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Bis(μ-pyridine-2,6-carboxylato-*O*,*N*,*O*′:*O*)bis[triaquamanganese(II)]–pyridine-2,6-dicarboxylic acid (1/2)

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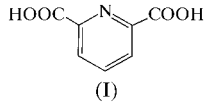
In the structure of the title compound, $[Mn_2(C_7H_3NO_4)_2(H_2O)_6]\cdot 2C_7H_5NO_4$, a centrosymmetric dinuclear complex, hexaaaquabis(pyridine-2,6-dicarboxylato)dimanganese(II) and free pyridine-2,6-dicarboxylic acid are present in a 1:2 ratio. In the complex, each Mn^{2+} ion is coordinated by three O atoms and one N atom from the pyridine-2,6-dicarboxylate ligands and by three water O atoms, resulting in a distorted pentagonal bipyramidal coordination. Within the centrosymmetric dinuclear complex, two Mn^{2+} ions are bridged by two carboxylate O atoms. The crystal structure is stabilized by hydrogen bonds involving all the H atoms of the water ligands.

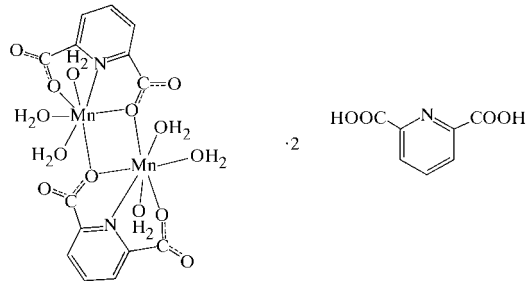
Comment

Pyridine-2,6-dicarboxylic acid (dipicolinic acid), (I), is present in large amounts in bacterial spores (Powell, 1953; Church & Halvorson, 1959). It is the main component of bacterial spores, in which it forms a metal complex with divalent metal ions, especially with the calcium ion. The Mn^{2+} ion appeared to substitute for the Ca^{2+} ion to some degree in conferring heat resistance (Chung *et al.*, 1971). It also has biological activity, such as inhibition of the zinc enzyme, bovine carbonic anhydrase (Pocker & Fong, 1980) or *E. coli* dihydrodipicolinate reductase (Scapin *et al.*, 1997), or selective activation of the metalloenzyme calmodulin-activated protein phosphatase calcineurin (Martin, 1997). The selective activation of calcineurin by pyridine-2,6-dicarboxylic acid is reduced by the Mn^{2+} ion, which may be explained by the formation of a manganese–pyridine-2,6-dicarboxylic acid complex (Martin, 1997). We have analyzed the title complex, (II), in order to confirm the coordination mode of a manganese–pyridine-2,6-dicarboxylic acid complex.

Crystals of (II) were obtained as a 1:2 mixture of the dinuclear metal complex and free pyridine-2,6-dicarboxylic acid (see Fig. 1 and Table 1). The dinuclear complex sits on a crystallographic inversion center. Each Mn^{2+} ion is coordinated by two O atoms and one N atom from one pyridine-2,6-dicarboxylic acid ligand, by one carboxylate O atom of the second pyridine-2,6-dicarboxylic acid ligand and by three water O atoms. In each dinuclear complex, the carboxylate group and the N atom form a five-membered chelate ring with the Mn^{2+} ion (N1/C1/C6/O2/Mn1 and N1/C5/C7/O4/Mn1), and



(I)



(II)

the two Mn^{2+} ions are bridged by two bifurcated coordination bonds of two carboxylate O atoms [O2 and O2^{i}; symmetry code: (i) $-x, -y, 1-z$]. Each Mn^{2+} ion has seven coordinate bonds forming a distorted pentagonal bipyramid, in which the N1, O2, O2^{i}, O9 and O4 atoms form the distorted pentagonal plane. The pentagonal bipyramidal coordination of the d^3sp^3 hybrid orbital of the Mn^{2+} ion seems to be rare; it usually forms an octahedral d^2sp^3 hybrid orbital consisting of six coordination bonds. The planar conformation of the free pyridine-2,6-dicarboxylic acid molecules cocrystallized with the chelate complex in (II) resembles the crystal structure of pyridine-2,6-dicarboxylic acid itself (Takusagawa *et al.*, 1973).

Up until now, many crystal structures of chelate compounds of pyridine-2,6-dicarboxylic acid with various metal ions have been determined: Ca^{2+} (Strahs & Dickerson, 1968), Ag^{2+} (Drew *et al.*, 1970), Ti^{2+} (Schwarzenbach, 1970), Sr^{2+} (Palmer *et al.*, 1972), Ni^{2+} (Quaglieri *et al.*, 1972), Fe^{2+} (Lainé, Gourdon & Launay, 1995; Lainé, Gourdon, Launay & Tuchagues, 1995), and Cu^{2+} and Zn^{2+} (Okabe & Oya, 2000). In most of these crystal structures, the pyridine-2,6-dicarboxylic acid ligand is

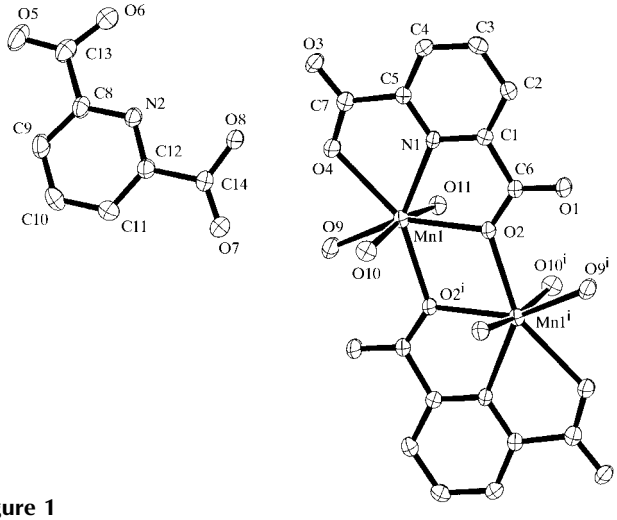


Figure 1
*ORTEP*II (Johnson, 1976) drawing of (I) with the atomic numbering scheme. Another free ligand molecule located centrosymmetrically has been omitted. Ellipsoids for non-H atoms correspond to 50% probability.

coordinated to a mononuclear metal ion and acts as a terdentate ligand, in which the central metal ion is bonded to two N and four O atoms of two ligand molecules. But the Ti^{5+} (Schwarzenbach, 1970), Fe^{2+} (Lainé, Gourdon, Launay & Tuchagues, 1995) and Ca^{2+} complexes (Strahs & Dickerson, 1968) are dinuclear, and the Sr^{2+} complex is polynuclear. Among these, the structure of the Fe^{2+} complex is isomorphous with the Mn^{2+} complex. Not only do these structures have the same geometry, but they also have the same space group and similar cell constants. Each metal has three bonds to one ligand molecule, one to the second ligand molecule and three to water molecules. Substitution of the Mn^{2+} ion for Ca^{2+} in bacterial spores in conferring heat resistance (Chung *et al.*, 1971) may be caused by the similarities of the coordination polyhedron of the dinuclear octacoordinated Ca^{2+} and the dinuclear heptacoordinated Mn^{2+} complexes.

In the crystal structure of (II), the complex molecules and free ligand molecules are connected by hydrogen bonds involving all the H atoms of the water ligands (Table 2). There are π-stacking interactions between the pyridine rings both in the metal complexes and in the free ligand along the *a* axis.

Experimental

The colorless pillar-shaped crystal used for analysis was obtained by slow evaporation from a 50% ethanol–water solution of pyridine-2,6-dicarboxylic acid and manganese chloride tetrahydrate in a 10:1 molar ratio at room temperature.

Crystal data

$[Mn_2(C_7H_3NO_4)_2(H_2O)_6]\cdot 2C_7H_5NO_4$
$M_r = 882.42$
Monoclinic, $P2_1/c$
$a = 9.166\ (3)$ Å
$b = 14.603\ (3)$ Å
$c = 12.192\ (3)$ Å
$\beta = 97.43\ (2)^\circ$
$V = 1618.2\ (7)$ Å^3
$Z = 2$
$D_x = 1.811$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 14.6$–15.0°
$\mu = 0.887$ mm^{-1}
$T = 296$ K
Pillar, colorless
0.60 × 0.30 × 0.10 mm

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.816$, $T_{max} = 0.915$
4093 measured reflections
3711 independent reflections
2524 reflections with $F^2 > 2\sigma(F^2)$
$R_{int} = 0.023$
$\theta_{max} = 27.5^\circ$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 18$
$l = -15 \rightarrow 15$
3 standard reflections
every 150 reflections
intensity decay: 0.4%

Refinement

Refinement on F^2
$R(F) = 0.037$
$wR(F^2) = 0.122$
$S = 1.101$
3711 reflections
253 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + \{0.06000 \times [\max(F_o^2) + 2F_c^2]/3\}^2]$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.67$ e Å^{-3}

The H atoms were located from difference Fourier maps.

Data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1992); program(s) used to solve structure: *SAPI*91 (Fan, 1991) and *DIRDIF* (Beurskens *et al.*, 1992); program(s) used to refine structure: *TEXSAN LS*; molecular graphics: *ORTEP*II (Johnson, 1976).

Table 1
Selected geometric parameters (Å, °).

Mn1—O2	2.312 (2)	Mn1—O10	2.192 (2)
Mn1—O2^{i}	2.313 (2)	Mn1—O11	2.305 (2)
Mn1—O4	2.467 (2)	Mn1—N1	2.283 (2)
Mn1—O9	2.176 (2)		
O2—Mn1—O2^{i}	69.39 (7)	O4—Mn1—O11	99.85 (7)
O2—Mn1—O4	136.61 (6)	O4—Mn1—N1	66.67 (7)
O2—Mn1—O9	151.61 (7)	O9—Mn1—O10	90.41 (8)
O2—Mn1—O10	91.87 (7)	O9—Mn1—O11	83.76 (8)
O2—Mn1—O11	88.06 (7)	O9—Mn1—N1	137.26 (7)
O2—Mn1—N1	70.29 (7)	O10—Mn1—O11	167.40 (7)
O4—Mn1—O9	71.71 (7)	O10—Mn1—N1	97.91 (7)
O4—Mn1—O10	88.83 (7)	O11—Mn1—N1	93.93 (7)

Symmetry code: (i) $-x, -y, 1-z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O6—H7···O11^{i}	0.90	2.00	2.841 (2)	156
O8—H8···O4	0.98	1.57	2.507 (3)	158
O9—H10···O1^{ii}	0.91	1.75	2.608 (2)	158
O9—H9···O7	0.83	2.00	2.821 (3)	169
O10—H11···O3^{iii}	0.87	1.87	2.724 (2)	167
O10—H12···O5^{iv}	0.94	1.83	2.756 (3)	170
O11—H13···O8^{v}	0.86	2.43	2.842 (3)	110
O11—H14···O3^{v}	0.86	2.09	2.934 (3)	168

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1553). Services for accessing these data are described at the back of the journal.

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