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Aqua(4,4'-dicarbomethoxy-2,2'-bipyridine-*N,N'*)(3,6-dichloro-4,5-dihydroxy-1,2-benzoquinonato-*O*⁴,*O*⁵)copper(II) Acetonitrile Hemisolvate†

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Abstract

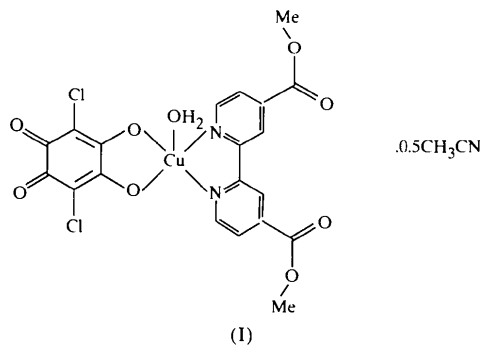
The title compound, [Cu(C₆Cl₂O₄)(C₁₄H₁₂N₂O₄)(H₂O)].0.5CH₃CN, adopts a slightly distorted square-pyramidal geometry around the five-coordinated Cu^{II} atoms, where the bidentate benzoquinone anion and the bidentate bipyridine ligand form the basal plane. The elongated apical position is occupied by a water molecule. The acetonitrile solvate molecule is disordered.

Comment

Attempts to build new metallic molecular materials using the oxalate ligand leads to three- and two-

† Systematic name: aqua(3,6-dichloro-4,5-dihydroxy-1,2-benzoquinonato-*O*⁴,*O*⁵)(dimethyl 2,2'-bipyridine-4,4'-dicarboxylato-*N,N'*)copper(II) acetonitrile hemisolvate.

dimensional compounds (Decurtins *et al.*, 1994; Pellaux *et al.*, 1997), while the 3,6-dichloro-4,5-dihydroxy-1,2-benzoquinone ligand (CA²⁻) has the potential for building up one-dimensional or two-dimensional transition metal polymers. The structures of several such polymers have been determined. Among these are the one-dimensional structures of [Cu(CA)(H₂O)₂]_n (Cueto *et al.*, 1992), {[Cu(CA)(H₂O)_m](G)}_n (*m* = 2, *G* = 2,5-dimethylpyrazine and phenazine; *m* = 1, *G* = 1,2,3,4,6,7,8,9-octahydrophenazine; Kawata *et al.*, 1996) and [Cu(CA)(CH₃OH)₂]_n (Kawata *et al.*, 1994), and the two-dimensional sheet structure of [Cu(CA)(pyz)]_n (pyz = pyrazine; Kawata *et al.*, 1994). We have recently succeeded in synthesizing the two chain compounds [Mn(bipy)(CA)]_n (bipy = 2,2'-bipyridine; Zheng *et al.*, 1996) and [Cu(DCMB)(CA)]_n (DCMB = 3,3'-dicarbomethoxy-2,2'-bipyridine) (Decurtins, Schmale, Zheng & Enslin, 1996). In our attempt to build new one- or two-dimensional bimetallic systems from an analogous precursor, [Cu(4-DCMB)]²⁺ (4-DCMB = 4,4'-dicarbomethoxy-2,2'-bipyridine), and a manganese(II) salt, a mononuclear compound, (I), was obtained.



The molecular structure of (I) is shown in Fig. 1. It exhibits a slightly distorted square-pyramidal coordination geometry about the Cu^{II} atom. Two N atoms from the 4-DCMB ligand [Cu—N = 1.984(2) and 1.985(2) Å, N1A—Cu—N1B = 81.7(1)°] and two O atoms from the CA²⁻ ligand [Cu—O = 1.938(2) and 1.947(2) Å, O1—Cu—O2 = 84.0(1)°] occupy the basal plane. All four atoms deviate by 0.007(1) Å from this plane. The Cu atom is pulled out of this least-squares plane [0.218(1) Å] towards the apically coordinated O11 atom [Cu—O11 = 2.216(2) Å]. The structure could be closely related to the mononuclear compound [Cu(DHBQ)(bipym)(H₂O)].5H₂O (DHBQ is the dianion of 2,5-dihydroxy-1,4-benzoquinone and bipym = 2,2'-bipyrimidine; Decurtins, Schmale, Schneuwly & Zheng, 1996), where the bond lengths Cu—N [1.983(3) and 2.004(3) Å] and Cu—O [1.928(3) and 1.947(3) Å] are comparable to those in the title compound, and the bond angles N—Cu—N [82.1(1)°] and O—Cu—O [85.1(1)°] are only slightly larger. The two pyridine

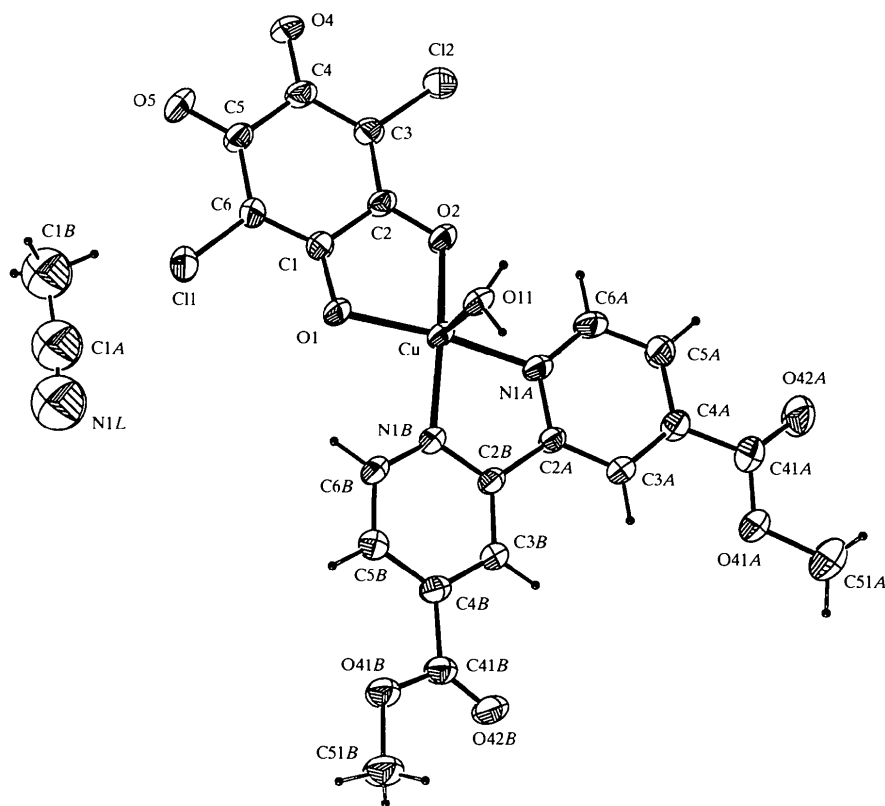


Fig. 1. ORTEP (Johnson, 1976) drawing of the title complex. Displacement ellipsoids are drawn at the 40% probability level. H atoms are shown as small circles of arbitrary radii.

rings in 4-DCMB are approximately planar with an angle of $4.6(2)^\circ$ between them. The CA^{2-} ring is planar with a maximum deviation of $0.024(2)$ Å for C3 and the four O atoms deviate by $0.002(5)$ – $0.052(4)$ Å from the plane. The neutral molecules are connected to each other through intermolecular hydrogen bonds. Details of the hydrogen bonds are listed in Table 2. The acetonitrile solvate molecule is disordered.

Experimental

4-DCMB was synthesized according to a published procedure (Sprintschnik *et al.*, 1977). $[Cu(4\text{-DCMB})_2(\text{ClO}_4)_2] \cdot 4\text{H}_2\text{O}$ was first obtained by slow evaporation of a mixture of $[Cu(\text{ClO}_4)_2] \cdot 6\text{H}_2\text{O}$ (0.5 mM) and 4-DCMB (1.5 mM) in 25 ml $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (4:1). A solution of this complex (5 mM) and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (2.5 mM) in $\text{CH}_3\text{CN}-\text{CH}_3\text{OH}$ (3:1) was placed on top of a sodium metasilica gel containing 5 mM H_2CA . Dark-red plate-like crystals appeared after two weeks.

Crystal data

$[Cu(\text{C}_6\text{Cl}_2\text{O}_4)(\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4) \cdot (\text{H}_2\text{O})] \cdot 0.5\text{C}_2\text{H}_3\text{N}$
 $M_r = 581.30$
 Triclinic
 $P\bar{1}$

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 5.9\text{--}10.4^\circ$

$a = 9.331(4)$ Å
 $b = 10.678(3)$ Å
 $c = 12.884(3)$ Å
 $\alpha = 65.94(2)^\circ$
 $\beta = 78.75(2)^\circ$
 $\gamma = 83.80(3)^\circ$
 $V = 1149.1(6)$ Å³
 $Z = 2$
 $D_x = 1.680$ Mg m⁻³
 D_m not measured

$\mu = 1.241$ mm⁻¹
 $T = 296(2)$ K
 Plate
 $0.35 \times 0.18 \times 0.05$ mm
 Dark red

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω - 2θ scan
 Absorption correction: numerical (Coppens *et al.*, 1965)
 $T_{\min} = 0.757$, $T_{\max} = 0.929$
 6936 measured reflections
 6661 independent reflections

3578 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.042$
 $\theta_{\max} = 29.97^\circ$
 $h = -13 \rightarrow 12$
 $k = -14 \rightarrow 13$
 $l = -18 \rightarrow 0$
 3 standard reflections every 400 reflections
 intensity decay: 2.8%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.145$

$w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 1.1681P]$
 where $P = (F_o^2 + 2F_c^2)/3$

S = 1.074

6661 reflections

326 parameters

H atoms treated by a
mixture of independent
and constrained refinement $(\Delta/\sigma)_{\max} = 0.003$ $\Delta\rho_{\max} = 0.486 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.579 \text{ e } \text{\AA}^{-3}$ Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)Table 1. Selected geometric parameters (\AA , $^\circ$)

Cu—O1	1.938 (2)	Cu—N1B	1.985 (2)
Cu—O2	1.947 (2)	Cu—O11	2.216 (2)
Cu—N1A	1.984 (2)		
O1—Cu—O2	83.95 (8)	N1A—Cu—N1B	81.65 (10)
O1—Cu—N1A	167.47 (10)	O1—Cu—O11	97.36 (9)
O2—Cu—N1A	96.18 (9)	O2—Cu—O11	99.16 (9)
O1—Cu—N1B	95.38 (9)	N1A—Cu—O11	94.99 (9)
O2—Cu—N1B	166.87 (10)	N1B—Cu—O11	93.94 (10)

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

D—H...A	D—H	H...A	D...A	D—H...A
O11—H111...O4 ⁱ	0.79 (1)	2.35 (2)	2.947 (3)	134 (1)
O11—H111...O5 ⁱ	0.79 (1)	2.27 (2)	2.999 (3)	153 (1)
O11—H112...O4 ⁱⁱ	0.81 (1)	1.97 (2)	2.777 (3)	173 (2)
C3A—H3A...N1L ⁱⁱⁱ	0.93	2.42	3.349 (10)	176.9
C3B—H3B...N1L ⁱⁱⁱ	0.93	2.48	3.403 (11)	174.9
C5A—H5A...O42A ^{iv}	0.93	2.51	3.210 (4)	132.6
C6B—H6B...O1	0.93	2.58	3.082 (4)	114.5
C6B—H6B...Cl1 ^v	0.93	2.767	3.541 (4)	141.3
C51B—H51D...O11 ^{vi}	0.96	2.387	3.292 (5)	157.1

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

The three coordinating ligands were refined anisotropically and the positions of the H atoms were calculated and refined using a riding model. The water H atoms at O11 were located in a difference electron-density map and were refined with isotropic displacement parameters using O—H and H...H distance restraints of 0.82 (2) and 1.30 (2) \AA , respectively. The acetonitrile solvent molecule was located by interpreting two electron-density peaks near a centre of symmetry with a very short inter-peak distance of about 1.10 \AA . Application of the symmetry operation resulted in four atomic positions of which the central generated peak to peak distance was approximately 1.45 \AA . Thus, the peak near the centre was assigned to a C atom and a rigid model of acetonitrile was refined with distance restraints [N1L—C1LA = 1.140 (15) and C1LA—C1LB = 1.453 (15) \AA]. The positions of the H atoms of the methyl C1LB atom were calculated in a previous refinement with *SHELXL97* (Sheldrick, 1997) using the *HFIX* 137 option and a dummy C atom. The H-atom coordinates were fixed in the final refinement cycles. All atoms of the acetonitrile solvent molecule were refined with a site occupancy factor of 0.5 and isotropic displacement parameters.

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*. Molecular graphics: *PLATON* and *PLUTON* (Spek, 1990). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1187). Services for accessing these data are described at the back of the journal.

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A New Dinuclear Molybdenum Compound, (Bu₄N)[Mo₂(CO)₆(SPh)₂(CH₂CCH₃COO)]

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Abstract

The crystal structure of the title compound, tetrabutylammonium bis(μ -benzenethiolato-*S:S*)- μ -methacrylate-*O:O'*-bis(tricarbonylmolybdenum)(*Mo—Mo*), (C₁₆H₃₆N)[Mo₂(C₄H₅O₂)(C₆H₅S)₂(CO)₆], shows that it contains a Bu₄N⁺ cation and a dinuclear anion with three bridging ligands, *i.e.* [Mo₂(CO)₆(SPh)₂(CH₂CCH₃COO)]⁻; the