# metal-organic compounds

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# $Cu_2(dien)_2Ag_5(CN)_9$ containing the one-dimensional polymeric cation $[Cu(dien)Ag(CN)_2]_n^{n+}$ and the unusual $[Ag_2(CN)_3]^-$ anion (dien is diethylenetriamine)

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From the 1:1 system of [Cu(dien)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> and K[Ag(CN)<sub>2</sub>] in water (dien is diethylenetriamine, C<sub>4</sub>H<sub>13</sub>N<sub>3</sub>), the novel compound *catena*-poly[bis][ $\mu$ -cyano-1:2 $\kappa^2 C$ :N-diethylenetriamine- $2\kappa^3 N$ -copper(II)silver(I)]- $\mu$ -cyano-1: $2\kappa^2 C$ :N] dicyanosilver(I) tricyanodisilver(I)], [CuAg(CN)<sub>2</sub>(dien)]<sub>2</sub>[Ag(CN)<sub>2</sub>]- $[Ag_2(CN)_3]$ , has been isolated. The structure is formed from positively charged  $[-Cu(dien)-NC-Ag-CN-]_n^{n+}$  chains and two isolated centrosymmetric  $[Ag(CN)_2]^-$  and  $[Ag_2(CN)_3]^$ anions. In the cationic chains, the Cu atoms are linked by bridging dicyanoargentate groups, and the deformed squarepyramidal coordination polyhedron of the Cu<sup>II</sup> cation is formed from a tridentate chelate-like bonded dien ligand and two N-bonded bridging cyano groups. One of the bridging cyano groups occupies the apical (ap) position [mean  $Cu-N_{eq} = 2.02 (2) \text{ Å}$ , and  $Cu-N_{ap} = 2.170 (3) \text{ Å}$ ; eq is equatorial]. Short argentophilic interactions in the range 3.16–3.30 Å are present in the crystal structure.

# Comment

The magnetic properties of cyano complexes are currently the subject of intensive study (Verdaguer *et al.*, 1999; Dunbar & Heintz, 1997). These complexes are suitable model compounds for the study of magnetic phenomena, due to the favourable properties of cyanometallate anions, *viz.* the geometric and magnetic variability of the anions with various central atoms, the rigidity and stability of the anions, and the Lewis basicity of the N atoms, which facilitates the bridging function of the cyano group. The dicyanoargentate anion  $[NC-Ag-CN]^-$ , with a linear geometry, may exhibit a bridging function, *e.g.* in the one-dimensional compound [Cd(N-M)]

 $Meim)_4Ag(CN)_2][Ag(CN)_2]$  (*N*-Meim is *N*-methylimidazole; Soma & Iwamoto, 1996), although it can also act as a terminal ligand, *e.g.* in the dinuclear compound  $[N(Ph)_4][ClPh_3Sn-NC-AgCN]$  (Carcelli *et al.*, 1992). In addition, it can simply play the role of a counter-ion, as in  $[Ni(en)_3][Ag(CN)_2]_2$  (en is ethylenediamine; Kappenstein *et al.*, 1988). A more complicated role is that which the cyanoargentate anion plays as part of the polymeric  $[Ag_3(CN)_5]^{2-}$  anion (Zhang *et al.*, 1999).

We are interested in the preparation, crystal chemistry and magnetic properties of low-dimensional cyano complexes. It is known that the Cu<sup>II</sup> cation in these cyano complexes, apart from the usual 4+2 coordination, often exhibits pentacoordination. This property can be used in the synthetic design of one-dimensional polymeric species; when three coordination sites are blocked by a suitable 3N-donor ligand, the presence of cyanometallate anions can lead to the formation of one-dimensional structures, *e.g.* in [Cu(dien)]<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub>·6H<sub>2</sub>O (Kou *et al.*, 1997). Following this idea, we reacted dien as a 3N-donor ligand with Cu<sup>II</sup>, and added dicyanoargentate anions with the intention that they would act as a bridging species. By this reaction, the title compound, (I), was formed and herein we report its crystal structure.

$$\begin{bmatrix} \sum_{N-U-NC-Ag-CN-}^{N-I} & n [NC-Ag-CN]^{n-I} & n [NC-Ag-CN]^{n-I} \\ & & (I) \end{bmatrix}$$

The structure of (I) is formed from  $[-Cu(dien)-NC-Ag-CN-]_n^{n+}$  cationic zigzag chains running parallel along the *y* axis (Fig. 1). The positive charge of these chains is counterbalanced by two different non-coordinated centrosymmetric cyanoargentate anions lying on special positions ( $\overline{1}$ ), namely one dicyanoargentate anion,  $[Ag(CN)_2]^-$  (Ag2), and one tricyanodiargentate anion,  $[Ag_2(CN)_3]^-$  (Ag3).

The Cu<sup>II</sup> cation exhibits pentacoordination in a form close to a deformed square pyramid, as is indicated by the the  $\tau$ parameter of 10.2 (Addison et al., 1984). As expected, three coordination sites in the basal plane are occupied by the chelate-bonded dien ligand, and the remaining two sites, one in the basal plane and the apical site, are occupied by the N atoms of the bridging cyano groups. The Cu-N distances in the basal plane (Table 1) are very similar despite the different nature of the ligands, with a mean value of 2.02 (2) Å, while the ligand in the apical position is at a longer distance of 2.170 (3) A. The Cu atom is displaced by 0.3052 (4) A from the mean basal plane toward the apical ligand. The geometric parameters of the dien ligand in (I) are similar to those found in similar compounds (Rodriguez et al., 1999). The presence of the dien ligand manifests itself in the form of various IR absorption bands due to  $\nu(NH_2)$ ,  $\nu(CH_2)$  and other types of vibrations; these are listed in the Experimental section. It is interesting to note that the electronic spectrum in the solid state exhibits only a single absorption band at  $16\,300\,\mathrm{cm}^{-1}$ . This displays only very weak asymmetry, which may indicate the presence of a shoulder on the lower energy side, as expected in such coordination (Lever, 1984). The possible

assignment(s) to the observed absorption band envelope can be given as  ${}^{2}E \leftarrow {}^{2}B_{1}$  and  ${}^{2}B \leftarrow {}^{2}B_{1}$ .

The tricyanodiargentate anion is found as a bridging species in some cyano complexes with Cd, e.g. [Cd(4-Mepy)<sub>4</sub>-Ag<sub>2</sub>(CN)<sub>3</sub>] (4-Mepy is 4-methylpyridine; Soma & Iwamoto, 1994) and  $[Cd(pyz){Ag_2(CN)_3}{Ag(CN)_2}]$  (pyz is pyrazine; Soma et al., 1994). In (I), the tricyanodiargentate anion is 'unbound' and is centrosymmetric. As a consequence, the cyano group linking the two Ag atoms is disordered [label (C,N)32]. The geometric parameters associated with the dicyanoargentate and tricyanodiargentate anions in (I) are unremarkable (Soma & Iwamoto, 1994). The Ag2 anion is perfectly linear (Ag2 lies on the symmetry centre), while the Ag1 and Ag3 anions are somewhat bent at atoms Ag1 and Ag3, respectively. The presence of crystallographically different cyano groups can be seen in the IR spectrum of (I). The absorption bands at 2118 and  $2133 \text{ cm}^{-1}$  can be ascribed to the stretching vibrations of terminal cyano groups, while the remaining two absorption bands at 2156 and  $2165 \text{ cm}^{-1}$  are due to the presence of bridging cyano groups.

Argentophilic interactions (Omary et al., 1998) are responsible for the supramolecular architecture of the struc-

ture of (I) (Fig. 2). The Ag···Ag distances are relatively short (Table 1) compared with the Ag—Ag distance of 2.89 Å in metallic silver (Wells, 1984), but are comparable with those found in similar compounds (Meske & Babel, 1988). If we also take into consideration the Ag2···Ag3 contacts of 3.5373 (5) Å, the Ag atoms form chains based on interconnected hexagons and extended along the *c* direction. Besides these argentophilic interactions, weak N—H···N hydrogen bonds between the terminal N atoms of the cyano groups and the NH groups of the amine ligand contribute to the packing mode of the structure (Table 2).

The outstanding feature of the structure of (I) is the onedimensional character of the polymeric cation. This can be classified as of the CT type (Černák *et al.*, 2002), as the bridging cyano groups are in neighbouring *cis* positions at the pentacoordinated Cu<sup>II</sup> cation and in *trans* positions (forced by the geometry of the anion) on the Ag<sup>I</sup> cation. Such a type of chain among dicyanoargentates was previously found only in  $[Cu(bipy)_2Ag_2(CN)_4]\cdotH_2O$ , where the *cis* positions of the bridging cyano groups in the 4+1+1-type coordination polyhedron of the Cu atom are forced by the presence of sterically demanding bipy ligands (bipy is 2,2'-bipyridine; Černák *et al.*, 1993).



#### Figure 1

A view of the basic structural units of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry codes: (i)  $\frac{1}{2} - x$ ,  $y - \frac{1}{2}$ ,  $\frac{1}{2} - z$ ; (ii)  $\frac{1}{2} - x$ ,  $\frac{1}{2} + y$ ,  $\frac{1}{2} - z$ ; (iii) -x, 1 - y, -z; (iv) -x, 1 - y, 1 - z].

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## Figure 2

(a) The cationic zigzag chains along **b** and the argentophilic interactions along **c** between the Ag atoms in the anions of (I) (dotted lines). (b) A view of the structure of (I) projected approximately along [001]. H atoms have been omitted for clarity.

# **Experimental**

The preparation of (I) was carried out as follows: a blue solution containing aqueous  $[Cu(dien)_2]^{2+}$  cations, formed by mixing a 0.1 M solution of copper nitrate (10 ml, 1 mmol) and dien (0.22 ml, 2 mmol), was mixed with a colourless solution of K[Ag(CN)<sub>2</sub>], formed by dissolving AgNO<sub>3</sub> (0.34 g, 2 mmol) in a 0.4 M solution of KCN (10 ml, 4 mmol). The resulting blue solution was left to crystallize. Blue single crystals of (I) suitable for X-ray analysis were obtained after 1-2 d; these were filtered off and dried in air. Analysis calculated for C17H26Ag5Cu2N15: C 18.45, H 2.35, N 18.98, Cu 11.48, Ag 48.72%; found: C 18.72, H 2.42, N 19.42, Cu 11.42, Ag 49.20%. An IR spectrum (KBr disc) was measured on a Nicolet 510 FT-IR spectrometer from 4000 to 400  $\text{cm}^{-1}$  with absorption bands (cm<sup>-1</sup>) at 3309 (vs), 3268 (vs), 3238 (vs), 3157 (s), 2165 (s), 2156 (vs), 2133 (s), 2118 (s), 1606 (s), 1598 (s), 1467 (m), 1457 (m), 1429 (m), 1257 (m), 1141 (s), 1086 (vs), 1057 (m), 1021 (vs), 946 (s), 835 (m), 710 (m), 645 (m), 533 (s) and 442 (vs). The electronic spectrum was measured by reflectance using a Specord M40 Instrument (Zeiss Jena) from 30 000 to 11 000 cm<sup>-1</sup> (BaSO<sub>4</sub> standard).

### Crystal data

[CuAg(CN)2(C4H13N3)]2- $[Ag(CN)_2][Ag_2(CN)_3]$  $M_r = 1106.96$ Monoclinic,  $P2_1/n$ a = 12.5588 (12) Åb = 17.8070 (12) Åc = 6.9608 (6) Å  $\beta = 90.794 (11)^{\circ}$ V = 1556.5 (2) Å<sup>3</sup> Z = 2 $D_x = 2.362 \text{ Mg m}^{-3}$  $D_m = 2.36 (1) \text{ Mg m}^{-3}$ 

### Data collection

Stoe IPDS diffractometer @ scans Absorption correction: numerical (SHELXTL; Sheldrick, 1995)  $T_{\rm min}=0.414,\;T_{\rm max}=0.809$ 18 169 measured reflections 4462 independent reflections

# Refinement

Refinement on $F^2$	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.031$	$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2]$
$wR(F^2) = 0.067$	where $P = (F_o^2 + 2F_c^2)/3$
S = 0.88	$(\Delta/\sigma)_{\rm max} < 0.001$
4462 reflections	$\Delta \rho_{\rm max} = 0.83 \ {\rm e} \ {\rm \AA}^{-3}$
219 parameters	$\Delta \rho_{\rm min} = -0.65 \text{ e } \text{\AA}^{-3}$

 $D_m$  measured by flotation in a

Cell parameters from 8000

 $0.33 \times 0.15 \times 0.05 \text{ mm}$ 

2988 reflections with  $I > 2\sigma(I)$ 

acetone

Mo  $K\alpha$  radiation

reflections

 $\theta = 2.8 - 30.3^{\circ}$  $\mu = 4.45 \text{ mm}^{-1}$ 

T = 293 (2) KParallelepiped, blue

 $R_{\rm int} = 0.056$ 

 $\theta_{\rm max} = 30.3^{\circ}$  $h = -17 \rightarrow 17$  $k = -25 \rightarrow 25$ 

 $l = -8 \rightarrow 9$ 

mixture of bromoform and

## Table 1

Selected geometric parameters (Å, °).

$\Delta \sigma 1 \dots \Delta \sigma 2$	3 2970 (4)	Cu-N3	2 026 (3)
Δσ1Δσ3	3 1635 (6)	Cu=N11	1.020(3)
Ag1 = C11	2.074(4)	Cu=N12	2170(3)
$\Delta g1 - C12$	2.074(4) 2.075(3)	N11 - C11	1.152(5)
$\Delta g^2 = C^{21}$	2.073(3)	N12 $C12^{i}$	1.132(3) 1.143(4)
Ag2 = C21 Ag3 = C31	2.062(4)	N12-C12 N21_C21	1.143(4) 1.142(5)
Cu=N1	2.003(4) 2.014(3)	N31_C31	1.142(5) 1 141(5)
Cu=N1 Cu=N2	2.014(3) 2.032(3)	101-051	1.141 (5)
Cu-112	2.032 (3)		
C11-Ag1-C12	169.69 (15)	N11-Cu-N12	102.07 (13)
N11-Cu-N1	95.89 (13)	N1-Cu-N12	100.33 (14)
N11-Cu-N3	91.11 (13)	N3-Cu-N12	98.41 (14)
N1-Cu-N3	158.13 (15)	N2-Cu-N12	93.47 (13)
N11-Cu-N2	164.12 (14)	C11-N11-Cu	164.2 (3)
N1-Cu-N2	84.36 (13)	C12 <sup>i</sup> -N12-Cu	167.7 (3)
N3-Cu-N2	83.34 (14)		

Symmetry code: (i)  $\frac{1}{2} - x$ ,  $y - \frac{1}{2}, \frac{1}{2} - z$ .

# Table 2

Hydrogen-bonding and short intermolecular contact geometry (Å, °).

$D - H \cdots A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - \mathbf{H} \cdots A$
$N1-H1A\cdots N21^{i}$	0.89 (5)	2.29 (5)	3.119 (5)	154 (4)
$N1 - H1B \cdot \cdot \cdot N31^{ii}$	0.86 (5)	2.20 (5)	3.055 (5)	175 (4)
$N2-H2\cdots N12$	0.97 (4)	2.70 (5)	3.061 (5)	103 (3)
N3−H3 <i>B</i> ···N31	0.85 (5)	2.39 (5)	3.194 (5)	159 (4)
$N3-H3A\cdots N21^{iii}$	0.88 (5)	2.35 (5)	3.189 (5)	161 (4)

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

The C,N site was refined as a 50:50 mixture of both C and N atoms. The Ag3 $\cdots$ (C,N)32 distance is 2.082 (3) Å and the (C,N)32–(C,N)32 distance is 1.141 (7) Å, similar to normal C–N bond lengths. The H-atom positions were refined with common isotropic displacement parameters for the NH<sub>2</sub> and CH<sub>2</sub> groups, respectively, giving C–H distances in the range 0.77 (5)–1.07 (5) Å and N–H distances in the range 0.86 (5)–0.97 (4) Å. There is a short contact between N2–H2 and a symmetry-related Ag3 atom, such that H2 $\cdots$ Ag3 is 2.73 (4) Å.

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, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); program used for geometrical analysis: *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1124). Services for accessing these data are described at the back of the journal.

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