

METAL-ORGANIC COMPOUNDS

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Aqua(5,6-dimethyl-1,10-phenanthroline-*N,N'*)(malonato-*O,O'*)copper(II) hydrate

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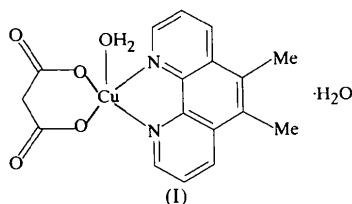
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Abstract

Each copper ion in the title complex, $[\text{Cu}(\text{C}_3\text{H}_2\text{O}_4)(\text{C}_{14}\text{H}_{12}\text{N}_2)(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$, displays a slightly distorted square-pyramidal coordination geometry, where the water molecule is in the apical position and two malonate O atoms and the phenanthroline N atoms define the base. The five-membered chelate ring defined by the phenanthroline molecule and the Cu atom is nearly planar with only slight distortion, while the ring defined by the malonate moiety and the Cu atom displays an envelope conformation. Hydrogen-bond and $\pi-\pi^*$ interactions define the crystal packing.

Comment

Our studies of the IR spectroscopic properties of several mixed phenanthroline and *O*-donor complexes has led us to prepare and crystallize, among others, the title $[\text{Cu}(\text{mal})(5,6\text{-dm-fen})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ complex, (I), where mal is malonate and 5,6-dm-fen is 5,6-dimethyl-1,10-phenanthroline.



Each Cu^{II} ion is surrounded by five ligand atoms in a slightly distorted square-pyramidal coordination geometry, where the water molecule is in the apical position [2.2751(2) Å] (Fig. 1). Two of the malonate

O atoms (O1 and O2) and both the phenanthroline N atoms (N1 and N2) define the base with negligible tetrahedral distortion; the average r.m.s. deviation from the four-atom least-squares plane is 0.0379 Å [distances: N1 0.0394(7), N2 -0.0394(7), O1 -0.0365(7) and O2 0.0364(7) Å]. The Cu1 atom is 0.2241(8) Å out of the least-squares plane and the O atom of the coordinated water molecule (O1W) is 2.495(2) Å from this plane.

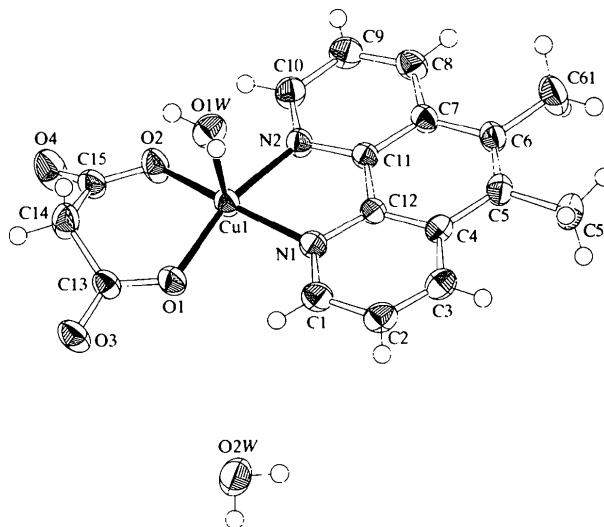


Fig. 1. ZORTEP plot (Zsolnai, 1997) of the molecular structure of $[\text{Cu}(\text{mal})(5,6\text{-dm-fen})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$. Displacement ellipsoids are drawn at the 50% probability level.

Other relevant mean planes in the molecule are the five-membered phenanthroline chelate ring defined by atoms N1, C12, C11, N2 and Cu1, which is planar with negligible distortion (average r.m.s. deviation from the five-atom plane is 0.0299 Å), and the plane defined by atoms O2, C13, C15, O1 and Cu1, which is roughly planar (average r.m.s. deviation from the five-atom plane is 0.0827 Å). The whole ligand displays an envelope conformation and deviates significantly from planarity. The distance of atom C14 from the latter plane is 0.632(3) Å.

The angle between the phenanthroline chelate plane (N1, C11, C12, N2 and Cu1) and the malonate moiety excluding the C14 atom (O1, C13, C15, O2 and Cu1) is 7.90(7)°. The angle between the planes of the coordination-plane atoms and the phenanthroline molecule is 6.08(6)°, and that formed with the malonate moiety is 1.85(8)°. Average Cu1—N distances [2.02(1) Å] are longer than Cu1—O distances [1.92(1) 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 & Bhadrade, 1997; Kawata *et al.*, 1995).

In complexes with malonate as the only ligand (Chattopadhyay *et al.*, 1993), Cu—O distances are longer [1.948 (3) Å] on average than in mixed complexes.

The Cu—O1W bond distance [2.275 (2) Å] is similar to those observed in related complexes, as in the case of phenanthroline [2.30 (3) Å; Kwik *et al.*, 1986; Borghi, 1987] or dimethylglyoxime [2.35 (1) Å; Kawata *et al.*, 1995] mixed complexes. However, when compared with non-aromatic amines, the bond is longer, as in 1-isopropyl-2-methylpropane-1,2-diamine [2.50 Å; Kansikas & Hamalainen, 1977] or in *N*-methylethylenediamine (2.51 Å; Hamalainen & Pajunen, 1973) mixed complexes. Finally, this bond is shorter than in the case of the simple bis(malonate) complex [2.46 (6) Å; Chattopadhyay *et al.*, 1993].

It is also observed that molecules in the crystal are arranged through weak hydrogen bonding (the main hydrogen-bonding distances are presented in Table 2), forming chains where the phenanthroline rings of neighbouring molecules lie parallel. It can be suggested that crystal packing is not only determined by hydrogen-bond interactions but probably also by π - π^* interactions among phenanthroline units. The distance between the nearest phenanthroline units in the cell is 3.3 (1) Å.

Experimental

The title complex was obtained by mixing Cu(NO₃)₂ (0.1 M, 2.5 ml) with 5,6,-dimethyl-1,10-phenanthroline (0.25 mmol) in methanol. To this solution was added malonic acid (0.1 M, 2.5 ml) dissolved in water. The mixture was neutralized with 0.1 M NH₄OH until a deep-blue colour was observed. The product was isolated as deep-blue prismatic crystals by filtration and drying. The product was recrystallized twice from water. Crystals suitable for X-ray analysis were grown by slow evaporation from a water solution.

Crystal data

[Cu(C₃H₂O₄)(C₁₄H₁₂N₂)·(H₂O)]·H₂O

M_r = 409.85

Monoclinic

*C*2/*c*

a = 24.772 (5) Å

b = 10.165 (2) Å

c = 15.362 (3) Å

β = 120.68 (3)°

V = 3326.8 (11) Å³

Z = 8

D_x = 1.637 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 11.5–24.4°

μ = 1.35 mm⁻¹

T = 293 (2) K

Prismatic

0.43 × 0.37 × 0.33 mm

Blue

Data collection

Enraf–Nonius CAD-4 diffractometer

3946 reflections with $I > 2\sigma(I)$

$\omega/2\theta$ scans

Absorption correction:

empirical ψ scan (North *et al.*, 1968)

T_{min} = 0.600, *T_{max}* = 0.640

5208 measured reflections

5033 independent reflections

R_{int} = 0.015

θ_{\max} = 30.41°

h = -30 → 35

k = 0 → 14

l = -21 → 0

3 standard reflections

frequency: 60 min

intensity decay: none

Refinement

Refinement on *F*²

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.096$

S = 1.057

5033 reflections

266 parameters

H atoms treated by a

mixture of independent

and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0560P)^2 + 1.6531P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.013$

$\Delta\rho_{\max} = 0.47 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.82 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu1—O2	1.915 (1)	Cu1—N2	2.028 (1)
Cu1—O1	1.935 (1)	Cu1—O1W	2.275 (2)
Cu1—N1	2.009 (2)		
O2—Cu1—O1	95.03 (6)	N1—Cu1—N2	81.06 (5)
O2—Cu1—N1	167.06 (6)	O2—Cu1—O1W	99.05 (6)
O1—Cu1—N1	90.38 (6)	O1—Cu1—O1W	97.55 (7)
O2—Cu1—N2	90.62 (6)	N1—Cu1—O1W	91.86 (5)
O1—Cu1—N2	163.17 (6)	N2—Cu1—O1W	97.19 (6)
N2—C11—C12—N1	-0.1 (2)	C13—C14—C15—O2	-52.1 (3)
O1—C13—C14—C15	44.3 (3)		

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1W—H1W···O3 ⁱ	0.89 (1)	1.93 (1)	2.806 (2)	170 (3)
O1W—H2W···O2W ^j	0.88 (1)	1.90 (1)	2.779 (2)	174 (3)
O2W—H3W···O4 ⁱⁱ	0.94 (1)	1.86 (1)	2.771 (1)	165 (3)
O2W—H4W···O3 ⁱⁱⁱ	0.93 (1)	1.93 (1)	2.864 (1)	177 (3)

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

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, 1997b). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a). Molecular graphics: *ZORTEP* (Zsolnai, 1997). Software used to prepare material for publication: *CIFTAB* in *SHELXS97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1113). Services for accessing these data are described at the back of the journal.

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(5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraene-*N,N',N'',N'''*)nickel(II) diperchlorate

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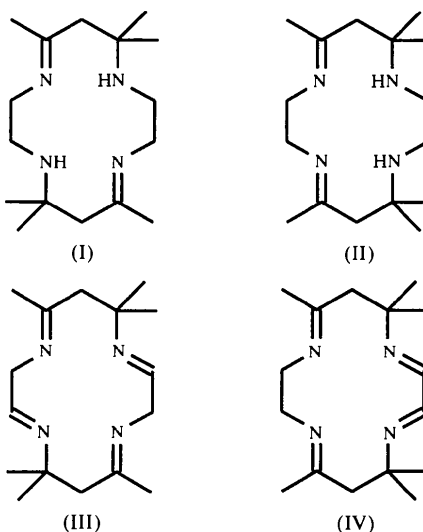
Abstract

In the title compound, [Ni(C₁₆H₂₈N₄)](ClO₄)₂, all the Ni—N distances are approximately equal [1.896 (3)–1.904 (2) Å]. There is no direct interaction between the Ni atoms and the perchlorate ions. Although most C···O interactions are close to or insignificantly less in size than those expected for van der Waals packing, one was found to be 3.105 (7) Å.

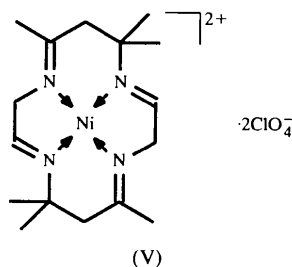
Comment

Tetraaza-macrocyclic compounds derived from condensation of amines (or their metal complexes) with

aliphatic carbonyl compounds (Curtis, 1968) remain classic objects for X-ray structural studies (Hu *et al.*, 1996; Lu *et al.*, 1996; Panneerselvam *et al.*, 1998; Simonov *et al.*, 1998; Wang *et al.*, 1996). The most important representatives, first of all due to their easy preparation, are Ni^{II} complexes with the neutral ligands composed of ethylenediamine and acetone fragments commonly called Me₆trans[14]dieneN₄, (I), and Me₆cis[14]dieneN₄, (II), as well as with the oxidized ligands Me₆trans[14]teteneN₄, (III), and Me₆cis[14]teteneN₄, (IV). While the structures of nickel complexes (I), (II) and (IV) (as perchlorate salts) were reported long ago (Bailey & Maxwell, 1972; Kilbourn *et al.*, 1969; Maxwell & Bailey, 1972), the corresponding complex of (III) has not been characterized.



We present here the X-ray structure determination of the latter compound, (5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraene-*N,N',N'',N'''*)nickel(II) diperchlorate, (V). All the Ni—N distances in the complex are approximately equal [Ni1—N1 1.904 (2) and Ni1—N5 1.896 (3) Å].



As in the three perchlorate salts studied before, there is no direct interaction between Ni atoms and the perchlorate ions (in the present case, the shortest Ni···O distance was 3.183 (6) Å for Ni1···O2). As a rule, the