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The first manganese(II) compound with the saccharinate ligand present both in the complex cation and as the counter-ion: $[Mn(bipy)_2(sac)(H_2O)]^+\cdot sac^-$

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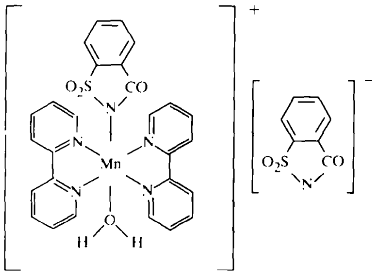
Abstract

The structure of the title compound, aqua[1,2-benzisothiazol-3(2*H*)-onato 1,1-dioxide-*N*]bis(2,2′-bipyridine-*N*,*N*′)manganese(II) 1,2-benzisothiazol-3(2*H*)-onate 1,1-dioxide, $[Mn(C_7H_4NSO_3)(C_{10}H_8N_2)_2(H_2O)](C_7H_4NSO_3)$, consists of $[Mn(bipy)_2(sac)(H_2O)]^+$ cations (bipy = 2,2′-bipyridine; sac = saccharinate, $C_7H_4NO_3S$) and non-coordinated saccharinate (sac^-) anions. The Mn^{II} ion constitutes the centre of a slightly distorted octahedron, with the water molecule hydrogen bonded to the N atom in the saccharinate counter-ion.

Comment

1,2-Benzisothiazol-3(2*H*)-one 1,1-dioxide, commonly known as saccharin, is widely used as a sweetening agent (Haider *et al.*, 1985). Research on the crystal structures of metal saccharinate (sac) complexes has been very extensive in the last 15 years, partly due to their potential effectiveness in biological systems (Haider *et al.*, 1983; Li *et al.*, 1991; Zhang, 1994). The synthesis and crystal structures of the metal complexes $[M(sac)_2(H_2O)_4]\cdot 2H_2O$, with *M* = Fe, Co, Ni (Haider *et al.*, 1983), Cu (Haider *et al.*, 1983; Ahmed *et al.*, 1981), Mn (Kamenar & Jovanovski, 1982), Zn, Cd (Haider *et al.*, 1984), Cr (Cotton *et al.*, 1984) or V (Cotton *et al.*, 1986), have all been reported. More recently, several structures have been described for various related species also containing bidentate pyridine ligands, such as 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen). These include examples where all the saccharinate ligands are attached to the metal $\{[Hg(bipy)(sac)_2]$; Hergold-Brundić *et al.*, 1989$\}$, where they are present simply as the counter-ion $\{[CuL(bipy)]sac\cdot 2H_2O$ (*L* = 2-formylpyridine thiosemicarbazonate) (Ainscough *et al.*, 1990), $[Mn(H_2O)_2phen_2]sac_2\cdot H_2O$ (Li, Chen *et al.*, 1993) and $[Fe(phen)_3]sac_2\cdot 4H_2O$ (Li, Wei *et al.*, 1993)$\}$ or, for some Cu complexes only, where they occur in both the cation and anion $\{[Cu(bipy)_2(sac)]sac\cdot 3H_2O$ (Li *et al.*, 1991), $[Cu(bipy)_2(sac)]sac\cdot 2H_2O$ (Hergold-Brundić *et al.*, 1991) and $[Cu(phen)_2(sac)]sac\cdot 2H_2O$ (Zhang *et al.*, 1994)$\}$. These last three complexes all exhibit distorted five-coordinate trigonal-bipyramidal structures for the cations. The title compound, (I), is the first manganese(II) compound with the saccharinate ligand present both in the complex cation and as the counter-ion.



(I)

The structure of the complex consists of cation chains composed of $[Mn(bipy)_2(sac)(H_2O)]^+$ units, and non-coordinated saccharinate anions. One of the independent structural units is shown in Fig. 1, together with the atom-numbering scheme. In the cation, the Mn—N_{bipy} average bond length is 2.259 (9) Å, with one of the bipy ligands (coordinating through N2 and N3) exhibiting rather more asymmetry in these bonds than the other. The Mn—N_{sac} bond length of 2.228 (4) Å compares with 2.281 (1) Å in $[Mn(sac)_2(H_2O)_4]\cdot 2H_2O$ (Kamenar & Jovanovski, 1982). Bond angles about Mn clearly show some distortion from idealized octahedral geometry [N5—Mn—O7 163.11 (14), N1—Mn—N3 168.06 (14) and N2—Mn—N4 168.69 (14)°], probably as a consequence of the steric restrictions imposed by the bipy chelate rings. The water molecule which completes the coordination about Mn appears to participate in hydrogen bonding to the N atom of the corresponding saccharinate anion (Fig. 1), with an N···H distance of 1.77 (5) Å. Even so, the Mn—O length of 2.127 (3) Å is significantly shorter than

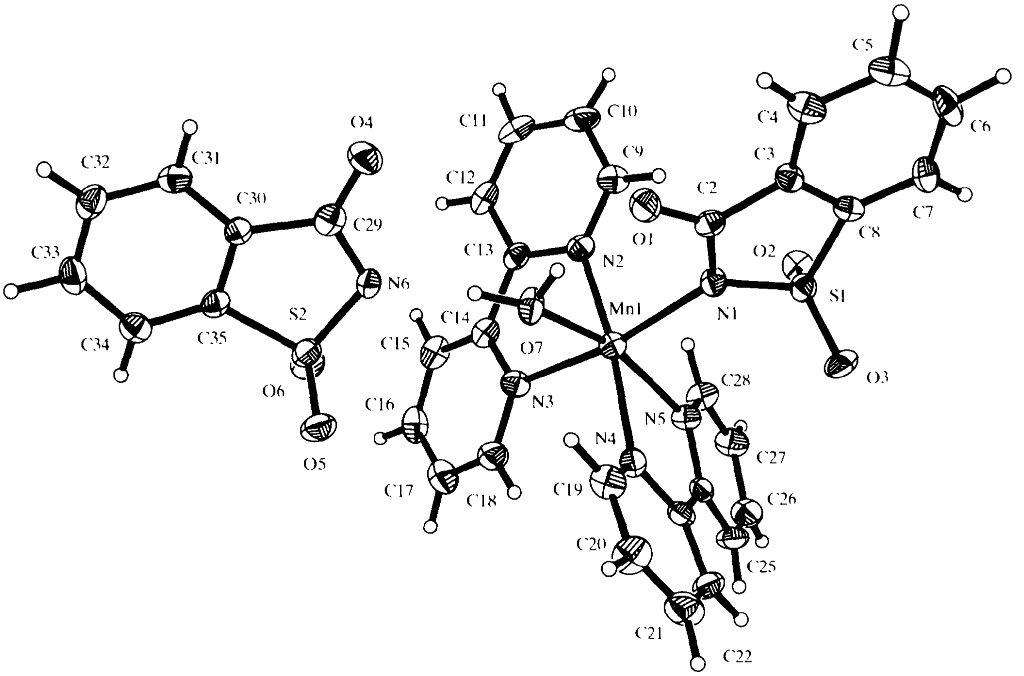


Fig. 1. The molecular structure of the title complex, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

the independent Mn—O bond lengths [2.162 (1) and 2.219 (2) Å] in $[Mn(sac)_2(H_2O)_4]\cdot 2H_2O$, where the water molecules are hydrogen bonded to saccharinate O atoms (Kamenar & Jovanovski, 1982). In contrast, the three Cu complexes containing saccharinate, both coordinated to the metal and as a counter-ion, are all known to possess five-coordinate cations, with no water present (Li *et al.*, 1991; Hergold-Brundić *et al.*, 1991; Zhang *et al.*, 1994). The free saccharinate anion in the title compound has very similar derived molecular parameters to those found in $K_2Na(sac)_3\cdot H_2O$ (Malik *et al.*, 1984).

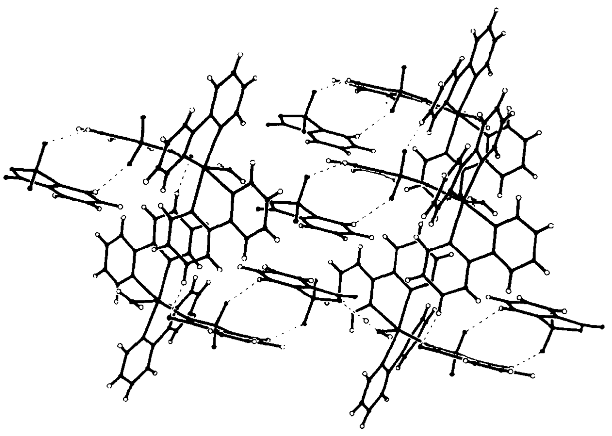


Fig. 2. Packing diagram of (I), illustrating the close intermolecular contacts (indicated by dotted lines).

The three-dimensional arrangement within the crystal structure is shown in Fig. 2, and involves stacking of alternate metal-bonded and free saccharinate groups in a staggered conformation. This structure includes reasonably close intermolecular contacts, as shown by dotted lines, between C=O (bound ligand) and a phenyl H atom from bipy at 2.47 (5) Å, between S=O (bound ligand) and H—C (free ligand) at 2.55 (4) Å, between S=O (free ligand) and H—C (bound ligand) at 2.51 (5) Å, and between S=O and a phenyl H from bipy at 2.59 (5) Å. While these distances are too long to represent strong hydrogen bonds, they play a role in determining the overall geometry and packing adopted by this interesting complex.

Experimental

A warm solution of 2,2′-bipyridine (0.448 g, 2.88 mmol) in water (50 ml) was added with stirring to a warm clear solution of $[Mn(sac)_2(H_2O)_4]\cdot 2H_2O$ (0.757 g, 1.44 mmol) in water (25 ml). A clear yellow solution formed. This was stirred for a time and left to stand for 3 d to give fine yellow shiny crystals (yield 0.660 g; 60.1%). The weakly diffracting nature of the crystals is reflected in the high value of $R_{\rm int}$.

Crystal data

$[Mn(C_7H_4NSO_3)(C_{10}H_8N_2)_2(H_2O)](C_7H_4NSO_3)$
$M_r = 749.67$
Monoclinic
$P2_1/n$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 300 reflections
$\theta = 3.24$–$17.31°$

$a = 7.7544 (2)$ Å
$b = 31.6493 (10)$ Å
$c = 13.2174 (4)$ Å
$\beta = 93.004 (1)°$
$V = 3239.4 (2)$ Å^3
$Z = 4$
$D_x = 1.537$ Mg m^{-3}
D_m not measured

$\mu = 0.597$ mm^{-1}
$T = 150$ K
Block
$0.3 \times 0.2 \times 0.1$ mm
Yellow

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.768$, $T_{\max} = 0.942$
16 761 measured reflections

4669 independent reflections
2852 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.103$
$\theta_{\max} = 25°$
$h = -8 \rightarrow 8$
$k = -35 \rightarrow 32$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.105$
$S = 1.064$
4665 reflections
529 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0366P)^2 + 0.5595P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.360$ e Å^{-3}
$\Delta\rho_{\min} = -0.368$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Mn1—O7	2.127 (3)	Mn1—N2	2.273 (4)
Mn1—N1	2.228 (4)	N1—C2	1.363 (5)
Mn1—N5	2.249 (4)	N1—S1	1.644 (4)
Mn1—N3	2.253 (4)	S2—N6	1.624 (4)
Mn1—N4	2.259 (4)	N6—C29	1.368 (6)
O7—Mn1—N1	90.74 (13)	N3—Mn1—N4	96.67 (14)
O7—Mn1—N5	163.11 (14)	O7—Mn1—N2	92.92 (13)
N1—Mn1—N5	95.52 (13)	N1—Mn1—N2	95.49 (14)
O7—Mn1—N3	90.92 (14)	N5—Mn1—N2	102.04 (14)
N1—Mn1—N3	168.06 (14)	N3—Mn1—N2	72.61 (14)
N5—Mn1—N3	86.20 (14)	N4—Mn1—N2	168.69 (14)
O7—Mn1—N4	90.80 (14)	C2—N1—S1	111.3 (3)
N1—Mn1—N4	95.13 (13)	C29—N6—S2	111.7 (3)
N5—Mn1—N4	73.06 (14)		

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1991). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1256). Services for accessing these data are described at the back of the journal.

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Bis(1,3-propanediamine-*N*,*N'*)bis(thiocyanato-*N*)nickel(II)

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Abstract

The title compound, $[Ni(NCS)_2\{H_2N(CH_2)_3NH_2\}_2]$, (I), is an octahedral complex of nickel(II) in which the thiocyanate ligands are bonded through nitrogen in a *cis* arrangement, while the 1,3-propanediamine lig-