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Structure and reactions of an eight-coordinate Mn(II) complex: [Mn(TMPA)$_2$](ClO$_4$)$_2$ (TMPA = tris[(2-pyridyl)methyl]amine)

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Abstract

The synthesis, structure and reaction products of an eight-coordinate Mn(II) complex are described. The reaction of $Mn(ClO_4)_2 \cdot 6H_2O$ with the tripodal amine ligand tris(2-methylpyridyl)amine (TMPA) yields the eight-coordinate complex [Mn(TMPA)$_2$](ClO$_4$)$_2$ (**1**) which crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.7063(3)$, $b = 10.929(3)$, $c = 18.378(7)$ Å, $\beta = 101.96(3)°$. The X-ray structure shows an eight-coordinate Mn(II) ion with coordination to six pyridyl and two amine nitrogens which form a bicapped trigonal antiprism geometry. The oxidation of the Mn(II) complex with H_2O_2 produces the dioxo-bridged dimeric Mn(III,IV) complex [Mn$_2$(μ-O)$_2$(TMPA)$_2$](ClO$_4$)$_3$ which shows antiferromagnetic coupling between the two valence trapped Mn ions leading to $S = 1/2$ ground state in a 16-line EPR spectrum typical of such dioxo-bridged mixed valent Mn complexes and similar to the EPR spectrum exhibited by the S_2 state Photosystem II. While the Mn(II) complex is stable to oxidation by O_2, in the presence of catechol in methanol solution, it is readily oxidized by O_2 to give the catecholate complex. The oxidation of 3,5-di-t-butylcatechol to the quinone by O_2 is catalyzed by **1**.

Introduction

The role of manganese as a redox catalyst in synthetic systems [1], as well as in metalloenzymes such as the water oxidizing complex in plants, Photosystem II (PS II) [2, 3], depends on its variable oxidation and coordination states [4–6]. In the S_1 state of PS II, coordination of 5 to 8 N and O donor groups to manganese ions in the average oxidation state of +2 to +3 has been proposed [7, 8]. In modeling the active site of PS II, complexes of chelating pyridine and other aromatic nitrogen donor ligands with manganese in oxidation states ranging form +2 to +4 and mixed valent complexes have been studied [9–14].

We report here the synthesis, structure and reactions of a unique, eight-coordinate Mn(II) complex of TMPA (TMPA = tris[(2-pyridyl)methyl]amine), [Mn(TMPA)$_2$](ClO$_4$)$_2$, the hydrogen peroxide oxidation of which yields a complex formulated as [Mn$_2$(TMPA)$_2$(O)$_2$](ClO$_4$)$_3$ (*vide infra*).

Experimental

Solvents were refluxed and distilled under argon atmosphere: methanol from magnesium methoxide and ether from Na/benzophenone.

Synthesis of the ligand TMPA

The ligand TMPA was prepared by the reaction of 2-aminomethylpyridine with picolyl chloride according to the literature [15].

Synthesis of the complex [Mn(TMPA)$_2$](ClO$_4$)$_2$

A solution of the ligand TMPA (1.63 g, 5.62 mmol) in methanol (25 ml) was added to a methanol solution (75 ml) of $Mn(ClO_4)_2 \cdot 6H_2O$ (1.00 g, 2.76 mmol). The mixture was stirred for 3 to 4 h, and filtered. Ether (100 ml) was then added while stirring to precipitate a white powder which was filtered and washed first with 20 ml methanol/ether (1/1) mixture and then with 20 ml ether, and dried in air yielding 2.15 g (93.4%) of the complex. It was recrystallized by adding ether to its methanol solution to the cloud point and standing overnight. *Anal.* Calc. for $C_{36}H_{36}Cl_2MnN_8O_8$: C, 52.8; H, 4.32; N, 13.43. Found: C, 51.72; H, 4.31; N, 13.38%.

Synthesis of the complex [Mn$_2$(TMPA)$_2$(μ-O)$_2$](ClO$_4$)$_3$

To a methanol solution (50 ml) of [Mn(TMPA)$_2$](ClO$_4$)$_2$ (1.67 g, 2.0 mmol) was added,

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dropwise while stirring, 2.0 ml of a 30% aqueous H_2O_2 solution. A green microcrystalline solid precipitated over 5 to 10 min. After filtration, the precipitate was washed with 15 ml methanol and dried to yield 0.95 g (93%) of the complex. *Anal.* Calc. for $C_{36}H_{36}Cl_3Mn_2N_8O_{14}$: C, 42.34; H, 3.53; N, 10.98. Found: C, 42.29; H, 3.61; N, 11.02%. The molar conductivity of this complex in DMF is that of a 1:3 electrolyte.

Synthesis of [Mn₂(TMPA)₂(μ-O)(catecholate)](ClO₄)₂

To a methanol solution (50 ml) of $Mn(TMPA)_2(ClO_4)_2$ (1.67 g, 2.0 mmol) was added with stirring a methanol solution (25 ml) of catechol (0.25 g, 2.1 mmol) and the mixture allowed to stir under O_2 atmosphere overnight. To the green solution formed was added ether to precipitate a green powdery solid which was redissolved in 20 ml methanol and reprecipitated by adding ether to yield 1.82 g (90.1%) of the green microcrystalline solid. *Anal.* Calc. for $C_{42}H_{40}Cl_2Mn_2N_8O_{11}$: C, 49.8; H, 3.95; N, 11.07. Found: C, 49.6; H, 3.97; N, 10.84%. The molar conductivity of this complex in DMF is that of a 1:2 electrolyte. The stoichiometry of the reaction of O_2 with the catechol and $Mn(TMPA)_2(ClO_4)_2$ mixture in methanol is $Mn:O_2=4:1$.

X-ray crystal structure of [Mn(TMPA)₂](ClO₄)₂

A Nicolet R3m/V diffractometer was used in the ω-scan mode to collect 2749 unique reflections of which 2128 reflections with $F_o \geq 6\sigma|F_o|$ were used in the solution and refinement. The positional parameters of the Mn atom were determined by the Patterson method. The remaining non-hydrogen atoms were located on subsequent difference Fourier maps. All atoms, with the exception of C and H, were refined anisotropically. The structure was refined to the current residual values of $R=0.057$ and $R_w=0.0571$ (Mo Kα, $\lambda=0.71073$ Å).

Results and discussion

The crystallographic data (Table 1), atomic coordinates (Table 2) and selected bond distances and angles (Tables 3 and 4) are shown. The structure of the dication $Mn(TMPA)_2^{2+}$ (Fig. 1) shows an eight-coordinate manganese ion at the center of symmetry of a bicapped trigonal antiprism (D_{3d} symmetry). The six pyridyl nitrogens form the corners of a trigonal antiprism and the two amine nitrogens (one of each ligand molecule) form the caps on the top and bottom trigonal faces. The geometry of the six pyridyl nitrogens could also be viewed as forming the corners of an octahedron that is distorted (flattened) by 14.9° such that the N–Mn–N angle made by two *cis* pyridyl nitrogens on the same ligand molecule is 104.9° while that made

TABLE 1. Crystallographic data for $[Mn(TMPA)_2](ClO_4)_2$

Temperature (K)	294
a (Å)	9.0706(3)
b (Å)	10.929(3)
c (Å)	18.378(7)
α (°)	90.00
β (°)	101.96(3)
γ (°)	90.00
V (Å³)	1908(1)
Molecular weight	837.8
F(000)	862
Z	2
ρ_{calc} (g/cm³)	
Space group	*P*2₁/*n*
Crystal dimensions (mm)	0.30×0.25×0.20
ω Scan rate (°/min)	3.0–20.0
Scan type	moving crystal, stationary counter
Scan width (°)	1.2
2θ Range (°)	0–45
R	0.057
R_w	0.0571

TABLE 2. Atom coordinates (×10⁴) and temperature factors (Å²×10³) for compound $[Mn(TMPA)_2](ClO_4)_2$

Atom	*x*	*y*	*z*	$U_{eq/iso}$
Mn(1)	0	0	10000	37(1)
N(1)	−1919(4)	1078(3)	10430(2)	42(1)
C(1)	−1838(5)	2295(4)	10482(3)	39(1)
C(2)	−2904(5)	3002(5)	10669(3)	53(1)
C(3)	−4097(6)	3417(5)	10802(3)	63(2)
C(4)	−4191(6)	1176(5)	10751(3)	58(1)
C(5)	−3084(5)	539(5)	10559(3)	51(1)
N(2)	765(4)	1450(3)	9089(2)	41(1)
C(6)	1656(5)	2346(4)	9384(3)	39(1)
C(7)	2443(5)	3004(5)	8960(3)	54(1)
C(8)	2301(6)	2723(5)	8223(3)	65(2)
C(9)	1386(6)	1815(5)	7912(3)	64(2)
C(10)	634(5)	1203(5)	8361(3)	52(1)
N(3)	1985(4)	−21(3)	11116(2)	42(1)
C(11)	2198(4)	987(4)	11539(2)	36(1)
C(12)	3274(5)	1088(5)	12160(3)	49(1)
C(13)	4159(6)	107(5)	12362(3)	62(1)
C(14)	3945(6)	−933(5)	11942(3)	57(1)
C(15)	2867(5)	−966(5)	11332(3)	50(1)
N(4)	684(3)	2073(3)	10509(2)	37(1)
C(16)	1140(5)	1991(4)	11323(2)	40(1)
C(17)	−548(5)	2878(4)	10306(3)	46(1)
C(18)	1851(5)	2568(4)	10199(3)	44(1)
Cl(1)	1190(1)	328(1)	3589(1)	52(1)
O(1)	421(6)	218(5)	4166(3)	119(3)
O(2)	462(5)	1075(4)	3000(3)	92(2)
O(3)	3641(4)	4147(3)	11698(2)	69(2)
O(4)	7537(5)	4180(5)	8882(3)	105(2)

[a] Asterisks indicate values of equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{11} tensor.

TABLE 3. Selected bond lengths (Å) in $[Mn(TMPA)_2](ClO_4)_2$

Mn(1)–N(1)	2.468(4)	Mn(1)–N(2)	2.526(4)
Ma(1)–N(3)	2.507(4)	Mn(1)–N(4)	2.488(4)
Mn(1)–N(1A)	2.468(4)	Mn(1)–N(2A)	2.526(4)
Mn(1)–N(3A)	2.507(4)	Mn(1)–N(4A)	2.488(4)

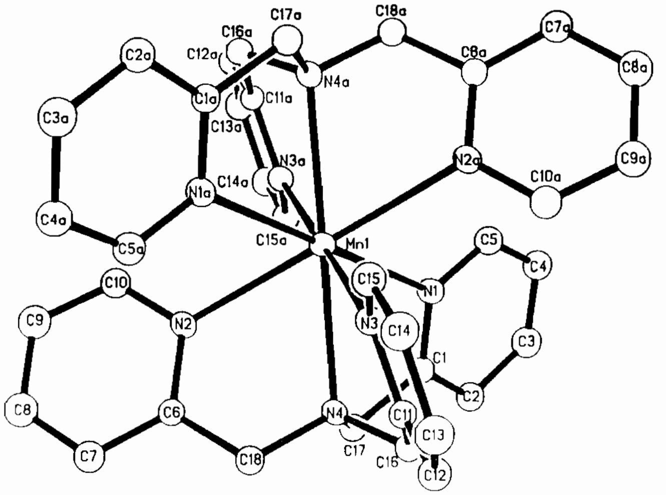

Fig. 1. ORTEP drawing of $Mn(TMPA)_2^{2+}$ showing the atom labeling scheme. H atoms are omitted for clarity.

by two *cis* pyridyl nitrogens on different ligand molecules is 75.1°. The N_{amine}–Mn–N_{py} angles are 65.5 to 66.8° within a coordinated ligand molecule. The average manganese–nitrogen distances (Mn–N(pyridyl) = 2.500, Mn–N(amine) = 2.468 Å) are significantly longer than the usually observed Mn–N(pyridyl) distances (2.20–2.30 Å) in six-coordinate Mn(II) complexes [16, 17], resulting most likely from ligand steric crowding at the metal center. A spherically symmetric high spin d^5 Mn(II) ion can achieve coordination stability by higher coordination at longer distances. The complex $[Mn(TMPA)_2](ClO_4)_2$ is the first example of a structurally characterized eight-coordinate Mn(II) complex in which all the donor nitrogens are part of chelating organic ligands.

The complex $[Mn(TMPA)_2](ClO_4)_2$ shows no absorption in the visible region of the spectrum, and it has a room temperature corrected magnetic moment of 5.84 BM both of which features are as expected for a high spin d^5 Mn(II) complex. The cyclic voltammetry in DMF shows an irreversible oxidation peak at 1.6 V (versus NHE) which is close to those of other similar pyridyl donor complexes [18, 19]. The compound is stable to oxidation by dioxygen both as a solid and in solution. However, in the presence of catechol in methanol, it reacts with dioxygen in a mole ratio of complex:O_2 = 4:1 with concomitant loss of one molecule of TMPA per Mn to give a green complex formulated from its elemental analysis, conductivity data and the O_2 reaction stoichiometry as $[Mn_2(TMPA)_2(O)(catecholate)](ClO_4)_2$ (visible spectrum in methanol with absorption maxima (nm) at 424 ($\epsilon = 1.92 \times 10^3$ M^{-1} cm^{-1}), 568 ($\epsilon = 1.48 \times 10^3$ M^{-1} cm^{-1}) and 606 ($\epsilon = 1.44 \times 10^3$ M^{-1} cm^{-1})). The oxidation of 3,5-di-t-butylcatechol to 3,5-di-t-butyl-*o*-benzoquinone by O_2 in methanol solution is catalyzed by $[Mn(TMPA)_2](ClO_4)_2$ ($t_{1/2}$ = 75 min in air in a 1.0 mM solution of 3,5-di-t-butyl-*o*-catechol and 0.1 mM complex as measured by the absorption at 400 nm of the quinone formed). The complex is then recovered unchanged. The reaction of $[Mn(TMPA)_2](ClO_4)_2$ in methanol with aqueous H_2O_2 results in the precipitation of a green complex that analyzes correctly and shows conductivity in solution consistent with the Mn(III,IV) complex $[Mn_2(TMPA)_2(O)_2](ClO_4)_3$ (absorption maxima (nm) at 448 ($\epsilon = 760$ M^{-1} cm^{-1}), 560 ($\epsilon = 370$ M^{-1} cm^{-1}) and 654 ($\epsilon = 300$ M^{-1} cm^{-1})), a compound whose structure (Fig. 2) has been previously shown to be a dioxo-bridged dimer [20]. The physical characteristics including the visible absorption, the solid state room temperature magnetic moment, cyclic voltammetric data and the DMF/methanol frozen solution EPR spectrum

TABLE 4. Selected bond angles (°) in $[Mn(TMPA)_2](ClO_4)_2$

N(1)–Mn(1)–N(2)	104.9(1)	N(1)–Mn(1)–N(3)	104.2(1)
N(2)–Mn(1)–N(3)	105.4(1)	N(1)–Mn(1)–N(4)	66.8(1)
N(2)–Mn(1)–N(4)	65.5(1)	N(3)–Mn(1)–N(4)	66.5(1)
N(1)–Mn(1)–N(1A)	180.0(1)	N(2)–Mn(1)–N(1A)	75.1(1)
N(3)–Mn(1)–N(1A)	75.8(1)	N(4)–Mn(1)–N(1A)	113.2(1)
N(1)–Mn(1)–N(2A)	75.1(1)	N(2)–Mn(1)–N(2A)	180.0(1)
N(3)–Mn(1)–N(2A)	74.6(1)	N(4)–Mn(1)–N(2A)	114.5(1)
N(1A)–Mn(1)–N(2A)	104.9(1)	N(1)–Mn(1)–N(3A)	75.8(1)
N(2)–Mn(1)–N(3A)	74.6(1)	N(3)–Mn(1)–N(3A)	180.0(1)
N(4)–Mn(1)–N(3A)	113.5(1)	N(1A)–Mn(1)–N(3A)	104.2(1)
N(2A)–Mn(1)–N(3A)	105.4(1)	N(1)–Mn(1)–N(4A)	113.2(1)
N(2)–Mn(1)–N(4A)	114.5(1)	N(3)–Mn(1)–N(4A)	113.5(1)
N(4)–Mn(1)–N(4A)	180.0(1)	N(1A)–MN(1)–N(4A)	66.8(1)
N(2A)–Mn(1)–N(4A)	65.5(1)	N(3A)–Mn(1)–N(4A)	66.5(1)

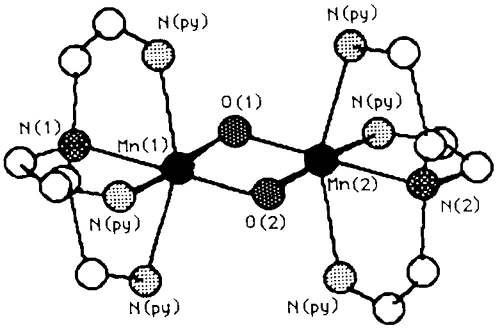

Fig. 2. The structure of the cation $[Mn_2(O)_2(TMPA)_2]^{3+}$ showing the coordination geometry of the oxide bridges (O(1), O(2)) and the TMPA ligand molecules (for clarity only the nitrogen donor atoms of the pyridine groups are shown).

(16 line) at liquid nitrogen temperature of this compound also match the features of the same compound synthesized also by the H_2O_2 oxidation of a 1:1 mole ratio reaction product of Mn(II) and the ligand (TMPA) in water solution [21]. The 16 line EPR spectrum is the same as those shown by other mixed valent dioxo-bridged dinuclear complexes of manganese [12b, 22]. The Mn center of PS II in its S_2 state [23, 24] and also of catalase [25] are known to show a similar multi-line spectrum at $g = 2$ suggesting that the active sites most likely have dinuclear manganese complexes.

Conclusions

We have structurally characterized the first eight-coordinate stable Mn(II) complex with all donors from chelating organic N ligands showing lability and oxidation by O_2 in the presence of catechol. It forms a dioxo-bridged dinuclear manganese(III,IV) oxidation product that exhibits an EPR spectrum characteristic of mixed valent dioxo-bridged dinuclear manganese complexes and similar to the EPR exhibited by the S_2 state of PS II. The finding also demonstrates the variability of the coordination properties of manganese in synthetic and possibly biological systems.

Supplementary material

Table of experimental details for data collection and refinement (Table SI, 2 pages), complete listings of bond lengths and bond angles (Table SII and SIII), anisotropic temperature factors (Table SIV), hydrogen atom coordinates and temperature factors (Table SV), and observed and calculated structure factors (Table SVI) (9 pages) are available from the authors on request.

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