Inorganica Chimica Acta, 92 (1984) 107–111

Molecular and Crystal Structure of Hexaaquamanganese(II) Bis{bis(N-salicylideneglycinato)manganate(III)} Dihydrate, $[Mn^{II}(H_2O)_6][Mn^{III}(Sal = Gly)_2]_2 \cdot 2H_2O$

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Received November 25, 1983

The crystal structure of hexaaquamanganese(II) bis{bis(N-salicylideneglycinato)manganate(III)} dihydrate has been determined by X-ray analysis. The complex crystallizes in the monoclinic space group I2/a, with unit-cell dimensions $a = 37.431(5)$, $b = 12.100(1)$, $c = 9.448(1)$ Å, $\beta = 92.31(1)°$. The structure was deduced by the direct method and refined by the block-diagonal least-squares technique to a final R value of 0.062 for 3904 observed reflections. The Mn(II) is octahedrally ligated by six water molecules, while Mn(III) is octahedrally chelated by two salicylideneglycinate ligands, of which one is nearly planar and the other considerably bent.

It was discovered that the crystal is, as a whole, of a 'sandwich' structure made of one central sheet containing hexaaquamanganese(II)'s and the water molecules of crystallization, and two outside sheets containing bis(N-salicylideneglycinato)manganate(III)'s.

Introduction

Trivalent manganese has received increasing attention because of its probable participation in a part of photosystem II to evolve oxygen [1] and in catalytic processes of purple phosphatase [2] and manganese-containing superoxide dismutase [3]. In addition, manganese within cells of *Lactobacillus plantarum* and related lactic acid bacteria [4] appears to have the same function as superoxide dismutase.

On the other hand, the coordinated phenolate imparts unique properties to iron containing enzymes such as transferrin [5], uteroferrin [6], beef spleen purple phosphatase [7], catechol dioxygenase [8], catalase and manganese-containing phosphatase [2]. In the present study, the manganese(III) complex hexaaquamanganese(II) bis{bis(N-salicylideneglycinato)manganate(III)} dihydrate, in which phenolates of N-salicylideneglycinates were, coordinated to manganese(III), was isolated and subjected to X-ray crystal analysis.

Experimental

Preparation

To the Schiff base derived from 1.22 g (0.01 mol) of salicylaldehyde and 0.75 g (0.01 mol) of glycine in aqueous ethanol was added 1.97 g (0.01 mol) of manganese(II) chloride tetrahydrate. Immediately after adjusting the pH of the solution to *ca.* 7 with sodium hydroxide, yellow prismatic crystals composed of manganese(II) and N-salicylideneglycinate in a 1:1 ratio separated out from a yellow solution. On allowing the filtrate to stand for several days, dark brown needles separated out from the solution which had turned brown as the result of oxidation with air. These dark brown needles were used in the X-ray crystal analysis. *Anal.* Found: C, 42.56; H, 4.36; N, 5.48%. Calcd for $M_{1.5}C_{18}H_{14}N_2O_64H_2O$: C, 42.49; H, 4.75; N, 5.51%.

Physical Measurements

The magnetic moment of the complex in DMSO-d_6 was determined by observing the paramagnetic shift of the methyl signal of t-butyl alcohol by manganese ions using a double coaxial cell on a Varian EM-360 NMR spectrometer. The determined magnetic moment of 5.4 B.M. per one manganese ion seems to agree with the expected value of 5.2 B.M. for one-third of Mn(II) and two-thirds of Mn(III).

Data Collection

Data were collected using a dark brown crystal with dimensions of 0.2 × 0.2 × 0.4 mm. Accurate unit cell constants were determined by least-squares refinement of the θ values of 50 reflections measured by the $\theta - 2\theta$ scan technique on a Rigaku four-circle diffractometer with graphite-monochromated MoKα radiation. The scan speed and scan width in ω were 4° $\min^{-1}$ and $(1.2 + 0.35 \tan\theta)°$, respectively. Of 4288 independent reflections collected up to $2\theta = 60°$, 3904 reflections with $|F_o| \geqslant 2\sigma(|F_o|)$ were used in the subsequent calculation. Corrections were made for Lorentz and polarization effects, but not for absorption.

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0020-1693/84/$3.00

Crystal data: Formula $[Mn(H_2O)_6][Mn(C_9H_7NO_3)_2]_2 \cdot 2H_2O$, asymmetric unit $[Mn(H_2O)_6]_{0.5}[Mn(C_9H_7NO_3)_2] \cdot H_2O$, monoclinic, space group I2/a, $a = 37.431(5)$, $b = 12.100(1)$, $c = 9.448(1)$ Å, $\beta = 92.31(1)°$, $V = 4275.7$ Å^3, $D_m = 1.58$, $D_x = 1.58$ g cm^{-3}, $Z = 8$ asymmetric units, $\mu = 10.1$ cm^{-1} (MoKα).

Structure Determination

The systematic absences, hkl, h + k + l = 2n + 1, h0l, h = 2n + 1 and l = 2n + 1, 0k0, k = 2n + 1 indicated the space group I2/a or Ia. The former was confirmed by a statistical distribution of E values and a successful refinement of the structure. Using 400 reflections with $|E| \geqslant 1.659$, the crystal structure was determined by the direct method with the program MULTAN 78 [10]. The E-maps and the subsequent successive weighed Fourier synthesis revealed the positions of all non-hydrogen atoms. Several cycles of block-diagonal least-squares refinement with isotropic temperature factors brought the R value to 0.113. After several further cycles of block-diagonal least-squares refinement with anisotropic temperature factors were carried out, R dropped to 0.076. At this stage, all hydrogen atoms were located from a difference synthesis. After several cycles of block-diagonal least-squares including the hydrogen atoms with fixed isotropic temperature factors (3.3 Å^2), the R value was reduced to 0.062. The function minimized was $\Sigma w(F_o - |F_c|)^2$ with w = 1.0. All the atomic scattering factors were taken from 'International Tables for X-Ray Crystallography' [11]. The computations were carried out on an ACOS-S700 computer at the Crystallographic Research Center, Institute for Protein Research Laboratory, Osaka University, with 'The Universal Crystallographic Computing System—Osaka' [12]..

Table I lists the final atomic and thermal parameters with their estimated standard deviations. The F_o and F_c tables, anisotropic temperature factors, and H-atom positional parameters have been deposited with the Editor. Bond distances and angles are shown in Table II.

TABLE I. Atomic Positional and Thermal Parameters.

Atom	*x*	*y*	*z*	B_{eq}
MN(1)	0.75000(0)	0.02367(8)	0.50000(0)	2.25
MN(2)	0.86946(2)	−0.02469(5)	0.90138(7)	2.13
O(1)	0.84077(9)	0.0429(3)	1.0856(3)	3.2
O(2)	0.89070(10)	−0.0344(3)	0.7056(4)	3.3
O(3)	0.82312(9)	−0.0657(3)	0.8198(3)	3.1
O(4)	0.91431(9)	−0.0030(3)	0.9893(4)	3.3
O(5)	0.79725(10)	0.1603(3)	1.1285(4)	3.6
O(6)	0.77620(10)	−0.1744(3)	0.8378(4)	4.4
O(7)	0.75000(0)	−0.1567(4)	0.5000(0)	4.0
O(8)	0.75000(0)	0.1983(4)	0.5000(0)	3.8
O(9)	0.76210(11)	0.0068(3)	0.2802(4)	4.4
O(10)	0.69258(9)	0.0332(3)	0.4448(3)	3.4
N(1)	0.85948(10)	0.1386(3)	0.8497(4)	2.3
N(2)	0.86518(10)	−0.1718(3)	0.9910(4)	2.7
C(1)	0.82193(12)	0.1268(4)	1.0572(5)	2.5
C(2)	0.83102(13)	0.1929(4)	0.9261(5)	2.8
C(3)	0.87721(12)	0.1976(4)	0.7647(5)	2.5
C(4)	0.90332(12)	0.1572(4)	0.6689(4)	2.3
C(5)	0.92195(14)	0.2374(4)	0.5934(5)	3.1
C(6)	0.94551(16)	0.2069(5)	0.4938(6)	4.0
C(7)	0.95096(15)	0.0958(6)	0.4673(6)	4.1
C(8)	0.93258(14)	0.0146(5)	0.5370(5)	3.6
C(9)	0.90828(12)	0.0427(4)	0.6410(5)	2.7
C(10)	0.80735(13)	−0.1508(4)	0.8685(5)	3.0
C(11)	0.83000(16)	−0.2229(4)	0.9667(7)	4.6
C(12)	0.88757(14)	−0.2184(4)	1.0777(5)	3.1
C(13)	0.92163(13)	−0.1730(4)	1.1202(5)	2.9
C(14)	0.94395(16)	−0.2363(5)	1.2131(7)	4.2
C(15)	0.97675(17)	−0.1980(6)	1.2576(7)	4.9
C(16)	0.98857(14)	−0.0980(5)	1.2084(7)	4.2
C(17)	0.96746(12)	−0.0332(4)	1.1200(5)	3.3
C(18)	0.93336(12)	−0.0690(4)	1.0722(5)	2.5
W	0.85581(11)	−0.0248(4)	0.3557(4)	5.4

TABLE II(a). The Bond Lengths (Å) with Their Estimated Standard Deviations in Parentheses.

I. $Mn^{II}(OH_2)_6$ cation			
MN(1)–O(7)	2.183(5)	O(7)–WH(7)	0.77(7)
MN(1)–O(8)	2.113(5)	O(8)–WH(8)	0.79(6)
MN(1)–O(9)	2.153(4)	O(9)–WH(9A)	0.87(6)
MN(1)–O(10)	2.194(4)	O(9)–WH(9B)	0.85(6)
		O(10)–WH(0A)	0.84(7)
		O(10)–WH(0B)	0.88(7)
II. Mn^{III}(Sal = Gly)$_2$ anion			
MN(2)–O(1)	2.236(4)	Mn(2)–O(3)	1.934(4)
MN(2)–O(2)	2.046(4)	MN(2)–O(4)	1.861(4)
MN(2)–N(1)	2.065(4)	MN(2)–N(2)	1.981(4)
O(1)–C(1)	1.259(6)	O(3)–C(10)	1.281(6)
C(1)–C(2)	1.524(7)	C(10)–C(11)	1.509(9)
C(2)–N(1)	1.466(6)	C(11)–N(2)	1.465(8)
C(1)–O(5)	1.233(6)	C(10)–O(6)	1.224(7)
O(2)–C(9)	1.307(6)	O(4)–C(18)	1.310(6)
N(1)–C(3)	1.280(6)	N(2)–C(12)	1.279(7)
C(3)–C(4)	1.444(7)	C(12)–C(13)	1.431(7)
C(4)–C(5)	1.406(7)	C(13)–C(14)	1.413(8)
C(5)–C(6)	1.365(8)	C(14)–C(15)	1.362(9)
C(6)–C(7)	1.384(9)	C(15)–C(16)	1.372(9)
C(7)–C(8)	1.382(9)	C(16)–C(17)	1.372(9)
C(8)–C(9)	1.408(8)	C(17)–C(18)	1.406(7)
C(9)–C(4)	1.424(7)	C(18)–C(13)	1.413(7)
C(2)–H(2A)	1.01(6)	C(11)–H(11A)	1.02(6)
C(2)–H(2B)	0.99(7)	C(11)–H(11B)	0.81(7)
C(3)–H(3)	0.95(7)	C(12)–H(12)	1.03(6)
C(5)–H(5)	1.04(7)	C(14)–H(14)	0.93(6)
C(6)–H(6)	0.97(7)	C(15)–H(15)	0.94(7)
C(7)–H(7)	0.94(7)	C(16)–H(16)	0.97(7)
C(8)–H(8)	1.04(7)	C(17)–H(17)	0.95(7)

(continued on facing page)

TABLE II *(continued)*

III. Water of crystallization			
W–WH(A)	0.80(7)	W–WH(B)	0.93(7)

TABLE II(b). The Bond Angles (°) with Their Estimated Standard Deviations in Parentheses.

I. $Mn^{II}(OH_2)_6$ cation			
O(7)–MN(1)–O(8)	180.0(2)	O(7)–MN(1)–O(9)	84.6(2)
O(7)–MN(1)–O(10)	93.0(2)	O(8)–MN(1)–O(9)	95.4(2)
O(8)–MN(1)–O(10)	87.0(2)	O(9)–MN(1)–O(10)	91.0(1)
O(9)–MN(1)–O(9)*	169.1(2)	O(9)–MN(1)–O(10)*	89.5(1)
O(10)–MN(1)–O(10)*	174.0(1)		
*The symmetry code is 3/2 – x, y, 1 – z			
II. Mn^{III} (Sal = Gly)$_2$ anion			
O(1)–MN(2)–O(2)	160.2(1)	O(1)–MN(2)–O(3)	87.3(1)
O(1)–MN(2)–O(4)	93.1(1)	O(1)–MN(2)–N(1)	75.3(1)
O(1)–MN(2)–N(2)	86.9(1)	O(2)–MN(2)–O(3)	90.0(1)
O(2)–MN(2)–O(4)	92.0(1)	O(2)–MN(2)–N(1)	85.1(1)
O(2)–MN(2)–N(2)	112.1(1)	O(3)–MN(2)–O(4)	172.8(1)
O(3)–MN(2)–N(1)	90.0(1)	O(3)–MN(2)–N(2)	81.5(1)
O(4)–MN(2)–N(1)	97.0(1)	O(4)–MN(2)–N(2)	91.3(2)
N(1)–MN(2)–N(2)	160.7(2)		
MN(2)–O(1)–C(1)	114.3(3)	MN(2)–O(3)–C(10)	118.8(3)
O(1)–C(1)–C(2)	117.0(4)	O(3)–C(10)–C(11)	115.4(5)
C(1)–C(2)–N(1)	110.8(4)	C(10)–C(11)–N(2)	109.3(5)
C(2)–N(1)–MN(2)	116.1(3)	C(11)–N(2)–MN(2)	113.6(4)
O(1)–C(1)–O(5)	125.0(4)	O(3)–C(10)–O(6)	123.4(5)
C(2)–C(1)–O(5)	117.9(4)	C(11)–C(10)–O(6)	121.1(5)
MN(2)–N(1)–C(3)	126.0(3)	MN(2)–N(2)–C(12)	127.4(4)
N(1)–C(3)–C(4)	125.8(4)	N(2)–C(12)–C(13)	124.3(5)
C(3)–C(4)–C(9)	122.8(4)	C(12)–C(13)–C(18)	122.5(4)
C(4)–C(9)–O(2)	122.4(4)	C(13)–C(18)–O(4)	124.5(4)
C(9)–O(2)–MN(2)	127.0(3)	C(18)–O(4)–MN(2)	129.8(3)
C(9)–C(4)–C(5)	120.4(4)	C(18)–C(13)–C(14)	119.9(5)
C(4)–C(5)–C(6)	120.7(5)	C(13)–C(14)–C(15)	120.7(6)
C(5)–C(6)–C(7)	119.4(6)	C(14)–C(15)–C(16)	119.5(6)
C(6)–C(7)–C(8)	121.6(6)	C(15)–C(16)–C(17)	121.5(6)
C(7)–C(8)–C(9)	120.6(5)	C(16)–C(17)–C(18)	120.8(5)
C(8)–C(9)–C(4)	117.2(4)	C(17)–C(18)–C(13)	117.5(4)

Results and Discussion

The title compound forms an ionic crystal composed of one cation of $[Mn^{II}(H_2O)_6]$ and two anions of $[Mn^{III}$ (Sal = Gly)$_2]$. The geometry and atom numbering are illustrated in Fig. 1 [13]. Hereafter, the two crystallographically independent ligands of the $[Mn^{III}$ (Sal = Gly)$_2]$ anion will be designated as Sal = Gly(1) and Sal = Gly(2) as shown in Fig. 1.

Geometry of the [Mn^{III} (Sal = Gly)$_2$] anion

The manganese(III) or MN(2) ion is in a distorted octahedral configuration coordinated by the two nitrogen and four oxygen atoms of (Sal = Gly)$_2$ ligand. The corresponding bond lengths and angles in the two Sal = Gly ligands show similar values except for the MN–O, MN–N bond lengths and N–MN–O angles. The bond lengths of MN(2)–O(1) (2.236 Å), MN(2)–O(2) (2.046 Å) and MN(2)–N(1) (2.065 Å) in the Sal = Gly(1) ligand are significantly longer than the corresponding ones of MN(2)–O(3) (1.934 Å), MN(2)–O(4) (1.861 Å) and MN(2)–N(2) (1.981 Å) in the Sal = Gly(2) ligand. The bond angles of N(1)–MN(2)–O(2) (85.1°) and N(1)–MN(2)–O(1) (75.3°) in the Sal = Gly(1) ligand are significantly smaller than the corresponding ones of N(2)–MN(2)–O(4) (91.3°) and N(2)–MN(2)–O(3) (81.5°) in the Sal = Gly(2) ligand. The bond distances in the Sal = Gly(1) and Sal = Gly(2) ligands are comparable to the corresponding ones in Sal = Gly ligands of N-salicylideneglycinato-aquacopper(II) hemihydrate (SGCH) [14] and tetrahydrate (SGCT) [15], diaqua(N-salicylidene-L-threoninate)copper(II) (DSTC) [16], (N^{α}-salicylidene-D-ornithinato) (N^{α}-salicylidene-L-ornithinato)dipalladium(II) dimethyl sulfoxide (SODDS) [17], and hexaaquacobalt(II) bis(N-salicylideneglycinato)cobaltate(III) dihydrate (HSCD) [18].

The three best planes are shown in Table III as the plane A through the 5-membered chelating ring, B through the 6-membered chelating ring and C through the benzene ring. Table IV shows the dihedral angles between these planes and the corresponding dihedral angles of Cu, Pd and Co derivatives cited above. It is found from this table that the Sal = Gly(1) ligand is considerably bent as well as the ligand(1) in the Co derivative: the dihedral angles between the planes of A and B, between the planes of B and C, and between the planes of A and C are 18.6°, 10.3° and 27.9°, respectively. On the other hand, the Sal = Gly(2) ligand is nearly planar: the corresponding dihedral angles are 3.1°, 1.5° and 1.9°, respectively.

Geometry of the [$Mn^{II}(H_2O)_6$]$^{2+}$ Ion

The coordination around the manganese(II) or MN(1) ion is distorted octahedral. The MN(1), O(7) and O(8) atoms lie on the two-fold axis. The MN(1)–O bond lengths range from 2.113 Å to 2.195 Å.

Crystal Structure

The crystal structure of the present Mn compound projected along the *c* axis is shown in Fig. 2. Inspection of Fig. 2 reveals that the structural unit is built up from one sheet containing the $[Mn^{II}(H_2O)_6]^{2+}$ ions and the water molecules of crystallization as a central part, and two sheets of the $[Mn^{III}$ (Sal = Gly)$_2]^-$ ions as the outside parts, and these sheets are hydrogen bonded to each other to form a 'sandwich' structure. Every sandwich unit is only weakly bound by van der Waals' forces.

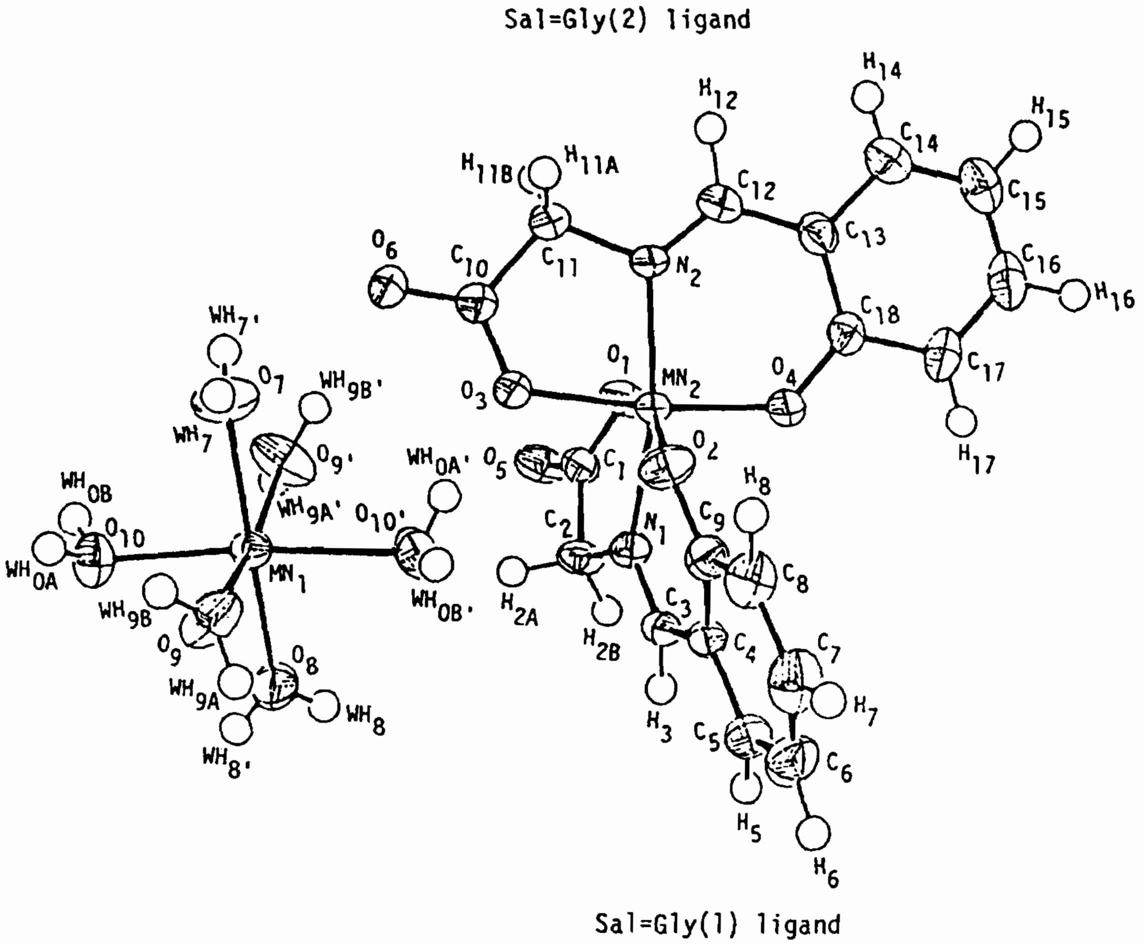

Fig. 1. ORTEP view of the Mn compound, showing the numbering of the atoms. The non-hydrogen atoms were drawn at the 50% probability level and the hydrogen atoms were drawn with an arbitrary diameter.

TABLE III. Equations of Least-squares Planes and Displacements (Å) of the Atoms from the Planes.

i) Sal = Gly(1) ligand

Plane A:
MN(2), O(1), C(1), C(2), N(1)
$-0.7784x - 0.3970y - 0.4862z + 29.2057 = 0$

MN(2)	0.119	C(2)	0.088
O(1)	−0.160	N(1)	−0.152
C(1)	0.107		

Plane B:
MN(2), N(1), C(3), C(4), C(9), O(2)
$-0.7937x - 0.0948y - 0.6008z + 30.4327 = 0$

MN(2)	−0.210	C(4)	−0.177
N(1)	0.176	C(9)	−0.043
C(3)	0.038	O(2)	0.221

Plane C:
C(4), C(5), C(6), C(7), C(8), C(9)
$-0.7102x + 0.0276y - 0.7034z + 28.2165 = 0$

C(4)	−0.007	C(7)	−0.010
C(5)	0.005	C(8)	0.008
C(6)	0.003	C(9)	0.000

TABLE III *(continued)*

ii) Sal = Gly(2) ligand

Plane A:
MN(2), O(3), C(10), C(11), N(2)
$-0.4242x + 0.4745y + 0.7713z + 7.2827 = 0$

MN(2)	0.045	C(11)	0.019
O(3)	−0.062	N(2)	−0.064
C(10)	0.062		

Plane B:
MN(2), N(2), C(12), C(13), C(18), O(4)
$-0.4517x + 0.4295y + 0.7820z + 8.0198 = 0$

MN(2)	−0.000	C(13)	−0.000
N(2)	−0.015	C(18)	−0.021
C(12)	0.018	O(4)	0.018

Plane C:
C(13), C(14), C(15), C(16), C(17), C(18)
$-0.4315x + 0.4453y + 0.7846z + 7.3306 = 0$

C(13)	−0.005	C(16)	−0.014
C(14)	−0.003	C(17)	0.006
C(15)	0.009	C(18)	0.002

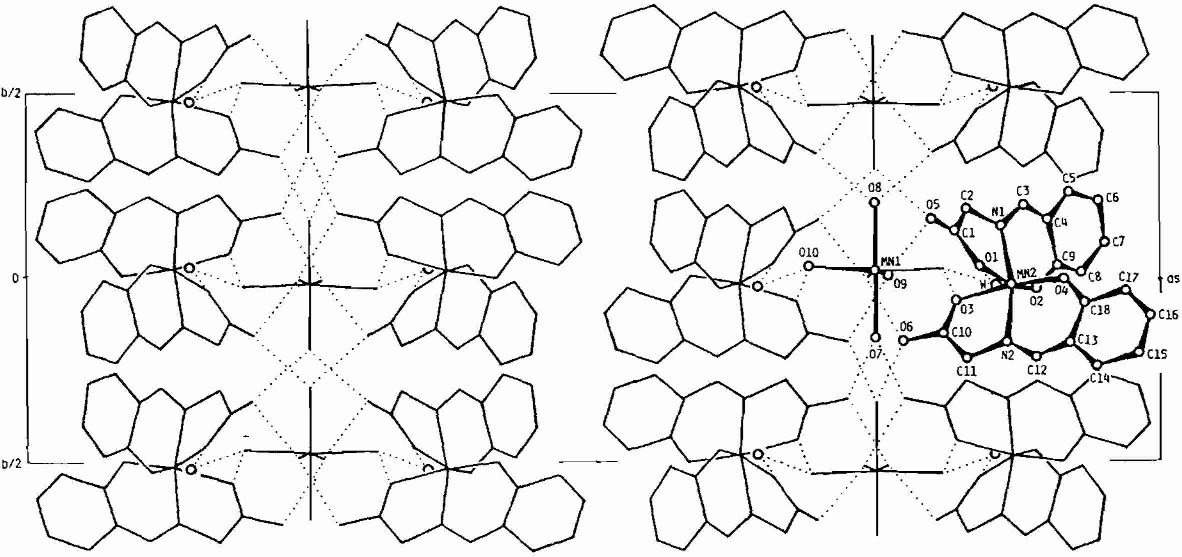

Fig. 2. Crystal structure of the Mn compound projected along the *c* axis. Dotted lines denote the hydrogen bonding.

TABLE IV. Dihedral Angles (°) between the Least-squares Planes.

	A and B	B and C	A and C	Reference
Sal = Gly(1)	18.6	10.3	27.9	Present work
Sal = Gly(2)	3.1	1.5	1.9	
SGCH	15.2	2.2	15.1	14
SGCT	8.7	1.7	10.2	15
DSTC	12.1	5.5	7.3	16
	12.7	5.6	7.4	
SODDS	7.4	5.2	12.3	17
HSCD	14.0	11.4	23.7	18
	8.7	3.7	12.2	

TABLE V. Hydrogen-bond Distances (Å).

$O(7)\cdots O(6)^{i}$	2.758(7)	$O(8)\cdots O(5)^{ii,iii}$	2.713(6)
$O(9)\cdots O(5)^{iv}$	2.718(6)	$O(9)\cdots O(6)^{v}$	2.824(6)
$O(10)\cdots O(3)^{v}$	2.813(5)	$O(10)\cdots W^{v}$	2.757(7)
$W\cdots O(1)^{iv}$	2.718(7)		

The symmetry code is the following:

i	x, −1/2 − y, −1/2 + z
ii	x, 1/2 − y, −1/2 + z
iii	x, 1/2 − y, 1/2 + z
iv	x, y, −1 + z
v	3/2 − x, y, 1 − z.

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