

As the [Ag₂I₆]⁴⁻ anion has no intermolecular distance shorter than 4.3 Å, it may be characterized as an isolated di- μ -iodo-bis[diiodoargentate(I)], which consists of two AgI₄ tetrahedra sharing a common edge (Fig. 2). In all known structures of iodoargentates the Ag atom is tetrahedrally coordinated by four I atoms, but the tetrahedra are connected over common corners, edges or planes building polymeric chains, layers or three-dimensional networks (Gilmore, Tucker & Woodward, 1971, and references therein; Coetzer, 1975; Coetzer & Thackeray, 1975; Thackeray & Coetzer, 1975*a*,*b*, 1978, and references therein; Geller, 1972; Geller & Dudley, 1978; Geller, Skarstad & Wilber, 1975). Structures with isolated iodoargentates have not yet been reported, though the existence of Ag₂I₆⁴⁻ in melts has been postulated by Holmberg (1973). The connection of the two tetrahedra in [Ag₂I₆]⁴⁻ causes a distortion of the tetrahedral coordination around Ag with the angle I(2)–Ag–I(2)' becoming much smaller than the others. The bridging Ag–I distance is longer than the terminal ones. These features are found for other M₂X₆ metal halides. The Ag–I distances lie in the range found for polymeric structures. The calculation of the bond-valence sum for Ag (Brown, Howard-Lock & Natarajan, 1977) yielded a value somewhat too small (0.93 instead of 1.00), again comparable to polymeric iodoargentates with values in the range 0.9 to 1.0.

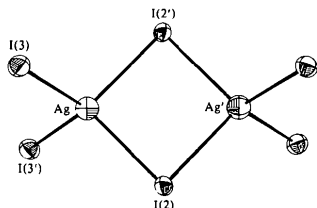


Fig. 2. ORTEP plot of the [Ag₂I₆]⁴⁻ anion.

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Bis[μ -(2-methylaminopyridine 1-oxide)- μ -O]-bis[dichloro(2-methylaminopyridine 1-oxide)copper(II)]

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Abstract. [Cu₂(C₆H₈N₂O)₄Cl₄], C₂₄H₃₂Cl₄Cu₂N₈O₄, *M_r* = 765.4, triclinic, *P*1, *a* = 11.0483 (11), *b* = 9.2975 (9), *c* = 9.4998 (9) Å, α = 124.61 (1), β = 92.85 (1), γ = 99.26 (1)°, at 298 K, *Z* = 1, *D_m* =

1.63 (2), *D_c* = 1.628 Mg m⁻³. The structure was solved by a combination of direct methods and Fourier synthesis techniques which led to a conventional *R* of 0.041 for the 255 parameters varied and 2147

observed reflections used in the refinement. The molecular structure consists of a centrosymmetric bridged dimer with each square-pyramidal Cu bonded to three terminal atoms (one O and two Cl) and two bridging O atoms with bonding distances of 1.928 (2), 2.231 (1), 2.515 (1), 1.988 (2) and 2.054 (2) Å respectively. The internal bridge angles are 71.1 (5)° at Cu and 108.9 (5)° at O.

Introduction. The title compound is one in a series of copper complexes under investigation which contain ring-substituted pyridine 1-oxide ligands. An ongoing correlative study is being made with respect to their chemical compositions, EPR spectra and molecular structures (Pavkovic & Brown, 1982; West, Pavkovic & Brown, 1980). The present structure determination was undertaken because the title compound differs markedly in its spectral and magnetic properties from previously available examples (West & Wang, 1979).

Amber crystals were obtained by slow evaporation from a methanol/ethyl orthoformate solution of the powdered compound. A fragment (measuring 0.15 × 0.24 × 0.36 mm) was mounted nearly parallel to the *a** axis, and all subsequent measurements were carried out with a Picker FACS-I automated diffractometer. The crystal belongs to the triclinic system and cell constants were determined by a least-squares refinement of 33 reflections (60 < |2θ| < 78°) measured with Cu Kα radiation [λ(Cu Kα₁) = 1.54050, λ(Cu Kα₂) = 1.54433 Å]. The structure was solved and is reported using the unit cell given in the *Abstract*. A reduced cell [*a* = 8.7381 (9), *b* = 9.2975 (9), *c* = 11.0483 (11) Å, α = 80.74 (1), β = 76.98 (1), γ = 63.48 (1)°] is obtained by transforming with the matrix whose rows 1–3 are: 011, 010, –100. The space group was assumed to be *P*1̄, and this choice was verified by a subsequent successful structure solution.

Intensities were measured with Ni-filtered Cu radiation (40 kV, 12 mA, take-off angle 2.5°). Data were collected using the coupled θ:2θ technique from 3 to 120°, with a scan rate of 2° min⁻¹ and range of 2.4 × (1 + 0.4 tan θ)°, with 10 s background measurements at both extremities of the scan. 2328 reflections were measured of which 2147 reflections having |*F*_o| > 3σ(*F*_o) were used in the structure solution and refinement; σ²(*F*_o) = 1/*w* = (*F*_o/2*I*_n)²[*I*_s + (*t*_s/*t*_b)²*I*_b + (0.02*I*_n)²], where *I*, *t*, *s*, *n* and *b* refer to intensity (counts), time (s), scan, net and background, respectively. Three standard reflections measured after every 50 data reflections showed an average intensity decrease of less than 1%. Intensities, which were corrected for absorption as a function of φ [linear μ = 4.98 mm⁻¹; maximum/minimum transmission (calculated) = 1.5, (observed) = 1.4] and Lorentz-polarization effects in the usual manner, were converted to structure factor amplitudes.

The structure was refined by a full-matrix least-squares program which minimized the function ∑ *w*(|*F*_o| – |*F*_c|)², utilized anisotropic temperature factors and included a correction for secondary extinction. Atomic scattering factors for nonhydrogen atoms were taken from tabulations of Cromer & Waber (1965) and for H atoms the values of Stewart, Davidson & Simpson (1965) were used; corrections for real and imaginary anomalous-dispersion effects were applied to scattering factors of copper and chlorine atoms (Cromer & Liberman, 1970).

A difference Fourier electron density map contained peaks near all 16 expected H atom positions. H atoms were included in the model structure and refined isotropically. Refinement converged to *R* = [∑ (|*F*_o| – |*F*_c|)/∑ (*F*_o)] = 0.041 and *R*_w = [∑ *w*(|*F*_o| – |*F*_c|)²/∑ *w*(*F*_o)²]^{1/2} = 0.047. There were no significant

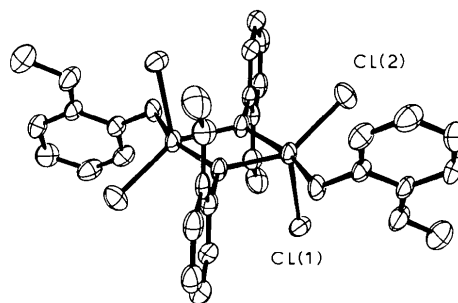


Fig. 1. A perspective view of the [C₁₂H₁₆Cl₂CuN₄O₂]₂ molecule (Johnson, 1965). The hydrogen atoms are omitted from the diagram and all other atoms are shown as ellipsoids of 50% probability.

Table 1. *Final positional parameters and equivalent isotropic thermal parameters*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)†
Cu	0.13625 (5)	0.11485 (7)	0.51611 (7)	2.29 (5)
Cl(1)	0.21958 (9)	–0.15175 (13)	0.30192 (13)	3.10 (8)
Cl(2)	0.17126 (10)	0.34030 (14)	0.48878 (13)	3.44 (8)
O(1)	–0.0358 (2)	–0.0011 (3)	0.3807 (3)	2.4 (2)
O(2)	0.2761 (2)	0.1996 (4)	0.6948 (3)	2.9 (2)
N(1)	–0.0909 (3)	0.0153 (4)	0.2613 (4)	2.3 (2)
N(2)	–0.0402 (3)	–0.2481 (5)	0.0524 (5)	3.1 (3)
N(3)	0.3555 (3)	0.3581 (4)	0.7620 (4)	2.7 (3)
N(4)	0.4574 (3)	0.2047 (6)	0.5340 (5)	3.7 (3)
C(1)	–0.0958 (3)	–0.1162 (5)	0.0908 (5)	2.5 (3)
C(2)	–0.1575 (4)	–0.0996 (6)	–0.0297 (6)	3.0 (3)
C(3)	–0.2092 (4)	0.0443 (7)	0.0262 (6)	3.5 (4)
C(4)	–0.2037 (4)	0.1742 (7)	0.2016 (6)	3.5 (4)
C(5)	–0.1428 (4)	0.1566 (6)	0.3161 (6)	2.9 (3)
C(6)	0.4516 (3)	0.3615 (6)	0.6789 (5)	2.7 (3)
C(7)	0.5356 (4)	0.5273 (7)	0.7553 (7)	3.6 (4)
C(8)	0.5193 (4)	0.6755 (7)	0.9056 (7)	4.2 (4)
C(9)	0.4202 (4)	0.6675 (7)	0.9857 (6)	4.0 (4)
C(10)	0.3397 (4)	0.5082 (6)	0.9119 (5)	3.2 (3)
C(11)	–0.0377 (6)	–0.3953 (7)	–0.1245 (7)	4.6 (4)
C(12)	0.5505 (6)	0.1891 (10)	0.4266 (9)	4.8 (5)

$$\dagger B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

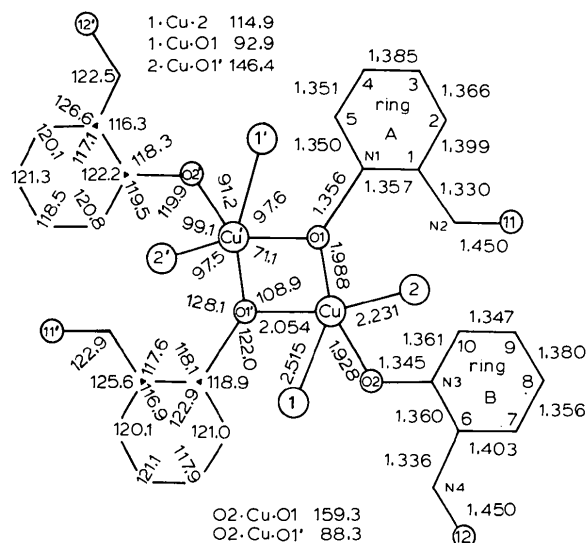


Fig. 2. A diagrammatic representation of the [C₁₂H₁₆Cl₂CuN₄O₂]₂ molecule showing bond distances (Å) and angles (°). Atoms on the right (unprimed symbols) are related to those on the left (primed symbols) by an inversion center. Bond distances and angles involving Cu have e.s.d.'s less than 0.003 Å and 0.10°; other distances and angles have e.s.d.'s of 0.004–0.007 Å and 0.25–0.50°.

shifts observed for nonhydrogen atom parameters in the final cycle of refinement. For H atom parameters the observed shifts were less than 0.3σ. Major peaks in the final difference Fourier electron density map have a maximum height of 0.5 e Å⁻³, and are located within 1.2 Å of the copper atom. Atomic coordinates are listed in Table 1, Fig. 1 is a perspective view of the complex, and Fig. 2 shows the atom numbering scheme and bonding distances and angles. E.s.d.'s (from the least-squares matrix) are less than 0.007 Å and 0.6° for all bond distances and angles. E.s.d.'s involving bonds to copper are less than 0.003 Å and 0.1°. Throughout the text primed atom symbols refer to inverted positions ($\bar{x}, \bar{y}, \bar{z}$) relative to their coordinates listed in Table 1.*

* Lists of structure factors, anisotropic thermal parameters and hydrogen atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36645 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The coordination geometry about Cu can be described as a distorted square pyramid. The square is composed of Cl(2) and three O atoms with Cl(2) and O(1') below and O(1) and O(2) above the idealized base plane by as much as 0.31 (1) Å. The Cu and Cl(1) are 0.41 (1) and 2.86 (1) Å above the idealized plane and the Cu–Cl(1) bond makes an angle of 77 (1)° to the plane. The two square pyramids in the dimer are related by an inversion center. They share O(1) and O(1') along a common base edge. The amine N atoms are not coordinated to Cu.

At the center of the molecule the separation between opposed atoms within the Cu–O(1)–Cu'–O(1') central ring is 2.351 (5) for O(1) and 3.289 (1) Å for Cu. The angle between the O(1')–Cu–O(2) and Cu–O(2)–N(3) planes is 34.2 (4)°. The dihedral angle between planes of the central ring and bridging pyridine ring (A) is 90 (1)° whereas for the terminal pyridine ring (B) the corresponding angle is 70 (1)°; between the planes of ring A and ring B the angle is 86 (1)°.

Amine H atoms from both rings are H bonded to Cl(1) and the parameters are H–Cl(1) = 2.58 (4), 2.41 (4); N–Cl(1) = 3.278 (4), 3.327 (4) Å; and N–H–Cl(1) = 147 (3), 166 (3)°, where the first value listed refers to ring A atoms and the second to ring B atoms. There are no H bonds to Cl(2). The tilt of ring B relative to the central ring serves to enhance H bonding to Cl(1) and reduce steric interactions between pyridine ring atoms and Cl(2).

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