Br(12)	0.7001 (2)	0.3827 (2)	0.3767 (2)	0.045 (1)
Br(13)	0.4696 (2)	0.1535 (2)	0.5853 (1)	0.033 (1)
Br(21)	0.2618 (2)	0.0296 (2)	0.1892 (1)	0.039 (1)
Br(22)	−0.0116 (2)	0.1683 (2)	0.5840 (1)	0.033 (1)
O(2)	0.2457 (12)	0.3153 (10)	0.3789 (9)	0.039 (4)
N(1)	0.9101 (19)	0.6804 (16)	−0.0680 (17)	0.061 (7)
C(2)	0.821 (2)	0.6818 (19)	0.0382 (18)	0.057 (8)
C(3)	0.715 (2)	0.5454 (17)	0.0682 (15)	0.046 (7)
C(4)	0.6997 (18)	0.4050 (15)	−0.0182 (14)	0.037 (6)
C(5)	0.7955 (19)	0.4134 (18)	−0.1304 (14)	0.044 (7)
C(6)	0.898 (2)	0.550 (2)	−0.1517 (16)	0.053 (8)
N(4)	0.5978 (18)	0.2642 (14)	0.0045 (15)	0.063 (7)

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

Centrosymmetrically related atoms within the same dimer are denoted by (*a*) and atoms in an adjacent dimer are denoted by (*b*).

Cu(1)—Br(11)	2.386 (2)	Cu(1)—Br(21*b*)	3.221 (2)
Cu(1)—Br(12)	2.417 (2)	Cu(1)—Br(22*b*)	3.240 (3)
Cu(1)—Br(13)	2.426 (2)	N(1)—C(2)	1.33 (3)
Cu(1)—Br(13*a*)	2.465 (2)	N(1)—C(6)	1.33 (2)
Cu(2)—Br(21)	2.399 (2)	C(2)—C(3)	1.38 (2)
Cu(2)—Br(22)	2.454 (2)	C(3)—C(4)	1.41 (2)
Cu(2)—O(2)	1.992 (9)	C(4)—C(5)	1.41 (2)
Cu(2)—Br(22*a*)	2.428 (2)	C(4)—N(4)	1.368 (18)
Cu(2)—Br(11*b*)	2.940 (2)	C(5)—C(6)	1.33 (2)
Cu(2)—Br(13*b*)	3.200 (2)		
Br(11)—Cu(1)—Br(12)	94.0 (1)	O(2)—Cu(2)—Br(22*a*)	169.6 (3)
Br(11)—Cu(1)—Br(13)	173.1 (1)	Cu(1)—Br(13)—Cu(1*a*)	95.6 (1)
Br(12)—Cu(1)—Br(13)	91.6 (1)	Cu(2)—Br(22)—Cu(2*b*)	92.3 (1)
Br(11)—Cu(1)—Br(13*a*)	90.1 (1)	C(2)—N(1)—C(6)	122.4 (15)
Br(12)—Cu(1)—Br(13*a*)	175.6 (1)	N(1)—C(2)—C(3)	120.4 (15)
Br(13)—Cu(1)—Br(13*a*)	84.4 (1)	C(2)—C(3)—C(4)	118.6 (15)
Br(21)—Cu(2)—Br(22)	177.3 (1)	C(3)—C(4)—C(5)	117.5 (13)
Br(21)—Cu(2)—O(2)	87.6 (3)	C(3)—C(4)—N(4)	122.4 (14)
Br(22)—Cu(2)—O(2)	90.6 (3)	C(5)—C(4)—N(4)	120.1 (13)
Br(21)—Cu(2)—Br(22*a*)	93.7 (1)	C(4)—C(5)—C(6)	120.6 (15)
Br(22)—Cu(2)—Br(22*a*)	87.7 (1)	N(1)—C(6)—C(5)	120.5 (16)

The structure solution was obtained *via* the direct-methods routine *SOLV* in the *SHELXTL* crystallographic program package (Sheldrick, 1985); refinement also used *SHELXTL*. A difference synthesis based on the Cu and Br positions thus obtained yielded the C-, N- and O-atom positions. H atoms were constrained to ideal positions (C—H and N—H = 0.96 Å) and assigned isotropic displacement parameters 1.2 times larger than those of the associated atoms. Because of the rather large residual electron density in the region of the heavy atoms (up to 2.6 e Å^{-3}), the accuracy of the absorption corrections seemed questionable. The data were further corrected utilizing a ΔF refinement with the program *XABS* (Sheldrick, 1990). This resulted in a reduction of *R* from 0.075 to 0.060, and a reduction of the residual electron density to ±1.8 e Å^{-3}.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and structure determination details, as well as a packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71385 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1014]

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Di-μ-chlorobis[chloro(4,7-diphenyl-1,10-phenanthroline)copper(II)]

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Abstract

The crystal structure of $[\{CuCl(C_{24}H_{16}N_2)\}_2(\mu\text{-}Cl)_2]$ contains dimers formed by pairs of $[CuCl_2(4,7\text{-diphenyl-}1,10\text{-phenanthroline-}N,N)]$ units related by an inversion centre.

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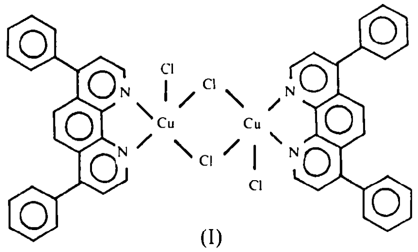
Comment

Cu(NN)X_2 (NN = a pyridine derivative, X = Cl, Br) complexes in which Cu^{II} has a coordination number of four, five or six are known. These complexes have been shown to exist in monomeric (Marsh, Hatfield & Hodgson, 1982), dimeric (Wilson, Hatfield & Hodgson, 1976) and at least four different polymeric forms (Morosin, 1975; Copeland, Hatfield & Hodgson, 1972; Copeland, Singh, Hatfield & Hodgson, 1973; Bream, Estes & Hodgson, 1975; Helis, Goodman, Wilson, Morgan & Hodgson, 1977; Swank & Willet, 1980). Previous work by our group has also led to the characterization of a number of 2,2′-bipyridine and 1,10-phenanthroline Cu^{II} complexes. The complexes [Cu(bipy)X_2] (bipy = 2,2′-bipyridine, X = Cl, Br) adopt alternately spaced polymeric structures (Garland, Grandjean, Spodine, Atria & Manzur, 1988*a*), [Cu(diMe-bipy)Cl_2].0.5H_2O (diMe-bipy = 4,4′-dimethylbipyridine) forms a dimeric μ-chloro-bridged complex (Gonzalez, Atria, Spodine, Manzur & Garland, 1993) and [Cu(diMe-bipy)Br_2] has a regular chain structure (Atria *et al.*, 1993). The unsubstituted 1,10-phenanthroline ligand gives a polymeric μ-bromo Cu^{II} complex (Garland, Grandjean, Spodine, Atria & Manzur, 1988*b*).

In this paper we report the synthesis and structure of the [Cu(diphenyl-phen)]Cl_2 complex (diphenyl-phen = 4,7-diphenyl-1,10-phenanthroline) (I). The crystal structure contains dimers formed by pairs of [CuCl_2(diphenyl-phen)] units related by an inversion centre (Fig. 1).



(I)

The coordination geometry of each Cu atom is square-pyramidal. The base plane of each pyramid is formed by the two N atoms from a diphenyl-phen ligand and two Cl atoms, while the apical Cl atom is part of the second [CuCl_2(diphenyl-phen)] unit within each dimer. The atoms N(1), N(2), Cl(1) and Cl(2) deviate from the best basal mean plane by −0.003 (5), 0.003 (5), 0.002 (2) and −0.002 (2) Å, respectively. The apical Cl atom and the Cu atom are −2.958 (1) and −0.157 (2) Å from the basal mean plane, respectively. The dihedral angle between the planes [N(1), N(2), Cu] and [Cl(1), Cl(2), Cu] is 11.6°. The core of the dimer is a planar [CuCl]$_2$ moiety with two identical Cu—Cl(1) bonds of 2.839 (2) Å between the [CuCl_2(diphenyl-phen)] units and two identical Cu—Cl(1) bonds of 2.266 (2) Å within each unit. The dihedral angles between the phenanthroline molecule and the two phenyl rings are 43.1 and 34.7°, and the bond lengths and angles in the aromatic rings are normal. The crystal structure is stabilized by van der Waals forces between the dimers.

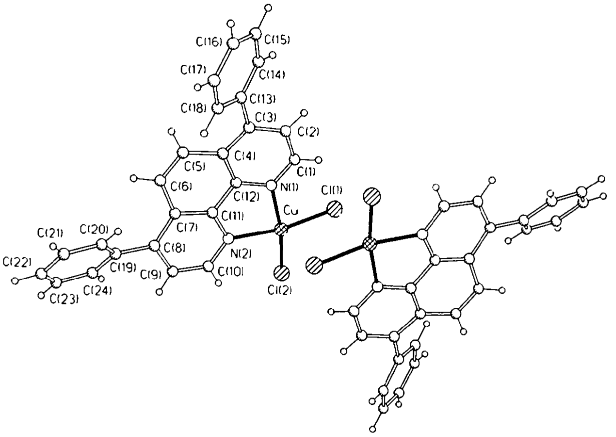


Fig. 1. A view of the dimer showing the labelling of the non-H atoms.

Experimental

The title compound was prepared by mixing a solution of $\text{CuCl}_2.6\text{H}_2\text{O}$ in ethanol with a solution of the ligand in the same solvent. Crystals were grown from a solution of dimethylacetamide.

Crystal data

[$\text{CuCl}_2(\text{C}_{24}\text{H}_{16}\text{N}_2)$]
M_r = 466.8
Triclinic
$P\bar{1}$
a = 10.165 (2) Å
b = 10.191 (2) Å
c = 11.004 (2) Å
α = 66.77 (1)°
β = 70.41 (1)°
γ = 87.56 (1)°
V = 981.6 (3) Å^3
Z = 2
D_x = 1.579 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 5-10°
μ = 1.398 mm^{-1}
T = 293 K
Polyhedron
0.22 × 0.18 × 0.14 mm
Light green

Data collection

Siemens $R3m$ diffractometer
$\theta/2\theta$ scans (4.19-29.3° min^{-1})
Absorption correction: none
3294 measured reflections
3098 independent reflections
2454 observed reflections [$F > 4.0\sigma(F)$]

R_{int} = 0.031
θ_{max} = 22.5°
$h = 0 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -11 \rightarrow 12$
2 standard reflections monitored every 98 reflections intensity variation: none

Refinement

Refinement on F
R = 0.036
wR = 0.036

$(\Delta/\sigma)_{\text{max}}$ = 0.069
$\Delta\rho_{\text{max}}$ = 0.34 e Å^{-3}
$\Delta\rho_{\text{min}}$ = −0.47 e Å^{-3}

$S = 1.35$
2454 reflections
262 parameters
H-atom parameters not refined
Unit weights applied

Atomic scattering factors from *International Tables for X-ray Crystallography* (1991, Vol. C Tables 6.1.1.4 and 6.1.1.5)

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}
Cu	0.0414 (1)	0.1961 (1)	0.4049 (1)	0.031 (1)
Cl(1)	0.1800 (2)	0.0259 (2)	0.4812 (2)	0.041 (1)
Cl(2)	0.1357 (2)	0.2181 (2)	0.1806 (2)	0.045 (1)
N(1)	−0.0344 (4)	0.2174 (4)	0.5910 (5)	0.029 (2)
N(2)	−0.0673 (4)	0.3701 (4)	0.3496 (5)	0.030 (2)
C(1)	−0.0202 (6)	0.1342 (6)	0.7118 (6)	0.035 (2)
C(2)	−0.0888 (6)	0.1522 (6)	0.8364 (6)	0.037 (3)
C(3)	−0.1720 (5)	0.2640 (6)	0.8381 (6)	0.031 (2)
C(4)	−0.1791 (5)	0.3610 (5)	0.7072 (6)	0.029 (2)
C(5)	−0.2456 (6)	0.4920 (5)	0.6833 (6)	0.032 (2)
C(6)	−0.2593 (5)	0.5720 (6)	0.5598 (6)	0.034 (3)
C(7)	−0.2120 (5)	0.5311 (5)	0.4421 (5)	0.028 (2)
C(8)	−0.2391 (5)	0.5980 (5)	0.3140 (6)	0.032 (2)
C(9)	−0.1714 (6)	0.5524 (6)	0.2072 (6)	0.038 (3)
C(10)	−0.0859 (6)	0.4415 (6)	0.2283 (6)	0.037 (3)
C(11)	−0.1308 (5)	0.4136 (5)	0.4564 (5)	0.028 (2)
C(12)	−0.1132 (5)	0.3309 (5)	0.5883 (5)	0.026 (2)
C(13)	−0.2580 (6)	0.2674 (6)	0.9767 (6)	0.034 (2)
C(14)	−0.2051 (7)	0.2278 (6)	1.0844 (6)	0.041 (3)
C(15)	−0.2909 (8)	0.2100 (8)	1.2202 (7)	0.055 (3)
C(16)	−0.4322 (8)	0.2349 (8)	1.2441 (8)	0.061 (4)
C(17)	−0.4851 (7)	0.2771 (7)	1.1378 (7)	0.051 (3)
C(18)	−0.3996 (6)	0.2953 (6)	1.0015 (7)	0.043 (3)
C(19)	−0.3385 (6)	0.7095 (6)	0.2906 (6)	0.032 (2)
C(20)	−0.4638 (6)	0.7022 (6)	0.3988 (6)	0.037 (2)
C(21)	−0.5573 (6)	0.8035 (6)	0.3725 (7)	0.041 (3)
C(22)	−0.5314 (6)	0.9091 (6)	0.2389 (7)	0.043 (3)
C(23)	−0.4087 (7)	0.9159 (6)	0.1307 (7)	0.045 (3)
C(24)	−0.3129 (6)	0.8171 (6)	0.1560 (6)	0.039 (3)

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

Cu—Cl(1)	2.266 (2)	C(7)—C(11)	1.412 (7)
Cu—Cl(1^{i})	2.839 (2)	C(8)—C(9)	1.389 (9)
Cu—Cl(2)	2.249 (2)	C(8)—C(19)	1.491 (8)
Cu—N(1)	2.028 (5)	C(9)—C(10)	1.389 (8)
Cu—N(2)	2.042 (4)	C(11)—C(12)	1.430 (8)
N(1)—C(1)	1.318 (7)	C(13)—C(14)	1.374 (10)
N(1)—C(12)	1.374 (7)	C(13)—C(18)	1.411 (8)
N(2)—C(10)	1.318 (8)	C(14)—C(15)	1.397 (9)
N(2)—C(11)	1.367 (8)	C(15)—C(16)	1.402 (11)
C(1)—C(2)	1.394 (9)	C(16)—C(17)	1.360 (12)
C(2)—C(3)	1.392 (8)	C(17)—C(18)	1.400 (9)
C(3)—C(4)	1.414 (8)	C(19)—C(20)	1.403 (7)
C(3)—C(13)	1.495 (8)	C(19)—C(24)	1.396 (7)
C(4)—C(5)	1.440 (8)	C(20)—C(21)	1.385 (8)
C(4)—C(12)	1.402 (9)	C(21)—C(22)	1.381 (8)
C(5)—C(6)	1.332 (8)	C(22)—C(23)	1.387 (8)
C(6)—C(7)	1.440 (10)	C(23)—C(24)	1.385 (9)
C(7)—C(8)	1.420 (9)		
Cl(1)—Cu—Cl(2)	93.4 (1)	C(7)—C(8)—C(19)	123.7 (6)
Ci(1)—Cu—Cl(1^{i})	88.3 (1)	C(9)—C(8)—C(19)	119.1 (6)
Cl(1)—Cu—N(1)	93.2 (1)	C(8)—C(9)—C(10)	121.0 (6)
Cl(2)—Cu—N(1)	169.0 (1)	N(2)—C(10)—C(9)	123.2 (6)
Cl(1)—Cu—N(2)	169.6 (2)	N(2)—C(11)—C(7)	123.5 (5)
Cl(2)—Cu—N(2)	92.0 (1)	N(2)—C(11)—C(12)	116.2 (5)
N(1)—Cu—N(2)	80.2 (2)	C(7)—C(11)—C(12)	120.3 (5)
Cu—N(1)—C(1)	127.8 (4)	N(1)—C(12)—C(4)	123.3 (5)
Cu—N(1)—C(12)	114.4 (4)	N(1)—C(12)—C(11)	115.4 (5)
C(1)—N(1)—C(12)	117.7 (5)	C(4)—C(12)—C(11)	121.3 (5)
Cu—N(2)—C(10)	128.8 (4)	C(3)—C(13)—C(14)	120.4 (5)
Cu—N(2)—C(11)	113.8 (4)	C(3)—C(13)—C(18)	119.3 (6)
C(10)—N(2)—C(11)	117.4 (5)	C(14)—C(13)—C(18)	119.9 (6)
N(1)—C(1)—C(2)	122.4 (5)	C(13)—C(14)—C(15)	121.0 (6)
C(1)—C(2)—C(3)	121.3 (5)	C(14)—C(15)—C(16)	118.5 (7)
C(2)—C(3)—C(4)	116.8 (5)	C(15)—C(16)—C(17)	121.1 (7)
C(2)—C(3)—C(13)	119.1 (5)	C(16)—C(17)—C(18)	120.6 (6)
C(4)—C(3)—C(13)	123.8 (5)	C(13)—C(18)—C(17)	118.9 (7)
C(3)—C(4)—C(5)	125.7 (6)	C(8)—C(19)—C(20)	121.2 (4)
C(3)—C(4)—C(12)	118.1 (5)	C(8)—C(19)—C(24)	119.8 (5)
C(5)—C(4)—C(12)	116.2 (5)	C(20)—C(19)—C(24)	118.8 (5)
C(4)—C(5)—C(6)	122.5 (6)	C(19)—C(20)—C(21)	120.1 (5)
C(5)—C(6)—C(7)	122.1 (5)	C(20)—C(21)—C(22)	120.7 (5)
C(6)—C(7)—C(8)	126.1 (5)	C(21)—C(22)—C(23)	119.6 (6)
C(6)—C(7)—C(11)	116.5 (5)	C(22)—C(23)—C(24)	120.4 (5)
C(8)—C(7)—C(11)	117.4 (6)	C(19)—C(24)—C(23)	120.5 (5)
C(7)—C(8)—C(9)	117.2 (5)		

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

Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991). Cell refinement: *P3/P4-PC Diffractometer Program*. Data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1991). Program(s) used to solve structure: *XS* in *SHELXTL/PC*. Program(s) used to refine structure: *XLS* in *SHELXTL/PC*. Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *XPUBL* in *SHELXTL/PC*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71816 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1079]

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