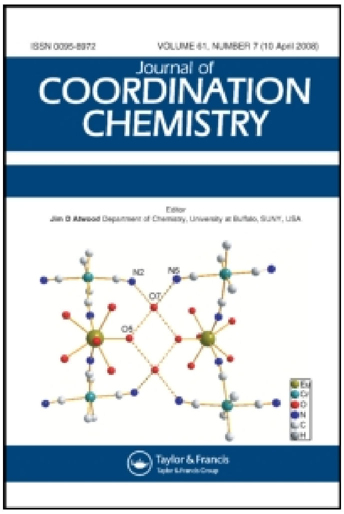

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A NEW POLYMERIC Mn(III) COMPLEX WITH A SCHIFF BASE: (μ-ACETATO)BIS(SALICYLIDENE)-PROPYLDIAMINOMANGANESE(III) DI(DICHLOROMETHANE)

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A NEW POLYMERIC Mn(III) COMPLEX WITH A SCHIFF BASE: (μ-ACETATO)BIS(SALICYLIDENE)-PROPYLDIAMINOMANGANESE(III) DI(DICHLOROMETHANE)

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As a mimic of the oxygen evolution complex in photosystem II, the title manganese(III) complex was synthesized. X-ray structure analysis shows that acetate anions bridge adjacent Mn(III) atoms to form a polymeric chain in the crystal. An anion of the Schiff base, *N,N′*-bis(salicylidene)-1,3-propyldiamine, coordinates to a Mn(III) atom with an umbrella configuration; the coordination geometry around the Mn(III) atom is flexible.

Keywords: Manganese; Schiff base; crystal structure; photosystem II

INTRODUCTION

Recently, intense efforts are concentrated on elucidating the nature of the biological unit responsible for water oxidation/oxygen evolution in the photosynthetic apparatus of green plants and cyanobacteria. The process of water splitting is generally believed to occur at a manganese cluster located in the reaction centre of photosystem II[1] and to accompany changes of oxidation states of manganese atoms.[2,3] It is considered that water coordination to Mn(III) is an important step for oxygen evolution in the photosynthetic process. In order to investigate the possibility of water coordination for

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mimics of oxygen evolution complex, a series of manganese complexes with different ligands has been synthesized in our laboratory. We present here the crystal structure of the title complex, which shows a flexible coordination geometry around the Mn(III) atom in the solid state.

EXPERIMENTAL

Preparation

Some 0.61 g (5.0 mmol) of salicylaldehyde and 0.185 g (2.5 mmol) of 1,3-propanediamine were dissolved in 25 cm^3 of methanol and the mixture refluxed for 1 h. Then, 0.2 g (5 mmol) of NaOH was added to the resulting yellow liquid with stirring, followed by 0.61 g (2.5 mmol) of $Mn(Ac)_2 \cdot 4H_2O$. After stirring for 1 h at 80°C in air, the solution changed colour to brown. The solution was filtered and left to stand for 1 month, when a black solid was obtained. The solid product was recrystallized from 40 cm^3 of 1 : 1 dichloromethane and heptane. The dark-green filtrate was set aside in the dark for two weeks to give well-formed, black, single crystals.

C, H and N were analysed using a Carlo-Erba 1160 instrument. *Anal.* Calc. for $C_{21}H_{23}N_2O_4Cl_4Mn$(%): C, 44.71, H, 4.11, N, 4.97; Found: C, 46.33, H, 4.22, N, 5.21. The significant difference for the C content might be due to partial loss of crystal CH_2Cl_2.

Infrared Measurements

Infrared spectra were recorded with a Shimadzu IR-470 spectrophotometer (4000–400 cm^{-1}) using a powdered sample spread on a KBr plate.

Crystal Structure Determination

A crystal was sealed in a Lindermann glass capillary. X-ray diffraction intensity data were collected on a Nonius CAD4 diffractometer to 2θ value of 50.4° with graphite-monochromatized MoKα radiation ($\lambda = 0.71073$ Å) by the ω–2θ scan technique. A total of 4537 independent reflections was collected, of which 2646 reflections were considered as observed [$I > 2\sigma(I)$] and used for the structure determination. Usual Lp and empirical absorption corrections were applied.

The structure was solved by the Patterson method followed by Fourier syntheses. Structure refinement was carried out by full-matrix least-squares procedures using the TEXSAN program package.[4] H atoms were located in a difference Fourier map. Anisotropic refinement including all the non-H atoms converged to agreement factors and $R = 0.059$ and $R_w = 0.062$, where $w = 1/\sigma^2(F)$. Atomic scattering factors were taken from International Tables for X-ray Crystallography.[5] All calculations were performed on a Micro VAX 3100 computer.

RESULTS AND DISCUSSION

Crystal Structure

Crystal data: $C_{21}H_{23}N_2O_4Cl_4Mn$, $M = 564.18$, monoclinic, space group $P2_1/c$, $a = 19.511(2)$, $b = 10.299(1)$, $c = 12.676(2)$ Å, $\beta = 100.85(1)°$, $V = 2501.7(9)$ Å^3, $Z = 4$, $D_c = 1.50\,\mathrm{g\,cm^{-3}}$, $\mu(\mathrm{MoK}\alpha) = 9.66\,\mathrm{cm^{-1}}$.

TABLE I Fractional atomic coordinates and equivalent isotropic thermal parameters for non-H atoms

Atom	*x/a*	*y/b*	*z/c*	B_{eq} (Å^2)
Mn	0.24572(5)	0.2138(1)	0.48654(6)	2.60(2)
Cl(1)	0.0502(1)	0.3614(3)	0.2116(2)	7.62(7)
Cl(2)	0.0975(2)	0.6109(3)	0.3012(2)	7.86(7)
Cl(3)	0.3058(2)	0.6493(4)	0.3131(3)	10.8(1)
Cl(4)	0.4070(2)	0.5837(4)	0.5003(4)	13.2(1)
O(1)	0.2386(2)	0.3963(4)	0.4981(3)	3.4(1)
O(2)	0.3426(2)	0.2337(5)	0.5047(3)	3.4(1)
O(3)	0.2262(2)	0.2309(5)	0.3129(3)	3.8(1)
O(4)	0.2446(2)	0.3085(5)	0.1591(3)	3.3(1)
N(1)	0.1396(3)	0.2021(6)	0.4670(4)	3.1(1)
N(2)	0.2585(3)	0.0182(5)	0.4791(4)	3.3(1)
C(1)	0.1932(4)	0.4613(6)	0.5428(5)	3.1(1)
C(2)	0.2110(4)	0.5873(7)	0.5826(5)	3.9(2)
C(3)	0.1638(4)	0.6590(7)	0.6269(6)	4.5(2)
C(4)	0.0986(4)	0.6101(8)	0.6338(6)	4.5(2)
C(5)	0.0809(4)	0.4883(8)	0.5958(5)	3.8(2)
C(6)	0.1272(3)	0.4113(7)	0.5500(5)	3.0(1)
C(7)	0.1026(3)	0.2896(8)	0.5020(5)	3.4(1)
C(8)	0.1101(4)	0.0924(8)	0.4084(6)	4.4(2)
C(9)	0.1318(4)	−0.0381(8)	0.4451(6)	4.4(2)
C(10)	0.2023(4)	−0.0641(7)	0.4186(6)	4.3(2)
C(11)	0.3153(4)	−0.0380(7)	0.5227(5)	3.9(2)
C(12)	0.3784(4)	0.0231(8)	0.5726(5)	4.0(2)
C(13)	0.4331(5)	−0.0548(9)	0.6292(7)	6.1(2)
C(14)	0.4967(5)	−0.003(1)	0.6703(8)	7.5(3)
C(15)	0.5085(5)	0.127(1)	0.6546(8)	7.1(3)
C(16)	0.4568(4)	0.206(1)	0.5997(6)	5.3(2)
C(17)	0.3906(3)	0.1558(8)	0.5578(5)	3.7(2)
C(18)	0.2624(3)	0.2346(7)	0.2404(4)	3.2(1)
C(19)	0.3264(4)	0.1522(9)	0.2495(5)	4.7(2)
C(20)	0.1245(4)	0.4594(9)	0.2595(6)	5.1(2)
C(21)	0.3555(6)	0.520(1)	0.3787(9)	8.6(3)

Fractional atomic coordinates and equivalent isotropic thermal parameters for all non-H atoms are listed in Table I. Selected bond distances and angles are listed in Table II. The molecular structure of the title complex is illustrated in Figure 1 with the atom-numbering scheme. The Mn(III) atom has an elongated octahedral coordination geometry. A dianion of the tetradentate Shiff base, *N*,*N*′-bis(salicylidene)1,3-propyldiamine, chelates the Mn(III) atom in the equatorial plane with two phenolate oxygen atoms and two imine nitrogen atoms; the average Mn–O distance of 1.882(3) Å and Mn–N distance of 2.038(4) Å are in agreement with 1.876(3) Å and 2.050(4) Å reported for $[Mn(2\text{-}OH\text{-}SALPN)(OAc)]_n$.[6] Acetate anions bridge adjacent Mn(III) atoms in the axial direction to form a linear polymeric chain along the *c* axis. The distances 2.169(3) and 2.204(3) Å between acetate O atoms and Mn(III) atom are about 0.3 Å longer than the Mn–O distance of 1.882(3) Å in the equatorial plane, consistent with Jahn–Teller distortion of this high-spin d^4 ion. Electron delocalization is observed in the carboxy group of the acetate anion as expected, the distances C(18)–O(3) and C(18)–O(4) being almost identical. Within

TABLE II Selected bond distances and angles

Bond distances (Å)			
Mn–O(1)	1.892(3)	Mn–O(2)	1.872(3)
Mn–O(3)	2.169(3)	Mn–O(4)^a	2.204(3)
Mn–N(1)	2.042(4)	Mn–N(2)	2.034(4)
O(1)–C(1)	1.321(5)	O(2)–C(17)	1.318(5)
O(3)–C(18)	1.261(5)	O(4)–C(18)	1.275(5)
N(1)–C(7)	1.284(6)	N(1)–C(8)	1.478(6)
N(2)–C(10)	1.481(6)	N(2)–C(11)	1.279(6)
C(6)–C(7)	1.436(7)	C(8)–C(9)	1.509(7)
C(9)–C(10)	1.501(7)	C(11)–C(12)	1.421(7)
C(18)–C(19)	1.497(6)		
Bond angles (°)			
O(1)–Mn–O(2)	88.2(1)	O(1)–Mn–O(3)	89.8(1)
O(1)–Mn–O(4)^a	90.7(1)	O(1)–Mn–N(1)	88.9(2)
O(1)–Mn–N(2)	176.9(2)	O(2)–Mn–O(3)	95.5(1)
O(2)–Mn–O(4)^a	95.0(1)	O(2)–Mn–N(1)	177.1(2)
O(2)–Mn–N(2)	89.1(2)	O(3)–Mn–O(4)^a	169.4(1)
O(3)–Mn–N(1)	84.3(1)	O(3)–Mn–N(2)	91.9(1)
O(4)^a–Mn–N(1)	85.1(1)	O(4)^a–Mn–N(2)	88.1(1)
N(1)–Mn–N(2)	93.8(2)	Mn–O(1)–C(1)	127.0(4)
Mn–O(2)–C(17)	126.9(4)	Mn–N(1)–C(7)	122.7(4)
Mn–N(1)–C(8)	120.9(3)	C(7)–N(1)–C(8)	116.4(3)
Mn–N(2)–C(10)	120.4(3)	Mn–N(2)–C(11)	122.1(3)
C(10)–N(2)–C(11)	117.4(4)	N(1)–C(8)–C(9)	113.0(4)
C(8)–C(9)–C(10)	114.7(5)	N(2)–C(10)–C(9)	113.7(4)
O(3)–C(18)–O(4)	120.2(4)		

Symmetry code: a: x, $0.5 - y$, $0.5 + z$.

the Schiff base ligand, all bond distances and angles are normal, both N–C distances [N(1)–C(7) = 1.284(6), N(2)–C(11) = 1.279(6) Å] and bond angles around N atoms show the character of the Schiff base and agree with the IR spectrum as discussed below.

The remarkable structural feature of the title complex is the umbrella-like spatial conformation around the Mn(III) atom as shown in Figure 1. Four donor atoms from a Schiff base ligand form a basal plane with the Mn(III) atom. Both salicylaldehyde moieties are planar but are inclined towards each other with a dihedral angle of 54.1(1)°. This may be due to repulsion between the phenyl ring and crystal CH_2Cl_2 as verified by the Cl(2)–C(1)

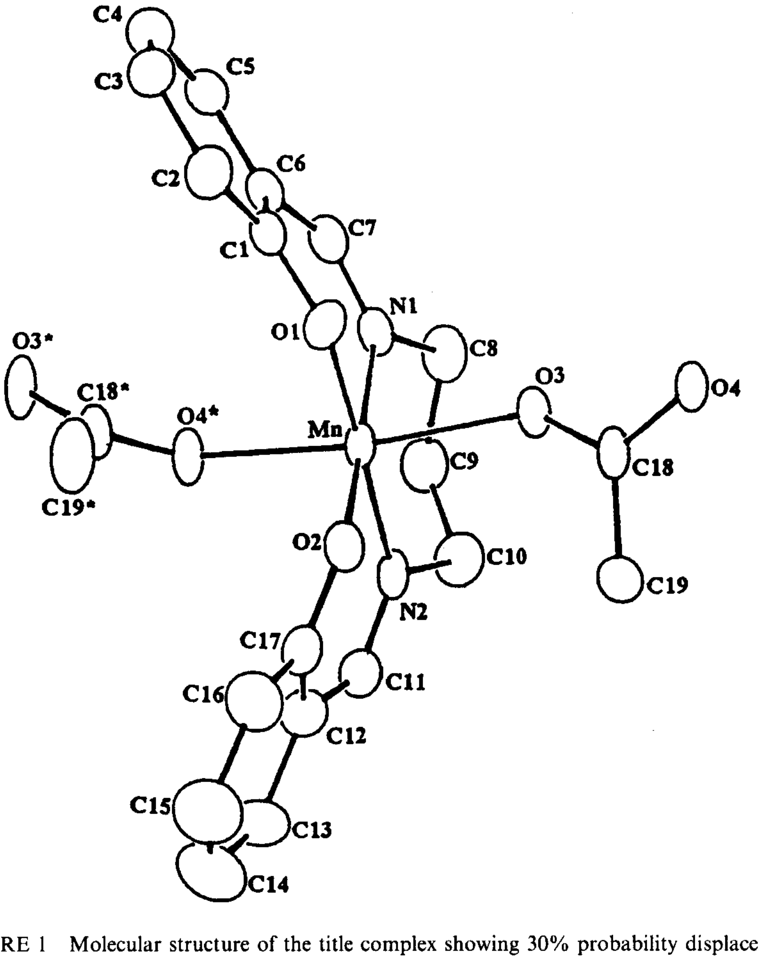

FIGURE 1 Molecular structure of the title complex showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.

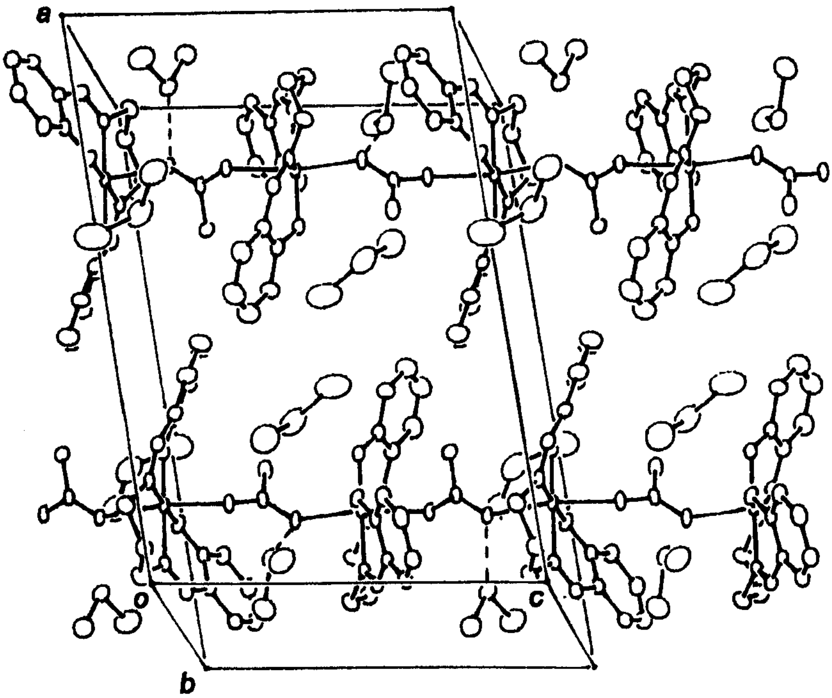

FIGURE 2 Packing diagram of polymeric chains in the unit cell; dashed lines show H-bonds.

distance of 3.618 Å. The umbrella structure shows the flexibility of the Schiff base ligand and suggests that the present complex may be a suitable chemical model for the oxygen evolution centre complex because the flexible structure is amenable to water molecule coordination during the water splitting process in photosystem II.

H-bonds between O and C atoms are noteworthy in the crystal. Similar H-bonds involving the C atom, for example, that between Cl and C atoms and between N and C atoms, have been reported previously.[7,8] An H-bond between O and C atoms is observed in the present crystal as shown in Figure 2. The distance O(3)–C(20) = 3.070 Å is about 0.3 Å shorter than the sum of the van der Waals radii of the methyl group and the oxygen atom.

Infrared Spectrum

The coordination pattern of a Schiff base ligand determines the C=N stretching vibration frequency. When the anionic ligand chelates to a metal atom by N and O atoms the ν(C=N) value is about 20 cm^{-1} smaller than in the free ligand, and when the neutral ligand coordinates to a metal atom by imine N atoms the ν(C=N) value is about 10 cm^{-1} larger than in the free ligand.[9] In the present complex, ν(C=N) is observed at 1620 cm^{-1}, which is 15 cm^{-1} smaller than (1635 cm^{-1}) in the free ligand. This agrees with a chelate anion.

For the acetate group of the complex, ν_{as}(COO) and ν_s(COO) are observed at 1540 and 1400 cm^{-1}, respectively, which are near values of 1560 and 1416 cm^{-1} for the free acetate group.[10] The $\Delta\nu$ [ν_{as}(COO) − ν_s(COO)] value of 140 cm^{-1} also agrees with those found in complexes bridged by the acetate group.[11]

Supplementary Material

Full lists of H atom positions, anisotropic thermal parameters for non-H atoms, and observed and calculated structure factors are available from the authors upon request.

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