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### SYNTHESIS AND CRYSTAL STRUCTURE OF A MANGANESE(II) COMPLEX, $\text{Mn}(\text{phen})_2(\text{phcoo})_2 \cdot 2\text{H}_2\text{O}$

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## SYNTHESIS AND CRYSTAL STRUCTURE OF A MANGANESE(II) COMPLEX, $\text{Mn}(\text{phen})_2(\text{phcoo})_2 \cdot 2\text{H}_2\text{O}$

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The title complex has been prepared by the reaction of  $\text{Mn}(\text{phcoo})_2$  with phen in EtOH/ $\text{H}_2\text{O}$  solution (where phcoo = the anion of benzoic acid, phen = 1,10-phenanthroline). The crystal structure has been determined by X-ray diffraction. The complex molecule has distorted octahedron geometry. Carboxyl O atoms coordinate to Mn(II) from unidentate ligands with a *cis*-configuration. Two uncoordinated O atoms of benzoate anions locate on the one side of the coordination plane so that there is free space on the other side of the plane; such a spatial arrangement may promote the attack of a water molecule at the manganese atom in the oxygen evolution process in photosystem II.

**Keywords:** Manganese(II); crystal structure; oxygen evolution; 1,10-phenanthroline; benzoic acid

### INTRODUCTION

Recently, intense efforts have concentrated on elucidating the nature of the biological unit responsible for water oxidation/oxygen evolution in the photosynthetic apparatus of green plants.<sup>1–3</sup> The process of water splitting is generally believed to occur at a manganese cluster located in the reaction centre of photosystem II<sup>4–6</sup> and to accompany changes of oxidation states of manganese atoms.<sup>7–9</sup> Direct biochemical and biophysical studies of the chloroplast-associated oxygen evolution centre have provided significant insight into the mechanism and structure of the enzyme complex responsible

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for the water splitting reaction.<sup>10,11</sup> In the framework of a systematic investigation on manganese complexes as mimics of the oxygen evolution complex performed in our laboratory, we prepared the title Mn(II) complex with 1,10-phenanthroline and the anion of benzoic acid. The crystal and molecular structure of the manganese(II) complex is reported here.

## EXPERIMENTAL

### Synthesis

Some 1.26 g (10 mmol) benzoic acid was added to an aqueous solution containing 0.40 g of NaOH with stirring at room temperature, and 0.99 g (5 mmol)  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  was dissolved in  $10 \text{ cm}^3$  of water. Mixing of the solutions gave white crystals of manganese(II) benzoate. Then, 1.98 g (10 mmol) of 1,10-phenanthroline was dissolved in  $25 \text{ cm}^3$  of mixed ethanol and water, when 2.97 g (10 mmol) of manganese benzoate obtained in the above step was added with stirring at  $60^\circ\text{C}$ , followed by refluxing for 20 min. The solution changed colour from colourless to yellow. The reaction mixture was cooled to room temperature and filtered. The filtrate was left to stand for ten days until well-formed, light yellow, single crystals were obtained.

### Elemental Analysis

C, H and N were analyzed using a Carlo-Erba 1160 instrument. *Anal.* Calc. for  $\text{C}_{38}\text{H}_{30}\text{N}_4\text{O}_6\text{Mn}$ (%): C 65.74, H 4.33, N 8.07%. Found: C 67.15, H 4.54, N 8.22.

### Infrared Spectra

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

### Crystal Structure Determination

A prismatic crystal of the title complex with approximate dimensions  $0.22 \times 0.20 \times 0.32 \text{ mm}$  was mounted on a glass fibre. X-ray intensity data were collected on a Rigaku AFC7R diffractometer up to a  $2\theta$  value of  $50.0^\circ$

with graphite-monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ) by the  $\omega$ - $2\theta$  scan technique. A total of 5935 independent reflections was collected, of which 4016 reflections were considered as observed [ $I > 3\sigma(I)$ ] and used for the structure determination. Usual  $L_p$  and empirical adsorption 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.<sup>12</sup> H atoms were located in a difference Fourier map, and coordinates and thermal parameters were fixed during structure refinement. Anisotropic refinement including all the non-H atoms converged to agreement factors  $R = 0.041$  and  $R_w = 0.051$ , where  $w = 1/\sigma^2(F)$ . Atomic scattering factors were taken from International Tables for X-ray Crystallography.<sup>13</sup>

### Crystal Data

$\text{C}_{38}\text{H}_{30}\text{N}_4\text{O}_6\text{Mn}$ ,  $M_r = 693.62$ , monoclinic,  $P2_1/n$ ,  $a = 11.137(2)$ ,  $b = 25.098(3)$ ,  $c = 11.756(2) \text{ \AA}$ ,  $\beta = 92.67(1)^\circ$ ,  $V = 3282.4(8) \text{ \AA}^3$ ,  $Z = 4$ ,  $F(000) = 1436$ ,  $D_c = 1.40 \text{ g} \cdot \text{cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 4.57 \text{ cm}^{-1}$ , No. of variables = 443,  $(\Delta/\sigma)_{\max} = 0.01$ ,  $(\Delta\rho)_{\max} = 0.47 \text{ e} \cdot \text{\AA}^{-3}$ .

## RESULTS AND DISCUSSION

### Crystal Structure

The molecular structure of the title complex is illustrated in Figure 1 with the atom numbering scheme. Final atomic coordinates and equivalent isotropic thermal parameters for all non-H atoms are presented in Table I. Selected bond distances and angles are listed in Table II. Two 1,10-phenanthroline molecules chelate to a Mn(II) atom with a *cis*-configuration. Two oxygen atoms from benzoate anions *cis*-coordinate to the Mn(II) atom to complete a distorted octahedral geometry. Two nitrogen atoms belonging to the different 1,10-phenanthroline molecules and coordinated carboxyl oxygen atoms form a basal plane around Mn(II); the other two nitrogen atoms of 1,10-phenanthroline molecules occupy the apical positions of the distorted octahedron. The molecular structure exhibits significant asymmetry. Bond angles between neighboring coordination atoms in the basal plane are near  $90^\circ$ , angles involving the apical coordination nitrogen atoms

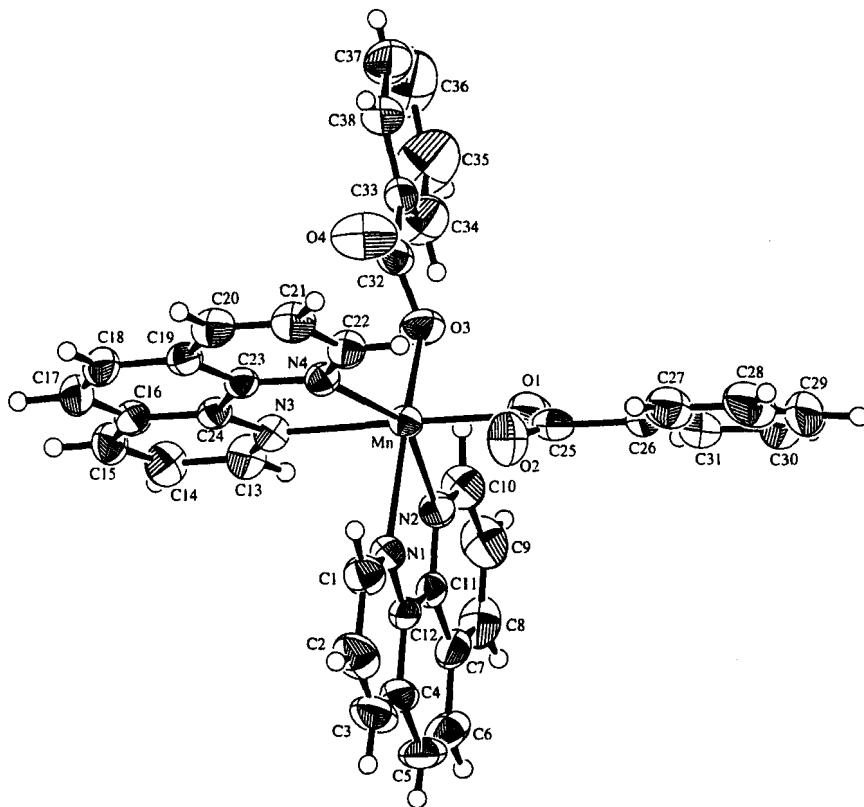


FIGURE 1 Molecular structure of the title complex showing 30% probability displacement ellipsoids and the atom numbering scheme.

are far from theoretical values. Both the N(2)–Mn–N(4) angle of  $150.90(9)^\circ$  and the O(3)–Mn–N(4) angle of  $109.91(9)^\circ$  the coordination between the N(4) and Mn(II) should be weaker. However it is surprising that the Mn–N(4) bond distance of  $2.268(2) \text{ \AA}$  in the axial direction is about  $0.1 \text{ \AA}$  shorter than the Mn–N(3) bond distance of  $2.362(2) \text{ \AA}$  in the basal plane. The carboxyl group of the benzoate anion coordinates to the Mn(II) atom *via* one oxygen atom as a unidentate; electron delocalization is observed in the carboxyl group. In the carboxyl group formed by C(32), O(3) and O(4) atoms the bond distance between the coordinated oxygen atom and the carbon atom is little longer than that between uncoordinated oxygen atom and the carbon atom as expected. However in the other carboxyl group formed by C(25), mother O(1) and O(2) atoms, the C(25)–O(1) distance of  $1.226(5) \text{ \AA}$  is significantly shorter than the C(25)–O(2) distance of

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

Atom	$x/a$	$y/b$	$z/c$	$B_{eq} (\text{\AA}^2)$
Mn(II)	0.26359(4)	0.13060(2)	0.69707(4)	3.173(10)
O(1)	0.1931(2)	0.1254(1)	0.5241(2)	6.77(8)
O(2)	0.3040(3)	0.1929(1)	0.4712(3)	7.91(9)
O(3)	0.0909(2)	0.1096(1)	0.7529(2)	5.48(6)
O(4)	0.0512(3)	0.1914(1)	0.8047(3)	7.87(9)
O(5)	0.5310(3)	0.2005(1)	0.3741(3)	8.58(10)
O(6)	0.4804(3)	0.4410(2)	0.0408(3)	11.8(1)
N(1)	0.4643(2)	0.1184(1)	0.6568(2)	3.76(6)
N(2)	0.3034(2)	0.04061(9)	0.6950(2)	3.83(6)
N(3)	0.3358(2)	0.12708(9)	0.8891(2)	3.51(6)
N(4)	0.3109(2)	0.21467(9)	0.7539(2)	3.33(5)
C(1)	0.5433(3)	0.1563(1)	0.6368(3)	4.84(9)
C(2)	0.6618(3)	0.1457(2)	0.6108(3)	6.4(1)
C(3)	0.6983(3)	0.0946(2)	0.6054(3)	6.8(1)
C(4)	0.6194(3)	0.0530(2)	0.6244(3)	5.25(9)
C(5)	0.6478(4)	-0.0031(2)	0.6153(3)	7.0(1)
C(6)	0.5684(5)	-0.0408(2)	0.6337(3)	6.7(1)
C(7)	0.4488(4)	-0.0285(1)	0.6616(3)	5.10(9)
C(8)	0.3603(5)	-0.0666(1)	0.6799(3)	6.3(1)
C(9)	0.2488(4)	-0.0511(1)	0.7050(4)	6.4(1)
C(10)	0.2227(3)	0.0029(1)	0.7115(3)	5.06(9)
C(11)	0.4159(3)	0.0256(1)	0.6709(2)	3.86(7)
C(12)	0.5020(3)	0.0670(1)	0.6511(2)	3.91(7)
C(13)	0.3454(3)	0.0849(1)	0.9566(3)	4.58(8)
C(14)	0.3931(3)	0.0873(1)	1.0682(3)	5.08(9)
C(15)	0.4305(3)	0.1346(1)	1.1119(3)	4.80(8)
C(16)	0.4220(3)	0.1803(1)	1.0442(3)	3.88(7)
C(17)	0.4583(3)	0.2318(1)	1.0849(3)	4.63(8)
C(18)	0.4437(3)	0.2749(1)	1.0192(3)	4.63(9)
C(19)	0.3916(3)	0.2712(1)	0.9061(3)	3.69(7)
C(20)	0.3718(3)	0.3154(1)	0.8354(3)	4.65(8)
C(21)	0.3231(3)	0.3090(1)	0.7289(3)	4.67(8)
C(22)	0.2945(3)	0.2579(1)	0.6900(3)	4.12(8)
C(23)	0.3579(2)	0.2212(1)	0.8613(2)	3.16(6)
C(24)	0.3727(2)	0.1746(1)	0.9331(2)	3.27(7)
C(25)	0.2286(3)	0.1562(2)	0.4521(3)	5.5(1)
C(26)	0.1773(3)	0.1501(1)	0.3308(3)	4.15(8)
C(27)	0.1859(3)	0.1922(2)	0.2557(4)	5.8(1)
C(28)	0.1409(4)	0.1874(2)	0.1449(4)	7.4(1)
C(29)	0.0900(4)	0.1411(3)	0.1096(4)	8.6(2)
C(30)	0.0816(4)	0.0991(2)	0.1817(4)	7.2(1)
C(31)	0.1244(3)	0.1037(2)	0.2923(3)	5.44(10)
C(32)	0.0258(3)	0.1442(2)	0.7978(3)	4.33(8)
C(33)	-0.0884(3)	0.1244(2)	0.8470(3)	4.52(8)
C(34)	-0.1095(4)	0.0717(2)	0.8576(4)	7.2(1)
C(35)	-0.2150(6)	0.0545(3)	0.9048(6)	11.5(2)
C(36)	-0.2974(6)	0.0905(4)	0.9376(6)	12.5(3)
C(37)	-0.2753(5)	0.1410(3)	0.9294(5)	10.8(2)
C(38)	-0.1719(3)	0.1601(2)	0.8837(3)	6.7(1)

TABLE II Selected bond distances (Å) and angles (°)

Mn–O(1)	2.149(3)	Mn–O(3)	2.127(2)
Mn–N(1)	2.326(3)	Mn–N(2)	2.302(2)
Mn–N(3)	2.362(2)	Mn–N(4)	2.268(2)
O(1)–C(25)	1.226(5)	O(2)–C(25)	1.259(5)
O(3)–C(32)	1.263(4)	O(4)–C(32)	1.220(4)
N(1)–C(1)	1.324(4)	N(1)–C(12)	1.361(4)
N(2)–C(10)	1.326(4)	N(2)–C(11)	1.351(4)
N(3)–C(13)	1.325(4)	N(3)–C(24)	1.357(3)
N(4)–C(22)	1.327(4)	N(4)–C(23)	1.354(3)
O(1)–Mn–O(3)	88.9(1)	O(1)–Mn–N(1)	96.40(9)
O(1)–Mn–N(2)	89.6(1)	O(1)–Mn–N(3)	174.2(1)
O(1)–Mn–N(4)	113.9(1)	O(3)–Mn–N(1)	157.13(10)
O(3)–Mn–N(2)	86.43(10)	O(3)–Mn–N(3)	88.21(9)
O(3)–Mn–N(4)	109.91(9)	N(1)–Mn–N(2)	71.43(9)
N(1)–Mn–N(3)	84.73(8)	N(1)–Mn–N(4)	88.28(9)
N(2)–Mn–N(3)	85.20(9)	N(2)–Mn–N(4)	150.90(9)
N(3)–Mn–N(4)	71.90(8)	Mn–O(1)–C(25)	120.0(3)
Mn–O(3)–C(32)	120.3(2)	Mn–N(1)–C(1)	126.5(2)
Mn–N(1)–C(12)	115.9(2)	Mn–N(2)–C(10)	124.5(2)
Mn–N(2)–C(11)	117.2(2)	Mn–N(3)–C(13)	128.1(2)
Mn–N(3)–C(24)	114.5(2)	Mn–N(4)–C(22)	124.7(2)
Mn–N(4)–C(23)	117.4(2)		

1.259(5) Å. The other notable feature of this structure is that the uncoordinated oxygen atoms of the benzoate anions are located on the one side of the coordination plane composed by the O(1), O(3), N(1) and N(3) atoms, and there is free space on the other side. Such a structure may promote the attack of a water molecule at manganese in the oxygen evolution process.

The crystal consists of the complexes and crystalline water molecules. H-bonding exists between the carboxyl groups and water as verified by the O(2)–O(5) distance of 2.828(5) Å and the O(4)–O(5) [ $-1/2 + x$ ,  $1/2 - y$ ,  $1/2 + z$ ] distance of 2.846(4) Å, so that the complex molecules form one-dimensional chains approximately parallel to the crystallographic glide plane.

The stretching vibration of the carboxyl group was observed at  $1605\text{ cm}^{-1}$  [ $\nu(\text{C}=\text{O})$ ] and  $1370\text{ cm}^{-1}$  [ $\nu(\text{C}-\text{O})$ ] in the title complex, in agreement with values reported previously.<sup>14</sup> The  $\Delta\nu$  value [ $\nu(\text{C}=\text{O}) - \nu(\text{C}-\text{O})$ ] of  $235\text{ cm}^{-1}$  suggests unidentate coordination of the carboxyl group;<sup>15</sup> it is also in agreement with the crystal structure as mentioned above.

### Acknowledgements

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### Supplementary Material

Full lists of crystallographic data are available from the author upon request.

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