

# Synthesis and structure of the first water-soluble chiral monomeric Mn<sup>IV</sup> complex: [ $\Delta$ -Mn<sup>IV</sup>(biguanide)<sub>3</sub>](ClO<sub>4</sub>)<sub>4</sub>·H<sub>2</sub>O

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The reaction of KMnO<sub>4</sub> with alkaline biguanide sulfate solution, followed by acidification of the resulting stable filtrate with concentrated HClO<sub>4</sub>, led to the title complex, **1**. The crystal structure of the [ $\Delta$ -Mn<sup>IV</sup>(bigH)<sub>3</sub>](ClO<sub>4</sub>)<sub>4</sub>·H<sub>2</sub>O (**1**, bigH: biguanide, C<sub>2</sub>H<sub>7</sub>N<sub>5</sub>) has a tetragonal chiral *P4<sub>1</sub>2<sub>1</sub>2* space group with *a* = *b* = 11.416(3) Å, *c* = 20.742(7) Å, *Z* = 4. The complex consists of one chiral [ $\Delta$ -Mn<sup>IV</sup>(bigH)<sub>3</sub>] tetracation, four ClO<sub>4</sub><sup>-</sup> anions, and one water molecule. In the tetracation, six N atoms from three neutral biguanide chelate coordinate to the Mn<sup>IV</sup> cation, forming an octahedron with  $\Delta$ -optical activity. The [ $\Delta$ -Mn<sup>IV</sup>(bigH)<sub>3</sub>] tetracation interconnects each other by numerous hydrogen bonds with N–H...O and O–H...O between biguanide moieties of the [ $\Delta$ -Mn<sup>IV</sup>(bigH)<sub>3</sub>] tetracations and counter-anions as well as water molecules, to construct a three-dimensional network.

**KEY WORDS:** Mn<sup>IV</sup> complex; biguanide; chirality; crystal structure.

## Introduction

The oxygen-evolving complex (OEC) of photosystem II (PS II) is a tetrameric manganese cluster where a cubane-like Mn<sub>3</sub>CaO<sub>4</sub> cluster is connected to another Mn by a mono- $\mu$ -oxo bridge.<sup>1</sup> The Mn cluster in PS II is known to cycle between five distinct oxidation levels labeled as S<sub>*n*</sub> states.<sup>2,3</sup> In these states, Mn ions are present in various combination of oxidation states, including Mn<sup>II</sup>, Mn<sup>III</sup>, Mn<sup>IV</sup>, and even Mn<sup>V</sup>.<sup>4</sup> The Mn

ions are bound to O- and/or N-based donor atoms from amino acid side chains.<sup>3</sup> Several structural as well as functional models of PS II are now available.<sup>3</sup> One of the basic units of PS II, *viz.* an authentic, mononuclear water-soluble Mn<sup>IV</sup> species is, however, rather uncommon. Only recently [Mn<sup>IV</sup>(bigH)]<sup>4+</sup> has been prepared from aqueous media and is stable in aqueous solution over a wide acidity range. Das *et al.*<sup>5</sup> prepared the Mn<sup>IV</sup>–biguanide complex with the composition [Mn<sup>IV</sup>(bigH)<sub>3</sub>]<sub>2</sub>SO<sub>4</sub>(NO<sub>3</sub>)<sub>6</sub>·3H<sub>2</sub>O (bigH: biguanide, C<sub>2</sub>H<sub>7</sub>N<sub>5</sub>). The lattice consists of two monomeric units held together by hydrogen bonds *via* the sulfato anion, acting as a bridge between the two. Following the same procedure for its preparation, Lu *et al.*<sup>6</sup> however, obtained a stoichiometrically different Mn<sup>IV</sup>–biguanide complex (bigH<sub>3</sub>)[Mn<sup>IV</sup>(bigH)<sub>3</sub>](NO<sub>3</sub>)<sub>6</sub> that may be viewed as a mixture of [Mn<sup>IV</sup>(bigH)<sub>3</sub>](NO<sub>3</sub>)<sub>4</sub> and

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(bigH<sub>3</sub>)·(NO<sub>3</sub>)<sub>2</sub>. Using the same methodology as described by Das *et al.*<sup>5</sup> for the preparation of Mn<sup>IV</sup> complex by reducing aqueous KMnO<sub>4</sub> with alkaline biguanide sulfate and subsequent treatment with concentrated HClO<sub>4</sub> we obtained perchlorate salt of the Mn<sup>IV</sup>-biguanide complex, [Δ-Mn<sup>IV</sup>(bigH)<sub>3</sub>](ClO<sub>4</sub>)<sub>4</sub>·H<sub>2</sub>O. We describe herein the structure of the chiral complex so prepared. The Mn<sup>IV</sup> complex thus prepared is monomeric and is simplest water-soluble stable form of Mn<sup>IV</sup>. We verified that the optical spectra of the ClO<sub>4</sub><sup>-</sup> salt prepared by us matches absolutely well with the reported values for the dimmer<sup>7,8</sup> that dissociates into two monomeric species in aqueous media.

The title complex is the first example of optically active aqueous monomeric Mn<sup>IV</sup> though very recently only a few structurally characterized optically active mononuclear nonaqueous Mn<sup>IV</sup> complexes are reported but the optical activity of these monomeric Mn<sup>IV</sup> result from chiral ligands<sup>9,10</sup> instead of chiral at metal. We describe herein the structural details of **1**, the first and simplest water soluble Mn<sup>IV</sup>.

## Experimental section

### *Preparation and optical activity of tris (biguanide)manganese(IV) perchlorate salt*

A solution of KMnO<sub>4</sub> (0.8 g in 25 mL water) was added dropwise with constant stirring to that of alkaline biguanide sulphate (bigH. H<sub>2</sub>SO<sub>4</sub>, 5.5 g in 75 mL of 4% NaOH solution) solution. The color of KMnO<sub>4</sub> solution first changed to green and finally to dark orange-red. The reduction of KMnO<sub>4</sub> is slow to begin with and gradually becomes rapid. It was filtered and the filtrate was kept for ~15 min, then the solution was further filtered, if necessary. The filtrate was then neutralized with concentrated HClO<sub>4</sub> and made the solution ~ 2(N) with respect to HClO<sub>4</sub>. If some precipitate appears then it was filtered again. The filtrate was kept in low temperature (~5°C) for around 1 month

when red crystals appeared. (Caution! Though perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with extreme care, we found that the synthetic procedure described here is safe.) The crystals were collected by filtration and crystallographically characterized as [Mn(bigH)<sub>3</sub>](ClO<sub>4</sub>)<sub>4</sub>·H<sub>2</sub>O, bigH: C<sub>2</sub>H<sub>7</sub>N<sub>5</sub>. The optical activity of **1** was recorded in Perkin Elmer 241 polarimeter with the value  $[\alpha]_D^{20} = -150^\circ$  ( $c = 6.7 \times 10^{-5}$ , water).

### *X-ray crystallography*

A deep red cubic crystal of the complex was mounted on a glass fiber and used for data collection. Cell dimensions and an orientation matrix

**Table 1.** Crystal Data and Structure Refinement for [Δ-Mn<sup>IV</sup>(bigH)<sub>3</sub>](ClO<sub>4</sub>)<sub>4</sub>·H<sub>2</sub>O

CCDC deposit no	CCDC-267925
Empirical formula	MnC <sub>6</sub> H <sub>23</sub> Cl <sub>4</sub> N <sub>15</sub> O <sub>17</sub>
Formula weight	774.13
Temperature (K)	293(2)
Wavelength (Mo Kα) (Å)	0.71073
Crystal system	Tetragonal
Space group	<i>P</i> 4 <sub>1</sub> 2 <sub>1</sub> 2
Crystal size (mm <sup>3</sup> )	0.30 × 0.30 × 0.20
Unit cell dimensions	
<i>a</i> = <i>b</i> (Å)	11.416(3)
<i>c</i> (Å)	20.742(7)
Volume (Å <sup>3</sup> )	2703.3(12)
<i>Z</i>	4
Calculated density (mg/m <sup>3</sup> )	1.902
$\theta$ range for data collection (°)	2.04–25.00
Reflections collected	12,911
Unique reflections	2373 [ <i>R</i> (int) = 0.0413]
<i>F</i> (0 0 0)	1572
Absorption coefficient (mm <sup>-1</sup> )	0.986
Maximum and minimum transmission	0.8272 and 0.7564
Index ranges	– 13 ≤ <i>h</i> ≤ 10 – 13 ≤ <i>k</i> ≤ 13 – 24 ≤ <i>l</i> ≤ 22
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.109
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.061, <i>wR</i> <sub>2</sub> = 0.1527
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0640, <i>wR</i> <sub>2</sub> = 0.1548
Absolute structure parameter <sup>13</sup>	0.06(6)
Largest diff. peak and hole (e Å <sup>-3</sup> )	0.975 and – 0.441

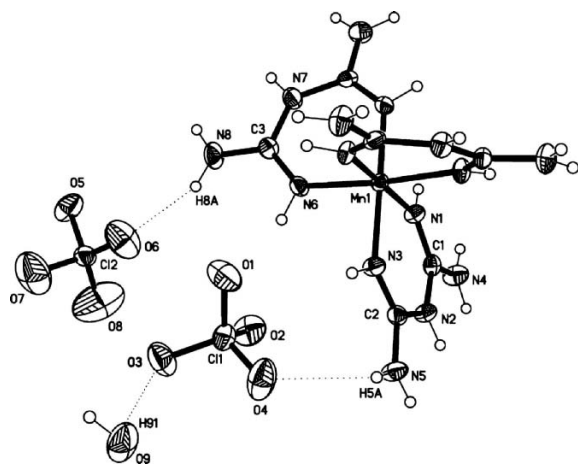
**[ $\Delta$ -Mn<sup>IV</sup>(biguanide)<sub>3</sub>](ClO<sub>4</sub>)<sub>4</sub>·H<sub>2</sub>O**

**Table 2.** Selected Bond Lengths (Å) and Angles (°)<sup>a</sup>

Bond lengths			
Mn(1)–N(6)	1.938(5)	Mn(1)–N(6)#1	1.938(5)
Mn(1)–N(3)#1	1.943(5)	Mn(1)–N(3)	1.943(5)
Mn(1)–N(1)	1.948(5)	Mn(1)–N(1)#1	1.948(5)
N(1)–C(1)	1.307(8)	N(4)–C(1)	1.322(8)
N(2)–C(2)	1.348(8)	N(2)–C(1)	1.373(8)
N(3)–C(2)	1.305(8)	N(5)–C(2)	1.341(8)
N(6)–C(3)	1.298(8)	N(7)–C(3)	1.369(7)
N(7)–C(3)#1	1.369(7)	N(8)–C(3)	1.322(9)
Bond angles			
N(6)–Mn(1)–N(6)#1	87.0(3)	N(6)–Mn(1)–N(3)#1	173.6(2)
N(6)#1–Mn(1)–N(3)#1	90.3(2)	N(6)–Mn(1)–N(3)	90.3(2)
N(6)#1–Mn(1)–N(3)	173.6(2)	N(3)#1–Mn(1)–N(3)	93.1(3)
N(6)–Mn(1)–N(1)	95.7(2)	N(6)#1–Mn(1)–N(1)	87.9(2)
N(3)#1–Mn(1)–N(1)	90.0(2)	N(3)–Mn(1)–N(1)	86.6(2)
N(6)–Mn(1)–N(1)#1	87.9(2)	N(6)#1–Mn(1)–N(1)#1	95.7(2)
N(3)#1–Mn(1)–N(1)#1	86.5(2)	N(3)–Mn(1)–N(1)#1	90.1(2)
N(1)–Mn(1)–N(1)#1	175.1(3)	C(2)–N(2)–C(1)	126.9(5)
C(3)–N(7)–C(3)#1	126.6(8)	N(1)–C(1)–N(4)	122.8(6)
N(1)–C(1)–N(2)	121.3(5)	N(4)–C(1)–N(2)	115.9(6)
N(3)–C(2)–N(5)	122.3(6)	N(3)–C(2)–N(2)	122.1(6)
N(5)–C(2)–N(2)	115.5(6)	N(6)–C(3)–N(8)	123.5(7)
N(6)–C(3)–N(7)	121.4(6)	N(8)–C(3)–N(7)	115.1(6)

<sup>a</sup>Symmetry code: #1  $y - 1, x + 1, -z$ .

for data collection were obtained by least-squares refinement of diffraction data from 2861 reflections with  $2.04 < \theta < 27.04^\circ$  using a Bruker



**Fig. 1.** The structure of [ $\Delta$ -Mn<sup>IV</sup>(bigH)<sub>3</sub>](ClO<sub>4</sub>)<sub>4</sub>·H<sub>2</sub>O with displacement ellipsoids at the 30% probability level and unlabeled half-structural domain generated at a symmetry element (a fourfold rotation axis,  $y - 1, x + 1, -z$ ).

SMART APEX CCD automatic diffractometer. Data were collected at 293 K using Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and the  $\omega$ -scan technique, and corrected for Lorentz and polarization effects (SADABS).<sup>11</sup>

The structure was solved by direct methods (SHELXS-97), refinement was done by full-matrix least-squares on  $F^2$  using the SHELXS-97 program suite.<sup>12</sup> In final cycles, all nonhydrogen positions were refined by anisotropic temperature factors. H atoms attached to N were positioned geometrically and refined as riding with the constraint  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$  and H atom attached to O was located in a difference map and refined as riding in its as-found relative position, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . A summary of the crystal data, experimental details, and refinement results is given in Table 1. The structure data has also been deposited with the Cambridge Crystallographic Data Center (No. 267925). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK

**Table 3.** Hydrogen Bond Parameters(Å, °)<sup>a</sup>

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(9)-H(91)...O(3)	0.84	2.20	2.954(9)	149.2
N(8)-H(8A)...O(6)	0.86	2.17	2.984(10)	156.8
N(7)-H(7)...O(9)#3	0.86	1.90	2.759(12)	180.0
N(5)-H(5B)...O(5)#4	0.86	2.25	2.936(8)	136.8
N(5)-H(5A)...O(4)	0.86	2.47	3.081(10)	128.3
N(3)-H(3)...O(5)#5	0.86	2.36	3.073(8)	140.8
N(2)-H(2)...O(1)#6	0.86	1.98	2.838(8)	178.0
N(4)-H(4A)...O(7)#7	0.86	2.03	2.889(11)	178.1

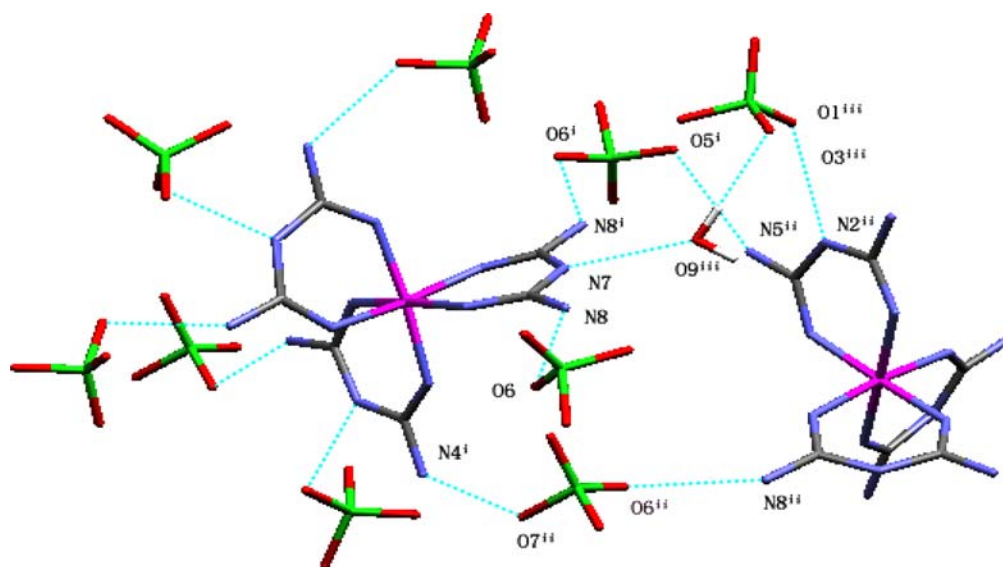
<sup>a</sup>Symmetry transformations used to generate equivalent atoms: #1  $y - 1, x + 1, -z$ ; #2  $y, x + 1, -z$ ; #3  $x, y + 1, z$ ; #4  $-x + 1/2, y - 1/2, -z + 1/4$ ; #5  $y - 1, x, -z$ ; #6  $-y + 1/2, x + 1/2, z + 1/4$ ; #7  $-x + 1/2, y + 1/2, -z + 1/4$

(Fax: int.code\_(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

## Results and discussion

Some features of the molecular geometry of **1** are shown in Fig. 1 and Table 2. The com-

plex **1** consists of one chiral  $[\Delta\text{-Mn}^{\text{IV}}(\text{bigH})_3]^{4+}$  cation, four  $\text{ClO}_4^-$  anions as counter ions, and one water molecule. The structure of the tetracation is similar to those reported before<sup>5,6</sup>, i.e. six N atoms from three neutral biguanide chelate coordinate to the  $\text{Mn}^{\text{IV}}$  atom in a *cis* configuration, forming an octahedron. However, the Mn-N bonds [1.938(5)–1.948(5) Å] and the bite angles [86.6(2), 95.7(2), 90.3(2)°] of the



**Fig. 2.** The hydrogen bonds (dotting lines) between neighboring tetracations and the surrounding  $\text{ClO}_4^-$  anions and water molecule. Red O, purple Mn, pale blue N, gray C, green Cl. Hydrogens except in water are omitted for clarity (symmetry code: i:  $1 + x, -1 + y, -z$ ; ii:  $1.5 - x, -0.5 + y, -0.25 + z$ ; iii:  $x, 1 + y, z$ ).

## $[\Delta\text{-Mn}^{\text{IV}}(\text{biguanide})_3](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$

biguanide ligands at the  $\text{Mn}^{\text{IV}}$  are a little changed comparing with  $(\text{bigH}_3)[\text{Mn}^{\text{IV}}(\text{bigH})_3](\text{NO}_3)_6$  [the Mn–N bonds, 1.918(2)–1.952(2) Å, the bite angles, 84.30(10), 85.68(10), 86.43(10)°] and  $[\text{Mn}^{\text{IV}}(\text{bigH})_3]_2\text{SO}_4(\text{NO}_3)_6 \cdot 3\text{H}_2\text{O}$  [the Mn–N bonds, 1.923(7)–1.943(7) Å, the bite angles 87.0(3), 87.0(3), 86.4(3)°] complexes, indicating that the conformation of the tetracation is slightly effected by different anions.

The hydrogen bonding geometry is listed in Table 3 and showed as Fig. 2. The crystal structure is stabilized by eight hydrogen bonds between biguanide moieties,  $\text{ClO}_4^-$  anions and water molecules. Every  $[\Delta\text{-Mn}^{\text{IV}}(\text{bigH})_3]$  tetracation directly links eight  $\text{ClO}_4^-$  anions and one water molecule by N–H...O hydrogen bonds, forming the pattern of eight  $\text{ClO}_4^-$  anions and one water molecule surrounding the tetracation. On the other hand, through these hydrogen bonds, neighboring tetracations are connected to each other by two  $\text{ClO}_4^-$  anions and one water molecule which is hydrogen bonded to another  $\text{ClO}_4^-$  anions. Therefore, every tetracation indeed links four neighboring tetracations, making the overall structure a complicated three-dimensional network.

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