Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Diaquamalonato(1,10-phenanthroline)zinc(II)

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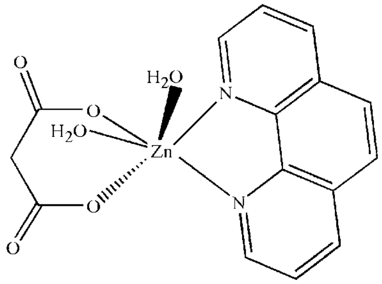
Received 26 September 2005
Accepted 18 November 2005
Online 10 December 2005

In the crystal structure of the title complex, $[Zn(C_3H_2O_4)(C_{12}H_8N_2)(H_2O)_2]$, the Zn^{II} atom displays a distorted octahedral geometry, being coordinated by two N atoms from the 1,10-phenanthroline ligand, two O atoms from different carboxylate groups of the chelating malonate dianion and two O atoms of *cis* water molecules. The complex molecules are linked to form a three-dimensional supramolecular array by both hydrogen-bonding interactions between coordinated water molecules and the uncoordinated carboxylate O atoms of neighboring molecules, and aromatic π–π stacking interactions between neighboring phenanthroline rings.

Comment

There has been considerable interest in the design and syntheses of transition metal complexes with carboxylate ligands in coordination chemistry, due to the fact that this type of complex has potential applications in molecular-based magnets, catalysis, supramolecular chemistry and biological systems (Li *et al.*, 2002; Shi *et al.*, 2000; Devereux *et al.*, 2000). As an important dicarboxylate ligand, the malonate dianion may act in a chelating bidentate manner and adopt different carboxylate bridging coordination modes, such as *syn–syn*, *syn–anti* and *anti–anti* (Li *et al.*, 1997; Lightfoot *et al.*, 1999; Lis *et al.*, 1979; Muro *et al.*, 1998). Zn^{II} complexes with the malonate ligand have potential applications in modified metalloenzymes and in precursor systems for Zn-containing ceramic materials. Several structures of Zn^{II} complexes with malonate (mal) have been reported, *viz.* $\{Na_2[Zn(mal)_2\cdot 2H_2O\}_n$ (Lin *et al.*, 2003), $\{[Zn_2(mal)_2(pym)(H_2O)]\cdot H_2O\}_n$ (pym is pyrimidine; Delgado *et al.*, 2003) and $[Zn_2(H_2O)_2(mal)_2(C_4H_4N_2)]$ (Zhang *et al.*, 2003). These structures were all found to be polymeric, with the malonate ligands serving as bridges. To the best of our knowledge, there have been no reports of mononuclear Zn^{II} complexes in which malonate acts as a chelating ligand via the carboxylate groups. We report here the crystal structure of one such complex, diaquamalonato(1,10-phenanthroline)zinc(II), (I).



(I)

The molecular structure of (I), shown in Fig. 1, consists of discrete monomers. The malonate dianion chelates the Zn^{II} atom through two O atoms from different carboxylate groups. The Zn^{II} atom is also coordinated by the two 1,10-phenanthroline N atoms and the O atoms of two *cis* water molecules. Each malonate ligand forms a six-membered chelate ring with one Zn^{II} ion in a boat-type configuration; the malonate ligand acts only as a chelating ligand and does not act as a bridge between metal atoms. The carboxylate chelating coordination

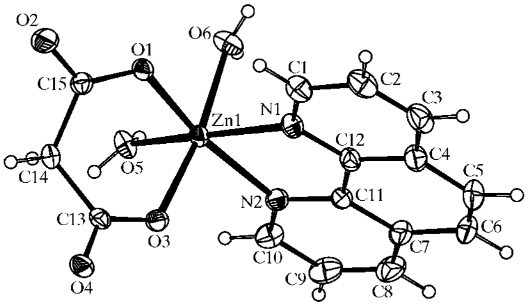


Figure 1
The molecular structure of (I), showing displacement ellipsoids at the 35% probability level.

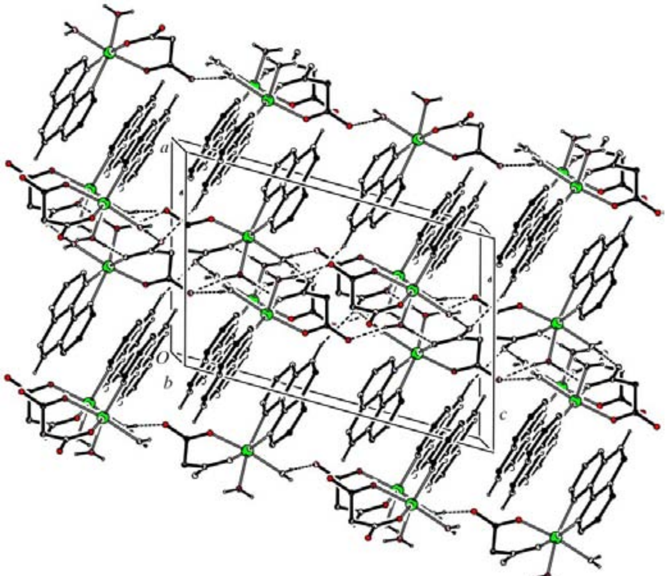


Figure 2
The molecular packing of (I), viewed along the *b* axis, showing π–π stacking and hydrogen-bond interactions. H atoms not involved in hydrogen bonding have been omitted.

DOI: 10.1107/S0108270105038047

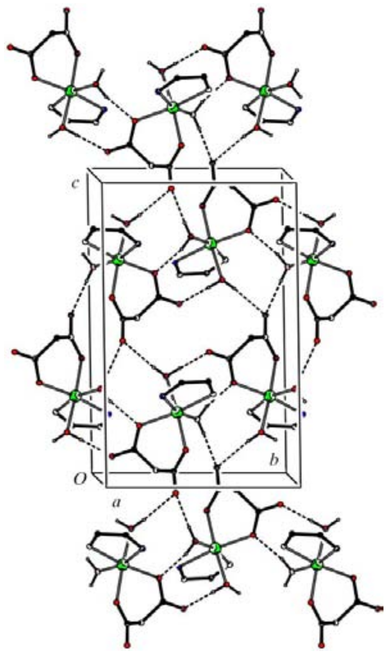


Figure 3
The hydrogen-bond interactions in a chain in (I), viewed along the *a* axis. Only the coordination five-numbered rings are shown for phen moieties.

mode is similar to those of [Mn(mal)(bipy)(H_2O)$_2$] (bipy is 2,2′-bipyridine; Sain *et al.*, 2003) and [Mn(mal)(phen)(H_2O)$_2$] (phen is 1,10-phenanthroline; Zhang *et al.*, 2004). The Zn^{II} atom exhibits distorted octahedral coordination, with the bond angles ranging from 166.21 (6) to 172.07 (6)° for *trans* angles and from 77.05 (6) to 99.19 (6)° for the other bond angles (Table 1). The Zn—O(carboxylate) bond distances are 2.0618 (13) and 2.0646 (15) Å. In [Zn_2(H_2O)$_2$(mal)$_2$($C_4H_4N_2$)] (Zhang *et al.*, 2003), the corresponding Zn—O(carboxylate) bond distances are 2.085 (2) and 2.082 (3) Å; the difference is probably due to the effect of the chelating coordination in (I). The Zn—O(water) distances of 2.1152 (17) and 2.1364 (16) Å are comparable to those found in {[Zn_2(mal)$_2$(pym)(H_2O)]·H_2O}$_n$ [2.175 (4) Å; Delgado *et al.*, 2003]. The Zn—N bond lengths are 2.1601 (17) and 2.1745 (17) Å, somewhat longer than in [Zn(male)(H_2O)(phen)]$_n$ [2.1295 (17) and 2.1741 (19) Å; male is maleate; Li *et al.*, 2005].

As shown in Fig. 2, the molecular packing of (I) exhibits a three-dimensional supramolecular structure in which both hydrogen-bonding and π–π stacking interactions play an important role. The complex molecules are linked to one another through hydrogen bonds between coordinated water molecules and the uncoordinated carboxylate O atoms of neighboring molecules to form layers in the (100) plane in the crystal structure (Table 2 and Fig. 3). Neighboring layers are linked to each other *via* π–π stacking interactions between the phen rings of adjacent molecules, characterized by interplanar distances in the range 3.446 (14)–3.542 (14) Å.

Experimental

ZnO (0.162 g, 2 mmol) was added slowly to an aqueous solution (15 ml) of malonic acid (0.104 g, 1 mmol). The reaction mixture was stirred for 1 h at 353 K, and then an ethanol solution (5 ml) of phen (0.198 g, 1 mmol) was added with continuous stirring. After 30 min, the reaction mixture was cooled to room temperature and filtered. Colorless single crystals were obtained from the filtrate after two weeks.

Crystal data

[Zn($C_3H_2O_4$)($C_{12}H_8N_2$)(H_2O)$_2$]
M_r = 383.65
Monoclinic, $P2_1/c$
a = 10.3369 (11) Å
b = 9.6662 (10) Å
c = 15.4737 (16) Å
β = 105.720 (2)°
V = 1488.3 (3) Å^3
Z = 4

D_x = 1.712 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3676 reflections
θ = 2.56–28.29°
μ = 1.69 mm^{-1}
T = 292 (2) K
Prism, colorless
0.27 × 0.20 × 0.18 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.659, T_{max} = 0.751
10345 measured reflections

3237 independent reflections
2572 reflections with $I > 2\sigma(I)$
R_{int} = 0.063
θ_{max} = 27.0°
$h = -13 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -16 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.071
S = 0.95
3237 reflections
229 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0343P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—O1	2.0618 (13)	Zn1—N2	2.1745 (17)
Zn1—O3	2.0646 (15)	O1—C15	1.276 (2)
Zn1—O6	2.1152 (17)	O2—C15	1.224 (2)
Zn1—O5	2.1364 (16)	O3—C13	1.262 (2)
Zn1—N1	2.1601 (17)	O4—C13	1.248 (3)
O1—Zn1—O3	88.45 (6)	O6—Zn1—N1	89.82 (7)
O1—Zn1—O6	85.67 (6)	O5—Zn1—N1	166.21 (6)
O3—Zn1—O6	172.07 (6)	O1—Zn1—N2	168.23 (6)
O1—Zn1—O5	99.19 (6)	O3—Zn1—N2	94.15 (6)
O3—Zn1—O5	93.61 (6)	O6—Zn1—N2	92.68 (7)
O6—Zn1—O5	82.10 (7)	O5—Zn1—N2	92.11 (6)
O1—Zn1—N1	91.27 (6)	N1—Zn1—N2	77.05 (6)
O3—Zn1—N1	95.64 (6)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5B···O1^i	0.85 (2)	1.94 (2)	2.772 (2)	168 (3)
O6—H6B···O4^{ii}	0.78 (2)	2.06 (2)	2.837 (2)	173 (3)
O5—H5C···O4^{iii}	0.78 (2)	2.02 (2)	2.792 (2)	169 (3)
O6—H6C···O2^i	0.81 (2)	1.81 (2)	2.617 (2)	179 (3)

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

The water H atoms were located in a difference Fourier map and their positional parameters were refined with O—H distances restrained to 0.78 (2)–0.85 (2) Å; the U_{iso}(H) values were fixed at 0.063 Å^2. The remaining H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H bond lengths of 0.93 or 0.97 Å [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C)].

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

The authors thank the Education Office of Anhui Province, People's Republic of China, for research grant No. 200161

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF1018). Services for accessing these data are described at the back of the journal.

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