

Low-dimensional compounds containing cyano groups. VI.¹ A unique two- and one-dimensional structure in amminebis(1,4-diaminobutane)tetrakis[dicyanoargentato(I)]-dicopper(II) dihydrate

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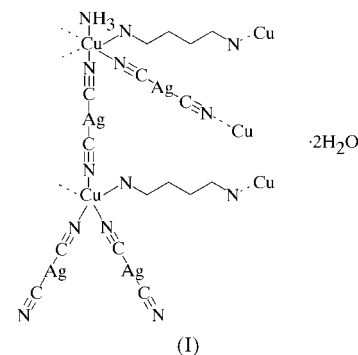
The title compound, $[\text{Cu}_2(\text{C}_4\text{H}_{12}\text{N}_2)_2\{\text{Ag}(\text{CN})_2\}_4(\text{NH}_3)] \cdot 2\text{H}_2\text{O}$ or $[\text{Ag}_4\text{Cu}_2(\text{CN})_8(\text{C}_4\text{H}_{12}\text{N}_2)_2(\text{NH}_3)] \cdot 2\text{H}_2\text{O}$, contains two crystallographically different Cu^{II} atoms lying on twofold axes. The first Cu atom is hexacoordinated in the form of an elongated tetragonal bipyramid and is part of a plane in which Cu atoms are connected by two bridging diaminobutane molecules [$\text{Cu}-\text{N} = 2.033$ (4) Å] and two dicyanoargentate anions [$\text{Cu}-\text{N} = 2.622$ (6) Å]. The ammine ligand stands perpendicular to this plane [$\text{Cu}-\text{N} = 2.011$ (6) Å] in a *trans* position to it. Another $[\text{Ag}(\text{CN})_2]^-$ anion connects the hexacoordinated Cu atom [$\text{Cu}-\text{N} = 1.997$ (8) Å] with the second Cu atom [$\text{Cu}-\text{N} = 2.026$ (7) Å], which is pentacoordinated in the form of a slightly distorted trigonal bipyramid by two monodentate dicyanoargentate anions [$\text{Cu}-\text{N} = 2.040$ (5) Å]. The axial positions are occupied by two bridging diaminobutane molecules [$\text{Cu}-\text{N} = 2.011$ (4) Å] that connect the Cu atoms into chains parallel to the above plane. The water molecules remain uncoordinated and thus a unique combination of two- and one-dimensional structures is formed.

Comment

Cyano complexes attract much attention in coordination chemistry because of the diversity of the crystal structures formed and their interesting properties, especially in the context of their magnetic behaviour (Iwamoto, 1996; Verdager *et al.*, 1999; Ohba & Okawa, 2000; Černák *et al.*, 2002). Dicyanoargentate complexes are mainly investigated from the

¹ Part V: Potočňák *et al.* (2002).

structural and magnetochemical points of view (Assefa *et al.*, 1995; Iwamoto, 1996; Comte *et al.*, 2000; Shek *et al.*, 2000; Dasna *et al.*, 2001, and references therein; Zhang *et al.*, 2002). Our interest has mainly focused on the preparation and study of low-dimensional magnetic materials (Černák *et al.*, 2002), and the present contribution is a continuation of our study of compounds having the general formula $\text{Cu}(\text{L})_2\text{Ag}_2(\text{CN})_4$, where *L* is either a bidentate chelating ligand, *viz.* 1,2-diaminoethane (Černák *et al.*, 1998), 1,3-diaminopropane



(Černák *et al.*, 2000) and 1,2-diaminopropane (Triščíková *et al.*, 2003a), or the monodentate 4-methylpyridine ligand (Triščíková *et al.*, 2002). With the aim of examining the effect on the structure of replacing the above bidentate ligands by larger ligands, we have used 1,4-diaminobutane (dabn). As a result, the title compound, (I), has been prepared, and we present here its crystal structure.

There are two crystallographically different Cu atoms in the structure of (I) (Fig. 1). Atom Cu1 is pentacoordinated in the form of a slightly distorted trigonal bipyramid by two mono-

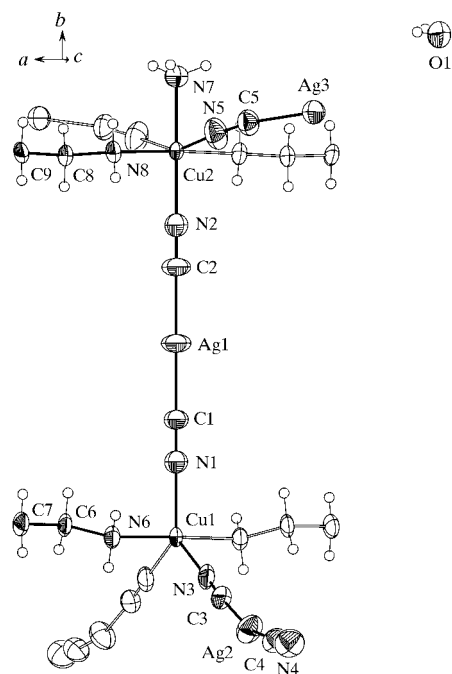


Figure 1

Part of the structure of (I), with labelling shown for the independent atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

dentate $[\text{Ag}(\text{CN})_2]^-$ anions (atoms Ag2) in the equatorial plane and by two bridging diaminobutane ligands in the axial positions, which connect neighbouring Cu1 atoms to form an infinite chain parallel to $[100]$. The third equatorial position is occupied by a bridging $[\text{Ag}(\text{CN})_2]^-$ anion (atom Ag1), which links atoms Cu1 and Cu2. The relatively small deviations of the bond angles around atom Cu1 (Table 1) from the corresponding values for an ideal trigonal bipyramid indicate that the degree of polyhedral distortion is small, as confirmed by the τ -parameter (Addison *et al.*, 1984) of 93.4 (ideal values are 100 for a trigonal bipyramid and 0 for a square pyramid). If we assign α_3 to the N3–Cu1–N3 angle, and α_1 and α_2 to the other two angles in the equatorial plane, then according to the criteria of Harrison & Hathaway (1980), which are based on the values of the three equatorial angles and their differences, the shape of the coordination polyhedron around atom Cu1 can be described as trigonal bipyramidal with C_{2v} symmetry. The C_2 axis passes through atom Cu1, the whole of the bridging $[\text{Ag}(\text{CN})_2]^-$ anion, atom Cu2 and atom N7 of the ammonia molecule coordinated to atom Cu2. Atom Cu2 is hexacoordinated by three dicyanoargentate anions, the ammonia molecule and two diaminobutane molecules. As a result of the Jahn–Teller effect, the coordination polyhedron of atom Cu2 adopts the shape of an elongated tetragonal bipyramid, with dicyanoargentate anions (atoms Ag3) in axial positions [Cu2–N5 = 2.622 (6) Å], while the four equatorial Cu–N bonds range from 1.997 (8) to 2.033 (4) Å. Only one N atom (ammine atom N7) in the coordination sphere of atom Cu2 originates from a monodentate ligand. The two diaminobutane ligands and all three $[\text{Ag}(\text{CN})_2]^-$ anions are bridging. The two diaminobutane ligands connect neighbouring Cu2 atoms to form infinite chains parallel to the chain containing atoms Cu1. Atoms Cu2 of neighbouring chains are

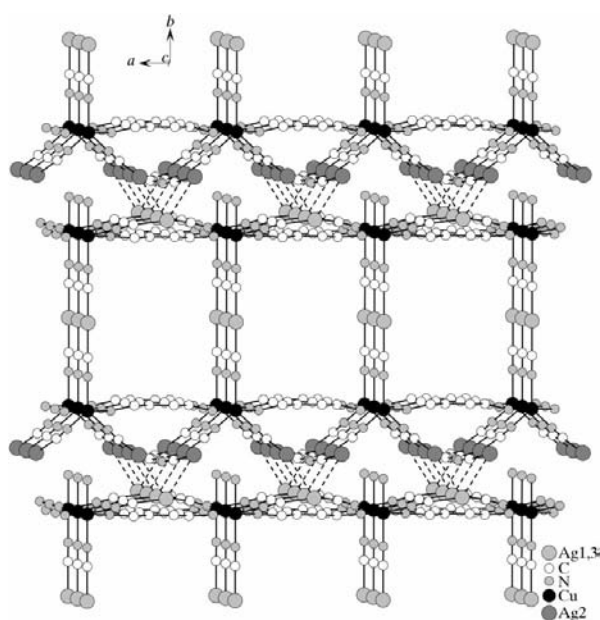


Figure 2

The packing of layers in (I), with the $\text{Ag} \cdots \text{Ag}$ interactions shown as dashed lines. Water molecules and H atoms have been omitted for clarity.

connected through the two $[\text{Ag}_3(\text{CN})_2]^-$ anions to form a chain parallel to $[001]$ and, as mentioned above, one $[\text{Ag}(\text{CN})_2]^-$ anion (Ag1 atom) connects atoms Cu1 and Cu2. Thus, atoms Cu2 lie in a plane parallel to (010) , which is formed by chains parallel to $[100]$ and $[001]$. The ammine ligands stand perpendicular to this plane, in *trans* positions to it, and $[\text{Ag}(\text{CN})_2]^-$ anions connecting atoms Cu1 and Cu2 hang from the plane (Fig. 2). Finally, we can describe the structure of (I) as a unique combination of two-dimensional plane with one-dimensional chains, both forming one layer. Water molecules remain uncoordinated and are involved in hydrogen bonds with the N atoms of an $[\text{Ag}(\text{CN})_2]^-$ anion (atom Ag2) and the diaminobutane molecule (Table 2).

One type of monodentate and two different types of bridging $[\text{Ag}(\text{CN})_2]^-$ anions are found in the structure of (I). The co-existence of both bridging and monodentate $[\text{Ag}(\text{CN})_2]^-$ anions in one compound is not common. Nevertheless, this situation has been observed in $[\text{Cd}(4\text{-ampy})_2\{\mu\text{-Ag}(\text{CN})_2\}_2]^-$ [Cd(mea)(4-ampy){ $\mu\text{-Ag}(\text{CN})_2$ }]₂ (4-ampy is 4-aminopyridine and mea is 2-aminoethanol; Soma & Iwamoto, 1996a), $[\text{Cu}(4\text{-Mepy})_2\text{Ag}_2(\text{CN})_4]$ (4-Mepy is 4-methylpyridine; Triščíková *et al.*, 2002) and $[\text{Cu}^{\text{II}}(4\text{-Mepy})_3\text{Ag}_{2-x}\text{Cu}_x^{\text{I}}(\text{CN})_4]$ ($x = 0.07$; Triščíková, Potočňák & Chomič, 2003). Dicyanoargentates with the general formula $\text{Cu}(L)_2\text{Ag}_2(\text{CN})_4$ [L is 1,2-diaminoethane (Černák *et al.*, 1998) or 2,2'-bipyridine (Černák *et al.*, 1993)] are one-dimensional polymers that contain one bridging and one isolated $[\text{Ag}(\text{CN})_2]^-$ anion. In contrast, the compound in which L is 1,3-diaminopropane contains non-polymeric binuclear cations, also with one isolated and one monodentate $[\text{Ag}(\text{CN})_2]^-$ anion (Černák *et al.*, 2000), and the compound in which L is 1,2-diaminopropane (pn) is built up of trinuclear $\text{NC}\text{--}\text{Ag}\text{--}\text{CN}\text{--}\text{Cu}(\text{pn})_2\text{--}\text{NC}\text{--}\text{Ag}\text{--}\text{CN}$ molecules and contains only monodentate $[\text{Ag}(\text{CN})_2]^-$ anions (Triščíková, Chomič *et al.*, 2003).

There are no unusual features in the bond lengths of the dicyanoargentate anions in (I). Although they are ligated differently, the equivalent bond lengths are almost equal. On the other hand, the Ag1 dicyanoargentate anion localized on a rotation axis is perfectly linear, while the Ag2 and Ag3 dicyanoargentate anions are substantially bent from linearity. In particular, the angles around atoms Ag1 and Ag3 are far from linear. Moreover, the bonding mode of the Ag3 dicyanoargentate anion can be considered as angular [C5–N5–Cu2 = 149.8 (4)°].

The bending of the two dicyanoargentate anions in (I) may be explained by argentophilic interactions between atoms Ag2 and Ag3 (Fig. 2); such reactions are characteristic of dicyanoargentates (Soma & Iwamoto, 1994, 1996b; Soma *et al.*, 1994; Černák *et al.*, 1998; Omary *et al.*, 1998). A typical range for these $\text{Ag} \cdots \text{Ag}$ contacts is $\sim 3.05\text{--}3.26$ Å, but both shorter [2.9264 (5) Å; Triščíková, Potočňák & Chomič, 2003] and longer [3.899 (1) Å; Omary *et al.*, 1998] contacts have been reported. In (I), the $\text{Ag}2 \cdots \text{Ag}3$ distance is 3.1152 (12) Å, and these argentophilic interactions connect the Cu1-containing chains from the upper layer with the Cu2-containing plane from the neighbouring lower layer, thus forming an infinite three-dimensional network.

Experimental

For the preparation of (I), a blue precipitate containing $[\text{Cu}(\text{dabn})_2]^{2+}$ cations, formed by mixing aqueous copper sulfate (10 ml, 1 mmol) and aqueous 1,4-diaminobutane (1 ml, 2 mmol), was dissolved by the addition of concentrated ammonia solution (26%, 1.5 ml). The resulting blue solution was mixed with aqueous $[\text{K}[\text{Ag}(\text{CN})_2]]$ (10 ml, 2 mmol) and the mixture was left to crystallize. Blue crystals of (I) suitable for X-ray analysis were obtained after 2 d, and these crystals were filtered off and dried in air.

Crystal data

$[\text{Ag}_4\text{Cu}_2(\text{CN})_8(\text{C}_4\text{H}_{12}\text{N}_2)_2(\text{NH}_3)] \cdot 2\text{H}_2\text{O}$	$D_x = 2.172 \text{ Mg m}^{-3}$
$M_r = 996.10$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 20 reflections
$a = 9.862 (6) \text{ \AA}$	$\theta = 8.1\text{--}11.6^\circ$
$b = 16.541 (5) \text{ \AA}$	$\mu = 3.93 \text{ mm}^{-1}$
$c = 10.210 (12) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 113.84 (4)^\circ$	Prism, blue
$V = 1523 (2) \text{ \AA}^3$	$0.45 \times 0.22 \times 0.15 \text{ mm}$
$Z = 2$	

Data collection

Stoe Stadi-4 diffractometer	$R_{\text{int}} = 0.062$
$\theta/2\theta$ scans	$\theta_{\text{max}} = 25.0^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -11 \rightarrow 11$
$T_{\text{min}} = 0.422$, $T_{\text{max}} = 0.619$	$k = -19 \rightarrow 0$
5248 measured reflections	$l = -12 \rightarrow 12$
2694 independent reflections	2 standard reflections
2160 reflections with $I > 2\sigma(I)$	frequency: 60 min
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0564P)^2 + 0.251P]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.113$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 1.10 \text{ e \AA}^{-3}$
2694 reflections	$\Delta\rho_{\text{min}} = -1.14 \text{ e \AA}^{-3}$
180 parameters	
H atoms treated by a mixture of independent and constrained refinement	

All diaminobutane and ammine H-atom positions were calculated using appropriate riding models and allowed for with isotropic displacement parameters, while water H-atom positions were found in a difference map and refined with free isotropic displacement parameters. Several peaks located closer than 1 Å from either Ag or Cu atoms were found in the difference map.

Table 1

Selected geometric parameters (Å, °).

Ag3—C5	2.080 (6)	C1—N1	1.140 (11)
Ag3—Ag2 ⁱ	3.1152 (12)	N1—Cu1	2.026 (7)
C5—N5	1.099 (7)	Cu1—N6	2.011 (4)
Cu2—N2	1.997 (8)	Cu1—N3	2.040 (5)
Cu2—N7	2.011 (6)	N3—C3	1.141 (7)
Cu2—N8	2.033 (4)	C3—Ag2	2.066 (6)
N2—C2	1.128 (11)	Ag2—C4	2.047 (7)
C2—Ag1	2.059 (8)	C4—N4	1.144 (8)
Ag1—C1	2.059 (8)		
C5 ⁱⁱ —Ag3—C5	165.6 (3)	N6 ⁱⁱⁱ —Cu1—N6	178.7 (3)
N5—C5—Ag3	171.3 (6)	N6—Cu1—N1	90.66 (13)
N2—Cu2—N7	180	N6 ⁱⁱⁱ —Cu1—N3	91.73 (18)
N2—Cu2—N8	88.69 (13)	N6—Cu1—N3	87.55 (18)
N7—Cu2—N8	91.31 (13)	N1—Cu1—N3	122.65 (14)
N8 ⁱⁱⁱ —Cu2—N8	177.4 (3)	N3—Cu1—N3 ⁱⁱⁱ	114.7 (3)

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

Table 2

Hydrogen bonds (Å, °) in (I).

$D\text{---}H\cdots A$	$D\cdots A$	$H\cdots A$	$D\text{---}H\cdots A$
N7—H7C ^{iv} ···O1 ^{iv}	3.143 (7)	2.26	169
N6—H6A ^v ···O1 ^v	3.096 (8)	2.27	152
O1—H1W ^{vi} ···N4 ^{vi}	2.903 (8)	2.14 (2)	160 (5)
O1—H2W ^{vii} ···N4 ^{vii}	3.144 (10)	2.38 (3)	162 (6)

Symmetry codes: (iv) $1 - x, y, \frac{3}{2} - z$; (v) $1 + x, -1 + y, z$; (vi) $x, 1 + y, 1 + z$; (vii) $1 - x, 1 + y, \frac{1}{2} - z$.

Data collection: *STADIA* (Stoe & Cie, 1996); cell refinement: *STADIA*; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1059). Services for accessing these data are described at the back of the journal.

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