Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

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

	x	y	z	U_{cq}
Pd	0.10212 (2)	0.935504 (12)	0.85106 (2)	0.03686 (9)
S1	0.02076 (8)	1.08333 (5)	0.79578 (7)	0.0499 (2)
S2	−0.10097 (7)	0.86091 (5)	0.73816 (6)	0.0467 (2)
O1	0.2907 (2)	0.99930 (11)	0.9532 (2)	0.0455 (4)
O2	0.1817 (2)	0.80262 (12)	0.9065 (2)	0.0473 (4)
N1	0.2881 (2)	1.09602 (14)	0.9554 (2)	0.0380 (4)
N2	0.0898 (2)	0.7295 (2)	0.8590 (2)	0.0394 (4)
C1	0.1679 (3)	1.1449 (2)	0.8897 (2)	0.0407 (5)
C2	0.1732 (4)	1.2454 (2)	0.8995 (3)	0.0523 (7)
C3	0.2948 (4)	1.2902 (2)	0.9717 (3)	0.0557 (7)
C4	0.4158 (4)	1.2371 (2)	1.0344 (3)	0.0507 (6)
C5	0.4119 (3)	1.1399 (2)	1.0258 (2)	0.0449 (5)
C6	−0.0433 (3)	0.7449 (2)	0.7773 (2)	0.0392 (5)
C7	−0.1299 (3)	0.6649 (2)	0.7294 (3)	0.0494 (6)
C8	−0.0830 (4)	0.5752 (2)	0.7662 (3)	0.0556 (7)
C9	0.0534 (4)	0.5622 (2)	0.8519 (3)	0.0551 (7)
C10	0.1383 (4)	0.6402 (2)	0.8964 (3)	0.0494 (6)

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

Pd—O1	2.031 (2)	S1—C1	1.724 (3)
Pd—O2	2.036 (2)	S2—C6	1.729 (3)
Pd—S1	2.2325 (7)	O1—N1	1.353 (2)
Pd—S2	2.2362 (7)	O2—N2	1.349 (3)
O1—Pd—O2	92.09 (6)	S1—Pd—S2	95.71 (3)
O1—Pd—S1	86.01 (5)	C1—S1—Pd	97.78 (8)
O2—Pd—S1	178.03 (5)	C6—S2—Pd	97.67 (8)
O1—Pd—S2	178.13 (5)	N1—O1—Pd	115.67 (13)
O2—Pd—S2	86.20 (5)	N2—O2—Pd	115.39 (13)

The H atoms were located from difference maps and refined isotropically. In the final difference map, there were two spurious peaks of 1 e Å^{-3} close to the Pd atom.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. 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. Geometrical calculations: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a packing diagram viewed down the *b* axis, have been deposited with the IUCr (Reference: MU1242). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dibromo[*N*-(2-pyridylmethylidene)-2-pyridylmethylamine-*N*,*N*′,*N*″]copper(II) Complex

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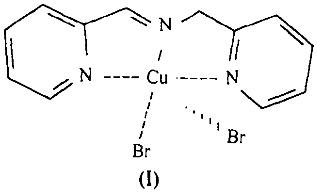
Abstract

The title complex, [$CuBr_2(C_{12}H_{11}N_3)$], is a monomer and the environment around the Cu^{2+} ion is that of a square pyramid, with one Br^- ion occupying the apical site and the other Br^- ion at a basal position.

Comment

The ligand [*N*-(2-pyridylmethylidene)-2-pyridylmethylamine-*N*,*N*′,*N*″] was prepared in order to compare its behaviour with that of the previously studied ligand [*N*-(2-pyridylmethylidene)-2-thienylmethylamine-*N*,*N*′] in copper(II) complexes (Atria *et al.*, 1994). Both ligands are Schiff bases which are prepared by the reaction of 2-pyridinecarboxaldehyde with 2-aminomethylpyridine and 2-aminomethylthiophene, respectively. The bromocopper(II) complex of the above mentioned ligand, (I), was prepared and the crystal structure determined in order to ascertain whether the metal center was coordinated to two or to all of the N atoms.



(I)

The environment around the Cu^{2+} ion is that of a square pyramid, with Br1 occupying the apical site, Br2 occupying one of the basal positions and the three remaining positions being occupied by the three N atoms of the organic ligand (Fig. 1) [N1—Cu1 = 2.045 (5), N2—Cu1 = 1.966 (4), N3—Cu1 = 2.041 (5), Br2—Cu1 = 2.412 (1) and Br1—Cu1 = 2.612 (1) Å]. The basal coordination plane, defined by N1, N2, N3, Br2 and N2, has a maximal displacement of 0.109 (4) Å. The apical bond Br1—Cu1 deviates 6.2 (1)° from the normal. The two Cu—Br bonds are quite different in length. This striking difference is probably due to the existence of two short intramolecular non-bonding H···Br2 contacts (C12—H12···Br2 = 2.91, C1—H1···Br2 = 2.87 Å). Their action is clearly to contract the Cu—Br2 bond, as shown in Fig. 1. The non-bonding interactions involving Br1 are all intermolecular and their action is the opposite of that of the H···Br2 contacts. The organic ligand as a whole shows a slight departure from planarity, the mean plane of the chelate unit defined by N3—C8—C7—N2—C6—C5—N1 having a maximal displacement of 0.071 (6) Å; Cu1 deviates by 0.248 (1) Å and the dihedral angle between the two pyridinic groups is 10.4 (2)°. The tridentate ligand does not display the short double-bond character of a C═N imine group: C6—N2 = 1.345 (7) and C7—N2 = 1.363 (7) Å. The two angles involved are also of the same magnitude: C5—C6—N2 = 112.9 (5) and C8—C7—N2 = 112.1 (5)°. These values are intermediate between pure sp^2 and sp^3 values, and indicate a high degree of delocalization. As a result, the three H atoms bonded to C6 and C7 could not be located precisely, and could only be treated in a disordered model, with site-occupancy factors of 0.5 each (Fig. 1). Therefore, this ligand presents a different behaviour from that of the parent ligand [*N*-(2-pyridylmethylidene)-2-thienylmethylamine-*N*,*N*′], reported previously, which coordinates only through two N atoms and shows a clear distinction between a short C═N bond [C6—N2 = 1.268 (5) Å] and a long C—N bond [C7—N2 = 1.483 (6) Å].

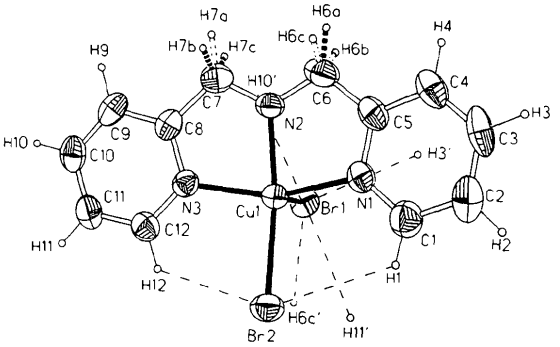


Fig. 1. View of the molecule showing the labelling of all atoms, as well as relevant Br···H interactions. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

Crystal data

$[CuBr_2(C_{12}H_{11}N_3)]$
$M_r = 420.60$
Monoclinic
$P2_1/n$
$a = 7.941\ (3)$ Å
$b = 12.810\ (4)$ Å
$c = 13.509\ (4)$ Å
$\beta = 90.93°$
$V = 1374.0\ (8)$ Å^3
$Z = 4$
$D_x = 2.033$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5–12.5°$
$\mu = 7.390$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.68 × 0.40 × 0.30 mm
Deep blue

Data collection

Siemens *R*3*m* diffractometer
$\theta/2\theta$ scans (4.19–29.3° min^{-1})
Absorption correction: ψ scan
$T_{min} = 0.502$, $T_{max} = 0.956$
2021 measured reflections
1785 independent reflections
1440 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0102$
$\theta_{max} = 22.52°$
$h = -3 \rightarrow 8$
$k = -2 \rightarrow 13$
$l = -14 \rightarrow 14$
2 standard reflections monitored every 98 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0301$
$wR(F^2) = 0.0731$
$S = 1.083$
1785 reflections
163 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.800$ e Å^{-3}
$\Delta\rho_{min} = -0.414$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
Br1	0.13491 (7)	0.27353 (5)	0.35676 (4)	0.0441 (2)
Br2	0.54997 (8)	0.14313 (5)	0.25117 (4)	0.0474 (2)
Cu1	0.41313 (8)	0.17649 (5)	0.40608 (5)	0.0353 (2)
N1	0.5548 (6)	0.3027 (4)	0.4481 (3)	0.0384 (11)
N2	0.3818 (6)	0.1730 (4)	0.5501 (3)	0.0372 (11)
N3	0.3038 (5)	0.0333 (3)	0.4208 (3)	0.0361 (11)
C1	0.6547 (8)	0.3607 (5)	0.3924 (5)	0.054 (2)
C2	0.7476 (9)	0.4428 (5)	0.4309 (6)	0.066 (2)
C3	0.7387 (9)	0.4644 (5)	0.5303 (6)	0.068 (2)
C4	0.6388 (8)	0.4052 (5)	0.5872 (5)	0.056 (2)
C5	0.5478 (7)	0.3241 (4)	0.5458 (4)	0.0428 (15)
C6	0.4409 (8)	0.2542 (5)	0.6033 (4)	0.054 (2)
C7	0.2948 (7)	0.0914 (5)	0.5890 (4)	0.046 (2)
C8	0.2536 (6)	0.0108 (4)	0.5134 (4)	0.0369 (14)
C9	0.1677 (7)	−0.0798 (5)	0.5344 (4)	0.044 (2)
C10	0.1290 (7)	−0.1493 (5)	0.4591 (5)	0.049 (2)
C11	0.1792 (7)	−0.1267 (5)	0.3653 (5)	0.048 (2)
C12	0.2657 (7)	−0.0348 (4)	0.3484 (4)	0.0421 (14)

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

Br1—Cu1	2.612 (1)	C1—C2	1.381 (8)
Br2—Cu1	2.412 (1)	C2—C3	1.374 (9)
Cu1—N2	1.966 (4)	C3—C4	1.348 (9)
Cu1—N3	2.041 (5)	C4—C5	1.379 (8)
Cu1—N1	2.045 (5)	C5—C6	1.465 (8)
N1—C1	1.330 (7)	C7—C8	1.484 (8)
N1—C5	1.349 (7)	C8—C9	1.378 (8)
N2—C6	1.345 (7)	C9—C10	1.383 (8)
N2—C7	1.363 (7)	C10—C11	1.366 (8)
N3—C12	1.340 (7)	C11—C12	1.383 (8)
N3—C8	1.351 (7)		
N2—Cu1—N3	79.8 (2)	C8—N3—Cu1	114.5 (4)
N2—Cu1—N1	79.7 (2)	N1—C1—C2	122.1 (6)
N3—Cu1—N1	156.5 (2)	C3—C2—C1	119.1 (7)
N2—Cu1—Br2	157.04 (13)	C4—C3—C2	119.0 (6)
N3—Cu1—Br2	97.09 (13)	C3—C4—C5	120.2 (6)
N1—Cu1—Br2	97.32 (14)	N1—C5—C4	121.3 (6)
N2—Cu1—Br1	98.23 (13)	N1—C5—C6	115.4 (5)
N3—Cu1—Br1	95.36 (12)	C4—C5—C6	123.3 (6)
N1—Cu1—Br1	98.86 (12)	N2—C6—C5	112.9 (5)
Br2—Cu1—Br1	104.72 (3)	N2—C7—C8	112.1 (5)
C1—N1—C5	118.4 (5)	N3—C8—C9	121.7 (5)
C1—N1—Cu1	128.0 (4)	N3—C8—C7	115.1 (5)
C5—N1—Cu1	113.6 (4)	C9—C8—C7	123.3 (5)
C6—N2—C7	124.2 (5)	C8—C9—C10	119.7 (5)
C6—N2—Cu1	117.5 (4)	C11—C10—C9	118.8 (6)
C7—N2—Cu1	118.2 (4)	C10—C11—C12	119.1 (6)
C12—N3—C8	118.0 (5)	N3—C12—C11	122.7 (5)
C12—N3—Cu1	127.3 (4)		

H atoms were placed in calculated positions, riding on their respective host atom. A disordered model was used for those H atoms attached to C6 and C7, to take account of the high degree of delocalization in the C—N bonds.

Data collection: *P3/P4/PC* (Siemens, 1991). Cell refinement: *P3/P4/PC*. Data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1991). Program(s) used to solve structure: *XS* in *SHELXTL/PC*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *CIFTAB* in *SHELXL93*; *PARST93* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1146). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dichloro(di-2-pyridylamine-*N*,*N*′)copper(II)

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Abstract

The title complex, [$CuCl_2(C_{10}H_9N_3)$], is a monomer, with the Cu atom in a rather distorted tetrahedral environment provided by two Cl^- ions and two N atoms from the bidentate bipyridine derivative. The group is bisected by a twofold axis passing through the cation and the amine N atom bridging the symmetry-related pyridine groups. The deformation of the coordination tetrahedron is due to the Cl^- ion taking part in intramolecular interactions.

Comment

Copper(II) complexes of formula [Cu(NN')X_2], where X is Cl or Br and NN' is a pyridine derivative, show different geometries with four-, five- and six-fold coordination. These complexes can crystallize as monomers, dimers and different kinds of polymers. Our previous work led to the characterization of a number of 2,2′-bipyridine complex deriva-