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(2,2′-Bipyridine-*N*,*N*′)(7-oxabicyclo[2.2.1]heptane-2-*exo*,3-*exo*-dicarboxylato-$\kappa^3O^{2,3,7}$)manganese(II)–7-oxabicyclo[2.2.1]heptane-2-*exo*,3-*exo*-dicarboxylic acid–water (1/1/1)

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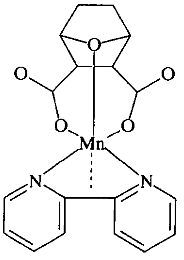
Abstract

In the title compound, $[Mn(C_8H_8O_5)(C_{10}H_8N_2)]\cdot C_8H_{10}O_5\cdot H_2O$, the Mn^{2+} ion is in an approximate six-coordinate octahedral environment composed of four O atoms, arising from tridentate chelation by one bicyclic ligand (L) and by one O atom of another L ligand, and two bipyridine N atoms. The complex entities are connected by carboxylate bridges into infinite zigzag chains. The uncoordinated molecules of the free acid (H_2L) are doubly hydrogen bonded into dimers, which are in turn linked to the complex chains through hydrogen bonds *via* the water molecules.

Comment

Under its trade name endothall, 7-oxabicyclo[2.2.1]heptane-2-*exo*,3-*exo*-dicarboxylic acid (H_2L) is used as a herbicide, but the compound is also known as a ligand for the formation of metal complexes with interesting properties. In most cases, the L^{2-} anion is a tridentate ligand chelating through the ether and two carboxylate O atoms, as exemplified in the ionic octahedral complex $[Cu(H_2O)_6][CuL_2]$ (Kennard & Smith, 1989). But L can also act as a bridging ligand and thus it shows a great variety in the complex structures it forms. So, for $[ZnL(H_2O)_2]$ (Wang *et al.*, 1984) and $[CaL(H_2O)_2]$ (Smith *et al.*, 1991), two different infinite chain structures, for the lanthanoid(III) complexes $[ML(HL(H_2O))]$ (M = La, Ce, Pr, Nd; Schüchner *et al.*, 1996), a polymeric layer structure, and for $K[NiL_2]\cdot 6H_2O$ (Wang *et al.*, 1988), a three-dimensional polymeric structure were found. Only two crystal structures built up from ternary metal complexes with L and *N*,*N*-donor ligands have been known until now. In $[CuL(bpy)]$ (bpy is bipyridine), L acts as a tridentate ligand and a square-pyramidal coordination is observed, but in the very similar complex $[CuL^1(en)]$ (L^1 is the 1-methyl homologue of L and en is ethylenediamine), the coordination number is increased to six by an O atom of a second $[CuL^1(en)]$ unit, resulting in a complex dimer with octahedrally coordinated Cu atoms (Kaplonek *et al.*, 1992).

The asymmetric unit of the title compound, (I), within the crystal lattice is shown in Fig. 1. It consists of a complex entity of chemical composition analogous to the above-mentioned copper complexes plus an H_2L and a water molecule. Each Mn^{2+} ion is coordinated by the ether and the carboxylate O atoms of the same ligand in facial mode and additionally by a fourth carboxylate O atom belonging to another ligand which is related to the first by the *c*-glide plane of the space group. The approximately octahedral coordination is completed by the two N atoms of the amine ligand. The rigidity of the 7-oxanorbornane skeleton is manifested by the good agreement of the geometric parameters in the two units L and H_2L in (I) with those in 7-oxabicyclo[2.2.1]heptane-2-*exo*,3-*exo*-dicarboxylic acid hydrate (Han *et al.*, 1983) and in the other complexes mentioned above. The *exo* positions of the carboxylate groups and their *cis* conformation are evident from the torsion angles given in Table 1. The bpy ligand is nearly exactly planar; the r.m.s. deviation of the fitted atoms from the least-squares plane is 0.011 Å and the interplanar angle between the two pyridine rings is only 1.09 (12)°. There is no significant difference between the two Mn—N bond lengths and no endocyclic torsion angle of the five-membered ring in which they are involved deviates significantly from 0°. The differences between the three Mn—O(carboxylate) distances are in a rather small range [mean value 2.116 (16) Å] and the Mn—O(ether) distance is unusually great compared with the corresponding values in other complexes with L as a ligand, except for the copper complexes, which are influenced by the Jahn–Teller effect (Kaplonek *et al.*, 1992). For example, in the chain structure of $[ZnL(H_2O)_2]$ (Wang *et al.*, 1984), which is similar to that of (I), the difference between the two kinds of metal–oxygen distances is only 0.109 Å.



$\cdot C_8H_{10}O_5\cdot H_2O$

(I)

The complex entities in (I) are linked together through carboxylate bridges (–Mn1—O3—C2—O4—Mn1′–) to form infinite zigzag chains running parallel to the *c* axis. The molecules of free dicarboxylic acid (H_2L) are doubly hydrogen bridged to dimers [O1*a*···O2*a*($1-x$, $1-y$, $-2-z$) 2.614 (3) Å]. The water molecules do

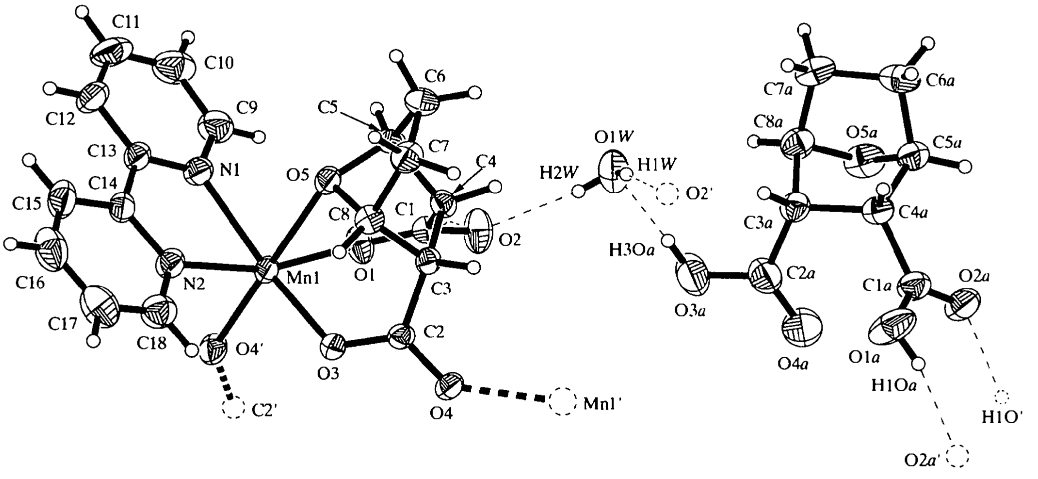


Fig. 1. The molecular structure and atomic numbering of the title compound (*XP*/*PC*; Siemens, 1990), with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii and hydrogen bonds are shown as thin dashed lines.

not belong to the coordination sphere of the Mn^{2+} ion, but they are of importance for the stability of the crystal lattice. Each of them is hydrogen bonded as an acceptor to an H_2L molecule and as a donor to two L ligands [O3*a*···O1*W* 2.583 (4), O1*W*···O2(x, $\frac{3}{2}-y$, $-\frac{1}{2}+z$) 2.718 (3) and O1*W*···O2 2.700 (3) Å]. In this way, a linkage between the chains of the complex entities and the H_2L dimers, as well as an additional connection between the chain links, is achieved. The crystal structure is illustrated in Fig. 2.

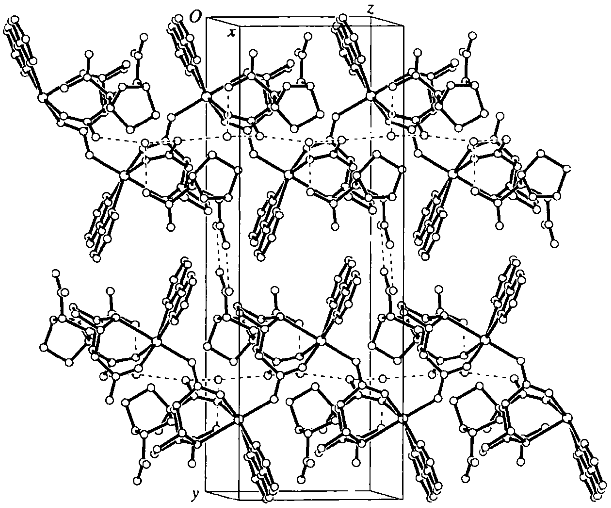


Fig. 2. The crystal packing of the title compound showing the hydrogen-bonding system as dashed lines. H atoms have been omitted for clarity.

Experimental

$Mn(NO_3)_2·4H_2O$ (5 mmol) and 2,2′-bipyridine (5 mmol) were dissolved at 333 K in an ethanol–water mixture (30 ml). A second solution, prepared by dissolution of 7-oxabicyclo[2.2.1]heptane-2-*exo*,3-*exo*-dicarboxylic acid (10 mmol) at 333 K in water (30 ml) and dropwise addition of 1 *M* NaOH (5 ml), was added slowly at 333 K under permanent stirring. The yellow mixture of the two solutions was reduced in a rotary evaporator to half of its volume and left to evaporate further in air. Yellow crystals of the title compound were obtained from a volume of 10 ml after 7 d, and were filtered off and dried in air.

Crystal data

[Mn($C_8H_8O_5$)($C_{10}H_8N_2$)]·$C_8H_{10}O_5$·H_2O
M_r = 599.44
Monoclinic
$P2_1/c$
a = 12.0311 (16) Å
b = 24.574 (3) Å
c = 8.9357 (11) Å
β = 99.245 (14)°
V = 2607.6 (6) $Å^3$
Z = 4
D_x = 1.527 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 76 reflections
θ = 8.5–17.9°
μ = 0.573 mm^{-1}
T = 293 (2) K
Prism
0.42 × 0.26 × 0.10 mm
Yellow

Data collection

Stoe Stadi-4 four-circle diffractometer
scan width (ω) = 1.02–1.23°, scan ratio $2\theta:\omega$ = 1.00, I(Net) and $\sigma(I)$ calculated according to Blessing (1987)
Absorption correction: none
15 166 measured reflections
7583 independent reflections

4904 reflections with $I > 2\sigma(I)$
R_{int} = 0.055
$\theta_{\max}$ = 29.96°
$h = -16 \rightarrow 16$
$k = -34 \rightarrow 34$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 60 min
intensity decay: 5.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.123

$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.398 e $Å^{-3}$
$\Delta\rho_{\min}$ = −0.326 e $Å^{-3}$

$S = 1.100$
7583 reflections
378 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.6916P]$ where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: *SHELXL*97
Extinction coefficient: 0.0021 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Mn1—O1	2.0980 (18)	O2—C1	1.249 (3)
Mn1—O4^{i}	2.1208 (17)	O3—C2	1.262 (3)
Mn1—O3	2.1297 (17)	O4—C2	1.262 (3)
Mn1—N1	2.236 (2)	O1*a*—C1*a*	1.306 (3)
Mn1—N2	2.245 (2)	O2*a*—C1*a*	1.224 (3)
Mn1—O5	2.4868 (16)	O3*a*—C2*a*	1.325 (4)
O1—C1	1.264 (3)	O4*a*—C2*a*	1.201 (4)
O1—Mn1—O4^{i}	101.10 (7)	O3—Mn1—N2	98.00 (7)
O1—Mn1—O3	88.36 (7)	N1—Mn1—N2	73.01 (8)
O4^{i}—Mn1—O3	96.25 (7)	O1—Mn1—O5	80.95 (6)
O1—Mn1—N1	97.09 (8)	O4^{i}—Mn1—O5	177.21 (7)
O4^{i}—Mn1—N1	97.96 (7)	O3—Mn1—O5	81.88 (6)
O3—Mn1—N1	163.49 (7)	N1—Mn1—O5	83.61 (7)
O1—Mn1—N2	164.12 (8)	N2—Mn1—O5	85.54 (7)
O4^{i}—Mn1—N2	92.69 (7)		
C2—C3—C4—C1	2.4 (3)	C2*a*—C3*a*—C4*a*—C1*a*	−14.9 (3)
C1—C4—C5—C6	−163.1 (2)	C1*a*—C4*a*—C5*a*—C6*a*	−154.1 (2)
C2—C3—C8—C7	163.7 (2)	C2*a*—C3*a*—C8*a*—C7*a*	170.4 (2)

Symmetry code: (i) $x, \frac{3}{2} - y, \frac{1}{2} + z$.

The quadrants $\pm h{+}k{+}l$ and $\pm h{-}k{-}l$ were measured. H-atom positions at C atoms were calculated geometrically and treated as riding, those at O atoms were located by a difference Fourier synthesis and refined with isotropic displacement parameters.

Data collection: *STADI*4 (Stoe & Cie, 1996*a*). Cell refinement: *STADI*4. Data reduction: *X-RED* (Stoe & Cie, 1996*b*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP*/*PC* (Siemens, 1990). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1307). Services for accessing these data are described at the back of the journal.

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Cadmium isopropylxanthate

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Abstract

The crystal structure of bis(*O*-isopropyl dithiocarbonato-*S*)cadmium(II), $[Cd(C_4H_7OS_2)_2]$, has been determined by X-ray crystallography. The crystals are orthorhombic (space group *Aba*2). The coordination about cadmium is distorted tetrahedral.

Comment

In our laboratories, we have been investigating the optical properties of novel metal–organic complexes. Some of the synthesized material was separated into powders of sizes in the range 12–350 µm and subjected to the Kurtz powder test (Kurtz & Perry, 1968; Kurtz & Dougherty, 1978). The powders were irradiated with an Nd:YAG laser operating at 1.064 µm and the intensity of the second harmonic (0.532 µm) was measured as a function of powder size. The results indicated that the title compound will phase match for 1.06 µm frequency doubling. Also, large single crystals can be grown from these materials, making them possible candidates for non-linear optical materials. Second-order non-linear optical materials have numerous applications as second-

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