

Orthorhombic

Pbca $a = 7.792(1) \text{ \AA}$ $b = 10.390(1) \text{ \AA}$ $c = 18.894(2) \text{ \AA}$ $V = 1529.6(3) \text{ \AA}^3$ $Z = 8$ $D_x = 2.618 \text{ Mg m}^{-3}$ D_m not measured

Cell parameters from 25 reflections

 $\theta = 2.50\text{--}17.25^\circ$ $\mu = 5.164 \text{ mm}^{-1}$ $T = 293(2) \text{ K}$

Block

 $0.1 \times 0.1 \times 0.1 \text{ mm}$

Colorless

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1168). Services for accessing these data are described at the back of the journal.

Data collection

Siemens P4-RA diffractometer

 $\theta/2\theta$ scans

Absorption correction:

semi-empirical via ψ

scan (XEMP in XSCANS; Siemens, 1994b)

 $T_{\min} = 0.583$, $T_{\max} = 0.621$

1582 measured reflections

1582 independent reflections

1262 reflections with

 $I > 2\sigma(I)$ $\theta_{\max} = 26.5^\circ$ $h = 0 \rightarrow 9$ $k = 0 \rightarrow 12$ $l = 0 \rightarrow 23$

3 standard reflections

every 150 reflections

intensity decay: none

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.025$ $wR(F^2) = 0.059$ $S = 1.053$

1572 reflections

122 parameters

H atoms constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0082P)^2 + 2.7273P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.660 \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = -0.886 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

| | | | |
|--|------------|---|------------|
| Ba1—O11 ⁱ | 2.712 (3) | Ba1—O41 ^l | 2.659 (3) |
| Ba1—O12 ⁱⁱ | 2.742 (3) | Ba1—O42 ^{ll} | 2.745 (3) |
| Ba1—O11 ⁱⁱⁱ | 2.757 (3) | Ba1—O41 | 2.806 (3) |
| Ba1—O12 ^{iv} | 2.868 (3) | Ba1—O42 | 2.944 (3) |
| O11 ⁱ —Ba1—O11 ⁱⁱⁱ | 148.50 (6) | O42 ^{ll} —Ba1—O12 ^{iv} | 134.55 (9) |
| O41 ^l —Ba1—O11 ⁱ | 135.10 (1) | O11 ⁱⁱⁱ —Ba1—O12 ^{iv} | 135.93 (9) |
| O41 ^l —Ba1—O12 ^{iv} | 148.10 (1) | O42 ^{ll} —Ba1—O42 | 151.71 (6) |
| O42 ^{ll} —Ba1—O41 | 140.7 (1) | O11 ⁱⁱⁱ —Ba1—O42 | 100.65 (9) |
| O41 ^l —Ba1—O12 ^{iv} | 69.6 (1) | O41—Ba1—O42 | 45.21 (9) |
| O12 ^{iv} —Ba1—O12 ^{iv} | 139.43 (9) | | |

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

A relatively small crystal was chosen to minimize absorption effects.

Data collection: XSCANS (Siemens, 1994b). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: XP (Siemens, 1994a).

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Acta Cryst. (1998). **C54**, 1848–1850

Aqua(4,4'-dimethyl-2,2'-bipyridine-*N,N'*)-(malonato-*O,O'*)copper(II) Dihydrate

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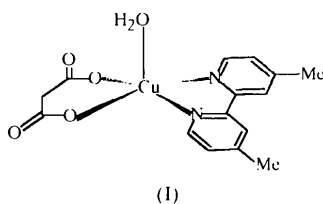
Abstract

The title compound, [Cu(C₃H₂O₄)(C₁₂H₁₂N₂)(H₂O)]·2H₂O, lies on a crystallographic mirror. The Cu^{II} ion in the complex has a slightly distorted square-pyramidal

coordination environment, with one water molecule in the apical position, and two malonate O atoms and both N atoms of the bipyridine ligand defining the base. The five-membered chelate ring defined by atoms N1, C5, C5', N1' and Cu1 is almost planar, while the chelate ring defined by the malonate ligand (O1, C7, C8, C7' and O1') and the Cu atom has an envelope conformation. Hydrogen bonding and π - π^* -orbital interactions between the bipyridine rings seem to determine the crystal packing.

Comment

Our study of the IR spectroscopic properties of several mixed aromatic diimine and oxygen-donor complexes has led us to prepare and crystallize, among others, the title complex, (I), in order to elucidate the relationships between structure and spectroscopic behaviour.



Each Cu^{II} ion is surrounded by five ligating atoms in a square-pyramidal arrangement. The mirror symmetry of the molecule requires atoms N1, N1', O1' and O1 to be coplanar; Cu1 deviates from this least-squares mean plane by $-0.239(2)$ Å. The O atom of the water molecule coordinated in the apical position deviates from this mean plane by $-2.533(3)$ Å. A similar coordination behaviour is observed in the unsubstituted bipyridine complex (Suresh & Bhadbhade, 1997), in which Cu deviates by -0.112 Å and OW by -2.651 Å from the corresponding basal plane. Differences between these two complexes are found in the disposition of the planes defined by the coordinating atoms of each ligand and Cu (*i.e.* the plane of N1, N1' and Cu1, and that of O1, O1' and Cu1, in the title complex): the interplanar angle is $19.24(7)^\circ$ in the title complex and $9.00(8)^\circ$ in the unsubstituted bipyridine complex.

Other relevant mean planes in the molecule are that of the five-membered bipyridine chelate ring defined by N1, C5, C5', N1' and Cu1, which is planar with negligible distortion (average r.m.s. deviation of the five fitted atoms is 0.0092 Å), and the plane defined by O1, C7, C7', O1' and Cu1, which is roughly planar (average r.m.s. deviation of the five fitted atoms is 0.1505 Å).

The chelate ring formed by the malonate ligand (O1, C7, C8, C7' and O1') and Cu1 has an envelope conformation; C8 deviates by $-1.126(5)$ Å from the plane of the other five atoms. This behaviour is also found in the unsubstituted bipyridine complex.

The angle between the least-squares mean plane of the bipyridine ring and that of the malonate ring, excluding C8, is $3.06(2)^\circ$. The angle between the mean plane of the coordinated atoms and the mean plane of the bipyridine chelate ring is $8.23(3)^\circ$, while the angle between the mean plane of the coordinated atoms and the mean plane of the malonate chelate ring is $14.54(4)^\circ$.

The Cu—N distances [$2.003(2)$ Å] are longer than the Cu—O distances [$1.931(2)$ Å], as observed in many complexes with amines and malonate (Kwik *et al.*, 1986; Borghi, 1987; Pajunen & Nasakkala, 1977; Hamalainen & Pajunen, 1973; Kansikas & Hamalainen, 1977; Suresh & Bhadbhade, 1997; Kawata *et al.*, 1995; Gasque *et al.*, 1998). Complexes with malonate as the only ligand, however, have Cu—O distances that are longer than in mixed-ligand complexes (Kiosse *et al.*, 1989).

The Cu—OW bond length [$2.297(4)$ Å] is similar to those in the related complexes with phenanthroline [$2.31(3)$ Å; Kwik *et al.*, 1986; Borghi, 1987], 5,6-dimethylphenanthroline (2.275 Å; Gasque *et al.*, 1998) or oxamide-oxime ligands (2.350 Å; Kawata *et al.*, 1995), but shorter than the Cu—OW bond in the simple parent bipyridine complex (2.523 Å; Suresh & Bhadbhade, 1997).

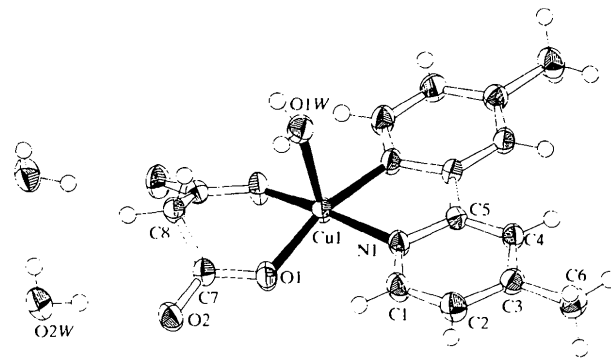


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

Relevant hydrogen bonds are listed in Table 2. Molecules in the crystal are linked by hydrogen bonding between water molecules and malonate O atoms, forming chains; the bipyridine rings in neighbouring chains are parallel to one another. It may be suggested that the crystal packing is not only determined by hydrogen-bond interactions, but also by π - π^* interactions among bipyridine units. The closest distance between bipyridine mean planes in the cell is $3.49(1)$ Å.

Experimental

The title compound was obtained by mixing Cu(NO₃)₂ (2.5 ml, 0.1 M) with 4,4'-dimethylbipyridine (0.25 mmol) in methanol. To this solution, malonic acid (2.5 ml, 0.1 M in water) was added. The mixture was then neutralized with 0.1 M NH₄OH until a deep-blue colour was observed. The product was isolated as prismatic deep-blue crystals. Recrystallization of the product was performed twice from a mixture of water and methanol in equal parts. Crystals suitable for X-ray analysis were grown by slow evaporation from a water/methanol solution.

Crystal data

| | |
|--|---|
| [Cu(C ₃ H ₂ O ₄)(C ₁₂ H ₁₂ N ₂)(H ₂ O)].2H ₂ O | Mo K α radiation |
| $M_r = 403.87$ | $\lambda = 0.71073 \text{ \AA}$ |
| Orthorhombic | Cell parameters from 25 reflections |
| <i>Pnma</i> | $\theta = 11.5\text{--}24.4^\circ$ |
| $a = 6.9780(1) \text{ \AA}$ | $\mu = 1.344 \text{ mm}^{-1}$ |
| $b = 17.156(3) \text{ \AA}$ | $T = 293(2) \text{ K}$ |
| $c = 13.996(3) \text{ \AA}$ | Prismatic |
| $V = 1675.5(5) \text{ \AA}^3$ | $0.35 \times 0.15 \times 0.10 \text{ mm}$ |
| $Z = 4$ | Blue |
| $D_x = 1.601 \text{ Mg m}^{-3}$ | |
| D_m not measured | |

Data collection

| | |
|---|---|
| Enraf-Nonius CAD-4 diffractometer | 1474 reflections with $I > 2\sigma(I)$ |
| $\omega/2\theta$ scan | $\theta_{\max} = 30.4^\circ$ |
| Absorption correction: ψ scan (North <i>et al.</i> , 1968) | $h = -9 \rightarrow 0$ |
| $T_{\min} = 0.821$, $T_{\max} = 0.874$ | $k = -24 \rightarrow 0$ |
| 2608 measured reflections | $l = -19 \rightarrow 0$ |
| 2608 independent reflections | 3 standard reflections every 60 reflections |
| | intensity decay: none |

Refinement

| | |
|---|--|
| Refinement on F^2 | $(\Delta/\sigma)_{\max} = 0.064$ |
| $R[F^2 > 2\sigma(F^2)] = 0.041$ | $\Delta\rho_{\max} = 0.55 \text{ e \AA}^{-3}$ |
| $wR(F^2) = 0.115$ | $\Delta\rho_{\min} = -0.43 \text{ e \AA}^{-3}$ |
| $S = 0.956$ | Extinction correction: none |
| 2608 reflections | Scattering factors from <i>International Tables for Crystallography</i> (Vol. C) |
| 128 parameters | |
| H atoms: see below | |
| $w = 1/[\sigma^2(F_o^2) + (0.0620P)^2]$ | |
| where $P = (F_o^2 + 2F_c^2)/3$ | |

Table 1. Selected geometric parameters (\AA , $^\circ$)

| | | | |
|--------------|-----------|------------|----------|
| Cu1—O1 | 1.931(2) | C5—C5' | 1.478(5) |
| Cu1—N1 | 2.003(2) | C7—C8 | 1.516(3) |
| Cu1—O1W | 2.297(3) | | |
| O1—Cu1—O1' | 91.3(1) | O1—Cu1—O1W | 99.17(8) |
| O1—Cu1—N1' | 165.03(9) | N1—Cu1—O1W | 94.61(8) |
| O1—Cu1—N1 | 92.21(8) | N1—C5—C5' | 114.4(1) |
| N1'—Cu1—N1 | 80.8(1) | C4—C5—C5' | 124.4(1) |
| O1—C7—C8—C7' | 53.2(4) | | |

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

| D—H...A | D—H | H...A | D...A | D—H...A |
|----------------|---------|---------|----------|---------|
| O1W—H1W...O2W' | 0.84(1) | 1.95(1) | 2.749(3) | 161(3) |
| O2W—H2W...O1' | 0.88(1) | 2.07(1) | 2.952(3) | 176(3) |
| O2W—H3W...O2 | 0.87(1) | 1.92(1) | 2.762(3) | 163(3) |

Symmetry code: (i) $x - \frac{1}{2}, y, \frac{1}{2} - z$.

Water H atoms were refined isotropically, while C—H H atoms were placed in calculated positions with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{attached C})$ for methyl H atoms and $1.2U_{\text{eq}}(\text{attached C})$ for others.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XPMA* and *ZORTEP* (Zsolnai, 1997). Software used to prepare material for publication: *CIFTAB* in *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1117). Services for accessing these data are described at the back of the journal.

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