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{4,4'-Dimethyl-6,6'-bis(1-morpholinio-methyl)-2,2'-[1,2-ethanediylbis(nitrilo-methylidene-*N*)]diphenolato-*O*,*O*′}-copper(II) diperchlorate monohydrate

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Abstract

The crystal structure of the title compound, $[Cu(C_{28}H_{38}N_4O_4)](ClO_4)_2 \cdot H_2O$, shows that the Cu^{II} ion is in a distorted square-pyramidal environment. The average Cu—O and Cu—N bond lengths are 1.916 (2) and 1.936 (3) Å, respectively. Both of the morpholino rings adopt a chair conformation. Even though enough chelating centres are available to coordinate more than one metal atom, because of the steric interaction of the morpholino rings only one Cu atom is coordinated to the ligand.

Comment

The function and properties of active sites in metal complexes are determined by the environment and coordination sites around the metal ion. Synthesis and structural studies of metal complexes should provide additional information on this issue. The mononuclear Cu site in the enzyme galactose oxidase is essential for catalysing a two-electron transfer reaction during the oxidation of primary alcohols to the corresponding aldehydes (Ito *et al.*, 1991). Galactose oxidase is unusual

among copper enzymes in participating in this catalysis of the two-electron redox chemistry of a mononuclear active site (Whittaker *et al.*, 1996). The study of metal complexes is focused very much towards the field of biomimicry, where they can be used as models for biological metallo-compounds, such as proteins and enzymes (Suzuki *et al.*, 1984). The present structural study of the title complex, (I), is the continuation of our previous work (Raj *et al.*, 1999).

(I)
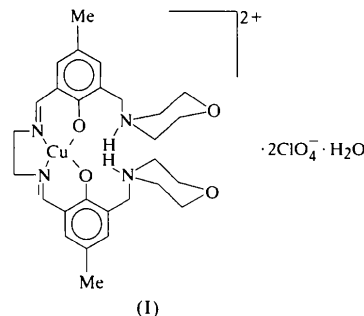
The O9 atom of the perchlorate ion coordinates with the Cu atom to make the metal pentacoordinate [Cu1···O9 2.832 (4) Å]. The Cu atom is in a distorted square-pyramidal environment, with the basal plane being defined by the two phenyloxy O atoms and the two imino N atoms. These O and N atoms extend the same type of coordination. The steric interaction of the morpholino rings restricts the coordination of a further metal atom in the other half of the complex, even though enough chelating centres are available (Kahn, 1982), where O1 and O4 can act as bridges. Due to steric interaction between the two bulky morpholino rings, the C2—C8—N1 [114.2 (2)°] and C21—C24—N4 [110.2 (2)°] angles are smaller than those of C6—C13—N2 [125.0 (3)°] and C17—C16—N3 [124.7 (3)°]. The bond lengths and angles in (I) are comparable with those of the ligand (Raj *et al.*, 1999). The five-membered ring, with Cu as one of the hetero atoms, is in a '*gauche*' conformation (Panneerselvam *et al.*, 1998) and the two six-membered rings are planar.

The decrease in the N2—Cu1—N3 angle [83.6 (1)°] may be due to the lack of macrocyclic closeness of the ligand. The N atoms of the morpholino rings are protonated and are involved in N—H···O hydrogen bonding. The morpholino rings adopt a chair conformation. The best plane passes through the central C atoms, leaving the N and O atoms above and below the plane. The deviations of these N and O atoms are 0.640 (3) and −0.677 (3) Å, respectively, for the ring consisting of atoms C9–C12, N1 and O1, and 0.645 (3) and −0.683 (3) Å, respectively, for the ring consisting of atoms C25–C28, N4 and O4.

The two phenyl rings are coplanar, making a dihedral angle of 3.8 (1)°, and the morpholino rings make
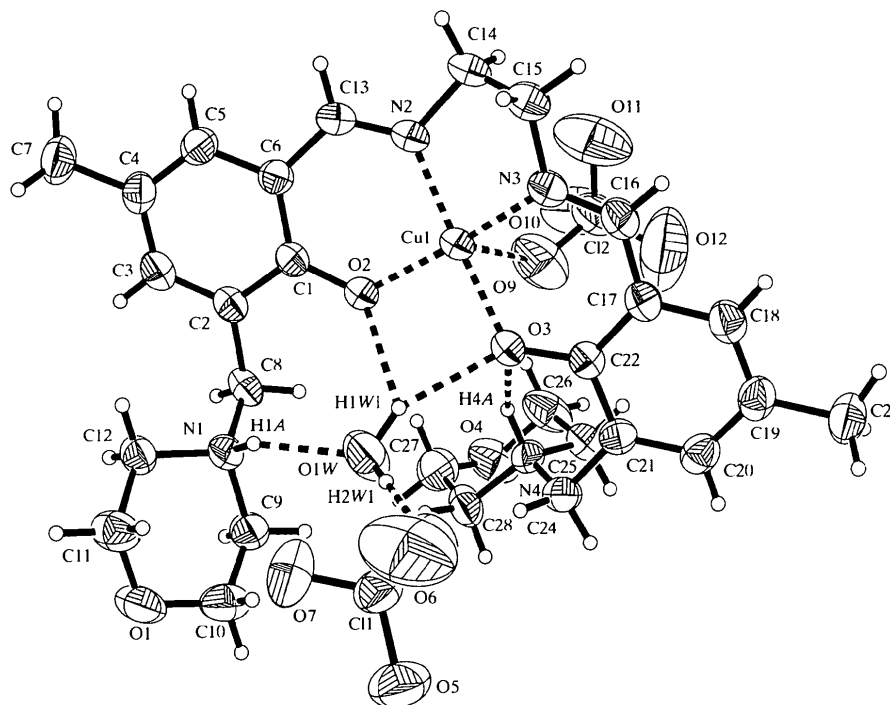
Fig. 1. *XP* (Sheldrick, 1997) plot of the title complex, showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as spheres of arbitrary radii.

dihedral angles of 68.7 (1) and 78.6 (1)° with the phenyl rings to which they are attached. The methylene group attached to the morpholino rings lies in an equatorial orientation. The packing is stabilized by N—H· · ·O and O—H· · ·O hydrogen bonds (Table 2) formed by the perchlorate ions and the water molecules.

Experimental

Paraformaldehyde (0.66 g, 0.022 mol) was mixed with morpholine (2.1 ml, 0.020 mol) in acetic acid and stirred overnight. To this, 5-methylsalicylaldehyde (2.7 g, 0.019 mol) was added. Stirring was continued for 1 d and the mixture was then refluxed for 8 h. The resulting compound was neutralized with saturated Na_2CO_3 and extracted with $CHCl_3$. The $CHCl_3$ extract was evaporated to obtain 4-methyl-2-formyl-6-(morpholin-1-ylmethyl)phenol. To this compound (4.70 g, 0.02 mol) in methanol (30 ml), 1,2-diaminoethane (0.7 ml, 0.01 mol) was added with stirring and the mixture was then refluxed for 2 h. The solvent was evaporated at room temperature to obtain bis[2-hydroxy-3-(morpholin-1-ylmethyl)-5-methyl-benzyl]ethylenediimine. To a mixture of this ligand (1.6 g, 0.0031 mol) and NaOH (0.26 g, 0.013 mol) in MeOH (30 ml), $Cu(ClO_4)_2$ (1.2 g, 0.0032 mol) was added in MeOH (20 ml) and the mixture refluxed for 2 h. The solvent was evaporated to obtain the title complex, which was separated by filtration, washed with MeOH, dried and recrystallized from a $CH_3CN/EtOH$ mixture (yield 60%, m.p. 343 K).

Crystal data

[Cu(C$_{28}$H$_{38}$N$_4$O$_4$)](ClO$_4$)$_2$·· H$_2$O
$M_r = 775.08$
Triclinic
$P\bar{1}$
$a = 8.9654\,(3)$ Å
$b = 9.6447\,(3)$ Å
$c = 20.0666\,(5)$ Å
$\alpha = 78.475\,(1)°$
$\beta = 81.518\,(1)°$
$\gamma = 83.786\,(1)°$
$V = 1675.99\,(9)$ Å^3
$Z = 2$
$D_x = 1.536$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 7132 reflections
$\theta = 1.45–33.17°$
$\mu = 0.881$ mm^{-1}
$T = 293\,(2)$ K
Block
$0.50 \times 0.38 \times 0.12$ mm
Dark brown

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical using *SADABS* (Sheldrick, 1996)
$T_{min} = 0.642$, $T_{max} = 0.891$
15 492 measured reflections
11 581 independent reflections

7898 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 33.13°$
$h = -13 \rightarrow 12$
$k = -13 \rightarrow 14$
$l = -29 \rightarrow 30$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.182$
$S = 1.117$
11 581 reflections
433 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2 + 1.6246P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.011$ e $Å^{-3}$
$\Delta\rho_{min} = -0.571$ e $Å^{-3}$
Extinction correction: none
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu1—O2	1.915 (2)	C11—O6	1.425 (3)
Cu1—O3	1.916 (2)	C11—O8	1.476 (5)
Cu1—N2	1.925 (3)	C12—O12	1.388 (5)
Cu1—N3	1.946 (3)	C12—O10	1.399 (4)
C11—O7	1.346 (4)	C12—O11	1.411 (4)
C11—O5	1.398 (3)	C12—O9	1.436 (4)
O2—Cu1—O3	89.66 (9)	O2—Cu1—N3	170.29 (11)
O2—Cu1—N2	93.29 (10)	O3—Cu1—N3	93.47 (10)
O3—Cu1—N2	177.02 (10)	N2—Cu1—N3	83.55 (11)
C12—N1—C9—C10	−52.9 (4)	C28—N4—C25—C26	53.0 (4)
C11—O1—C10—C9	−62.9 (4)	C27—O4—C26—C25	61.9 (5)
N1—C9—C10—O1	59.2 (4)	N4—C25—C26—O4	−57.5 (5)
C10—O1—C11—C12	62.3 (4)	C26—O4—C27—C28	−62.8 (4)
C9—N1—C12—C11	52.1 (4)	O4—C27—C28—N4	59.4 (4)
O1—C11—C12—N1	−57.5 (4)	C25—N4—C28—C27	−53.9 (4)

Table 2. Hydrogen-bonding geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1W	0.91	2.012	2.779 (4)	140.9
N4—H4A···O3	0.91	2.186	2.840 (3)	128.2
O1W—H1W1···O2	0.94	2.282	2.933 (3)	125.9
O1W—H1W1···O3	0.94	2.110	2.972 (4)	152.3
O1W—H2W1···O6	0.94	1.911	2.852 (4)	175.5

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 30 s covered 0.3° in ω. The crystal-to-detector distance was 4 cm and the detector swing angle was −35°. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the duplicate reflections; it was found to be negligible.

Data collection: SMART (Siemens, 1996). Cell refinement: SAINT (Siemens, 1996). Data reduction: SAINT. Program(s) used to solve structure: SHELXTL (Sheldrick, 1997). Program(s) used to refine structure: SHELXTL. Molecular graphics: XP in SHELXTL. Software used to prepare material for publication: SHELXTL and PARST (Nardelli, 1995).

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A neutral cobalt(II) complex of a Schiff base ligand containing mixed O2S2N2 donors

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Abstract

In the title compound, {1,1'-[2,2'-ethylenedioxybis-(benzylidenehydrazono)]-3,3'-diphenylbis(2-thiapropane-thiolato-S)}cobalt(II), [Co(C32H28N4O2S4)], the configuration about the cobalt(II) ion is distorted octahedral, involving two ethereal O, two β-N and two mercapto S atoms from the doubly deprotonated Schiff base ligand. The distorted octahedral configuration arises from a series of five- and six-membered chelate rings.

Comment

There is considerable interest in complexes containing sulfur donors due to their biological relevance. The