C6	−0.0677 (3)	0.5829 (3)	0.2388 (2)	0.0460 (5)
C7	−0.0690 (2)	0.1813 (2)	0.1497 (2)	0.0315 (4)
C8	−0.1495 (3)	0.1076 (2)	0.0663 (2)	0.0360 (5)
C9	−0.2596 (2)	−0.0213 (2)	0.1202 (2)	0.0332 (4)
C10	−0.3127 (2)	−0.0943 (2)	0.0292 (2)	0.0323 (4)
C11	−0.4368 (2)	−0.2166 (2)	0.0652 (2)	0.0293 (4)

Table 2. *Selected geometric parameters (Å, °)*

Cu—N3	1.995 (2)	N2—C4	1.488 (3)
Cu—N1	2.006 (2)	N3—C6	1.474 (3)
Cu—O1	2.023 (1)	C1—C2	1.506 (3)
Cu—N2	2.038 (2)	C2—C3	1.504 (4)
Cu—O5	2.482 (2)	C4—C5	1.507 (4)
O1—C7	1.265 (2)	C5—C6	1.509 (3)
O2—C7	1.233 (3)	C7—C8	1.516 (3)
O3—C11	1.237 (3)	C8—C9	1.524 (3)
O4—C11	1.264 (2)	C9—C10	1.521 (3)
N1—C1	1.481 (3)	C10—C11	1.523 (3)
N2—C3	1.482 (3)		
N3—Cu—O1	86.61 (7)	C3—C2—C1	113.4 (2)
N1—Cu—O1	84.15 (7)	N2—C3—C2	114.3 (2)
N3—Cu—N2	92.06 (7)	N2—C4—C5	113.9 (2)
N1—Cu—N2	97.22 (7)	C4—C5—C6	113.5 (2)
N3—Cu—O5	88.90 (7)	N3—C6—C5	111.0 (2)
N1—Cu—O5	91.89 (6)	O2—C7—O1	123.8 (2)
O1—Cu—O5	86.19 (5)	O2—C7—C8	121.3 (2)
N2—Cu—O5	91.12 (6)	O1—C7—C8	115.0 (2)
C7—O1—Cu	122.04 (13)	C7—C8—C9	117.1 (2)
C1—N1—Cu	125.06 (14)	C10—C9—C8	110.6 (2)
C3—N2—C4	108.7 (2)	C9—C10—C11	117.1 (2)
C3—N2—Cu	116.80 (14)	O3—C11—O4	123.5 (2)
C4—N2—Cu	115.09 (13)	O3—C11—C10	120.8 (2)
C6—N3—Cu	120.38 (15)	O4—C11—C10	115.7 (2)
N1—C1—C2	111.9 (2)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O4^{i}	2.12	2.964 (2)	164
N1—H2···O9	2.29	3.098 (3)	152
N2—H3···O3^{ii}	2.25	3.011 (2)	159
N3—H4···O5^{iii}	2.34	3.026 (2)	148
N3—H5···O1^{iii}	2.33	3.099 (2)	149
O5—H51···O4^{ii}	1.91	2.723 (2)	173
O5—H52···O4^{i}	2.10	2.796 (2)	173
O6—H61···O2	2.00	2.747 (3)	173
O6—H62···O8	1.80	2.760 (3)	172
O7—H71···O3^{iv}	2.01	2.714 (3)	157
O7—H72···O8	2.03	2.689 (3)	176
O8—H81···O2^{iv}	2.00	2.732 (3)	165
O8—H82···O9	1.92	2.736 (3)	167
O9—H91···O6^{iv}	2.17	2.910 (3)	163
O9—H92···O7^{v}	1.97	2.724 (3)	148

Symmetry codes: (i) $-x, -y, -z$; (ii) $1 + x, 1 + y, z$; (iii) $-x, 1 - y, -z$; (iv) $-x, -y, 1 - z$; (v) $1 - x, -y, 1 - z$.

The H atoms involved in the hydrogen bonds were located from a difference synthesis; all other H atoms were included in calculated positions with fixed displacement parameters (1.2 times the displacement parameter of the host atom).

Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: MU1258). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A New Bimetallic Complex of Ethylenediaminetetraacetic Acid: $Ag[Cu(C_{10}H_{13}N_2O_8)(H_2O)].H_2O$

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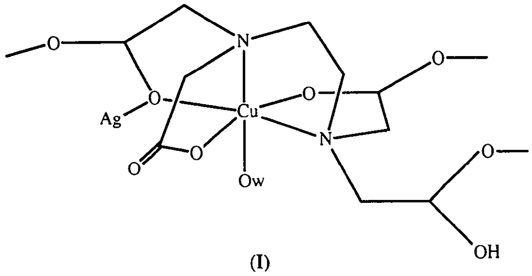
Abstract

The structure of silver aqua(hydrogen ethylenediaminetetraacetato)cuprate(II) monohydrate, $Ag[Cu(C_{10}H_{13}N_2O_8)(H_2O)].H_2O$, is described. This molecular compound is only the second complex of ethylenediaminetetraacetic acid (edta) with silver to be reported. It crystallizes as a three-dimensional network which can be described as stacked layers connected by Cu^{2+} ions.

Comment

This work is a continuation of the study of complexes used as molecular precursors of oxide and sulfide materials (Brouca-Cabarrecq, Galy & Trombe, 1991). Carboxylate ligands are known to be good complexing agents and we are investigating edta in particular. Numerous complexes of the edta ligand have been studied and described in the literature [see for example: H_2Cu(edta) (Stephens, 1969); CaCo(edta), H_2Co(edta) (Nesterova & Porai-Koshits, 1982); Co_xNi_{2-x}(edta) (Gomez-Romero, Jameson, Casan-Pastor, Coronado & Beltran, 1986, and references therein)]. A recent study has been carried out on complexes with formula [*M*Cu(edta)].$4H_2O$ (*M* = Ca, Sr, Ba) which are used for the soft synthesis of pure $MCuO_2$ (Insausti *et al.*, 1994). We are particularly interested in bimetallic complexes of copper as precursors to copper-containing materials. The crystal structure of the title complex Ag[Cu(Hedta)(H_2O)].H_2O, (I), has been determined. To our knowledge it is the second edta complex containing an Ag^+ ion to be reported, the first being Ag[Fe(edta)(H_2O)].$2H_2O$ (Solans, Font Altaba & Garcia-Oricain, 1984).



(I)

As illustrated in Fig. 1, the edta ligand is coordinated by one Cu^{2+} and four Ag^+ ions. The edta must be protonated (Hedta) to maintain electroneutrality; the proton was located, near O5, from a difference Fourier synthesis. Examination of C—O bond lengths reveals that C8—O6 and C8—O5 differ, the first being shorter indicating conjugation of the double bond after deprotonation (Summers, Abboud, Farrah & Palenik, 1994). A difference between the lengths of C4—O2 and C4—O1 was also found, the latter being longer. This can probably be explained by the fact that O1 is coordinated to the Cu atom whereas O2 is not coordinated.

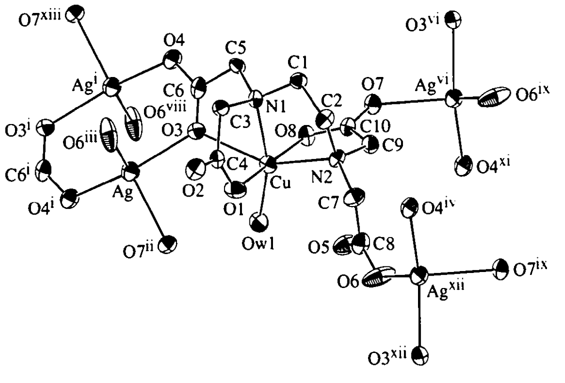


Fig. 1. *ORTEP*II (Johnson, 1976) diagram of the [CuAg(edta)(H_2O)] complex with labelling scheme, showing 50% probability displacement ellipsoids. H atoms are omitted for clarity. Symmetry codes are reported in Table 2 except for (xi) $\frac{3}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z$; (xii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (xiii) $\frac{3}{2}-x, y-\frac{1}{2}, -\frac{1}{2}-z$.

The edta acts as a pentadentate ligand towards Cu^{II}, the six-coordination being completed by the water molecule Owl. The octahedral geometry around the Cu^{2+} ion is distorted with the bond lengths in two groups; there are four equatorial bonds of 1.933 (4)–2.073 (4) Å involving the atoms O1, O8, N1, Owl and two longer axial bonds [Cu—O3 2.528 (4), Cu—N2 2.344 (5) Å]. The deviation of the Cu^{2+} ion from the mean equatorial plane through O1, O8, N1 and Owl is 0.130 (7) Å. Atom O3 bridges the Cu^{2+} and Ag^+ ions [Cu···Ag = 4.221 (1) Å] leading to a much longer Cu—O3 bond.

Unlike in Ag[Fe(edta)(H_2O)].$2H_2O$ where the Ag^+ ion is six-coordinate (Solans, Font Altaba & Garcia-Oricain, 1984), the Ag^+ ion in the title compound, is coordinated by four O atoms. The Ag—$O4^{i}$ and Ag—O3 distances are nearly equivalent [2.237 (4) and 2.256 (4) Å] while those for Ag—$O7^{ii}$ and Ag—$O6^{iii}$ are significantly longer [2.365 (4) and 2.499 (5) Å]. If only the O atoms are considered, the coordination geometry about the Ag^+ ion is a highly distorted tetrahedron. Indeed, angular deformations are important with the O—Ag—O angles ranging from 85.6 (2) to 154.0 (2)°. Two Ag^+ ions (at *x*, *y*, *z* and $2-x$, $-y$, $-z$) connected by two carboxylate groups (O4,C6,O3) form a dimer (Fig. 1) with an Ag···Ag distance of 2.857 (1) Å. The Ag^+ ion is therefore surrounded by four O atoms and one other Ag^+ ion. Its coordination sphere can be described as a distorted square pyramid. Atoms O3, $O4^{i}$, $O7^{ii}$ and Ag^{i} form the base plane with a maximum deviation from this plane of −0.10 (5) Å. The Ag is situated 0.51 (6) Å above the base plane; $O6^{iii}$ occupies the apical position.

Four chelating five-membered rings (three glycine and one ethylenediamine) lie around the metallic Cu^{II} ion. The glycine rings of edta are not at the same inclination to the ethylenediamine fragment; the dihedral angles between the mean plane through the *E* ring (Cu,N1,C1,C2,N2) and those through the glycine rings *G* (Cu,N1,C5,C6,O3), *R*1 (Cu,N1,C3,C4,O1) and *R*2 (Cu,N2,C9,C10,O8) are 13 (1), 87.8 (2) and 90.5 (2)°, respectively. In accordance with the nomenclature suggested by Porai-Koshits, Pozhidaev & Polynova (1974), an edta ligand can adopt three conformations. The conformation observed here is a classic *E*, *G*/*R* situation, *i.e.* methylene groups of the $N(CH_2)_3$ unit belonging to the *E* and *G* rings are located on the same side of the N1,Cu,N2 plane and the methylene groups of the *R* rings lie on the other side. The values of the dihedral angles N—C—C—N and N—C—C—O for the four rings *E*, *G*, *R*1 and *R*2 are 60.0 (6), −21.6 (7), −14.9 (7) and −15.8 (7)°, respectively, showing their strong deviations from the planarity.

Ag[Cu(edta)(H_2O)] adopts a very intricate three-dimensional network structure. As already mentioned, two Ag^+ ions form a dimer resulting in the formation of an eight-membered ring between two centrosymmetric units (Fig. 1). Connections between these dimers are achieved through Cu^{2+} ions and fragments of edta, O—C—O and N—C—C—O. The resulting structural unit can be described as a layer (Fig. 2) in which the Ag dimers form a pseudo-hexagonal network. These layers are stacked in the [100] direction and connected to each other through Cu^{2+} ions (Fig. 2.). Surprisingly, a very similar supramolecular arrangement has already been observed in [SbLi(edta)(H_2O)] (Marrot, Brouca-Cabarrecq & Mosset, 1996) which comprises an hexagonal network of lithium dimers forming layers connected through Sb atoms.

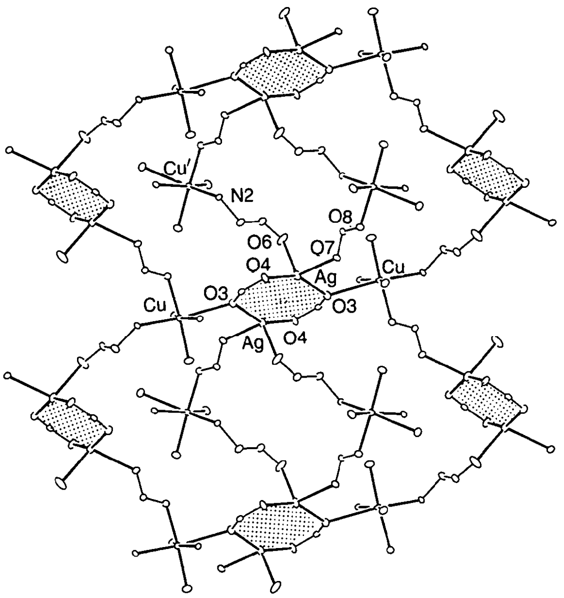


Fig. 2. View of a layer. For clarity, only the copper environment and fragments of edta ligands involved in the connection between dimers are shown. The Cu atom connecting the layers is denoted Cu'.

Hydrogen bonds and intra- and interlayer van der Waals interactions strengthen the cohesion of the lattice. Two van der Waals interactions involve atom O6 which may explain its large anisotropic displacement parameters.

Experimental

The complex was prepared by the reaction of stoichiometric amounts of copper hydroxyde, silver acetate and ethylenediaminetetraacetic acid (5 mmoles) in water. This solution was refluxed for 3 h (pH = 3). The reaction mixture was cooled. Single crystals were obtained by slow evaporation at room temperature and were filtered. Microanalysis results were: calculated Cu 12.79, Ag 21.75, C 24.17, N 5.64, O 32.22, H 3.42%; found Cu 12.8, Ag 19.76, C 24.53, N 5.56, O 33.82, H 3.53% (%O calculated by difference).

Crystal data

$Ag[Cu(C_{10}H_{13}N_2O_8)(H_2O)].H_2O$
$M_r = 496.5$
Monoclinic
$P2_1/n$
$a = 8.3490\,(7)$ Å
$b = 17.725\,(2)$ Å
$c = 10.129\,(2)$ Å
$\beta = 90.866\,(9)°$
$V = 1498.7\,(3)$ Å^3
$Z = 4$
$D_x = 2.201$ Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 4–13°$
$\mu = 12.80$ mm^{-1}
$T = 293$ K
Parallelepiped
0.275 × 0.125 × 0.075 mm
Blue

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical (Coppens, Leiserowitz & Rabinovich, 1965)
$T_{min} = 0.58$, $T_{max} = 0.83$
2498 measured reflections
2097 independent reflections
1725 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.0233$
$\theta_{max} = 60°$
$h = 0 \rightarrow 9$
$k = -19 \rightarrow 0$
$l = -11 \rightarrow 11$
3 standard reflections
frequency: 120 min
intensity decay: −3.5%

Refinement

Refinement on F
$R = 0.0297$
$wR = 0.0331$
$S = 0.883$
1725 reflections
268 parameters
Only coordinates of H atoms refined
$w = 0.9544/[\sigma^2(F) + 0.002F^2]$
$(\Delta/\sigma)_{max} = 0.489$
$\Delta\rho_{max} = 0.68$ e Å^{-3}
$\Delta\rho_{min} = -0.62$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ag	1.02596 (6)	0.04725 (2)	0.11259 (5)	0.0335 (3)
Cu	0.7371 (1)	0.24042 (5)	0.05721 (8)	0.0237 (5)
O1	0.7148 (5)	0.2141 (3)	0.2412 (4)	0.034 (3)
O2	0.5747 (5)	0.1425 (2)	0.3778 (4)	0.031 (2)
O3	0.8361 (5)	0.1104 (2)	−0.0034 (4)	0.029 (2)
O4	0.7462 (5)	0.0183 (2)	−0.1342 (5)	0.035 (2)
O5	0.8147 (5)	0.4152 (3)	0.1204 (5)	0.040 (3)
O6	0.7025 (6)	0.4887 (3)	0.2681 (6)	0.058 (3)
O7	0.6230 (5)	0.3418 (2)	−0.2839 (4)	0.027 (2)
O8	0.7324 (5)	0.2726 (2)	−0.1261 (4)	0.026 (2)
Ow1	0.9646 (5)	0.2716 (2)	0.0847 (4)	0.032 (2)
Ow2	0.4344 (6)	0.9973 (3)	0.3646 (4)	0.036 (2)
N1	0.5406 (5)	0.1713 (3)	0.0229 (4)	0.020 (2)
N2	0.5428 (5)	0.3357 (3)	0.0664 (5)	0.021 (2)
C1	0.4020 (7)	0.2197 (3)	−0.0088 (5)	0.023 (3)
C2	0.3970 (7)	0.2884 (3)	0.0794 (6)	0.025 (3)
C3	0.5176 (7)	0.1292 (3)	0.1494 (6)	0.025 (3)
C4	0.6056 (7)	0.1645 (3)	0.2666 (5)	0.021 (3)
C5	0.5689 (7)	0.1178 (3)	−0.0854 (6)	0.023 (4)

C6	0.7313 (7)	0.0791 (3)	−0.0718 (5)	0.025 (3)
C7	0.5436 (8)	0.3918 (4)	0.1727 (6)	0.032 (4)
C8	0.6949 (8)	0.4368 (3)	0.1919 (6)	0.031 (3)
C9	0.5496 (7)	0.3708 (3)	−0.0644 (6)	0.025 (3)
C10	0.6423 (7)	0.3246 (3)	−0.1643 (6)	0.022 (3)

Table 2. *Selected geometric parameters* (Å, °)

Around Cu			
Cu—O1	1.933 (4)	Cu—O3	2.528 (4)
Cu—O8	1.942 (4)	Cu—Ow1	1.994 (4)
Cu—N1	2.073 (4)	Cu—N2	2.344 (5)
O1—Cu—O8	172.6 (2)	O8—Cu—O3	92.1 (1)
O1—Cu—Ow1	92.2 (2)	Ow1—Cu—N1	159.6 (2)
O1—Cu—N1	86.0 (2)	Ow1—Cu—N2	116.9 (2)
O1—Cu—N2	93.4 (2)	Ow1—Cu—O3	88.4 (2)
O1—Cu—O3	92.9 (2)	N1—Cu—N2	83.5 (2)
O8—Cu—Ow1	93.3 (2)	N1—Cu—O3	71.4 (2)
O8—Cu—N1	90.5 (2)	N2—Cu—O3	153.6 (1)
O8—Cu—N2	79.8 (2)		
Around Ag			
Ag—O4^{i}	2.237 (4)	Ag—O3	2.256 (4)
Ag—O7^{ii}	2.365 (4)	Ag—O6^{iii}	2.499 (5)
O4^{i}—Ag—O3	154.0 (2)	O3—Ag—O7^{ii}	93.0 (1)
O4^{i}—Ag—O7^{ii}	95.9 (2)	O3—Ag—O6^{iii}	85.6 (2)
O4^{i}—Ag—O6^{iii}	113.0 (2)	O7^{ii}—Ag—O6^{iii}	112.9 (2)
Edta molecule			
O1—C4	1.295 (7)	N1—C3	1.497 (7)
O4—C6	1.255 (7)	N2—C2	1.485 (7)
O7—C10	1.258 (7)	C5—C6	1.525 (8)
N1—C1	1.473 (7)	O3—C6	1.239 (7)
N2—C7	1.466 (8)	O6—C8	1.201 (8)
C3—C4	1.520 (8)	N1—C5	1.472 (7)
C9—C10	1.522 (8)	N2—C9	1.465 (7)
O2—C4	1.224 (7)	C1—C2	1.511 (8)
O5—C8	1.301 (8)	C7—C8	1.504 (9)
O8—C10	1.248 (7)		
O1—Cu—O8	172.4 (2)	N1—C1—C2	111.7 (4)
O1—Cu—Ow1	92.2 (2)	O2—C4—O1	123.9 (5)
O1—Cu—N1	86.0 (2)	N1—C5—C6	112.0 (4)
O1—Cu—N2	93.4 (2)	O4—C6—C5	115.8 (5)
O1—Cu—O3	92.9 (2)	O6—C8—C7	121.6 (6)
O8—Cu—Ow1	93.3 (2)	O8—C10—O7	123.1 (5)
O8—Cu—N1	90.5 (2)	C5—N1—C3	110.0 (4)
O8—Cu—N2	79.8 (2)	C9—N2—C2	111.2 (4)
O8—Cu—O3	92.1 (1)	N2—C2—C1	111.9 (5)
Ow1—Cu—N1	159.6 (2)	O2—C4—C3	118.8 (5)
Ow1—Cu—N2	116.9 (2)	O3—C6—O4	126.3 (6)
Ow1—Cu—O3	88.4 (2)	N2—C7—C8	116.7 (5)
O4^{i}—Ag—O3	154.0 (2)	O5—C8—C7	115.0 (5)
O4^{i}—Ag—O7^{ii}	95.9 (2)	O8—C10—C9	120.1 (5)
O4^{i}—Ag—O6^{iii}	113.0 (2)	C1—N1—C3	111.5 (4)
O3—Ag—O7^{ii}	93.0 (2)	C7—N2—C2	108.2 (5)
O3—Ag—O6^{iii}	85.6 (2)	N1—C3—C4	113.4 (5)
O7^{ii}—Ag—O6^{iii}	112.9 (2)	O1—C4—C3	117.2 (5)
N1—Cu—N2	83.5 (2)	O3—C6—C5	117.9 (5)
N1—Cu—O3	71.4 (2)	O6—C8—O5	123.3 (6)
N2—Cu—O3	153.6 (1)	N2—C9—C10	113.6 (5)
C5—N1—C1	110.3 (4)	O7—C10—C9	116.8 (5)
C9—N2—C7	112.1 (4)		
Contact distances			
O2···O8^{iv}	3.230 (6)	O6···Ow2^{iii}	3.338 (7)
O3···O6^{iii}	3.234 (7)	O7···O3^{vi}	3.352 (6)
O5···Ow2^{iii}	2.553 (7)	Ow2···Ow2^{vii}	2.939 (9)
O5···Ow2^{v}	3.193 (7)		

Hydrogen-bonding geometry

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
Ow1—H2*w*1···O2^{viii}	1.85 (5)	2.758 (6)	158 (5)
Ow2—H1*w*2···O4^{ix}	1.85 (5)	2.773 (6)	161 (6)
Ow2—H2*w*2···O2^{x}	1.95 (4)	2.831 (6)	152 (6)

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

The structure was solved by initial location of heavy atoms Cu and Ag using the Patterson method (*SHELXS*86; Sheldrick, 1985). All the other atoms were found using Fourier and difference Fourier maps. Lorentz and polarization corrections were applied. H atoms were found from difference Fourier maps and refined with isotropic displacement parameters and fixed distances (0.97 Å) to the bonded C atoms.

Data collection: *CAD*-4 *EXPRESS Software* (Enraf–Nonius, 1993). Cell refinement: *CAD*-4 *EXPRESS Software*. Data reduction: *CADAK* (Savariault, 1991*a*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TABPUB* (Savariault, 1991*b*).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1208). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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