)] and a small number of green crystals of (I) appeared the next day. The crystals were filtered off, dried in air and mechanically separated under a microscope.

Crystal data

[Cu(C₂N₃)₂(C₁₀H₈N₂)]	$D_x = 1.633$ Mg m^{-3}
$M_r = 351.82$	Mo $K\alpha$ radiation
Monoclinic, Cc	Cell parameters from 7754
$a = 8.6495$ (18) Å	reflections
$b = 17.118$ (4) Å	$\theta = 1.7–26.1°$
$c = 10.568$ (2) Å	$\mu = 1.54$ mm^{-1}
$\beta = 113.85$ (2)°	$T = 220$ (2) K
$V = 1431.1$ (5) Å^3	Prism, green
$Z = 4$	$0.30 \times 0.27 \times 0.21$ mm

Data collection

Stoe IPDS diffractometer	2491 independent reflections
φ scans	2434 reflections with $I > 2\sigma(I)$
Absorption correction: numerical	$R_{int} = 0.028$
(*FACE* in *IPDS*; Stoe & Cie,	$\theta_{max} = 25.9°$
1999)	$h = -10 \rightarrow 10$
$T_{min} = 0.671$, $T_{max} = 0.776$	$k = -20 \rightarrow 20$
5294 measured reflections	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.023$	$+ 0.6066P]$
$wR(F^2) = 0.064$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} < 0.001$
2491 reflections	$\Delta\rho_{max} = 0.25$ e Å^{-3}
208 parameters	$\Delta\rho_{min} = -0.39$ e Å^{-3}
H-atom parameters constrained	Absolute structure: Flack (1983),
	1224 Friedel pairs
	Flack parameter = -0.012 (11)

All H atoms were placed in calculated positions, with C—H = 0.93 Å, and refined using the appropriate riding models.

Data collection: *EXPOSE* in *IPDS* (Stoe & Cie, 1999); cell refinement: *CELL* in *IPDS*; data reduction: *INTEGRATE* in *IPDS*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Crystal Impact, 1999).

Table 1
Selected geometric parameters (Å, °).

Cu1—N2	1.963 (4)	Cu1—N10	2.018 (4)
Cu1—N5	2.001 (2)	Cu1—N20	2.025 (2)
Cu1—N6	2.159 (2)		
N2—Cu1—N5	90.46 (12)	N5—Cu1—N6	94.67 (11)
N2—Cu1—N10	172.06 (15)	N10—Cu1—N6	91.95 (12)
N5—Cu1—N10	92.19 (10)	N20—Cu1—N6	111.18 (11)
N2—Cu1—N20	93.72 (11)	C2—N2—Cu1	163.6 (3)
N5—Cu1—N20	153.26 (11)	C5—N5—Cu1	167.8 (2)
N10—Cu1—N20	80.60 (9)	C6—N6—Cu1	158.2 (2)
N2—Cu1—N6	95.29 (15)		

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

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