Smith, R. A. (1975*b*). *Acta Cryst.* B**31**, 2347–2348.
Sorokina, N. I., Molchanov, V. N., Turskaya, T. N., Furmanova, N. G. & Belikova, G. S. (1989). *Kristallografiya*, **34**, 112–116.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Teplova, T. B., Turskaya, T. N., Shibanova, T. A., Nekrasov, Yu. V. & Belikova, G. S. (1986). *Kristallografiya*, **31**, 187–189.
Teplova, T. B., Turskaya, T. N., Tovbis, A. B., Zavodnik, V. E., Shibanova, T. A. & Belikova, G. S. (1984). *Kristallografiya*, **29**, 726–730.
Town, W. G. & Small, R. W. H. (1973). *Acta Cryst.* B**29**, 1950–1955.
Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1993). C**49**, 1294–1296

catena-Poly[silver(I)-μ-(cyano-*C*:*N*)-*cis*-bis-(2,2′-bipyridine-*N*,*N*′)copper(II)-μ-(cyano-*N*:*C*)] Dicyanoargentate(I) Monohydrate

JURAJ ČERNÁK†

Laboratoire de Chimie Minérale, Université de Poitiers, 40 Avenue du Recteur Pineau, 86 022 Poitiers, France

FRANÇOIS GÉRARD

Laboratoire de la Cristallochimie Minérale, Université de Poitiers, France

JOZEF CHOMIČ

Department of Inorganic Chemistry, P. J. Šafárik University, Moyzesova 11, 041 54 Košice, Czechoslovakia

(*Received* 27 *April* 1992; *accepted* 11 *January* 1993)

Abstract

The structure of the title complex is built up of positively charged zigzag chains running parallel to the *b* axis with the composition cis[-μ-CN-Cu(bpy)$_2$-μ-NC-Ag-]$^+$ (bpy = 2,2′-bipyridine), isolated $[Ag(CN)_2]^-$ anion and non-coordinated water molecule. The Cu atom is coordinated in the form of a very deformed tetragonal bipyramid (4 + 1 + 1) with unequal distortion of the axial bonds [2.239 (4) and 2.676 (5) Å]. Three crystallographically independent Ag atoms are coordinated linearly by two cyano groups and they are placed along the *b* axis forming an infinite chain with short Ag···Ag distances [3.0439 (4) and 2.9866 (4) Å]. One of the two non-coordinated independent water molecules shows partial occupancy of its disordered position.

Comment

The structure determination of the title complex forms a continuation of the study on the preparation, structure, thermal and other properties of bimetallic dicyanoargentates with nitrogen-containing ligands (Kappenstein, Ouali, Guerin, Černák & Chomič, 1988; Chomič, Černák, Potočňák, Zvereva & Saveljeva, 1993).

From a chemical point of view, two features of the studied structure are outstanding: the coordination mode of the Cu^{II} atom and the existence of infinite chains of Ag atoms with short Ag···Ag distances.

The coordination number of the Cu^{II} atom is six in the form 4 + 1 + 1. Four N atoms (three from bpy and one from a bridging cyano group) lie in the equatorial plane at normal distances (Table 2, Fig. 1); the axial positions are occupied by one N atom from bpy at a somewhat longer distance of 2.239 (4) Å, and one N atom from the bridging cyano group at a long distance of 2.676 (5) Å. A search in the Cambridge Structural Database (Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink, Hummelink-Peters, Kennard, Motherwell, Rodgers & Watson, 1991) among the CuN_6 hexacoordinated Cu complexes showed that similar distortion exists in the structure of $[Cu(bpy)_3](ClO_4)_2$ with somewhat shorter second axial Cu—N bonds: 2.226 (7) and 2.450 (7) Å (Anderson, 1972). A value of 2.627 (9) Å for the Cu—N bond was found in the complex $[Cu_3(bep)_2(\mu\text{-}N_3)_6]$ [bep = 2-benzoylpyridine (Goher & Mak, 1985)] and Cu—N bonds with values of 2.593 Å were found in two complexes: $[Cu(aep)_2(NCS)_2]$ [aep = 2-(2-aminoethyl)pyridine (Kozlowski & Hodgson, 1975)] and $[Cu(im)_6](NO_3)_2$ [im = imidazole (McFadden, McPhail, Garner & Mabbs, 1975)]. The formation of a deformed coordination polyhedron around the Cu atom is a manifestation of the Jahn–Teller effect. The bond distances and angles in the bpy ligands are normal (Manríquez, Brito, Andrade, Wittke, von Schnering & Peters, 1988).

The distances between Ag atoms are short (Table 2) and account for the metal–metal interaction. The distances are shorter than the 3.222 (1) Å found in the similar complex $[Zn(en)_2NCAgCN][Ag(CN)_2]$ (Kappenstein, Ouali, Guerin, Černák & Chomič, 1988) and comparable with the value of 3.032 (1) Å found in $Ag_3(NSO_2)_3.3H_2O$ (Dalgaard, Hazell & Hazell, 1974). The comparable distance in the metal is 2.89 Å (Wells, 1984). The bond distances and angles in the $[Ag(CN)_2]^-$ anions are normal (Zabel, Kühnel & Range, 1989).

† On leave from Department of Inorganic Chemistry, P. J. Šafárik University, Košice, Czechoslovakia.

The non-coordinated water molecule exhibits high thermal motion and is placed in the free space in the lattice. Some of the intermolecular distances of the type O···N(CN) indicate the formation of hydrogen bonds.

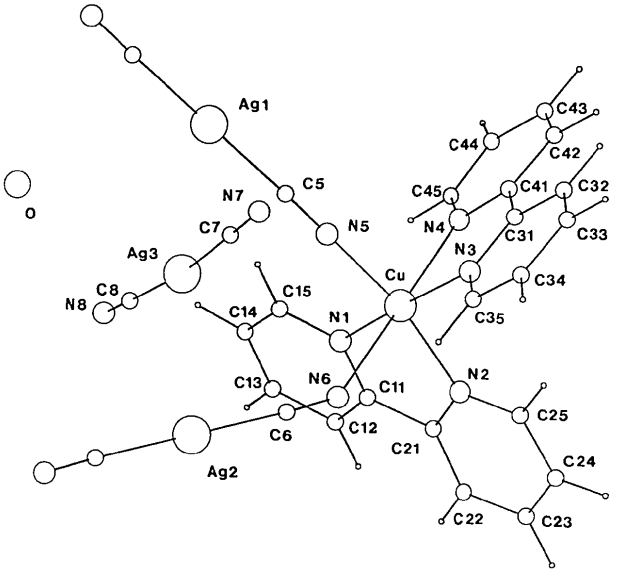

Fig. 1. View (Kappenstein & Raimi, 1987) of the structure of $Cu(bpy)_2Ag_2(CN)_4.H_2O$ along with the atom-numbering scheme for non-H atoms. H atoms are drawn as small circles.

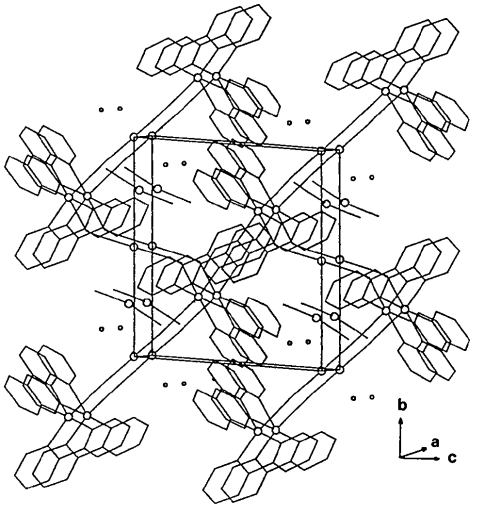

Fig. 2. Packing diagram of the structure of $Cu(bpy)_2$-$Ag_2(CN)_4.H_2O$. H atoms are omitted for clarity.

Experimental

Crystal data

$[AgCu(CN)_2(C_{10}H_8N_2)_2]$-$[Ag(CN)_2].H_2O$

Mo $K\alpha$ radiation
λ = 0.7093 Å

M_r = 713.74
Triclinic
$P\bar{1}$
a = 11.302 (2) Å
b = 11.814 (1) Å
c = 10.457 (1) Å
α = 97.09 (2)°
β = 109.44 (2)°
γ = 77.89 (1)°
V = 1285.2 (5) Å^3
Z = 2
D_x = 1.844 Mg m^{-3}
D_m = 1.85 (2) Mg m^{-3}

Cell parameters from 25 reflections
θ = 10.80–14.90°
μ = 2.35 mm^{-1}
T = 295 K
Parallelepiped
0.25 × 0.20 × 0.15 mm
Blue
Crystal source: polycrystalline product recrystallized from water-ethanol (1:1) solution

Data collection

CAD-4L diffractometer
ω scans
Absorption correction: none
5169 measured reflections
4891 independent reflections
4308 observed reflections $[F_o \geq 4\sigma(F_o)]$
R_{int} = 0.0199

θ_{max} = 27.5°
$h = -14 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = 0 \rightarrow 13$
3 standard reflections monitored every 100 reflections
intensity variation: ≤±2%

Refinement

Refinement on F
Final R = 0.0291
wR = 0.0387
S = 1.1911
4308 reflections
344 parameters
Only H-atom U's refined
$w = 0.7148/[\sigma^2(F_o)]$
$(\Delta/\sigma)_{max}$ = 0.111

$\Delta\rho_{max}$ = 1.14 (see below), 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}
Atomic scattering factors from *SHELX*76 (C, H, N, O); *International Tables for X-ray Crystallography* (1974, Vol. IV) (Cu, Ag)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = \frac{8\pi^2}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ag(1)	0.0000	0.0000	0.0000	3.48 (1)
Ag(2)	0.0000	0.5000	0.0000	3.64 (1)
Ag(3)	0.04343 (3)	0.24111 (3)	−0.02406 (4)	4.18 (1)
Cu	−0.19742 (4)	0.29480 (4)	0.32173 (3)	2.61 (1)
O	0.5945 (7)	0.1102 (6)	0.7927 (8)	14.8 (4)
N(1)	−0.3660 (3)	0.3399 (3)	0.1779 (3)	2.84 (8)
N(2)	−0.2752 (3)	0.4336 (2)	0.4238 (3)	2.67 (8)
N(3)	−0.0401 (3)	0.2506 (2)	0.4834 (3)	2.60 (8)
N(4)	−0.2504 (3)	0.1570 (3)	0.4102 (3)	2.9 (1)
N(5)	−0.1249 (3)	0.1788 (3)	0.1984 (3)	2.9 (1)
N(6)	−0.0908 (4)	0.4430 (3)	0.2408 (4)	4.4 (1)
N(7)	0.3243 (5)	0.1569 (6)	0.1750 (7)	8.7 (2)
N(8)	−0.2417 (4)	0.2872 (4)	−0.2273 (5)	6.3 (2)
C(11)	−0.4467 (3)	0.4287 (3)	0.2147 (4)	2.8 (1)
C(12)	−0.5713 (4)	0.4610 (4)	0.1316 (4)	3.9 (1)
C(13)	−0.6120 (4)	0.4022 (4)	0.0064 (5)	4.6 (1)
C(14)	−0.5286 (4)	0.3132 (4)	−0.0310 (5)	4.5 (1)
C(15)	−0.4053 (4)	0.2844 (4)	0.0577 (4)	3.9 (1)
C(21)	−0.3924 (3)	0.4864 (3)	0.3506 (4)	2.8 (1)
C(22)	−0.4560 (4)	0.5871 (3)	0.4005 (5)	3.8 (1)
C(23)	−0.3971 (4)	0.6324 (4)	0.5297 (5)	4.3 (1)
C(24)	−0.2795 (4)	0.5770 (4)	0.6048 (5)	4.1 (2)
C(25)	−0.2213 (4)	0.4773 (3)	0.5483 (4)	3.2 (1)
C(31)	−0.0392 (3)	0.1652 (3)	0.5602 (3)	2.5 (1)
C(32)	0.0672 (4)	0.1297 (3)	0.6687 (4)	3.3 (1)

C(33)	0.1732 (4)	0.1826 (4)	0.7012 (4)	3.8 (1)
C(34)	0.1707 (4)	0.2693 (4)	0.6243 (4)	3.9 (1)
C(35)	0.0631 (4)	0.3003 (3)	0.5158 (4)	3.4 (1)
C(41)	−0.1569 (3)	0.1144 (3)	0.5202 (4)	2.6 (1)
C(42)	−0.1702 (4)	0.0301 (3)	0.5921 (4)	3.6 (1)
C(43)	−0.2844 (5)	−0.0140 (4)	0.5462 (5)	4.5 (2)
C(44)	−0.3787 (4)	0.0270 (4)	0.4330 (5)	4.6 (2)
C(45)	−0.3585 (4)	0.1135 (4)	0.3679 (4)	3.8 (1)
C(5)	−0.0824 (4)	0.1126 (3)	0.1289 (4)	3.0 (1)
C(6)	−0.0568 (4)	0.4662 (3)	0.1591 (4)	3.4 (1)
C(7)	0.2279 (5)	0.1900 (4)	0.1030 (6)	5.2 (2)
C(8)	−0.1413 (5)	0.2730 (4)	−0.1584 (5)	4.3 (2)

Table 2. *Geometric parameters* (Å, °)

Ag(1)—Ag(3)	3.0439 (4)	Ag(2)—Ag(3)	2.9866 (4)
Ag(1)—C(5)	2.080 (4)	C(5)—N(5)	1.142 (5)
Ag(2)—C(6)	2.078 (5)	C(6)—N(6)	1.130 (7)
Ag(3)—C(7)	2.074 (5)	C(7)—N(7)	1.120 (7)
Ag(3)—C(8)	2.079 (4)	C(8)—N(8)	1.114 (6)
Cu—N(1)	2.010 (3)	Cu—N(2)	2.046 (3)
Cu—N(3)	2.030 (3)	Cu—N(4)	2.239 (4)
Cu—N(5)	2.003 (3)	Cu—N(6)	2.676 (5)
N(1)—C(11)	1.347 (5)	N(3)—C(31)	1.363 (5)
N(1)—C(15)	1.325 (5)	N(3)—C(35)	1.340 (5)
C(11)—C(12)	1.388 (5)	C(31)—C(32)	1.381 (4)
C(12)—C(13)	1.385 (6)	C(32)—C(33)	1.390 (6)
C(13)—C(14)	1.369 (7)	C(33)—C(34)	1.368 (7)
C(14)—C(15)	1.392 (5)	C(34)—C(35)	1.377 (5)
C(11)—C(21)	1.489 (5)	C(31)—C(41)	1.486 (5)
N(2)—C(21)	1.352 (4)	N(4)—C(41)	1.344 (4)
N(2)—C(25)	1.331 (5)	N(4)—C(45)	1.342 (6)
C(21)—C(22)	1.393 (5)	C(41)—C(42)	1.380 (6)
C(22)—C(23)	1.389 (6)	C(42)—C(43)	1.406 (7)
C(23)—C(24)	1.371 (6)	C(43)—C(44)	1.363 (6)
C(24)—C(25)	1.389 (6)	C(44)—C(45)	1.390 (8)
Ag(1)—C(5)—N(5)	176.4 (4)	C(21)—N(2)—C(25)	118.8 (3)
Ag(3)—C(7)—N(7)	175.1 (6)	N(2)—C(21)—C(22)	121.7 (4)
C(5)—Ag(1)—C(5^{i})	180	C(21)—C(22)—C(23)	118.5 (4)
C(7)—Ag(3)—C(8)	173.6 (2)	C(22)—C(23)—C(24)	119.5 (4)
C(5)—N(5)—Cu	179.4 (3)	C(23)—C(24)—C(25)	118.9 (4)
N(1)—Cu—N(2)	80.8 (1)	C(24)—C(25)—N(2)	122.5 (4)
N(1)—Cu—N(4)	97.8 (1)	N(2)—C(21)—C(11)	114.9 (3)
N(1)—Cu—N(6)	92.2 (1)	C(22)—C(21)—C(11)	123.4 (4)
Ag(2)—C(6)—N(6)	176.1 (4)	N(2)—Cu—N(5)	170.0 (1)
Ag(3)—C(8)—N(8)	177.0 (5)	N(3)—Cu—N(4)	77.4 (1)
C(6)—Ag(2)—C(6^{ii})	180	N(3)—Cu—N(6)	92.9 (1)
C(6)—N(6)—Cu	147.2 (4)	N(4)—Cu—N(6)	169.9 (1)
N(1)—Cu—N(3)	172.8 (1)	Cu—N(3)—C(31)	118.2 (3)
N(1)—Cu—N(5)	94.1 (1)	Cu—N(3)—C(35)	122.9 (3)
N(2)—Cu—N(3)	94.4 (1)	C(31)—N(3)—C(35)	118.9 (3)
N(2)—Cu—N(4)	96.9 (1)	N(3)—C(31)—C(32)	120.3 (4)
N(2)—Cu—N(6)	87.2 (1)	C(31)—C(32)—C(33)	119.9 (4)
N(3)—Cu—N(5)	91.5 (1)	C(32)—C(33)—C(34)	119.3 (4)
N(4)—Cu—N(5)	92.2 (1)	C(33)—C(34)—C(35)	118.6 (4)
N(5)—Cu—N(6)	84.4 (1)	C(34)—C(35)—N(3)	122.9 (4)
Cu—N(1)—C(11)	115.2 (3)	N(3)—C(31)—C(41)	116.4 (3)
Cu—N(1)—C(15)	125.4 (3)	C(32)—C(31)—C(41)	123.3 (3)
C(11)—N(1)—C(15)	119.2 (4)	Cu—N(4)—C(41)	112.4 (3)
N(1)—C(11)—C(12)	121.6 (4)	Cu—N(4)—C(45)	129.2 (3)
C(11)—C(12)—C(13)	118.9 (4)	C(41)—N(4)—C(45)	118.4 (3)
C(12)—C(13)—C(14)	119.0 (5)	N(4)—C(41)—C(42)	122.1 (4)
C(13)—C(14)—C(15)	119.2 (4)	C(41)—C(42)—C(43)	118.5 (4)
C(14)—C(15)—N(1)	122.1 (4)	C(42)—C(43)—C(44)	119.7 (5)
N(1)—C(11)—C(21)	114.9 (3)	C(43)—C(44)—C(45)	118.1 (5)
C(12)—C(11)—C(21)	123.5 (4)	C(44)—C(45)—N(4)	123.2 (4)
Cu—N(2)—C(21)	113.9 (2)	N(4)—C(41)—C(31)	115.6 (3)
Cu—N(2)—C(25)	127.3 (3)	C(42)—C(41)—C(31)	122.3 (4)

Symmetry code: (i) $-x, -y, -z$; (ii) $-x, 1-y, -z$.

Data reduction: *LOPOTRI* (Gravereau, 1982). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1986). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). The final difference map showed an important peak of 1.14 e Å^{-3} near the inversion centre (0.5,0,0). It was possible to refine it as a disordered O atom, accompanied by slight dropping of the R factor, but its thermal parameter was very high (B = 18 Å^2). It is known that intensity-measurement errors are manifested by spurious electron density at special positions (Jones, Schelbach, Schwarzmann & Thöne, 1988), so this peak is interpreted as a ghost peak. Geometric analysis: *PARST* (Nardelli, 1983). H atoms of bpy were placed in calculated positions at a distance of 1.08 Å (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987) and their U_{iso} values were refined. H atoms of the water molecule were not included in the refinement.

The authors are indebted to Professors C. Kappenstein and A. Hardy for valuable discussions and Mrs A. M. Hardy for data collection on the diffractometer.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and intermolecular contacts <3.5 Å have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71008 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1014]

References

Allen, F. H., Bellard, S. A., Brice, M. D., Cartwright, B. A., Doubleday, A., Higgs, H., Hummelink, T., Hummelink-Peters, B. G., Kennard, O., Motherwell, W. D. S., Rodgers, J. R. & Watson, D. G. (1991). *Cambridge Structural Database System (CSDS)*. Version 4.60. Univ. of Cambridge, England.

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.

Anderson, O. P. (1972). *J. Chem. Soc. Dalton Trans.* pp. 2597–2601.

Chomič, J., Černák, J., Potočňák, I., Zvereva, I. A. & Saveljeva, N. V. (1993). *Chem. Pap.* In the press.

Dalgaard, G. A. P., Hazell, A. C. & Hazell, R. G. (1974). *Acta Cryst.* B**30**, 2721–2724.

Goher, A. S. & Mak, T. C. W. (1985). *Inorg. Chim. Acta*, **99**, 223–229.

Gravereau, P. (1982). *LOPOTRI*. Program for data reduction. Univ. of Bordeaux, France. Unpublished.

Jones, P. G., Schelbach, R., Schwarzmann, E. & Thöne, C. (1988). *Acta Cryst.* C**44**, 1196–1198.

Kappenstein, C., Ouali, A, Guerin, M., Černák, J. & Chomič, J. (1988). *Inorg. Chim. Acta*, **147**, 189–197.

Kappenstein, C. & Raimi, M. (1987). *AL*1. Program for drawing crystal structures. Univ. of Poitiers, France. Unpublished.

Kozlowski, L. & Hodgson, D. J. (1975). *J. Chem. Soc. Dalton Trans.* pp. 55–58.

McFadden, D. L., McPhail, A. T., Garner, C. D. & Mabbs, F. E. (1975). *J. Chem. Soc. Dalton Trans.* pp. 263–268.

Manríquez, V., Brito, I., Andrade, C., Wittke, O., von Schnering, H. G. & Peters, K. (1988). *Acta Cryst.* C**44**, 1191–1193.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1986). *SHELXS*86. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

Wells, A. F. (1984). *Structural Inorganic Chemistry*, 5th ed., p. 1098. Oxford: Clarendon Press.

Zabel, M., Kühnel, S. & Range, K.-J. (1989). *Acta Cryst.* C**45**, 1619–1621.