

Low-dimensional compounds containing cyano groups. I. *catena*-Poly[[[dicyanoargentato(I)- κ N]-bis(4-methylpyridine- κ N)copper(II)]- μ -dicyanoargentato(I)- κ^2 N:N']

Ľubica Triščíková,^a Ivan Potočňák^{a*} and Christoph Wagner^b

^aDepartment of Inorganic Chemistry, Faculty of Science, P. J. Šafárik University, Moyzesova 11, SK-041 54 Košice, Slovakia, and ^bInstitute of Inorganic Chemistry, Martin Luther University, Halle-Wittenberg, Kurt Mothes Straße 2, D-06120 Halle, Germany

Correspondence e-mail: potocnak@kosice.upjs.sk

Received 29 November 2001

Accepted 1 February 2002

Online 21 March 2002

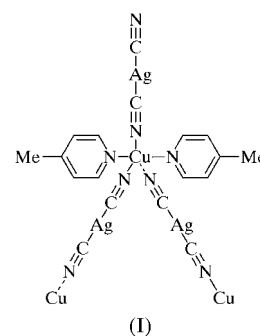
The structure of the title compound, [Cu(C₆H₇N)₂-{Ag(CN)₂}]_n, is made up of neutral zigzag chains of [-NC-Ag-CN-Cu(4-Mepy)₂{Ag(CN)₂}-NC-Ag-CN-] (4-Mepy is 4-methylpyridine). Neighbouring chains are linked by weak argentophilic interactions, with Ag...Ag distances of 3.2322 (12) Å. The Cu atom, which lies on a twofold rotation axis, is pentacoordinated by one monodentate Ag(CN)₂⁻ anion [Cu—N 1.985 (3) Å], the atoms of which lie on the same rotation axis, and by bridging dicyanoargentate anions [2 × Cu—N 2.0827 (19) Å], with Ag atoms on inversion centres. The coordination polyhedron is completed by two 4-Mepy molecules [2 × Cu—N 2.038 (2) Å], which occupy the axial positions of a distorted trigonal bipyramid.

Comment

Cyano complexes possessing various degrees of dimensionality and containing paramagnetic central atoms have often been the subject of magnetic studies (Verdaguer *et al.*, 1999; Ohba & Okawa, 2000). In previous papers by our research group (Černák *et al.*, 1998, 2000), we have outlined our interest in low-dimensional solids. A brief description of the structures and magnetic properties of known one-dimensional cyano complexes was given in a review by Černák *et al.* (2001). The construction of such solids requires linking of the paramagnetic centres by suitable bridging species. The ability of a cyano group to form μ_2 bridges of the $M-C\equiv N-M'$ type makes cyano complexes well suited to this. The low values of exchange coupling in this class of one-dimensional compounds make them especially suitable for experimental investigation of systems with strong crystal field anisotropy, systems with

comparable exchange and dipolar coupling and, potentially, Heisenberg antiferromagnetic chains with alternating spins.

The preparation of solid cyano complexes is based on a combination of suitable building blocks; this is the so-called 'bricks and mortar' method (Willet *et al.*, 1993). The building blocks in solution are formed by complex cations with at least two coordination sites occupied by weak ligands (bricks), and bridging cyano complex anions (mortar) which can replace the weak ligands, thus inducing polymerization of the structure in the solid state. Such a method was also used in the preparation of the title one-dimensional compound, [Cu(4-Mepy)₂Ag₂(CN)₄] (4-Mepy is 4-methylpyridine), (I), and we present its structure in this paper.



The structure of (I) is made up of neutral zigzag chains, and part of one chain is shown in Fig. 1. The backbone of the chain (-NC-Ag-CN-Cu-NC-Ag-CN-) is formed by pentacoordinate Cu^{II} atoms lying on the twofold rotation axis, which are connected by bridging Ag(CN)₂⁻ anions with Ag atoms on inversion centres. The remaining three coordination sites are occupied by monodentate ligands, *i.e.* one Ag(CN)₂⁻ anion and two 4-Mepy molecules.

The longest Cu—N distances in the coordination polyhedron are two Cu1—N1 distances of 2.0827 (19) Å [N1 from the bridging Ag(CN)₂⁻ anion]. All atoms of the terminally bonded dicyanoargentate anion lie on the same rotation axis as the Cu atom. These monodentate Ag(CN)₂⁻ anions are oriented perpendicular to the chain, directed to alternate sides.

In contrast with the Cu1—N1 distances above, the Cu1—N2 bond [N2 from the terminal Ag(CN)₂⁻ anion] is the shortest in the coordination polyhedron [1.985 (3) Å], although both dicyanoargentate anions are coordinated in the equatorial plane.

The two 4-Mepy molecules are coordinated in axial positions, at a distance of 2.038 (2) Å, with the two Cu1—N10 bonds oriented nearly perpendicular both to the terminal Ag(CN)₂⁻ anion and to the chain direction.

Thus, the chromophore in (I) is {CuN₅} and the coordination polyhedron adopts the shape of a distorted trigonal bipyramid. The degree of distortion is only small, as confirmed by the τ parameter (Addison *et al.*, 1984) of 84.6 (ideal values are 100 for a trigonal bipyramid and 0 for a tetragonal pyramid). In accordance with this statement, if we assign α_3 to the N1—Cu1—N1 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), the shape of the coordination

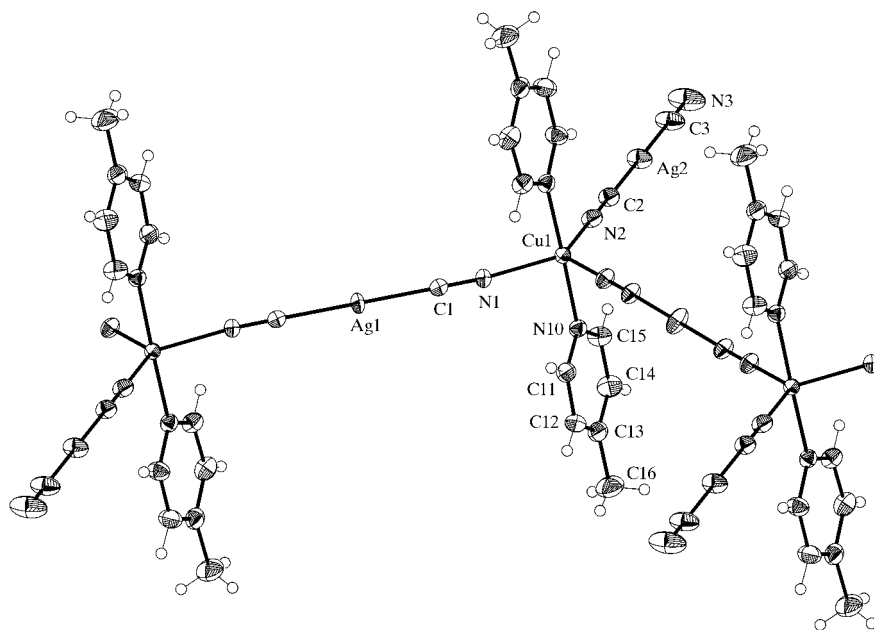


Figure 1

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

polyhedron in (I) can be described as trigonal bipyramidal with near C_{2v} symmetry. The C_2 axis passes through atoms N2 and Cu.

Bond distances and angles within the planar 4-Mepy ring [the largest deviation from the mean plane is of 0.005 (3) Å for C14] are normal for aromatic rings, and range from 1.337 (3) to 1.388 (4) Å and from 116.6 (2) to 123.3 (3)°, respectively, while the C13–C16 single-bond length is 1.497 (4) Å.

There are no unusual features in the dicyanoargentate anions. Although they are differently ligated, equivalent bond lengths and angles are almost equal. The co-existence of both bridging and monodentate $\text{Ag}(\text{CN})_2^-$ anions in one compound is not common. Nevertheless, it has been observed in $[\text{Cd}(4\text{-ampy})_2\{\mu\text{-Ag}(\text{CN})_2\}_2][\text{Cd}(\text{mea})(4\text{-ampy})\{\text{Ag}(\text{CN})_2\}\{\mu\text{-Ag}(\text{CN})_2\}_2]$ (4-ampy is 4-aminopyridine and mea is 2-aminoethanol; Soma & Iwamoto, 1996a). It is worth noting that in the related clathrate compound $[\text{Cd}(4\text{-Mepy})_2\text{Ag}_2(\text{CN})_4]\cdot 4\text{-Mepy}$, in which the host part exhibits the same stoichiometry as (I), only bridging $\text{Ag}(\text{CN})_2^-$ anions were observed. This reflects the preference of Cd for hexacoordination. As a consequence, the host part of the clathrate consists of a three-dimensional framework and not of chains (Soma & Iwamoto, 1994). Other dicyanoargentates with the general formula $[\text{Cu}(L)_2\text{Ag}_2(\text{CN})_4]$, analogous to (I) [L is ethylenediamine (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 where 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).

The chains in (I) are linked by weak argentophilic interactions, which are characteristic of dicyanoargentates (Omary

et al., 1998; Soma & Iwamoto, 1994, 1996b; Soma *et al.*, 1994; Černák *et al.*, 1998). A typical range for these $\text{Ag}\cdots\text{Ag}$ contacts is *ca* 3.05–3.26 Å, but both shorter [2.9879 (9) Å; Soma & Iwamoto, 1994] and longer [3.899 (1) Å; Omary *et al.*, 1998] contacts have been reported. In (I), the zigzag chains are stacked into layers parallel to (010) (Fig. 2). Monodentate $\text{Ag}(\text{CN})_2^-$ anions are directed from the 'peaks' of the zigzag chains of one layer to the 'valleys' between two neighbouring chains in the layers above and below. As a consequence, each Ag1 atom [from a bridging $\text{Ag}(\text{CN})_2^-$ anion] is surrounded by two Ag2 atoms [from monodentate $\text{Ag}(\text{CN})_2^-$ anions], and each Ag2 atom is surrounded by two Ag1 atoms from two chains in neighbouring layers. The Ag1 \cdots Ag2 distance is 3.2322 (12) Å, and the Ag1 \cdots Ag2 \cdots Ag1 and Ag2 \cdots Ag1 \cdots Ag2 angles are 157.262 (13) and 180.0°, respectively.

These argentophilic interactions connect the chains to form an infinite three-dimensional network.

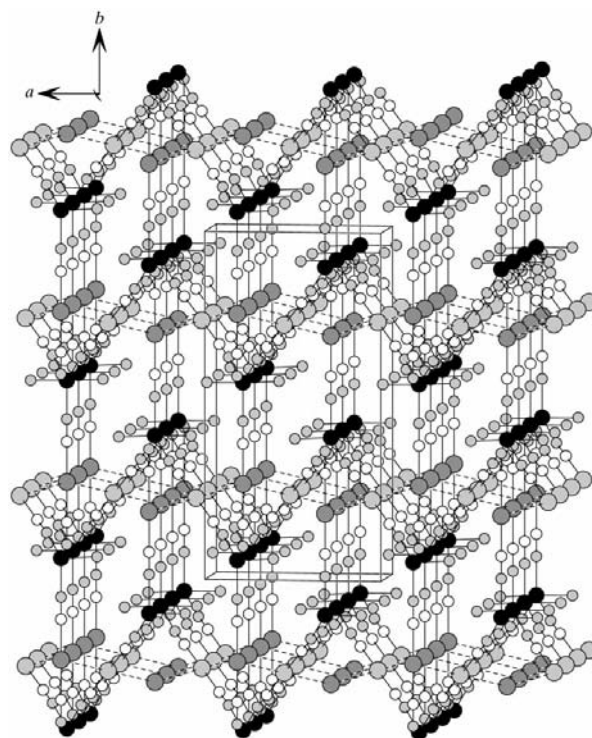


Figure 2

The packing of chains in (I), with the $\text{Ag}\cdots\text{Ag}$ interactions shown as dashed lines. Cu atoms are shown as black circles, C as white, N as small light grey, Ag1 as large light grey and Ag2 as large dark grey. Only the N atoms of the 4-Mepy molecules are shown for clarity.

Experimental

Crystals of (I) were prepared by successive addition of 2 M aqueous 4-methylpyridine (1 ml) and 0.2 M aqueous K[Ag(CN)₂] (10 ml) to 0.1 M aqueous CuSO₄ (10 ml). The precipitate which formed was dissolved by addition of concentrated (26%) ammonia solution (1.5 ml). A mixture of green crystals (0.085 g) and pale-blue crystals of (I) (0.256 g) appeared within 1 d. The crystals were filtered off, washed with a small amount of cold water and dried in air. The crystals of (I) were mechanically separated under a microscope. Elemental analysis of (I), calculated for C₁₆H₁₄Ag₂CuN₆: C 33.74, H 2.48, N 14.75, Ag 37.87, Cu 11.16%; found: C 33.79, H 2.29, N 14.32, Ag 38.81, Cu 11.45%. IR [KBr disc, $\nu(\text{CN})$, cm⁻¹]: 2137 (*m*), 2163 (*s*), 2172 (*vs*). The green crystals are still under investigation; elemental analysis (found: C 40.75, H 3.60, N 15.27, Ag 26.65, Cu 12.45%) corresponds best to a mixed-valence compound with the formula [Cu^{II}(4-Mepy)₃Ag_{2-x}Cu₁(CN)₄], with *x* = 0.26. Analysis calculated for C₂₂H₂₁Ag_{1.74}Cu_{1.26}N₇ (*M_r* = 651.21): C 40.58, H 3.25, N 15.12, Ag 28.82, Cu 12.30%. IR [$\nu(\text{CN})$, cm⁻¹]: 2108 (*w*), 2136 (*s*), 2168 (*s*).

Crystal data

[Ag ₂ Cu(CN) ₄ (C ₆ H ₇ N) ₂]	<i>D_x</i> = 1.982 Mg m ⁻³
<i>M_r</i> = 569.61	Mo <i>K</i> α radiation
Monoclinic, <i>C</i> ₂ / <i>c</i>	Cell parameters from 6639 reflections
<i>a</i> = 11.752 (3) Å	<i>θ</i> = 1.7–26.1°
<i>b</i> = 17.795 (3) Å	<i>μ</i> = 3.15 mm ⁻¹
<i>c</i> = 9.594 (3) Å	<i>T</i> = 220 (2) K
<i>β</i> = 107.95 (3)°	Prism, pale blue
<i>V</i> = 1908.7 (8) Å ³	0.18 × 0.12 × 0.05 mm
<i>Z</i> = 4	

Data collection

Stoe IPDS diffractometer	1591 reflections with <i>I</i> > 2σ(<i>I</i>)
φ scans	<i>R</i> _{int} = 0.033
Absorption correction: numerical	<i>θ</i> _{max} = 25.8°
(<i>IPDS FACE</i> ; Stoe & Cie, 1999)	<i>h</i> = -14 → 14
<i>T</i> _{min} = 0.674, <i>T</i> _{max} = 0.859	<i>k</i> = -21 → 21
6594 measured reflections	<i>l</i> = -11 → 11
1835 independent reflections	

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.031P)^2 + 0.277P]$
$R[F^2 > 2\sigma(F^2)] = 0.019$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.049$	(Δ/σ) _{max} = 0.001
<i>S</i> = 1.01	$\Delta\rho_{\text{max}} = 0.27 \text{ e } \text{Å}^{-3}$
1835 reflections	$\Delta\rho_{\text{min}} = -0.52 \text{ e } \text{Å}^{-3}$
119 parameters	
H-atom parameters constrained	

H-atom positions were calculated and then refined using a riding model or rigid methyl groups, with C–H = 0.93–0.96 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C).

Data collection: *EXPOSE* in *IPDS* (Stoe & Cie, 1999); cell refinement: *CELL* in *IPDS*; data reduction: *INTEGRATE* in *IPDS*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997);

Table 1

Selected geometric parameters (Å, °).

Ag2–C3	2.055 (4)	Ag1–C1	2.077 (2)
Ag2–C2	2.063 (3)	Ag1 ⁱ ···Ag2 ⁱ	3.2322 (12)
Cu1–N2	1.985 (3)	N1–C1	1.149 (3)
Cu1–N10	2.038 (2)	N2–C2	1.146 (5)
Cu1–N1	2.0827 (19)	N3–C3	1.137 (5)
C3–Ag2–C2	180.0	C1 ^v –Ag1–C1	180.0
Ag1 ⁱⁱ ···Ag2 ⁱ ···Ag1 ⁱⁱⁱ	157.262 (13)	Ag2 ⁱ ···Ag1 ⁱ ···Ag2 ^{vi}	180.0
N2–Cu1–N10	91.12 (5)	C1–N1–Cu1	175.2 (2)
N10–Cu1–N10 ^{iv}	177.76 (11)	N1–C1–Ag1	179.0 (2)
N2–Cu1–N1	127.00 (6)	C2–N2–Cu1	180.0
N10–Cu1–N1	89.09 (8)	N2–C2–Ag2	180.0
N10 ^{iv} –Cu1–N1	89.57 (8)	N3–C3–Ag2	180.0
N1 ^{iv} –Cu1–N1	106.00 (11)		

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

molecular graphics: *DIAMOND* (Crystal Impact, 1999); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Grant Agency VEGA (grant No. 1/7426/20). The authors thank Dr J. Černák for valuable comments on the manuscript.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1492). Services for accessing these data are described at the back of the journal.

References

- Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
- Černák, J., Abboud, K. A., Chomič, J., Meisel, M. W., Orendáč, M., Orendáčová, A. & Feher, A. (2000). *Inorg. Chim. Acta*, **311**, 126–132.
- Černák, J., Chomič, J., Gravereau, P., Orendáčová, A., Orendáč, M., Kováč, J., Feher, A. & Kappenstein, C. (1998). *Inorg. Chim. Acta*, **281**, 134–140.
- Černák, J., Gérard, F. & Chomič, J. (1993). *Acta Cryst.* **C49**, 1294–1296.
- Černák, J., Orendáč, M., Potočňák, I., Chomič, J., Orendáčová, A., Skoršepa, J. & Feher, A. (2001). *Coord. Chem. Rev.* **224**, 51–66.
- Crystal Impact (1999). *DIAMOND*. Release 2.1.e. Crystal Impact, D-53002 Bonn, Germany.
- Harrison, W. D. & Hathaway, B. J. (1980). *Acta Cryst.* **B36**, 1069–1074.
- Ohba, M. & Okawa, H. (2000). *Coord. Chem. Rev.* **198**, 313–328.
- Omary, M. A., Webb, T. R., Assefa, Z., Shankle, G. E. & Patterson, H. H. (1998). *Inorg. Chem.* **37**, 1380–1386.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Soma, T. & Iwamoto, T. (1994). *Chem. Lett.* pp. 821–824.
- Soma, T. & Iwamoto, T. (1996a). *Acta Cryst.* **C52**, 1200–1203.
- Soma, T. & Iwamoto, T. (1996b). *Inorg. Chem.* **35**, 1849–1856.
- Soma, T., Yuge, H. & Iwamoto, T. (1994). *Angew. Chem. Int. Ed. Engl.* **33**, 1665–1666.
- Stoe & Cie (1999). *IPDS*. Version 2.90. Stoe & Cie, Darmstadt, Germany.
- Verdaguer, M., Bleuzen, A., Marvaud, V., Vaissermann, J., Seuleiman, M., Desplanches, C., Scuiller, A., Train, C., Garde, R., Gelly, G., Lomenech, C., Rosenman, I., Veillet, P., Cartier, C. & Villain, F. (1999). *Coord. Chem. Rev.* **190–192**, 1023–1047.
- Willet, R. D., Wang, Z., Molnar, S., Brewer, K., Landee, C. P., Turnbull, M. M. & Zhang, W. (1993). *Mol. Cryst. Liq. Cryst.* **233**, 277–282.