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Bis(μ-cantharidinato)bis[(1,10-phenanthroline)-manganese(II)] hexahydrate

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Key indicators

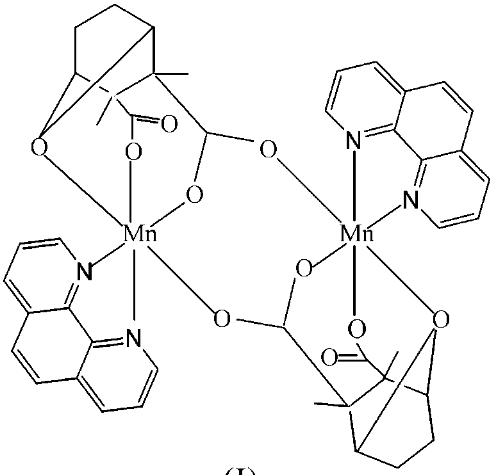
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.002 Å
R factor = 0.030
wR factor = 0.074
Data-to-parameter ratio = 16.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound {systematic name: bis(μ-2,3-dimethyl-7-oxobicyclo[2.2.1]heptane-2,3-dicarboxylato)bis[(1,10-phenanthroline)manganese(II)] hexahydrate}, $[Mn_2(C_{10}H_{12}O_5)_2(C_{12}H_8N_2)_2]\cdot6H_2O$, comprises centrosymmetric dinuclear neutral molecules in which two Mn^{II} centers are bridged by a single carboxylate group of each of two cantharidinate ligands, together with water molecules. In the complex, each Mn^{II} atom is in a distorted octahedral geometry, being coordinated by two N atoms of one 1,10-phenanthroline ligand, three O atoms from one cantharidinate dianion and one carboxylate O atom from another cantharidinate dianion. Adjacent molecules link to each other through hydrogen bonds involving solvent water molecules and carboxylate groups, forming a three-dimensional network.

Comment

Cantharidine has long been used as a Chinese medicine (Li, 1957). In the past few decades, several studies showed that cantharidine and its derivatives presented potential antitumor capability against lung, colon and breast cancer (Cui *et al.*, 1984; Li *et al.*, 1984; Shimi *et al.*, 1982). A few metal cantharidinate complexes have been synthesized. Some platinum cantharidine complexes have shown effective antitumor activity. To our knowledge, one platinum and one copper complex with cantharidinate have been structurally characterized (Wang *et al.*, 1997; Yin *et al.*, 2003). We report here the preparation and structure of a manganese(II) complex with cantharidinate and 1,10-phenanthroline.



(I)

The molecular structure of the title complex, (I), is shown in Fig. 1. This complex exists as discrete centrosymmetric

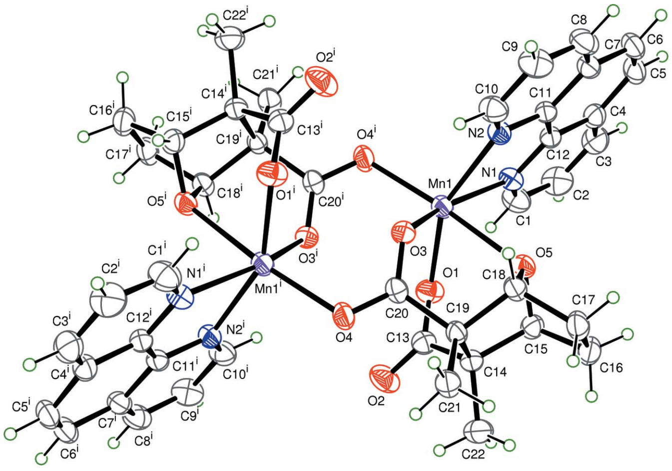


Figure 1

Molecular structure of (I), showing 50% probability displacement ellipsoids. Water molecules have been omitted. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

dinuclear molecules. A cantharidinate dianion chelates an Mn^{II} atom by two O atoms from one carboxylate group and one bridging oxo O atom. The Mn^{II} atom is also coordinated by two N atoms of one 1,10-phenanthroline ligand and one carboxylate O atom from another cantharidinate dianion. Each Mn site exhibits a distorted octahedral coordination, with *trans* bond angles ranging from 153.59 (4) to 168.22 (4)° and *cis* angles from 73.51 (4) to 105.02 (4)° (Table 1). The Mn—O(carboxylate) bond distances are comparable with those in $[Mn(phen)(cyclohexane\text{-}1,1\text{-}diacetato)(H_2O)_2]$ trihydrate (Shen *et al.*, 2005). The Mn—O(bridging oxo) bond distance of 2.4032 (11) Å is much longer than those of Mn—O(carboxylate). The Mn—N bond lengths are comparable to the corresponding ones found in $[Mn_2(mal)(phen)_3(H_2O)_2Cl]Cl$ (Sain *et al.*, 2003). Cantharidinate adopts a chair conformation in this complex. One of the carboxylate groups behaves as a monodentate ligand, and the other carboxylate acts in a common *syn–anti* bridging coordination mode (Policar *et al.*, 1999). The manganese–manganese separation is 4.441 (5) Å.

The hydrogen-bonding interactions (Table 2) play an important role in the solid-state structure of the title complex, (I). Adjacent molecules are linked to form a three-dimensional chain by hydrogen bonds between a coordinated O atom and water, and between water molecules.

Experimental

An aqueous solution (20 ml) of 2,3-dimethyl-7-oxobicyclo-[2,2,1]-heptane-2,3-dicarboxylic acid (0.214 g, 1 mmol) and $Mn_2(OH)_2CO_3$ (0.102 g, 0.5 mmol) was heated to reflux temperature on a water-bath for 8 h and was then filtered. To this hot filtrate, an aqueous solution (10 ml) containing 1,10-phenanthroline (0.180 g, 1 mmol) was added. The reaction mixture was stirred at reflux temperature for 12 h. Yellow crystals were collected after cooling the reaction mixture. Yellow single crystals of (I) were obtained by recrystallizing from water.

Crystal data

$[Mn_2(C_{10}H_{12}O_5)_2(C_{12}H_8N_2)_2]\cdot 6H_2O$
$M_r = 1002.79$
Monoclinic, $C2/c$
$a = 17.806\ (5)$ Å
$b = 20.600\ (5)$ Å
$c = 11.982\ (3)$ Å
$\beta = 90.812\ (11)°$
$V = 4395\ (2)$ Å^3
$Z = 4$
$D_x = 1.515$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.65$ mm^{-1}
$T = 298\ (1)$ K
Needle, yellow
0.30 × 0.15 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.830$, $T_{max} = 0.937$
21189 measured reflections
5033 independent reflections
3904 reflections with $F^2 > 2\sigma(F^2)$
$R_{int} = 0.029$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.074$
$S = 1.00$
5033 reflections
303 parameters
H-atom parameters constrained
$w = 1/[0.0003F_o^2 + \sigma(F_o^2)]/(4F_o^2)$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Mn1—O1	2.1206 (11)	Mn1—N2	2.2353 (11)
Mn1—O3	2.1276 (10)	O1—C13	1.2824 (18)
Mn1—O4^i	2.1222 (11)	O2—C13	1.2344 (18)
Mn1—O5	2.4032 (11)	O3—C20	1.2533 (16)
Mn1—N1	2.3042 (12)	O4—C20	1.2597 (16)
O1—Mn1—O3	95.40 (4)	O4^i—Mn1—N2	101.08 (4)
O1—Mn1—O4^i	104.27 (4)	O4^i—Mn1—O5	168.22 (4)
O1—Mn1—N1	92.69 (4)	O5—Mn1—O1	78.08 (4)
O1—Mn1—N2	153.59 (4)	O5—Mn1—O3	76.85 (4)
O3—Mn1—O4^i	91.41 (4)	O5—Mn1—N1	86.27 (4)
O3—Mn1—N1	159.30 (4)	O5—Mn1—N2	78.63 (4)
O3—Mn1—N2	91.27 (4)	N1—Mn1—N2	73.51 (4)
O4^i—Mn1—N1	105.02 (4)		

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

Table 2

Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O6—H601···O9^i	0.91	2.04	2.949 (2)	174
O7—H701···O9^i	0.90	1.91	2.809 (2)	176
O8—H801···O2	0.91	1.84	2.7466 (18)	176
O8—H802···O7^{ii}	0.92	1.95	2.836 (2)	161
O9—H901···O1	0.91	1.87	2.7710 (17)	178
O9—H902···O8	0.92	1.95	2.772 (2)	147

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

All the water H atoms were located in a difference Fourier map and the remaining H atoms were placed in calculated positions, with C—H = 0.93–0.98 Å and O—H = 0.90–0.92 Å. All H atoms were included in the final cycle of refinement in riding mode, with $U_{iso}(H) = 1.2U_{eq}(C,O)$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SIR97* (Altomare *et*

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al., 1999); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure* (Rigaku/MSC, 2004).

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