

A novel triply bridged dinuclear manganese(III) complex containing the $[\text{Mn}_2\text{O}(\text{OAc})_2]^{2+}$ core: synthesis, crystal structure and properties of $[\text{Mn}_2(\mu\text{-O})(\mu\text{-OAc})_2(\text{bpea})_2](\text{ClO}_4)_2$ [☆]

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Abstract

The reaction of $\text{Mn}(\text{O}_2\text{CCH}_3)_3 \cdot 2\text{H}_2\text{O}$ with the ligand *N,N*-bis(2-pyridylmethyl)ethylamine (bpea) in a 1:1 ratio in methanol followed by the addition of NaClO_4 afforded the title compound $[\text{Mn}_2\text{O}(\text{O}_2\text{CCH}_3)_2(\text{bpea})_2](\text{ClO}_4)_2$ (**1**) in 75% yield. Compound **1** was characterized by using several physical methods including single-crystal X-ray diffractometry. Compound **1**·0.5H₂O crystallizes in the orthorhombic space group *Pbca* (No. 61) with $a = 38.780(2)$, $b = 22.058(4)$, $c = 19.719(5)$ Å, $V = 16\,868(8)$ Å³ and $Z = 16$. There are two independent equivalents of compound **1** in the crystallographic asymmetric unit and there is a single unique water molecule in the crystal lattice. Both manganese atoms in each of the independent dinuclear units are in the +3 oxidation state and they are bridged by one oxo ligand (O^{2-}) and two acetate groups. Each manganese atom is also bound to one facially-coordinating tridentate bpea ligand, with the aliphatic nitrogen donor situated *trans* to an acetate oxygen atom. Deviations from idealized octahedral symmetry at each manganese center are consistent with expectations for a d^4 electronic configuration. Compound **1** has an average Mn···Mn separation of 3.11 Å and an average Mn–($\mu\text{-O}$)–Mn angle of 122.7°. The electronic absorption spectrum of **1** in CH_3CN is very similar to other compounds that contain the $[\text{Mn}_2(\mu\text{-O})(\mu\text{-O}_2\text{CCH}_3)_2]^{2+}$ core. A cyclic voltammogram of **1** in CH_3CN exhibits an oxidation wave (III,III to III,IV) at +0.66 V and a reduction wave (III,III to III,II) at –0.39 V versus the ferrocene/ferrocenium (Fc/Fc⁺) couple. The IR spectrum of **1** reveals two strong bands at 1566 and 1432 cm^{-1} corresponding to the bridging acetate groups present in the compound. The X-band electron paramagnetic resonance (EPR) spectrum of **1** in dry CH_3CN at 77 and 4 K is featureless. Compound **1** disproportionates in an $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ solvent mixture to give the (III,IV) binuclear species $[\text{Mn}_2\text{O}_2(\text{O}_2\text{CCH}_3)(\text{bpea})_2]^{2+}$, which displays a characteristic 16-line $g = 2$ EPR signal.

Keywords: Manganese complexes; Photosystem II model; Crystal structures

1. Introduction

Although Photosystem II (PSII) has been studied intensively for many years, the catalytic site for water

Abbreviations: PSII, photosystem II; WO, water oxidase; EXAFS, extended X-ray absorption fine structure; EPR, electron paramagnetic resonance; UV, ultraviolet; IR, infrared; NIR, near-infrared; Vis, visible; SCE, saturated calomel electrode; OAc, acetate ion; TEAP, tetraethylammonium perchlorate; bpea, *N,N*-bis(2-pyridylmethyl)ethylamine; bpy, 2,2'-bipyridine; tacn, 1,4,7-triazacyclononane; Me₃tacn, 1,4,7-trimethyltriazacyclononane; HB(pz)₃[−], hydrotris(pyrazol-1-yl)borate; tmip, tris(*N*-methylimidazol-2-yl)phosphine; bbiaac, 2-[bis(benzimidazole-2-ylmethyl)-amino]ethanol; pepmma, (2-pyridylethyl)(2-pyridylmethyl)methylamine.

[☆] This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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oxidation therein, a polynuclear manganese complex, is relatively poorly understood with respect to its structure and mechanism of action. While the crystal structure for the membrane bound multisubunit water oxidase (WO) has not been determined, some insight regarding the structure of the manganese aggregate has been gleaned from biochemical and spectroscopic studies on isolated PSII particles [1]. Elemental analyses [2] indicate that the WO manganese cluster likely contains four manganese atoms, while manganese extended X-ray absorption fine structure (EXAFS) data reveal the presence of at least two 2.7 Å Mn···Mn vectors [3–5]. A peak in the Mn EXAFS Fourier transform consistent with a 3.3 Å Mn···Mn interaction is also evident [3,5,6], although it is likely that at least a part of this feature is due to an Mn···Ca interaction [7]. Electron

paramagnetic resonance (EPR) studies of the PSII Kok S₂ state using X-band microwave frequencies reveal the presence of two characteristic signals associated with the manganese aggregate; a 19–21 line signal centered at $g=2$ [8,9] and a broader signal centered at $g=4.1$ [10,11]. Recently, nuclear hyperfine interactions for this latter signal were detected for oriented PSII samples [12]. These EPR data are consistent with the notion that the manganese atoms at the WO active site are assembled as a spin-coupled aggregate.

We and others have been engaged in a biomimetic synthetic approach to the problem of structural elucidation of the PSII manganese complex [13,14]. In recent years a large number of oxo-bridged manganese complexes, including a variety of tetranuclear species [15], have been characterized. One synthetic approach to an active site model being explored in our laboratory is the controlled aggregation of preformed dinuclear species that contain $\{\text{Mn}_2\text{O}_2\}^{2+,3+,4+}$ [16], $\{\text{Mn}_2\text{O}_2(\text{O}_2\text{CR})\}^{2+,3+}$ [17,21], and $\{\text{Mn}_2\text{O}(\text{O}_2\text{CR})_2\}^{2+,3+}$ [18] cores. This is due to the fact that di- μ -oxo dinuclear manganese complexes have Mn···Mn separations of approximately 2.7 Å and species with the $\{\text{Mn}_2\text{O}(\text{OAc})_2\}^{2+}$ core have ~3.2 Å Mn···Mn distances, consistent with the EXAFS data for the PSII WO mentioned above.

Prior to this work, structurally characterized dinuclear manganese complexes containing the $\{\text{Mn}_2\text{O}(\text{O}_2\text{CR})_2\}^{2+}$ core were reported either with rigid tridentate capping ligands, e.g. tacn, Me₃tacn, HBpz₃⁻ and tmip, or with bidentate bpy as terminal ligand. In the past few years we have investigated the higher valent manganese oxo coordination chemistry of several aminopolypyridyl ligands including the tridentate ligand bpea (*N,N*-bis(2-pyridylmethyl)ethylamine) [19–21]. The ligand bpea has a potential advantage over the aforementioned tridentate ligands due to the fact that it can bind to the metal both in facial and meridional fashion [20] and is likely to be less rigidly coordinated, features that we expect to be useful in mediating controlled aggregation reactions. In order to develop further the coordination chemistry of bpea and with the intent of preparing starting materials for subsequent synthesis we set out to make the dinuclear complex of the ligand bpea containing an $\{\text{Mn}_2\text{O}(\text{OAc})_2\}$ core. Another general motivating factor in this work is to gain an understanding of the factors that dictate polynuclear core assembly as a function of the terminal ligand, an area that has received relatively little attention. In this article we wish to report that the desired dinuclear complex, $[\text{Mn}_2\text{O}(\text{OAc})_2(\text{bpea})_2](\text{ClO}_4)_2$ (**1**), can be prepared in good yield and we describe its crystal structure along with several chemical and physical properties.

2. Experimental

2.1. Materials and methods

All manipulations were carried out under ambient conditions unless otherwise stated. Solvents used in this work were of analytical grade. Chemicals were obtained from the following sources: $\text{Mn}(\text{O}_2\text{C}-\text{CH}_3)_3 \cdot 2\text{H}_2\text{O}$ and 2-picolyl chloride hydrochloride, Aldrich Chemical Company; ethyl amine, Eastman Kodak Company. The ligand bpea was prepared as described previously [21]. Acetonitrile used for electrochemical experiments was distilled from CaH_2 and stored over 3 Å molecular sieves prior to use. The supporting electrolyte tetraethylammonium perchlorate (TEAP) was prepared by following a literature procedure [22].

2.2. Physical measurements

The IR spectrum of compound **1** as a KBr pellet was recorded in the range 4000–400 cm⁻¹ with use of a Nicolet DX FTIR spectrometer. The electronic absorption spectrum in the region 900–300 nm was recorded for a CH₃CN solution of **1** in quartz cells with a Cary 2400 or a Perkin-Elmer Lambda 3B UV–Vis–NIR spectrophotometer. The EPR spectra were recorded at liquid nitrogen temperature using an immersion ‘finger’ dewar and at liquid helium temperature using an Oxford cryostat and transfer line with a Bruker ECS 106 spectrometer. Cyclic voltammetric measurements were carried out with an EG&G PAR model 273 potentiostat/galvanostat equipped with a PAR model RE 0091 X–Y recorder. A typical three-electrode cell employing a platinum disk as working electrode, platinum wire as auxiliary electrode and a saturated calomel electrode as reference electrode [22] under a dry and purified dinitrogen atmosphere was used for the cyclic voltammetry study. No attempts were made to correct the potentials reported here for junction contributions. Under the conditions described above the ferrocene/ferrocenium couple had a reversible ($\Delta E_p = 70$ mV and $i_a/i_c = 1$) wave at +0.36 versus SCE. Elemental analyses were performed by Robertson Microlit Laboratories, Inc., Madison, NJ.

2.3. Preparation of $[\text{Mn}_2\text{O}(\text{OAc})_2(\text{bpea})_2](\text{ClO}_4)_2$ (**1**)

A portion of solid $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ (536 mg, 2.00 mmol) was added to a methanolic solution (30 ml) of the bpea ligand (454 mg, 2.00 mmol). After stirring for 30 min, the mixture was filtered and then solid $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (280 mg, 2.00 mmol) was added to the filtrate. Stirring was continued for another 1 h and then the solvent was removed under vacuum. The residue was redissolved in dry dichloromethane and filtered to remove a white solid and the dichloromethane

solution was allowed to evaporate in an open container overnight. The beautiful red–brown rectangular crystals that formed were collected by filtration, providing a yield of 670 mg (75%). *Anal. Calc.* for $C_{33}H_{41.5}N_{6.5}O_{13}Cl_2Mn_2$: C, 42.81; H 4.46; N, 9.36. Found: C, 43.65; H, 4.51; N, 9.40%. IR bands (KBr pellet) (cm^{-1}): 3113(w), 3081(w), 2978(w), 2947(w), 1608(s), 1576(sh), 1566(s), 1483(w), 1432(s), 1352(w), 1308(w), 1292(m), 1269(w), 1248(w), 1226(w), 1161(m), 1120(sh), 1093(vs), 1032(m), 1018(m), 930(w), 768(m), 730(w), 722(w), 660(w), 623(s). Electronic spectral data (in CH_3CN) (λ (nm) (ϵ ($M^{-1} cm^{-1}$)): 728(112), 569(sh), 545(sh), 521(372), 487(517), 377(sh) (vs, very strong; s, strong; m, medium; w, weak; sh, shoulder).

Compound **1** is soluble in methanol, dichloromethane and acetonitrile giving red–brown colored solutions. Dark brown single crystals of compound **1**, suitable for X-ray diffraction studies, were obtained when a small portion was dissolved in methanol and the resulting solution was allowed to evaporate very slowly.

Caution! Although we have not experienced any problems in working with the title compound, perchlorate salts of compounds containing organic ligands are potentially explosive [23].

2.4. X-ray crystallography

Crystals of compound **1** were very sensitive to solvent loss and therefore single crystals for this study were immersed under oil (a mixture of mineral and Paratone-N oil in a 1:1 ratio) after transferring them from the mother liquor in a small evaporating dish. A single crystal of suitable size ($0.4 \times 0.1 \times 0.05$ mm) was mounted on the tip of a thin glass fiber using a small amount of grease and then transferred to the cold stream of dinitrogen of the low temperature device attached to an automated four-circle Rigaku AFC5R diffractometer equipped with monochromated Cu $K\alpha$ radiation. A zigzag search of reciprocal space in the range $6 < 2\theta < 55^\circ$ gave 25 reflections which were indexed to give the orthorhombic crystal system. The 2θ – ω scan technique (rate: $8^\circ/min$) was used to collect data points over an octant of reciprocal space. The three reflections monitored periodically during the data collection showed no significant change in intensity during 131 h of X-ray exposure. Lorentz and polarization corrections were applied to the data as well as an empirical absorption correction based on ψ -scans of several reflections with χ near 90° [24]. The orthorhombic space group $Pbca$ (No. 61) was uniquely determined by systematic absences and this choice was confirmed by successful refinement of the structure. The unit cell volume suggested the presence of two independent dinuclear complexes. Positions for all atoms heavier than carbon were obtained from a SHELXS-86 direct method solution [25]. The remaining non-hydrogen atoms were located and refined

Table 1
Crystallographic data for $[Mn_2O(OAc)_2(bpea)_2](ClO_4)_2 \cdot 0.5H_2O$

Formula	$C_{32}H_{41}Cl_2Mn_2N_6O_{13.5}$
Formula weight	906.5
Space group	$Pbca$ (No. 61)
a (Å)	38.780(2)
b (Å)	22.058(4)
c (Å)	19.719(5)
α ($^\circ$)	90.00
β ($^\circ$)	90.00
γ ($^\circ$)	90.00
V (Å ³)	16868(8)
Z	16
D_{calc} ($g cm^{-3}$)	1.462
μ (Cu $K\alpha$) (cm^{-1})	68.229
Radiation used, λ (Å)	Cu $K\alpha$, 1.540598
Temperature ($^\circ C$)	– 50
Transmission factors, max., min. (%)	100.00, 23.12
R^a	0.086
R_w^b	0.094

$$^a R = \sum |F_o| - |F_c| / \sum |F_o|.$$

$$^b R_w = [\sum w(|F_o| - |F_c|) / \sum w|F_o|]^{1/2}; w = 1/\sigma^2(|F_o|).$$

by alternating difference Fourier maps and full-matrix least-squares refinement cycles, based on F derivatives, employing the TEXSAN software package [26]. A single unique water of crystallization per two dinuclear units was located in the lattice. For the two independent dinuclear units, two ethyl carbon atoms in two of the four bpea ligands and one methyl carbon atom in one of the four acetate groups were disordered over two positions with a total occupancy of 1.0. Three oxygen atoms in two of the four perchlorate ions were also disordered and modelled accordingly. Due to the limited number of data, only the core atoms of the dinuclear units ($Mn_2O_5N_6$) and the ordered ClO_4^- units were refined with anisotropic thermal parameters. Isotropic thermal parameters were assigned to all other atoms. The disorder problems noted above are assumed to account for the relatively high R values obtained. Several efforts to grow crystals of higher quality failed. Although the hydrogen atoms were not located on the difference maps, they were included (except those of the solvent molecule) at idealized positions ($C-H=0.95$ Å) during the final refinement cycles. The final difference Fourier map was relatively featureless with no peak greater than $1 e \text{ \AA}^{-3}$. The crystal parameters and basic information related to data collection and structure refinement are summarized in Table 1. The final positional and thermal parameters for this structure are listed in Table 2.

3. Results and discussion

3.1. Synthesis

Syntheses of complexes containing the $[Mn_2O(OAc)_2]^{2+}$ core have been carried out under

Table 2

Positional and isotropic equivalent thermal parameters for the cations in $[\text{Mn}_2\text{O}(\text{OAc})_2(\text{bpea})_2](\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ *

Atom	x	y	z	B_{eq} (\AA^2)
Mn(1)	0.44388(8)	0.2365(2)	0.4865(2)	3.6(2)*
Mn(2)	0.46539(8)	0.3101(2)	0.6161(2)	3.9(2)*
Mn(3)	0.22282(8)	0.2012(2)	0.0113(2)	4.6(2)*
Mn(4)	0.25597(9)	0.3257(2)	-0.0336(2)	4.3(2)*
O(1)	0.4722(3)	0.2507(7)	0.5567(6)	3.8(7)*
O(2)	0.3994(3)	0.2470(8)	0.5366(7)	5(1)*
O(3)	0.4144(3)	0.2971(7)	0.6343(6)	4.3(8)*
O(4)	0.4426(4)	0.3256(8)	0.4493(7)	6(1)*
O(5)	0.4552(4)	0.3793(7)	0.5457(8)	5(1)*
O(6)	0.2244(3)	0.2664(7)	-0.0431(7)	4.5(8)*
O(7)	0.2289(3)	0.2492(8)	0.1013(7)	5(1)*
O(8)	0.2507(4)	0.3400(8)	0.0661(7)	5(1)*
O(9)	0.2717(4)	0.1743(7)	-0.0016(8)	6(1)*
O(10)	0.2971(3)	0.2634(8)	-0.0303(8)	5(1)*
N(1)	0.4454(5)	0.1344(7)	0.501(1)	4(1)*
N(2)	0.4138(4)	0.207(1)	0.4072(8)	3(1)*
N(3)	0.4892(4)	0.2092(9)	0.4290(8)	4(1)*
N(4)	0.5212(4)	0.315(1)	0.635(1)	5(1)*
N(5)	0.4677(4)	0.3803(8)	0.6844(8)	4(1)*
N(6)	0.4771(5)	0.2377(9)	0.6942(9)	5(1)*
N(7)	0.1657(4)	0.202(1)	0.017(1)	7(1)*
N(8)	0.2044(6)	0.145(1)	-0.078(1)	6(1)*
N(9)	0.2159(4)	0.1260(9)	0.0729(9)	5(1)*
N(10)	0.2585(4)	0.343(1)	-0.1424(8)	5(1)*
N(11)	0.2160(4)	0.3957(9)	-0.055(1)	5(1)*
N(12)	0.2934(4)	0.3915(8)	-0.033(1)	5(1)*
C(1)	0.3950(6)	0.270(1)	0.593(1)	4.6(6)
C(2)	0.3568(5)	0.267(1)	0.620(1)	6.3(6)
C(3)	0.4462(7)	0.373(1)	0.486(2)	5.8(7)
C(4)	0.449(1)	0.438(2)	0.445(2)	5(1)
C(4')	0.427(1)	0.430(2)	0.455(3)	6(1)
C(5)	0.4297(7)	0.120(1)	0.569(2)	7.9(8)
C(6)	0.4366(7)	0.054(1)	0.591(1)	9.3(9)
C(7)	0.4271(7)	0.106(1)	0.444(2)	8.3(8)
C(8)	0.4100(6)	0.148(1)	0.395(1)	5.0(6)
C(9)	0.3911(6)	0.122(1)	0.344(1)	5.1(6)
C(10)	0.3741(5)	0.164(1)	0.304(1)	4.7(6)
C(11)	0.3762(6)	0.225(1)	0.312(1)	6.0(6)
C(12)	0.3981(5)	0.245(1)	0.367(1)	4.6(6)
C(13)	0.4824(7)	0.120(1)	0.498(1)	7.2(7)
C(14)	0.5018(6)	0.153(1)	0.443(1)	4.8(6)
C(15)	0.5336(6)	0.132(1)	0.417(1)	5.8(6)
C(16)	0.5503(6)	0.173(1)	0.376(1)	6.8(7)
C(17)	0.5392(7)	0.231(1)	0.362(1)	7.6(8)
C(18)	0.5068(6)	0.247(1)	0.389(1)	5.2(6)
C(19)	0.5396(8)	0.346(2)	0.578(2)	9.0(9)
C(20)	0.537(1)	0.404(3)	0.567(3)	10(2)
C(20')	0.578(2)	0.365(4)	0.573(4)	10(2)
C(21)	0.5252(6)	0.350(1)	0.699(1)	6.0(7)
C(22)	0.4971(6)	0.395(1)	0.713(1)	4.5(6)
C(23)	0.5012(6)	0.444(1)	0.759(1)	5.2(6)
C(24)	0.4728(6)	0.479(1)	0.773(1)	5.5(6)
C(25)	0.4427(6)	0.467(1)	0.741(1)	6.0(6)
C(26)	0.4400(6)	0.414(1)	0.699(1)	5.3(6)
C(27)	0.5336(5)	0.251(1)	0.644(1)	4.9(6)
C(28)	0.5094(7)	0.218(1)	0.689(1)	5.4(6)
C(29)	0.5190(7)	0.165(2)	0.723(2)	8.6(8)
C(30)	0.4955(7)	0.131(1)	0.758(1)	7.2(7)
C(31)	0.4626(7)	0.152(1)	0.763(1)	7.3(7)
C(32)	0.4539(6)	0.206(1)	0.731(1)	5.2(6)

(continued)

Table 2 (continued)

Atom	x	y	z	B_{eq} (\AA^2)
C(33)	0.2384(6)	0.304(1)	0.107(1)	4.4(6)
C(34)	0.2306(6)	0.333(1)	0.176(1)	8.6(8)
C(35)	0.2967(6)	0.208(1)	-0.021(1)	5.1(6)
C(36)	0.3295(6)	0.173(1)	-0.041(1)	6.6(7)
C(37)	0.155(1)	0.252(2)	0.053(2)	12(1)
C(38)	0.156(2)	0.306(4)	0.048(4)	14(3)
C(38')	0.116(2)	0.271(3)	0.041(3)	12(2)
C(39)	0.1531(6)	0.202(1)	-0.050(2)	7.4(7)
C(40)	0.1722(8)	0.164(1)	-0.092(1)	7.0(8)
C(41)	0.1571(8)	0.141(2)	-0.158(2)	11(1)
C(42)	0.1810(8)	0.106(1)	-0.190(1)	8.6(9)
C(43)	0.2122(8)	0.087(1)	-0.183(2)	10(1)
C(44)	0.2254(7)	0.112(2)	-0.114(2)	8.3(9)
C(45)	0.1559(6)	0.145(1)	0.056(1)	6.8(7)
C(46)	0.1841(6)	0.114(1)	0.089(1)	4.8(6)
C(47)	0.1767(6)	0.068(1)	0.137(1)	5.5(6)
C(48)	0.2015(6)	0.035(1)	0.167(1)	6.3(7)
C(49)	0.2355(6)	0.048(1)	0.149(1)	5.9(7)
C(50)	0.2408(6)	0.096(1)	0.101(1)	5.3(6)
C(51)	0.2756(6)	0.292(1)	-0.178(1)	5.6(6)
C(52)	0.2762(6)	0.294(1)	-0.254(1)	8.2(8)
C(53)	0.2218(6)	0.351(1)	-0.164(1)	5.5(6)
C(54)	0.2048(6)	0.395(1)	-0.117(1)	4.5(6)
C(55)	0.1775(7)	0.433(1)	-0.140(1)	7.0(7)
C(56)	0.1607(7)	0.470(2)	-0.094(2)	10(1)
C(57)	0.1739(7)	0.472(1)	-0.028(2)	9.1(8)
C(58)	0.2016(7)	0.433(1)	-0.010(1)	7.9(8)
C(59)	0.2780(6)	0.400(1)	-0.153(1)	6.2(7)
C(60)	0.2999(6)	0.418(1)	-0.094(1)	5.4(6)
C(61)	0.3285(7)	0.465(1)	-0.096(1)	7.3(7)
C(62)	0.3444(6)	0.479(1)	-0.037(2)	7.4(8)
C(63)	0.3380(7)	0.451(1)	0.020(1)	7.3(7)
C(64)	0.3116(6)	0.405(1)	0.020(1)	6.3(7)

* Only starred atoms were refined anisotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab\{\cos \gamma\}B_{12} + ac\{\cos \beta\}B_{13} + bc\{\cos \alpha\}B_{23}]$. Numbers in parentheses are e.s.d.s in the least significant digits.

a variety of conditions. The most common methods involve either the use of commercially available 'Mn(OAc)₃·2H₂O' along with some additional acetate source or the oxidation of Mn(II) salts by MnO₄⁻ in an appropriate solvent at a particular effective pH [18]. The title compound was prepared in good yield by using 'Mn(OAc)₃·2H₂O' in methanol. Addition of solid Mn(OAc)₃·2H₂O to a stirred methanol solution of the ligand bpea gave a deep brown solution within 30 min by which time all of the manganese starting material was dissolved. To the reaction mixture (after filtration), NaClO₄ was added to supply the counter anion and an excess of it along with NaOAc was separated when the MeOH was evaporated and the compound was redissolved in CH₂Cl₂. Compound 1 was obtained in pure form simply by removal of CH₂Cl₂ without requiring crystallization. We will discuss the structure of this complex first and follow with a summary of its physical properties.

3.2. Description of the structure

There are two independent molecules of compound **1** in the crystallographic asymmetric unit. The structures of the two independent cations of **1**, which are not significantly different, are shown in Fig. 1. For each pair of molecules of compound **1** there is one molecule of water in the lattice. The cations each possess a dinuclear oxo-bis(acetato) bridged core structure. The Mn atoms are in a distorted octahedral environment of three oxygen atoms and three nitrogen atoms. The bpea ligand is coordinated to the metal center in a facial mode as dictated by the orientation of the bridging ligands. Both cations have pseudo two-fold symmetry with the bpea aliphatic nitrogen atoms situated *cis* to the bridging oxo group. Selected bond distances and angles for **1** are presented in Table 3. For **1**, the Mn···Mn separation of 3.11 Å falls in the range observed for other species that contain the $\{\text{Mn}_2\text{O}(\text{O}_2\text{CR})_2\}^{2+}$ core (3.08–3.17 Å, see Table 4) [18]. The ranges for Mn–O_{oxo} distances (1.74–1.81 Å) and Mn–O–Mn angles (117.9–125.1°) for this class of compounds also encompass the corresponding average parameters found for **1** (1.77 Å, 122.7°, respectively). The manganese to carboxylate distances for **1** are in the range 2.00–2.09 Å, with no dramatic variation resulting

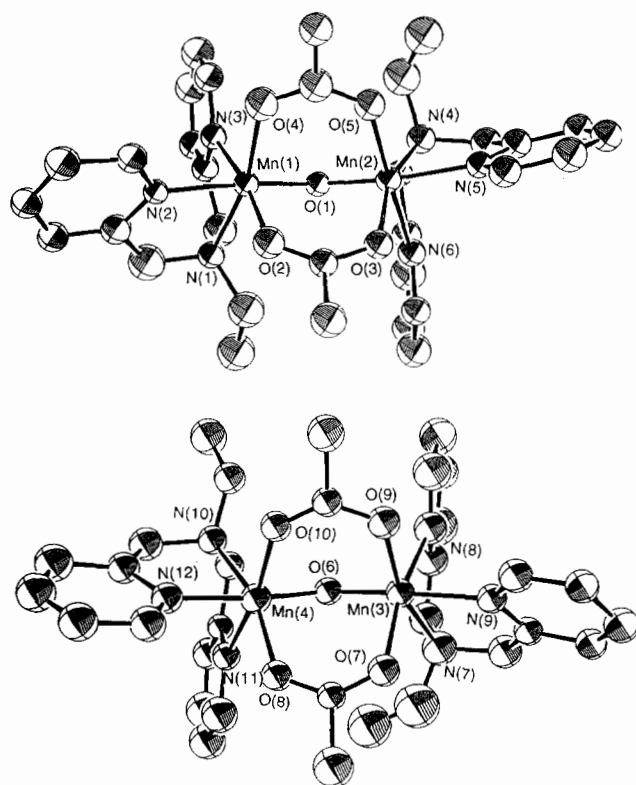


Fig. 1. ORTEP drawings of the two independent cations in **1**. Atoms are drawn at the 35% probability level; hydrogen atoms are not included for clarity. Only one orientation for the disordered atoms is shown.

Table 3

Selected bond distances (Å) and angles (°) for $[\text{Mn}_2\text{O}(\text{OAc})_2(\text{bpea})_2](\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ ^a

Bond distances			
Mn(1)–O(1)	1.79(1)	Mn(3)–O(6)	1.77(2)
Mn(1)–O(2)	2.00(2)	Mn(3)–O(7)	2.07(2)
Mn(1)–O(4)	2.06(2)	Mn(3)–O(9)	2.00(2)
Mn(1)–N(1)	2.22(2)	Mn(3)–N(7)	2.22(2)
Mn(1)–N(2)	2.05(2)	Mn(3)–N(8)	2.25(2)
Mn(1)–N(3)	2.17(2)	Mn(3)–N(9)	2.04(2)
Mn(2)–O(1)	1.75(2)	Mn(4)–O(6)	1.78(2)
Mn(2)–O(3)	2.03(1)	Mn(4)–O(8)	2.00(2)
Mn(2)–O(5)	2.07(2)	Mn(4)–O(10)	2.09(2)
Mn(2)–N(4)	2.20(2)	Mn(4)–N(10)	2.18(2)
Mn(2)–N(5)	2.03(2)	Mn(4)–N(11)	2.20(2)
Mn(2)–N(6)	2.24(2)	Mn(4)–N(12)	2.03(2)
Bond angles			
O(1)–Mn(1)–O(2)	97.3(6)	O(6)–Mn(3)–O(9)	96.9(6)
O(1)–Mn(1)–O(4)	97.4(6)	O(6)–Mn(3)–N(7)	93.7(7)
O(1)–Mn(1)–N(1)	93.0(7)	O(6)–Mn(3)–N(8)	87.9(7)
O(1)–Mn(1)–N(2)	171.7(7)	O(6)–Mn(3)–N(9)	174.5(6)
O(1)–Mn(1)–N(3)	87.3(6)	O(7)–Mn(3)–O(9)	98.4(6)
O(2)–Mn(1)–O(4)	92.8(6)	O(7)–Mn(3)–N(7)	93.8(8)
O(2)–Mn(1)–N(1)	94.1(7)	O(7)–Mn(3)–N(8)	167.4(7)
O(2)–Mn(1)–N(2)	85.5(6)	O(7)–Mn(3)–N(9)	84.5(7)
O(2)–Mn(1)–N(3)	170.4(7)	O(9)–Mn(3)–N(7)	162.7(9)
O(4)–Mn(1)–N(1)	166.7(7)	O(9)–Mn(3)–N(8)	92.6(7)
O(4)–Mn(1)–N(2)	90.3(7)	O(9)–Mn(3)–N(9)	88.2(6)
O(4)–Mn(1)–N(3)	94.9(7)	N(7)–Mn(3)–N(8)	74.1(9)
N(1)–Mn(1)–N(2)	79.0(7)	N(7)–Mn(3)–N(9)	80.8(8)
N(1)–Mn(1)–N(3)	77.2(7)	N(8)–Mn(3)–N(9)	89.8(7)
N(2)–Mn(1)–N(3)	88.8(6)	O(6)–Mn(4)–O(8)	98.3(6)
O(1)–Mn(2)–O(3)	99.3(6)	O(6)–Mn(4)–O(10)	93.7(6)
O(1)–Mn(2)–O(5)	96.2(6)	O(6)–Mn(4)–N(10)	93.0(7)
O(1)–Mn(2)–N(4)	90.0(6)	O(6)–Mn(4)–N(11)	89.4(6)
O(1)–Mn(2)–N(5)	168.8(6)	O(6)–Mn(4)–N(12)	173.8(8)
O(1)–Mn(2)–N(6)	85.3(6)	O(8)–Mn(4)–O(10)	98.5(6)
O(3)–Mn(2)–O(5)	91.9(6)	O(8)–Mn(4)–N(10)	160.8(7)
O(3)–Mn(2)–N(4)	159.2(6)	O(8)–Mn(4)–N(11)	90.6(7)
O(3)–Mn(2)–N(5)	91.7(6)	O(8)–Mn(4)–N(12)	87.8(7)
O(3)–Mn(2)–N(6)	88.9(6)	O(10)–Mn(4)–N(10)	96.3(7)
O(5)–Mn(2)–N(4)	105.6(7)	O(10)–Mn(4)–N(11)	169.8(7)
O(5)–Mn(2)–N(5)	85.1(6)	O(10)–Mn(4)–N(12)	84.5(6)
O(5)–Mn(2)–N(6)	178.2(6)	N(10)–Mn(4)–N(11)	73.9(7)
N(4)–Mn(2)–N(5)	79.0(7)	N(10)–Mn(4)–N(12)	81.4(9)
N(4)–Mn(2)–N(6)	73.3(7)	N(11)–Mn(4)–N(12)	91.4(7)
N(5)–Mn(2)–N(6)	93.2(6)	Mn(1)–O(1)–Mn(2)	123.3(7)
O(6)–Mn(3)–O(7)	96.8(7)	Mn(3)–O(6)–Mn(4)	122.1(8)

^a E.s.d.s in the least significant figure are given in parentheses.

from *trans* ligation differences, in contrast to what is seen for the bpy-ligated $\{\text{Mn}_2\text{O}(\text{O}_2\text{CR})_2\}^{2+}$ core species (Table 4). The pyridine rings in each bpea ligand can be placed into two different groups; the nitrogen atoms in set I are *trans* to the bridging oxo group while the nitrogens in set II are *cis* to the bridging oxo group and *trans* to one of the bridging acetate oxygen atoms. The average Mn–N distance for set I is 2.04 Å while that for the pyridine rings in set II is 2.21 Å. This marked shortening of Mn–N bonds *trans* to the bridging oxo group attached to an Mn(III) center was also noted for the $[\text{Mn}_2\text{O}(\text{OAc})_2(\text{HBpz}_3)_2]$ complex [18b]. One

Table 4

Comparison of some structural data ^a and spin exchange coupling constants ^b for the complexes ^c containing the [Mn₂(μ-O)(μ-OAc)₂]²⁺ core

Compound	Mn–Mn (Å)	Mn–μ-O (Å)	Mn–O _{carb} (Å)	∠Mn–O–Mn (°)	<i>J</i> (cm ⁻¹)	Ref.
[Mn ₂ O(OAc) ₂ (bpea) ₂](ClO ₄) ₂ (1) ^d	3.120(5) 3.106(6)	1.79(1) 1.75(2) 1.77(2) 1.78(2)	2.00(2) 2.06(2) 2.03(1) 2.07(2) 2.07(2) 2.00(2) 2.00(2) 2.09(2)	123.3(7) 122.1(8)	^e	this work
[Mn ₂ O(OAc) ₂ (bpy) ₂ (H ₂ O)(S ₂ O ₈)]·H ₂ O (2)	3.145(5)	1.735(10) 1.810(10)	1.949(12) 2.147(11) 1.933(11) 2.152(12)	125.1(6)	n.r.	[18d]
[Mn ₂ O(OAc) ₂ (H ₂ O) ₂ (bpy) ₂]- (PF ₆) ₂ ·1.75H ₂ O (3a)	3.132	1.781(5) 1.784(5)	2.142(6) 1.937(5) 1.939(5) 2.174(6)	122.9	-3.4	[18c]
[Mn ₂ O(OAc) ₂ (H ₂ O) ₂ (bpy) ₂](ClO ₄) ₂ (3b)	3.152(2)	1.793(4) 1.800(4)	2.175(4) 1.946(4) 1.939(4) 2.164(4)	122.7(2)	n.r.	[18i]
[Mn ₂ O(OAc) ₂ (HB(pz) ₃) ₂]·4CH ₃ CN (4a)	3.159(1)	1.773(2) 1.787(2)	2.044(2) 2.083(2) 2.085(3) 2.053(2)	125.1(1)	-0.2	[18b]
[Mn ₂ O(OAc) ₂ (HB(pz) ₃) ₂]·CH ₃ CN (4b)	3.175(1)	1.790(3)	2.001(6) 2.133(6)	125.0(3)	-0.7	[18b]
[Mn ₂ O(OAc) ₂ (tacn) ₂](ClO ₄) ₂ (5)	3.084(3)	1.80(1)	1.94(1) 2.05(1)	117.9(2)	n.r.	[18a]
[Mn ₂ O(OAc) ₂ (Me ₃ tacn) ₂](ClO ₄) ₂ ·H ₂ O (6a)	n.r.	1.810(4)	2.047(4)	120.9(1)	+9.0	[18a,e]
[Mn ₂ O(OAc) ₂ (Me ₃ tacn) ₂](I ₃)I·H ₂ O (6b)	3.096(2)	1.790(6) 1.787(6)	2.057(6) 2.059(6) 2.072(6) 2.063(6)	119.9(3)	n.r.	[18f]
[Mn ₂ O(OAc) ₂ (tacn)(Me ₃ tacn)](ClO ₄) ₂ (7) ^f					+7.0	[18g]
[Mn ₂ O(OAc) ₂ (tmip) ₂](ClO ₄) ₂ ·2CH ₃ CN·0.5(CH ₃) ₂ CO (8a)	3.164(5)	1.797(11) 1.781(11)	2.115(13) 2.155(13) 1.993(13) 1.965(13)	124.4(6)	-0.5	[18h]
[Mn ₂ O(OAc) ₂ (tmip) ₂](PF ₆) ₂ (8b) ^f					-0.2	[18h]
[Mn ₂ O(OAc) ₂ (bbiae) ₂](ClO ₄) ₂ ·2CH ₃ CN (9) ^f					-1.72	[18j]
[Mn ₂ O(O ₂ CC ₆ H ₅) ₂ (N ₃) ₂ (bpy) ₂] (10)	3.153(4)	1.802(4)	2.131(7) 2.043(7)	122.0(5)	+8.8	[18i]
[Mn ₂ O(OAc) ₂ Cl ₂ (bpy) ₂]·CH ₃ COOH·H ₂ O (11)	3.153(4)	1.788(11) 1.777(12)	2.214(12) 2.196(13) 1.955(13) 1.934(13)	124.3(7)	-4.1	[18i]

^a O_{carb} = oxygen atom from bridging carboxylate group.^b Values using $\mathcal{H} = -2JS_1 \cdot S_2$ convention: $J > 0$ implies weakly ferromagnetic, $J < 0$ implies weakly antiferromagnetic.^c For abbreviations of the ligands see p. 1.^d There are two independent molecules in the asymmetric unit.^e Will be reported elsewhere.^f Not structurally characterized.

n.r. = not reported.

Table 5

Comparison of spectroscopic ^{a,b} and electrochemical ^c data for the complexes ^d containing the [Mn₂(μ-O)(μ-OAc)₂]²⁺ core

Compound	UV-Vis λ (nm) (ε (M ⁻¹ cm ⁻¹))	IR ν(μ-OAc) (cm ⁻¹)	Electrochemical data		Ref.
			E _{1/2} ^{ox}	E _{1/2} ^{red}	
[Mn ₂ O(OAc) ₂ (bpea) ₂](ClO ₄) ₂ (1)	728(112) ^c 569, sh 545, sh 521(372) 487(517) 377, sh	1566 1432	+0.66 ⁱ	-0.39 ^j	this work
[Mn ₂ O(OAc) ₂ (H ₂ O) ₂ (bpy) ₂](PF ₆) ₂ ·1.75H ₂ O (3a)	640(108) ^c 490(146) 385(300) 295(5670) 240(5800)	1600 1420			[18c]
[Mn ₂ O(OAc) ₂ (HB(pz) ₃) ₂] (4)	760(58) ^b 582, sh(95) 540, sh(165) 524, sh(175) 503, sh(190) 486(210) 458, sh(165) 385, sh(405) 283(6000)	1580 1410	+0.51 ⁱ +1.22 ⁱ	-1.20 ^j	[18b]
[Mn ₂ O(OAc) ₂ (tacn) ₂](ClO ₄) ₂ (5)	910(40) ^c 665(95) 570, sh 560, sh 545, sh 520(250) 495(324) 280(3800) 232(3400)	1570 1450 1415	+0.28 ⁱ	-1.0 ^j	[18a,e]
[Mn ₂ O(OAc) ₂ (Me ₃ tacn) ₂](ClO ₄) ₂ ·H ₂ O (6a)	1000(63) ^c 720(104) 521(638) 486(667) 300(14000) 250, sh	1570 1450 1415	+0.585	-0.50 ^j	[18a,e]
[Mn ₂ O(OAc) ₂ (tacn)(Me ₃ tacn)](ClO ₄) ₂ (7)	680, sh(200) ^c 521(740) 481(770) 304(12000) 246(11000)	n.r.	n.r.		[18g]
[Mn ₂ O(OAc) ₂ (tmip) ₂](ClO ₄) ₂ ·2CH ₃ CN·0.5(CH ₃) ₂ CO (8a)	736(106) ^c 568, sh(216) 521, sh(349) 497(383) 484(405) 464(330) 376(844) 255(23900)	n.r.	+0.59 ⁱ	-0.70 ^j	[18h]
[Mn ₂ O(OAc) ₂ (tmip) ₂](PF ₆) ₂ (8b)	757(130) ^c 568, sh(240) 521, sh(400) 502(430) 485(460) 464, sh(360) 372, sh(840) 249(24900)	n.r.	n.r.		[18h]

(continued)

Table 5 (continued)

Compound	UV-Vis λ (nm) (ϵ ($M^{-1} \text{ cm}^{-1}$))	IR $\nu(\mu\text{-OAc})$ (cm^{-1})	Electrochemical data		Ref.
			$E_{1/2}^{\text{ox}}$	$E_{1/2}^{\text{red}}$	
$[\text{Mn}_2\text{O}(\text{C}_6\text{H}_5\text{CO}_2)_2(\text{N}_3)_2(\text{bpy})_2]$ (10)	416, sh(492) ^f 280(17000)	n.r.	+0.18 ⁱ +0.51 ^j	n.c.	[18i]
$[\text{Mn}_2\text{O}(\text{OAc})_2\text{Cl}_2(\text{bpy})_2] \cdot \text{CH}_3\text{COOH} \cdot \text{H}_2\text{O}$ (11)	556(246) ^g 492(361)	n.r.	+0.38 ⁱ +0.95 ^j	n.c.	[18i]
$[\text{Mn}_2\text{O}(\text{O}_2\text{CC}_2\text{H}_5)_2\text{Cl}_2(\text{bpy})_2] \cdot 3\text{C}_2\text{H}_5\text{COOH} \cdot \text{H}_2\text{O}$ (12)	468, sh(275) ^f 283(7000)	n.r.	+0.40 ⁱ	n.c.	[18i]
$[\text{Mn}_2\text{O}(\text{O}_2\text{CC}_6\text{H}_5)_2\text{Cl}_2(\text{bpy})_2] \cdot 2\text{H}_2\text{O}$ (13)	502, sh(135) ^f 340, sh(740) 280(15000)	n.r.	+0.41 ⁱ +0.95 ^j	n.c.	[18i]
$[\text{Mn}_2\text{O}(\text{OAc})_2(\text{pepmma})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (14)	n.a.	n.a.	+0.84 ^h	-0.36 ^j	[18k]

^a All electronic spectra were recorded in solution.

^b All IR spectra were recorded in the solid state.

^c All potentials reported vs. Fc^+/Fc couple.

^d For abbreviations of the ligands see p. 1.

^e CH_3CN as solvent.

^f DMF as solvent.

^g CH_2Cl_2 as solvent.

^h Originally reported as vs. SCE (-0.36 correction factor).

ⁱ Quasi-reversible.

^j Irreversible.

n.r. = not reported; n.a. = not available from the paper; n.c. = not conclusive as indicated in the reference.

interpretation for this phenomenon, as set out previously, is that the N atom *trans* to the oxo group lies along an empty d_σ orbital while the *cis* N atom lone pair is directed toward a half-filled d_σ orbital. Thus, with less antibonding electron density in the *trans* Mn–N region, one can rationalize the shorter bond observed.

3.3. Physical properties

As for other complexes containing the $\{\text{Mn}_2\text{O}(\text{O}_2\text{CCH}_3)_2\}^{2+}$ core [18], the IR spectrum of compound **1** displays prominent ν_{as} (1566 cm^{-1}) and ν_{s} (1432 cm^{-1}) vibrations of the O–C–O portion of the μ -acetate group. Data for related species are supplied in Table 5, inspection of which reveals that the ranges for O–C–O ν_{as} and ν_{s} frequencies for carboxylates in the $\{\text{Mn}_2\text{O}(\text{O}_2\text{CCH}_3)_2\}^{2+}$ core are 1410–1450 and 1566–1600 cm^{-1} , respectively.

The electronic absorption spectrum of $[\text{Mn}_2\text{O}(\text{OAc})_2(\text{bpea})_2]^{2+}$ in acetonitrile (not shown) from 300–900 nm shows maxima at 728 ($\epsilon = 112 \text{ M}^{-1} \text{ cm}^{-1}$), 521 ($\epsilon = 372 \text{ M}^{-1} \text{ cm}^{-1}$), and 487 ($\epsilon = 517 \text{ M}^{-1} \text{ cm}^{-1}$) nm. In addition to these peaks three shoulders at 569, 545 and 377 nm are also observed. The spectrum of **1** has features in common with other species possessing the same bridged core (Table 5), indicating that these bands are characteristic for this structural type. For example, a peak is observed in the range 481–492 nm for many of the species in Table 5, including $\{\text{Mn}_2\text{O}(\text{O}_2\text{CR})_2\text{L}_2\}$ where L = bpea, tacn, Me_3tacn ,

HBpz_3^- , tmip, and the mixed ligand sets (bpy, H_2O) and (bpy, Cl). Several of the above species display a neighboring maximum in the vicinity of 520 nm, and then there is usually a series of shoulders. Visible spectra of the Me_3tacn , HBpz_3^- and tmip compounds have bands which appear to correlate with the 728 nm band for **1** at 720, 760 and 736 nm, respectively. Definitive assignment of the above features awaits an examination of the magnetic circular dichroism spectra, a task that was recently carried out for compounds with the $\{\text{Mn}_2\text{O}_2(\text{O}_2\text{CCH}_3)_2\}^{2+}$ core [27]. It is likely that the broad, structured maximum at 487 nm in **1** is principally oxo-to-Mn charge transfer in origin.

Cyclic voltammetric studies (E_{pa} , anodic peak potential; E_{pc} , cathodic peak potential; $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$; $\Delta E_{\text{p}} = E_{\text{pa}} - E_{\text{pc}}$) of **1** in acetonitrile at 298 K indicate one quasi-reversible oxidation wave at $E_{1/2} = +0.66 \text{ V}$ ($\Delta E_{\text{p}} = 80 \text{ mV}$) versus external Fc/Fc^+ , and an irreversible reduction at $E_{\text{pc}} = -0.39 \text{ V}$ versus external Fc/Fc^+ with no corresponding oxidation peak. Both processes are assumed to be metal-centered. The values for **1** are close to those reported for the related pepmma complex (Table 5); an expected result as the ligands differ by only one methylene unit. A more basic ligand such as tacn stabilizes the higher oxidation state as is evident from the 0.38 V shift in its oxidation potential relative to **1**. It is interesting to note that the oxidation potential can be tuned over a range of +0.18 to +0.84 V by variation of terminal and R group of the bridging carboxylate ligands. The first reduction potentials in

Table 5 are spread over a similarly wide range with the bpea and pepmma complexes being the easiest to reduce.

Compound **1** is very moisture sensitive and similar behavior has been observed for other complexes [13c,18b]. It is stable in dry acetonitrile for at least a week, however in a 1:1 mixture of acetonitrile and water the color of the solution changed from red–brown to deep green in several minutes. Addition of excess NaClO₄ to the green solution gives a green precipitate. This green precipitate has been shown to be [Mn₂O₂(OAc)(bpea)₂](ClO₄)₂ by UV–Vis and EPR spectroscopy. While the title compound does not show any EPR signal under very dry conditions, this latter complex displays a 16-line $g = 2$ EPR signal. This mixed-valent (III,IV) complex has been structurally characterized and reported recently from our laboratory [20].

4. Conclusions

A novel binuclear manganese(III) species has been prepared, purified and characterized using single crystal X-ray diffraction techniques. The solid state structural, IR and solutions properties are in accord with other species possessing the [Mn₂O(O₂CCH₃)₂]²⁺ core. Complex **1** is prone to disproportionation in the presence of water. We plan to use it as starting material for further controlled aggregation chemistry with goal of mimicking the PSII active site aggregate.

5. Supplementary material

Full tables of crystallographic parameters and structure refinement, positional and isotropic thermal parameters, bond distances, bond angles and components of the anisotropic thermal parameters for **1** (27 pages), and observed and calculated structure factors (25 pages) for **1** are available from author W.H.A.

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