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Synthesis and characterization of a new dinuclear bis(μ -oxo)manganese(III)/manganese(IV) complex

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Abstract

[(pmap)Mn-(μ -O)₂-Mn(pmap)](ClO₄)₃, a dinuclear bis(μ -oxo)manganese (III, IV) complex, was synthesized by the reaction of Mn(ClO₄)₂ with bis[2-(2-pyridyl)ethyl]-2-pyridylmethylamine (= pmap) and hydrogen peroxide. The complex was characterized structurally and EPR-measurements showed the characteristic 16 line signal for a bis-(μ -oxo)Mn(III)/Mn(IV) dimer. The corresponding complex with tris[2-(2-pyridyl)ethyl]amine (= tepa) could not be synthesized; it is most likely that in this complex, the Mn–Mn separation would be too long for a bis(μ -oxo) bridge. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Manganese complexes; Tripodal ligand complexes; Oxo-bridged complexes; Crystal structures

1. Introduction

Interest in the chemistry of dinuclear and polynuclear manganese complexes derives mainly from the fact that such species are involved in important electron transfer reactions in biological systems. For example, the dioxygen-evolving complex in photosystem II of green plants consists of a tetranuclear manganese cluster, probably built by bis(μ -oxo) dimeric manganese units [1]. After these findings, a large number of different dinuclear manganese complexes in variable oxidation states have been synthesized and investigated [2]. More recently, a functional model for the O–O bond formation by the dioxygen-evolving complex in photosystem II was presented, based on the complex [H₂O(terpy)Mn(O)₂Mn(terpy)OH₂](NO₃)₃ (terpy = 2,2':6',2''-terpyridine) [3].

The tripodal ligand tmpa (= tris(2-pyridylmethyl)amine, Fig. 1) has proven to be a versatile ligand in bioinorganic chemistry; different metal complexes with this ligand have been synthesized and characterized

(examples are given in the references) [4–9]. In the case of manganese, a mononuclear eight coordinated Mn(II) complex with two tmpa ligands could be isolated and characterized structurally [6]. Furthermore, it was possible to obtain the dinuclear bis-(μ -oxo) complexes Mn(III)–Mn(IV) and Mn(IV)–Mn(IV) [6,10,11].

If the ligand tmpa is coordinated to a metal ion, each of its pyridine arms forms a five membered chelate ring. An increasing arm length leads to the ligand series shown in Fig. 1.

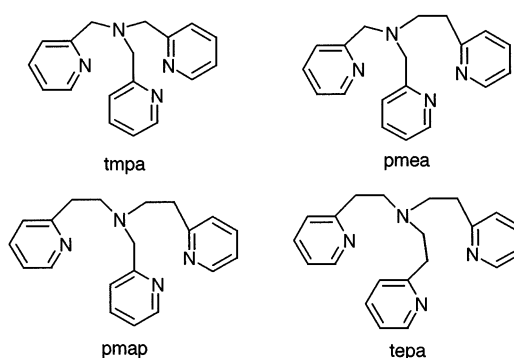


Fig. 1. Tripodal ligand series derived from tmpa by increasing the length of the pyridine arms.

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Table 1

Complex	1 ·CH ₃ CN
Empirical formula	C ₄₂ H ₄₇ Cl ₃ Mn ₂ N ₉ O ₁₄
Formula weight	1118.12
Temperature (K)	200(2)
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$ (no. 2)
<i>a</i> (Å)	10.4277(2)
<i>b</i> (Å)	12.39840(10)
<i>c</i> (Å)	19.4145(3)
α (°)	83.3406(9)
β (°)	86.6774(4)
γ (°)	68.6677(11)
<i>V</i> (Å ³)	2321.95(6)
<i>Z</i>	2
<i>D</i> _{calc} (Mg m ^{−3})	1.599
Absorption coefficient (mm ^{−1})	0.794
<i>F</i> (000)	1150
Crystal size (mm ³)	0.3 × 0.4 × 0.2
θ Range for data collection	1.77–28.25
Index ranges	−13 = <i>h</i> = 13, −16 = <i>k</i> = 15, −25 = <i>l</i> = 25
Reflections collected/unique	23389/10727 [<i>R</i> _{int} = 0.0460]
Completeness to $\theta = 28.25$	93.5%
Data/restraints/parameters	10727/10/739
Goodness of fit on <i>F</i> ²	1.115
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0776, <i>wR</i> ₂ = 0.1644
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1222, <i>wR</i> ₂ = 0.1845
Largest difference peak and hole (e Å ^{−3})	1.268 and −0.615

The bis(μ -oxo)dimanganese(III, IV) dimer of pmea (= [2-(2-pyridyl)ethyl]bis(2-pyridylmethyl)amine) has been synthesized and studied thoroughly [12]. In contrast, manganese complexes with pmap (bis[2-(2-pyridyl)ethyl]-2-pyridylmethylamine) or tepa (tris[2-(2-pyridyl)ethyl]amine) are unknown so far.

An increase in the size of the chelate rings is expected to favor low oxidation states. We therefore decided to test whether it is still possible to synthesize the bis(μ -oxo)dimanganese(III, IV) dimers with pmap and tepa. An additional aim was to prepare the corresponding Mn(III)–Mn(III) complex since such complexes are extremely rare [13].

2. Experimental

2.1. Materials and methods

Reagents and solvents used were of commercially available reagent grade quality. pmap was synthesized as described earlier [4]. tepa was prepared according to the literature [14]. UV–Vis spectra were measured on a

Hewlett Packard 8452 A spectrophotometer. Cyclic voltammetry was performed with an EG&G potentiostat (model 263) at 25°C with a scan rate of 100 mV s^{−1}. Solutions studies contained 1 mM manganese complex and 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile. A conventional H-type cell was used with a glassy carbon, Pt and Ag/AgCl as working, counter and reference electrodes, respectively. Ferrocene was added as an internal standard at the end of each measurement. Electron spin resonance measurements at X-band frequency were obtained using a Bruker EMX-113 spectrometer. Samples in *N*-methylformamide were measured at 100 K. All EPR spectra were simulated with the Bruker SIMFONIA program.

2.1.1. [(pmap)Mn-(μ -O)₂-Mn(pmap)](ClO₄)₃·CH₃CN (**1**·CH₃CN)

To 0.5 g (1.57 mmol) of pmap in a small amount of ethanol 0.6 g (1.65 mmol) of Mn(ClO₄)₂·6 H₂O dissolved in 10 ml of water was added. A few drops of H₂O₂ (30%) were added and the solution was stirred for 1 h. The solid material was collected in a glass frit and redissolved in acetonitrile. This solution was filtered, then slow evaporation of acetonitrile was allowed. After a few days dark green crystals suitable for X-ray crystal structure analysis were obtained (yield: 0.3 g, 34%). When the crystals were dried in air, the acetonitrile was lost. *Anal.* Calc. for C₄₀H₄₄Cl₃Mn₂N₈O₁₄: C, 44.61; H, 4.12; N, 10.40. Found: C, 44.07; H, 4.32; N, 10.44%.

2.2. X-ray data collection and structure refinement details

Crystal data and experimental conditions are listed in Table 1. The molecular structure is illustrated in Fig. 2. Selected bond lengths and bond angles with standard deviations in parentheses are presented in Table 2. Intensity data were collected on a Siemens SMART 5000 CCD-diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The exposure time was 10 s per frame collected with the ω -scan technique ($\Delta\omega = 0.3^\circ$). The collected reflections were corrected for Lorentz, polarization and absorption effects. The structures were solved by direct methods and refined by full-matrix least-squares methods on *F*² [15–17].

3. Results and discussion

So far, only in a very few cases, pmap was used as a ligand in metal complexes [4,18]. Its synthesis is straightforward; in contrast to tmpa, it forms one five membered and two six membered chelate rings when coordinated to a metal ion. Efforts to isolate the man-

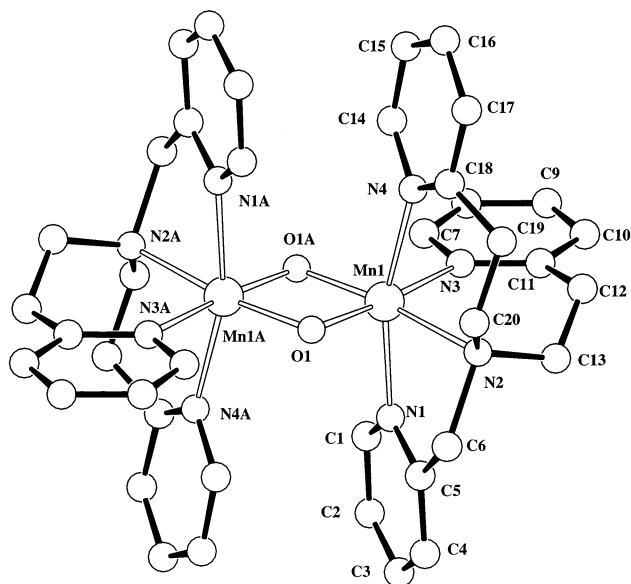


Fig. 2. Molecular structure of the cation of **1** (only one of the molecular structures in the crystal is shown; atoms with index A are obtained by symmetry operations).

Table 2
Selected bond lengths (Å) and angles (°) for **1**·CH₃CN

Mn1–O1A	1.813(3)	Mn2–O2A	1.811(3)
Mn1–O1	1.821(3)	Mn2–N5	2.110(4)
Mn1–N2	2.114(5)	Mn2–N6	2.121(5)
Mn1–N3	2.123(4)	Mn2–N7	2.123(5)
Mn1–N1	2.134(4)	Mn2–N8	2.155(5)
Mn1–N4	2.154(5)	Mn2–Mn2A	2.7379(13)
Mn1–Mn1A	2.7393(13)	Mn2–O2	1.819(3)
O1A–Mn1–O1	82.15(13)	O2–Mn2–N5	91.27(14)
O1A–Mn1–N2	172.12(17)	O2A–Mn2–N5	173.29(14)
O1–Mn1–N2	91.23(17)	O2–Mn2–N6	172.34(19)
O1A–Mn1–N3	91.86(14)	O2A–Mn2–N6	91.34(17)
O1–Mn1–N3	173.99(15)	N5–Mn2–N6	95.23(17)
N2–Mn1–N3	94.78(17)	O2–Mn2–N7	97.56(16)
O1A–Mn1–N1	97.01(15)	O2A–Mn2–N7	93.18(15)
O1–Mn1–N1	94.53(15)	N5–Mn2–N7	86.78(15)
N2–Mn1–N1	79.2(2)	N6–Mn2–N7	78.8(2)
N3–Mn1–N1	86.68(15)	O2–Mn2–N8	96.52(16)
O1A–Mn1–N4	96.83(16)	O2A–Mn2–N8	95.05(16)
O1–Mn1–N4	94.53(15)	N5–Mn2–N8	86.56(16)
N2–Mn1–N4	87.9(2)	N6–Mn2–N8	87.9(2)
N3–Mn1–N4	85.63(15)	N7–Mn2–N8	164.54(16)
N1–Mn1–N4	164.36(15)	O2–Mn2–Mn2A	41.15(10)
O1A–Mn1–Mn1A	41.19(9)	O2A–Mn2–Mn2A	40.94(9)
O1–Mn1–Mn1A	40.96(10)	N5–Mn2–Mn2A	132.41(11)
N2–Mn1–Mn1A	132.05(14)	N6–Mn2–Mn2A	132.16(14)
N3–Mn1–Mn1A	133.05(11)	N7–Mn2–Mn2A	97.12(12)
N1–Mn1–Mn1A	97.66(11)	N8–Mn2–Mn2A	97.68(12)
N4–Mn1–Mn1A	97.54(11)	Mn1A–O1–Mn1	97.85(13)
O2–Mn2–O2A	82.08(14)	Mn2–O2–Mn2A	97.92(14)

ganese(II) complex with pmap as a ligand were unsuccessful. In contrast, the dinuclear bis μ -oxo manganese(III, IV) complex, [(pmap)Mn-(μ -O)₂-Mn(pmap)]-(ClO₄)₃ (**1**), was prepared easily in the usual way by

reacting Mn(ClO₄)₂ with pmap and hydrogen peroxide in water. The powder obtained was recrystallized from acetonitrile to yield crystals suitable for X-ray analysis. The molecular structure of the cation of **1** is shown in Fig. 2.

Complex **1** crystallizes in the triclinic space group $P\bar{1}$ with one acetonitrile solvent molecule. There is a crystallographic inversion center in the middle of the dimer; Fig. 2 was obtained by a symmetry operation on one half of the cation. Two of the three perchlorate ions are disordered. The crystallographically independent unit of the elementary cell contained two half molecules of the dimeric manganese complex (only one of the molecular structures in the crystal is shown in Fig. 2). Two of the ethylpyridine arms were disordered in the dimer. The Mn–Mn separation increases from 2.643(1) Å in [(tpma)Mn-(μ -O)₂-Mn(tpma)](ClO₄)³⁺ and 2.693(1) Å in [(pmea)Mn-(μ -O)₂-Mn(pmea)]³⁺ to 2.7379(13) Å in **1**. The considerably longer bond distance results obviously from increasing the chelate ring sizes in the dimeric complex.

The two manganese centers in **1** are equivalent crystallographically. This does not imply that the two centers are chemically equivalent — this was discussed in detail for [(pmea)Mn-(μ -O)₂-Mn(pmea)]³⁺ which also has a crystallographic inversion center in the middle of the dimer [12]. In **1**, the bridging Mn–O bond lengths of 1.811(3)–1.821(3) Å, as well as the bridging Mn–O–Mn angles of 97.85(13) and 97.92(14)° are similar to those found in other systems [12,19,20].

The geometry at each manganese center is distorted octahedral with the methylpyridyl and one of the ethylpyridyl groups in the axial positions. In general, the structure is similar to [(pmea)Mn-(μ -O)₂-Mn(pmea)]³⁺ but bond distances and angles are slightly different because the methylpyridyl has been replaced through an ethylpyridyl group.

The UV–Vis spectrum of **1** in acetonitrile showed two absorbance maxima at 556 and 662 nm, which are similar to the values reported for [(tpma)Mn-(μ -O)₂-Mn(tpma)]³⁺ (560 and 654(8) nm) [6,11] and for [(pmea)Mn-(μ -O)₂-Mn(pmea)]³⁺ (557 and 668 nm) [12]. These bands were assigned to the Mn(IV) center and specifically to charge-transfer transitions from the oxo groups to the metal $d\pi^*$ orbitals [12].

The cyclic voltammogram of **1** in acetonitrile exhibits two quasi-reversible redox waves with $E_{1/2}$ values at 0.293 and 1.241 V versus Ag/AgCl (the $E_{1/2}$ of ferrocene was 0.4300 vs. Ag/AgCl). These potentials correspond to the redox reactions of Mn(III, IV)/Mn(III, III) and Mn(IV, IV)/Mn(III, IV) and are similar to the potentials reported for [(tpma)Mn-(μ -O)₂-Mn(tpma)]³⁺ and [(pmea)Mn-(μ -O)₂-Mn(pmea)]³⁺ [12].

The EPR spectrum of **1** was measured at 100 K in *N*-methylformamide (Fig. 3). It showed the characteris-

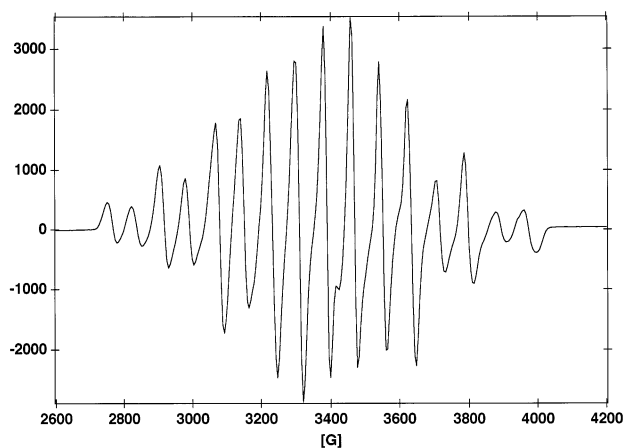


Fig. 3. EPR spectrum of **1** in *N*-methylformamide at 100 K.

tic 16 line signal centered around $g = 2.003$; it could be simulated assuming two unequivalent ^{55}Mn nuclei with the hyperfine coupling constants $A_1 = 162$ G and $A_2 = 79$ G. This type of spectrum is known to be diagnostic for the $S = 1/2$ ground state of a bis- μ -oxo Mn(III)/Mn(IV) dimer [2]. However, all of these dimers known so far give rise to almost identical EPR parameters. Therefore, although the spectra of the complexes of tmpa [11], pmea [12] and pmap show small differences, it is not possible at present to interpret these differences in terms of variations in the structure or electron density.

Substitution of the last methylpyridyl by an ethylpyridyl group would be expected to result in an even larger Mn–Mn separation in the tepa bis(μ -oxo)dimanganese(III, IV) dimer. However, so far all efforts to synthesize $[(\text{tepa})\text{Mn}(\mu\text{-O})_2\text{Mn}(\text{tepa})]^{3+}$ were unsuccessful. Only brown impure powders were obtained when manganese perchlorate was reacted with tepa and hydrogen peroxide.

Most likely, the $[(\text{tepa})\text{Mn}(\mu\text{-O})_2\text{Mn}(\text{tepa})]^{3+}$ was not formed because the Mn–Mn distance would become too long for a bis(μ -oxo) bridge. Therefore, formation of a Mn(III)-(μ -O) $_2$ -Mn(III) dimer would be favored. A brown product was also obtained using the ligand bispicMe $_2$ en (= *N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-1,2-ethanediamine), which was shown to be the corresponding bis(μ -oxo) Mn(III)–Mn(III) complex [13]. The formation of a similar bis(μ -oxo) Mn(III)–Mn(III) dimer in our experiments cannot be confirmed in the absence of suitable crystals.

4. Conclusions

The metal–metal distances in bis(μ -oxo) bridged Mn(III)–Mn(IV) complexes are known to lie within a very narrow range, between 2.64 and 2.74 Å [2]. The ligand series discussed here presents complexes with

increasing Mn–Mn distances, going from the lower extreme (tmpa) to the upper extreme (pmap) of this range. For the last ligand of the series, tepa, an even larger Mn–Mn separation would be expected, but this is probably no longer compatible with the structural requirements of a rigid bis(μ -oxo) Mn(III)–Mn(IV) complex unit. We therefore predict that it is unlikely that $[(\text{tepa})\text{Mn}(\mu\text{-O})_2\text{Mn}(\text{tepa})]^{3+}$ is a stable complex. On the other hand, this suggests that tepa may be an ideal ligand for the preparation of manganese dimers with lower oxidation states, such as Mn(III)–Mn(III) etc. Further experiments are planned to investigate this possibility.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 136915. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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