

Cu₂(dien)₂Ag₅(CN)₉ containing the one-dimensional polymeric cation [Cu(dien)Ag(CN)₂]_nⁿ⁺ and the unusual [Ag₂(CN)₃]⁻ anion (dien is diethylenetriamine)

Juraj Černák,^{a*} Jozef Chomič^a and Werner Massa^b

^aDepartment of Inorganic Chemistry, P. J. Šafárik University, Moyzesova 11, 041 54 Košice, Slovakia, and ^bFachbereich Chemie der Universität Marburg, Hans-Meerwein Straße, D-35043 Marburg, Germany
Correspondence e-mail: cernakju@kosice.upjs.sk

Received 3 July 2002

Accepted 23 July 2002

Online 21 September 2002

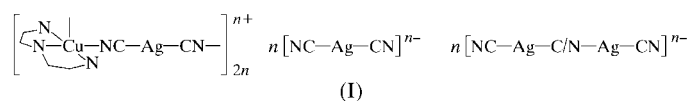
From the 1:1 system of [Cu(dien)₂](NO₃)₂ and K[Ag(CN)₂] in water (dien is diethylenetriamine, C₄H₁₃N₃), the novel compound *catena*-poly[bis[[μ-cyano-1:2κ²C:N-diethylenetriamine-2κ³N-copper(II)silver(I)]-μ-cyano-1:2'κ²C:N] dicyano-silver(I) tricyanodisilver(I)], [CuAg(CN)₂(dien)]₂[Ag(CN)₂]₃[Ag₂(CN)₃], has been isolated. The structure is formed from positively charged [-Cu(dien)-NC-Ag-CN]_nⁿ⁺ chains and two isolated centrosymmetric [Ag(CN)₂]⁻ and [Ag₂(CN)₃]⁻ anions. In the cationic chains, the Cu atoms are linked by bridging dicyanoargentate groups, and the deformed square-pyramidal coordination polyhedron of the Cu^{II} 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) Å, and Cu-N_{ap} = 2.170 (3) 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-

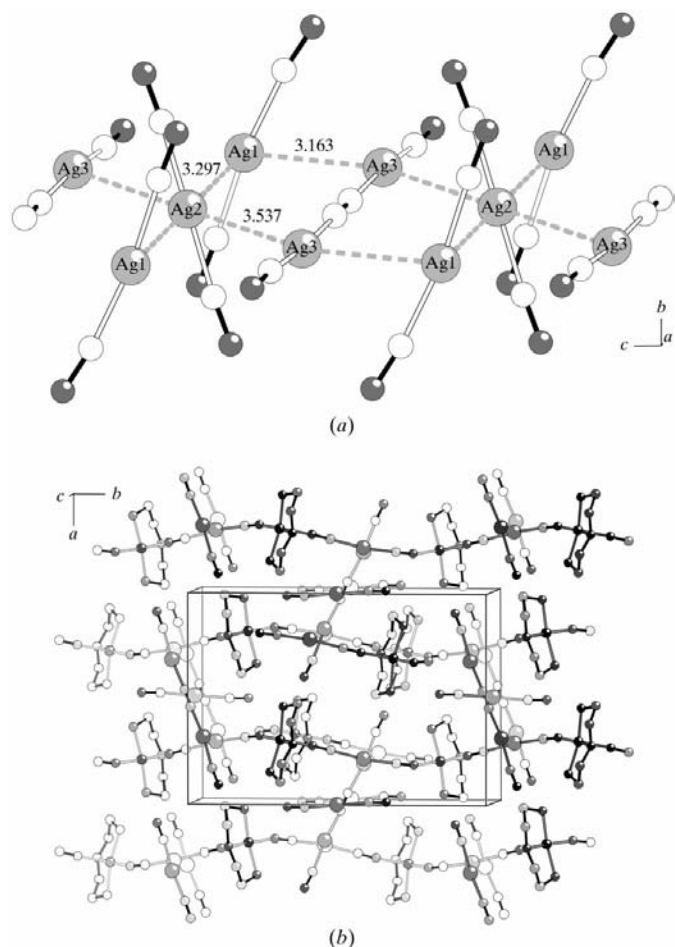
Meim)₄Ag(CN)₂][Ag(CN)₂] (*N*-Meim is *N*-methylimidazole; Soma & Iwamoto, 1996), although it can also act as a terminal ligand, *e.g.* in the dinuclear compound [N(Ph)₄][ClPh₃Sn-NC-AgCN] (Carcelli *et al.*, 1992). In addition, it can simply play the role of a counter-ion, as in [Ni(en)₃][Ag(CN)₂]₂ (en is ethylenediamine; Kappenstein *et al.*, 1988). A more complicated role is that which the cyanoargentate anion plays as part of the polymeric [Ag₃(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^{II} 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)₃][Fe(CN)₆]₂·6H₂O (Kou *et al.*, 1997). Following this idea, we reacted dien as a 3N-donor ligand with Cu^{II}, 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.



The structure of (I) is formed from [-Cu(dien)-NC-Ag-CN]_nⁿ⁺ 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 ($\bar{1}$), namely one dicyanoargentate anion, [Ag(CN)₂]⁻ (Ag2), and one tricyanodiargentate anion, [Ag₂(CN)₃]⁻ (Ag3).

The Cu^{II} cation exhibits pentacoordination in a form close to a deformed square pyramid, as is indicated by the τ 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) Å. The Cu atom is displaced by 0.3052 (4) Å 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 (Rodríguez *et al.*, 1999). The presence of the dien ligand manifests itself in the form of various IR absorption bands due to $\nu(\text{NH}_2)$, $\nu(\text{CH}_2)$ 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 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


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 $[\text{Cu}(\text{dien})_2]^{2+}$ 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 $\text{K}[\text{Ag}(\text{CN})_2]$, formed by dissolving AgNO_3 (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 $\text{C}_{17}\text{H}_{26}\text{Ag}_5\text{Cu}_2\text{N}_{15}$: 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 cm^{-1} with absorption bands (cm^{-1}) 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 $11\,000\text{ cm}^{-1}$ (BaSO₄ standard).

Crystal data

$[\text{CuAg}(\text{CN})_2(\text{C}_4\text{H}_{13}\text{N}_3)_2]_2$
 $[\text{Ag}(\text{CN})_2][\text{Ag}_2(\text{CN})_3]$
 $M_r = 1106.96$
 Monoclinic, $P2_1/n$
 $a = 12.5588$ (12) Å
 $b = 17.8070$ (12) Å
 $c = 6.9608$ (6) Å
 $\beta = 90.794$ (11)°
 $V = 1556.5$ (2) Å³
 $Z = 2$
 $D_x = 2.362\text{ Mg m}^{-3}$
 $D_m = 2.36$ (1) Mg m^{-3}

D_m measured by flotation in a mixture of bromoform and acetone
 Mo $K\alpha$ radiation
 Cell parameters from 8000 reflections
 $\theta = 2.8$ – 30.3°
 $\mu = 4.45\text{ mm}^{-1}$
 $T = 293$ (2) K
 Parallelepiped, blue
 $0.33 \times 0.15 \times 0.05\text{ mm}$

Data collection

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

2988 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.056$
 $\theta_{\max} = 30.3^\circ$
 $h = -17 \rightarrow 17$
 $k = -25 \rightarrow 25$
 $l = -8 \rightarrow 9$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.067$
 $S = 0.88$
 4462 reflections
 219 parameters

All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0352P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.83\text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.65\text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ag1...Ag2	3.2970 (4)	Cu—N3	2.026 (3)
Ag1...Ag3	3.1635 (6)	Cu—N11	1.988 (3)
Ag1—C11	2.074 (4)	Cu—N12	2.170 (3)
Ag1—C12	2.075 (3)	N11—C11	1.152 (5)
Ag2—C21	2.082 (4)	N12—C12 ⁱ	1.143 (4)
Ag3—C31	2.065 (4)	N21—C21	1.142 (5)
Cu—N1	2.014 (3)	N31—C31	1.141 (5)
Cu—N2	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 ⁱ —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, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A...N21 ⁱ	0.89 (5)	2.29 (5)	3.119 (5)	154 (4)
N1—H1B...N31 ⁱⁱⁱ	0.86 (5)	2.20 (5)	3.055 (5)	175 (4)
N2—H2...N12	0.97 (4)	2.70 (5)	3.061 (5)	103 (3)
N3—H3B...N31	0.85 (5)	2.39 (5)	3.194 (5)	159 (4)
N3—H3A...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...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 NH₂ and CH₂ 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...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).

This work was supported by the Slovak Grant Agency VEGA (1/7426/20). One of the authors (JČ) thanks DAAD for its support of a study visit to the University of Marburg.

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.

References

- Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
- Brandenburg, K. (1999). *DIAMOND*. Release 2.1c. Crystal Impact GbR, Bonn, Germany.
- Carcelli, M., Ferrari, C., Pelizzi, C., Pelizzi, G., Predieri, G. & Solinas, C. (1992). *J. Chem. Soc. Dalton Trans.* pp. 2127–2128.
- Černák, J., Gérard, F. & Chomič, J. (1993). *Acta Cryst.* **C49**, 1294–1297.
- Černák, J., Orendáč, M., Potočňák, I., Chomič, J., Orendáčová, A., Skoršepa, J. & Feher, A. (2002). *Coord. Chem. Rev.* **224**, 51–66.
- Dunbar, K. R. & Heintz, R. A. (1997). *Prog. Inorg. Chem.* **45**, 283–391.
- Kappenstein, C., Ouali, A., Guerin, M., Černák, J. & Chomič, J. (1988). *Inorg. Chim. Acta*, **147**, 189–197.
- Kou, H.-Z., Liao, D.-Z., Cheng, P., Jiang, Z.-H., Yan, S.-P., Wang, G.-L., Yao, X.-K. & Wang, H.-G. (1997). *J. Chem. Soc. Dalton Trans.* pp. 1503–1506.
- Lever, A. B. P. (1984). *Inorganic Electronic Spectroscopy*, 2nd ed., pp. 568–569. Amsterdam: Elsevier.
- Meske, W. & Babel, D. (1988). *Z. Naturforsch. Teil B*, **43**, 1167–1173.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Omary, M. A., Webb, T. R., Shankle, G. E. & Paterson, H. H. (1998). *Inorg. Chem.* **37**, 1380–1386.
- Rodríguez, V., Gutierrez-Zorilla, J. M., Vitoria, P., Luque, A., Román, P. & Martínez-Ripoll, M. (1999). *Inorg. Chim. Acta*, **290**, 57–63.
- Sheldrick, G. M. (1985). *SHELXS86*. University of Göttingen, Germany.
- Sheldrick, G. M. (1995). *SHELXTL*. Release 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Soma, T. & Iwamoto, T. (1994). *Chem. Lett.* pp. 821–824.
- Soma, T. & Iwamoto, T. (1996). *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.
- Verdaguier, M., Bleuzen, A., Marvaud, V., Vaissermann, J., Seuleiman, M., Desplanches, C., Scuille, A., Train, C., Garde, R., Gelly, G., Lomenech, C., Rosenman, I., Veillet, P., Cartier, C. & Villain, F. (1999). *Coord. Chem. Rev.* **1023**, 190–192.
- Wells, A. F. (1984). *Structural Inorganic Chemistry*, 5th ed., p. 1098. Oxford: Clarendon Press.
- Zhang, H.-X., Chen, Z.-N., Su, C.-Y., Ren, C. & Kang, B.-S. (1999). *J. Chem. Crystallogr.* **29**, 1239–1243.