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MANGANESE(II) SACCHARINATE HEXAHYDRATE, $Mn(C_7H_4NO_3S)_2 \cdot 6H_2O$, AND ISOMORPHISM WITH THE ANALOGOUS Fe, Co, Ni, Zn and Cd COMPLEXES

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Preliminary information. Font-Altaba (1956) was first who published his attempt to solve the structure of Mn saccharinate. Since his result was unsatisfactory and incomplete we decided to solve the structure of this complex in the course of our investigation of metal saccharinates (Jovanovski & Kamenar, 1981a). We found that the title compound is not tetrahydrate as firstly described by Defournel (1901) and accepted by Font-Altaba but hexahydrate. Its actual chemical formula is $Mn(H_2O)_4(C_7H_4NO_3S)_2 \cdot 2H_2O$.

Crystal data. From single crystal diffractometry, Mo$K\alpha$, λ = 0.7107 Å: a = 7.955(2), b = 16.131(6), c = 7.784(1) Å, β = 99.70(3)°, V = 984.6 Å^3, Z = 2, D_{obs} = 1.73, D_{calc} = 1.780 g cm^{-3}, $F(000)$ = 542, μ(Mo$K\alpha$) = 9.82 cm^{-1}, space group $P2_1/c$.

Intensity data, structure determination and refinement. The intensities of 2197 independent reflections from a prismatic specimen (0.17 x 0.18 x 0.25 mm^3) were collected up to 2θ = 60° on a four circle diffractometer Philips PW 1100 (graphite monochromatized Mo$K\alpha$ radiation, θ - 2θ scan technique, scan width 1.50°, scan speed 0.05° s^{-1}). The 2107 reflections with

$I>3\sigma(I)$ were used in the structure analysis. Neither absorption nor extinction corrections were applied. The structure was solved by means of three-dimensional Fourier synthesis based upon the manganese atom coordinates. The hydrogen atoms were located in a difference Fourier map. The structure was refined by full matrix least-squares method with anisotropic thermal parameters for all atoms except hydrogens for which isotropic parameter B = 2.5 was assigned. The final R factor was 0.028. The anomalous dispersions for manganese and sulphur atoms were included in the F_c calculations (International Tables for X-ray Crystallography, 1974).

Table 1. Atomic coordinates ($x10^4$, for H $x10^3$) with their e.s.d.'s

	x/a	*y/b*	*z/c*		*x/a*	*y/b*	*z/c*
Mn	0	0	0	Ow(3)	-20(2)	1127(1)	4941(2)
N	1891(2)	931(1)	1438(2)	Ow(2)	-1757(2)	386(1)	1784(2)
S	3522(1)	599(0)	2830(1)	Ow(1)	-942(2)	1006(1)	-1733(2)
C(1)	4389(2)	1573(1)	3445(2)	H(2)	658	132	511
C(2)	5886(2)	1756(1)	4570(3)	H(3)	727	272	559
C(3)	6272(3)	2595(1)	4812(3)	H(4)	542	380	408
C(4)	5196(3)	3200(1)	3982(3)	H(5)	294	340	232
C(5)	3702(3)	2998(1)	2861(3)	H(11)	-71	99	-277
C(6)	3305(2)	2164(1)	2587(3)	H(12)	-49	148	-118
C(7)	1842(2)	1774(1)	1406(3)	H(21)	-276	32	173
O(3)	715(2)	2177(1)	479(2)	H(22)	-135	66	281
O(2)	4653(2)	119(1)	1965(2)	H(31)	23	165	501
O(1)	2923(2)	201(1)	4276(2)	H(32)	92	90	490

Comments.Tables 1 and 2 give atomic coordinates and interatomic distances and angles. The manganese atom, positioned on a symmetry centre, is octahedrally coordinated by four oxygen atoms from water molecules and two nitrogen atoms from saccharinate ions (see Figure). The Mn-O bond lengths are 2.162 (2x) and 2.219 Å (2x), while the Mn-N bond length is 2.281 Å (2x). Within the coordination octahedron the angles range from 86.6 to 93.4°. Four water molecules coordinated to manganese atom as well as two non-coordinated water molecules participate in hydrogen bonding with saccharinate oxygen atoms. Bond lengths and angles within planar saccharinate ligands are very close

to the values found in sodium and magnesium saccharinate (Jovanovski & Kamenar, 1982b).

The title compound is isomorphous with the analogous iron, cobalt, nickel, zinc and cadmium saccharinates. Table 3 gives their unit cell parameters.

Table 2. Interatomic distances and angles with their e.s.d.'s

Distances (Å)

Mn-N	2.281(1)	C(3)-C(4)	1.385(3)
Mn-Ow(1)	2.162(1)	C(4)-C(5)	1.390(3)
Mn-Ow(2)	2.219(2)	C(5)-C(6)	1.390(3)
S-N	1.634(2)	C(2)-H(2)	0.94
S-C(1)	1.749(2)	C(3)-H(3)	0.93
S-O(1)	1.445(2)	C(4)-H(4)	0.98
S-O(2)	1.437(2)	C(5)-H(5)	0.94
N-C(7)	1.360(2)	Ow(1)-H(11)	0.86
C(7)-O(3)	1.237(2)	Ow(1)-H(12)	0.92
C(6)-C(7)	1.495(2)	Ow(2)-H(21)	0.80
C(1)-C(6)	1.381(2)	Ow(2)-H(22)	0.93
C(1)-C(2)	1.386(2)	Ow(3)-H(31)	0.86
C(2)-C(3)	1.393(3)	Ow(3)-H(32)	0.84

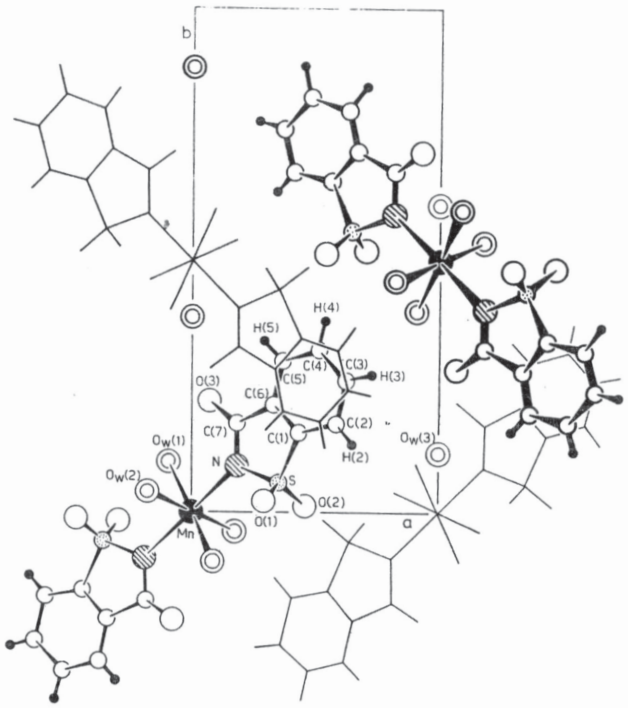
Hydrogen bonds

Ow(1)...Ow(3)^{iii}	2.814(2)	Ow(2)...O(2)^{ii}	2.915(1)
Ow(1)...O(3)	2.740(2)	Ow(3)...O(1)$_{iv}$	2.896(2)
Ow(2)...Ow(3)	2.869(2)	Ow(3)...O(3)^{iv}	2.814(1)

Angles (°)

Ow(1)-Mn-Ow(2)	89.5(1)	C(1)-C(6)-C(5)	119.1(2)
Ow(1)-Mn-N	86.7(1)	C(5)-C(6)-C(7)	129.5(2)
Ow(2)-Mn-N	86.6(1)	S-C(1)-C(6)	107.6(1)
Mn-N-S	119.6(1)	S-C(1)-C(2)	128.4(1)
Mn-N-C(7)	129.4(1)	C(2)-C(1)-C(6)	124.0(2)
		C(1)-C(2)-C(3)	116.0(2)
S-N-C(7)	110.9(1)	C(2)-C(3)-C(4)	121.1(2)
C(1)-S-N	96.9(1)	C(3)-C(4)-C(5)	121.6(2)
O(1)-S-O(2)	116.1(1)	C(4)-C(5)-C(6)	118.2(2)
O(1)-S-C(1)	110.6(1)	C(1)-C(2)-H(2)	120
O(1)-S-N	109.5(1)	C(3)-C(2)-H(2)	124
O(2)-S-N	110.8(1)	C(2)-C(3)-H(3)	117
O(2)-S-C(1)	111.3(1)	C(4)-C(3)-H(3)	122
N-C(7)-C(6)	113.2(1)	C(3)-C(4)-H(4)	125
N-C(7)-O(3)	123.5(2)	C(5)-C(4)-H(4)	114
O(3)-C(7)-C(6)	123.3(2)	C(4)-C(5)-H(5)	123
C(1)-C(6)-C(7)	111.4(2)	C(6)-C(5)-H(5)	119

(ii=x-1,y,z; iii=x,y,z-1; iv=x,1/2-y,1/2+z)



Figure

Table 3. The unit cell parameters of isomorphous Mn(II), Fe(II), Co(II), Ni(II), Zn(II), Cd(II) saccharinates hexahydrates

Metal	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
Mn	7.955(2)	16.131(6)	7.784(1)	99.70(3)	984.6
Fe	7.922(4)	16.129(5)	7.737(3)	99.77(9)	974.2
Co	7.901(4)	16.134(7)	7.688(7)	99.52(3)	966.5
Ni	7.921(2)	16.135(5)	7.655(3)	100.00(2)	963.5
Zn	7.954(4)	16.157(7)	7.709(5)	99.91(2)	975.9
Cd	8.031(2)	16.133(18)	7.870(6)	100.26(3)	1003.4

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