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N,*N*,*N*′,*N*′-Tetrakis(2-quinolylmethyl)-2-hydroxy-1,3-propanediamine (Htqhpn) as a Supporting Ligand for a Low-Valent $(\mu\text{-O})_2$ Tetranuclear Manganese Core

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A new heptadentate N6–O1 ligand, *N*,*N*,*N*′,*N*′-tetrakis(2-quinolylmethyl)-2-hydroxy-1,3-propanediamine (Htqhpn), was synthesized and used to generate compounds with linearly ordered $Mn^{II}Mn^{III}$-$Mn^{III}Mn^{II}$ tetranuclear cores. This is the lowest valent tetranuclear manganese complex that exhibits a $(\mu_2\text{-O})_2Mn_2$ core in the molecule. The electron paramagnetic resonance and magnetic measurements of these tetranuclear complexes suggest moderately strong antiferromagnetic coupling for the central Mn^{III}_2 core, with weak coupling between the Mn^{II} and Mn^{III} centers.

The control of structural arrangements and oxidation states of metal ions in multinuclear metal complexes continues to attract interest in the development of metal-based materials. The synthesis of novel magnetic materials such as a single-molecule magnet is an important objective for such investigations.[1] Among these complexes, the assembly of manganese clusters is of particular importance and has additional relevance to the oxygen-evolving complex (OEC) of photosystem II found in green plants.[2] Because a high-valent oxomanganese species is proposed as a key intermediate for dioxygen evolution from OEC, terminal oxomanganese(V) complexes have been extensively studied using porphyrin,[3] porphyrinoid,[4] and amido-containing ligands.[5] Other types of high-valent, multinuclear μ-oxomanganese complexes with nitrogen-containing heteroaromatic ligands,[6] together with carboxylates[7] or other oxygen-atom donors as bridging ligands,[8] have also been exploited for this goal. On the other hand, the introduction of steric hindrance, for instance, the introduction of 6-methyl substituents in (2-pyridylmethyl)-amine-based tripodal ligands, stabilizes lower oxidation states (Mn^{III}) in the dinuclear manganese metal center as a result of a Jahn–Teller distortion.[9] Other structural modification of the ligand molecules such as chelate ring-size alternation would afford a range of oxidation states of the manganese center and add a new dimension of aggregation property into the manganese clusters.[6e,10]

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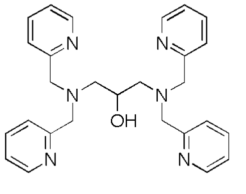
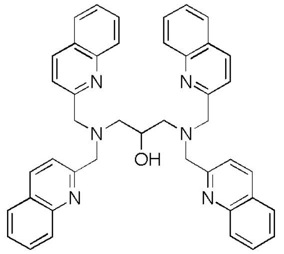
In this paper, we report the synthesis, structural characterization, and spectroscopic analysis of two tetranuclear (μ-O)$_2$ manganese complexes **1** and **2**, where both structures are chelated by a novel quinoline-based ligand, *N,N,N′,N′*-tetrakis(2-quinolylmethyl)-2-hydroxy-1,3-propanediamine (Htqhpn). This ligand was designed based on *N,N,N′,N′*-tetrakis(2-pyridylmethyl)-2-hydroxy-1,3-propanediamine (Htphpn), which supports several types of manganese clusters.[11] Replacement of the pyridine ring with a quinoline ring affords steric hindrance and reduced basicity of the aromatic nitrogen donor atom, forcing the stabilization of low-valent manganese centers, namely, (μ-O)$_2$Mn$^{III}_2$ rather than (μ-O)$_2$-Mn^{III}Mn^{IV} or (μ-O)$_2$Mn$^{IV}_2$, for the central oxomanganese unit.


Htphpn


Htqhpn

Htqhpn was obtained in 75% yield from the reaction of (2-chloromethyl)quinoline hydrochloride with 1,3-diamino-2-propanol. The product was characterized by ^{1}H/^{13}C NMR, mass spectrometry, elemental analysis, and X-ray crystallography (Figure S1 of the Supporting Information).

An acetonitrile solution of Htqhpn containing manganese(II) perchlorate hexahydrate (2 equiv) and triethylamine (1 equiv) was stirred at room temperature open to air. A green-white precipitate appeared and was collected after 2 days. This material was recrystallized from two different solvent systems: acetonitrile−ether afforded green crystals, while DMF−ether gave brown crystals. X-ray crystallography revealed that both are tetranuclear manganese complexes. Figures 1 and 2 show the cationic parts of the molecular structures of [Mn$_4$(tqhpn)$_2$(μ-O)$_2$(H$_2$O)$_2$](ClO$_4$)$_4$·6CH$_3$CN·2Et$_2$O (**1**·6CH$_3$CN·2Et$_2$O)[12] and [Mn$_4$(tqhpn)$_2$(μ-O)$_2$(H$_2$O)$_2$(DMF)$_2$](ClO$_4$)$_4$·6DMF (**2**·6DMF),[13] which were obtained from acetonitrile−ether and DMF−ether, respectively.

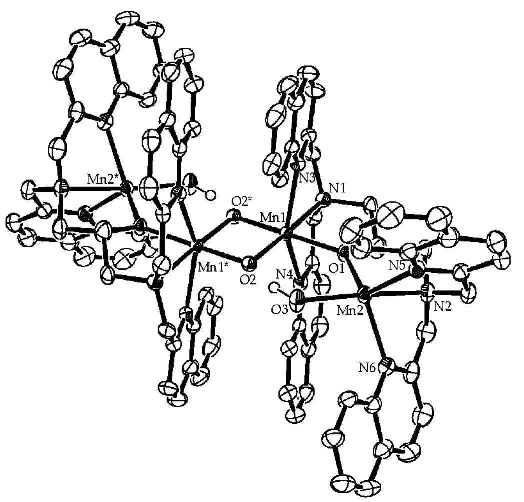


Figure 1. ORTEP plot for [Mn$_4$(tqhpn)$_2$(μ-O)$_2$(H$_2$O)$_2$]$^{4+}$. Selected interatomic distances (Å) and angles (deg): Mn1−O1, 1.981(2); Mn1−O2, 1.8508(19); Mn−O2*, 1.860(2); Mn1−N1, 2.111(2); Mn1−N3, 2.361(2); Mn1−N4, 2.326(2); Mn2−O1, 2.092(2); Mn2−O3, 2.045(2); Mn2−N2, 2.238(3); Mn2−N5, 2.197(3); Mn2−N6, 2.236(3); Mn1···Mn1*, 2.7496(8); Mn1···Mn2, 3.7353(5); O2···O2*, 2.492(2); O2···O3, 2.467(3); Mn1−O2−Mn1*, 95.63(8); Mn1−O1−Mn2, 133.0(1); O2−Mn1−O2*, 84.37(9).

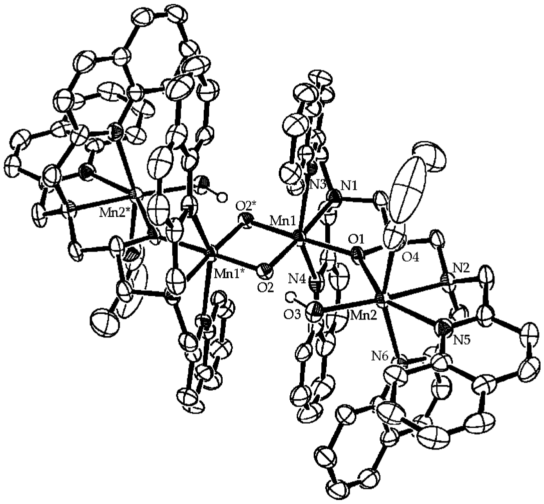


Figure 2. ORTEP plot for [Mn$_4$(tqhpn)$_2$(μ-O)$_2$(H$_2$O)$_2$(DMF)$_2$]$^{4+}$. Selected interatomic distances (Å) and angles (deg): Mn1−O1, 1.950(2); Mn1−O2, 1.857(2); Mn−O2*, 1.849(2); Mn1−N1, 2.119(3); Mn1−N3, 2.424(3); Mn1−N4, 2.390(3); Mn2−O1, 2.153(2); Mn2−O3, 2.122(2); Mn2−O4, 2.187(3); Mn2−N2, 2.273(3); Mn2−N5, 2.359(3); Mn2−N6, 2.323(3); Mn1···Mn1*, 2.7288(6); Mn1···Mn2, 3.7867(7); O2···O2*, 2.507(4); O2···O3, 2.549(4); Mn1−O2−Mn1*, 94.9(1); Mn1−O1−Mn2, 134.66(12); O2−Mn1−O2*, 85.1(1).

The former complex (**1**, Figure 1) was composed of four manganese ions, two equivalents of ligand, two water molecules, four perchlorate anions, and a (μ-O)$_2$ core, as well as solvent molecules in the crystal lattice. The Mn2−O3 bond distance is 2.045(2) Å, indicating that this is a water molecule and neither OH$^-$ nor O^{2-}.[11c,d] In addition, one of two hydrogen atoms of this water molecule is hydrogen-bonded to the μ-oxo oxygen atom of the center of the molecule. The total charge of the manganese cluster is 10+, judged by the number of counteranions. A comparison of the bond lengths around the manganese atoms with related structure[11a−d] reveals the manganese oxidation states as a Mn^{II}Mn^{III}Mn^{III}-

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(12) Crystal data for **1**·6CH$_3$CN·2Et$_2$O: formula C$_{106}$H$_{116}$Cl$_4$N$_{18}$Mn$_4$O$_{24}$, triclinic, space group $P\bar{1}$, a = 14.178(4) Å, b = 14.300(4) Å, c = 15.741(4) Å, α = 73.948(12)°, β = 69.661(11)°, γ = 69.339(11)°, V = 2756.7(13) Å^3, Z = 1, T = −100 °C, 21 800 data collected, 8244 data with $I > 2\sigma(I)$, R1 = 0.054, wR2 (all data) = 0.129, GOF = 1.005.

(13) Crystal data for **2**·2DMF: formula C$_{110}$H$_{134}$Cl$_4$N$_{20}$Mn$_4$O$_{30}$, monoclinic, space group $P2_1/c$, a = 14.9507(11) Å, b = 26.6917(13) Å, c = 16.8354(11) Å, β = 118.376(3)°, V = 5911.1(7) Å^3, Z = 2, T = −100 °C, 46 330 data collected, 8091 data with $I > 2\sigma(I)$, R1 = 0.061, wR2 (all data) = 0.133, GOF = 1.084.

Mn^{II} composition in complex **1**.[14] The Mn^{III} centers are ligated in an octahedral geometry, whereas the Mn^{II} centers were coordinated in a trigonal-bipyramidal configuration. While tetranuclear manganese complexes with *μ-alkoxo* moieties exhibit II,II,II,II[15] or II,II,III,III[16] formulations, the lowest valent tetranuclear *μ-oxo*manganese complexes reported are II,II,III,III[11a,b,17] and II,II,II,IV[18] formulations. These complexes have linear (μ_2-O)Mn_2,[11a,b] (μ_3-O)$_2$$Mn_4$,[17a−c] and ($\mu_4$-O)$Mn_4$[17d,e,18] bridging moieties. To our best knowledge, complex **1** is the first example of a species that has a (μ_2-O)$_2$$Mn_2$ core in the Mn_4 cluster with an average manganese oxidation state of 2.5+.

One characteristic of the quinoline ring is the stacking interaction between two ligand molecules located at the center of the complex. When compared with corresponding complexes having a pyridine-based ligand, Htphpn, the extra benzene ring of Htqhpn plays an important role in the efficient overlap of the aromatic rings that shield the Mn^{III}_2-(μ-O)$_2$ core in the center of the complex from the surrounding environment. Reduced basicity and steric hindrance due to the *peri*-hydrogen in the quinoline ring are also important for the present ligand design; both effects weaken the coordination ability of the nitrogen to the metal center, forcing the manganese atoms to adopt high-spin d^4 Mn^{III} states with elongated axial bonds by Jahn−Teller distortion.[9]

The latter complex (**2**, Figure 2) also has a (μ-O)$_2$ tetranuclear $Mn^{II}Mn^{III}Mn^{III}Mn^{II}$ core similar to that of complex **1**.[14] The structural difference between **1** and **2** is that complex **2** has a DMF molecule bound to the Mn^{II} center, affording four octahedral manganese atoms in the molecule. The three nitrogens of the tqhpn ligand chelated to this terminal Mn^{II} end adopt a facial (*fac*) mode, in contrast to the pyridine-based tphpn complexes, in which the corresponding moiety binds in a meridional (*mer*) fashion.[11a−d] As a result, the plane of the DMF molecule is perpendicular to the Mn_4(μ-O)$_2$ axis and parallel to the adjacent quinoline ring ligated to the central Mn^{III}.

Magnetic susceptibility measurements on complexes **1** and **2** were performed (Figures 3 and S2 of the Supporting Information).[19] At room temperature, both complexes show a smaller magnetic moment per molecule ($\mu_{eff} = 9.0\ \mu_B$ for **1** and 8.3 μ_B for **2**) than the expected value (10.86 μ_B) for a $Mn^{III}_2Mn^{II}_2$ system with no magnetic coupling. In addition, at low temperature, the magnetic moment significantly decreases, indicating that moderately strong antiferromagnetic interaction is present in both complexes. The curve fitting of temperature-dependent magnetic data for complex **1** gave the values of exchange interaction parameters J_1 (for Mn1···Mn1*) and J_2 (for Mn1···Mn2) and the g value as −41.7 cm^{-1}, −2.8 cm^{-1}, and 1.95, respectively. Similar values are obtained for complex **2** (see the Supporting Information), and these values are in good agreement with those for previously reported a tetranuclear manganese(II,III,III,II) complex.[11a]

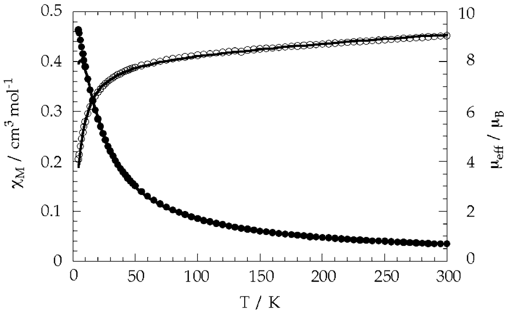

Figure 3. Variable-temperature magnetic moment (open circles) and magnetic susceptibility (filled circles) of complex **1**. Solid lines represent the best fit of the data with the model described in the Supporting Information.[19]

Electron paramagnetic resonance (EPR) spectra of complexes **1** and **2** in frozen acetonitrile were also measured at 77 K (Figure S3 of the Supporting Information). Both complexes exhibit a broad signal centered at $g = 2.0$ ($W_{pp} \approx 130$ mT for **1** and 120 mT for **2**), which is consistent with the presence of the magnetic interactions between the Mn ions.

In conclusion, Htqhpn, the quinoline-based heptadentate N6−O1 ligand, supports Mn_4 complexes that exhibit low oxidation states for the manganese ions. Steric and electronic properties of the quinoline ring nitrogen should provide new characteristics into multinuclear metal complexes.

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Supporting Information Available: Preparation and characterization details of the compounds and CIF files for Htqhpn, **1**·6CH_3CN·2Et_2O, and **2**·6DMF. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) The assignments of manganese oxidation states are also supported by bond valence sum analysis. See the Supporting Information.

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(19) For the simulation of the magnetic susceptibility data, we used the following spin Hamiltonian: $H = -2J_1S_2S_3 - 2J_2(S_1S_2 + S_3S_4) + g_{II}\mu_BB(S_1 + S_4) + g_{III}\mu_BB(S_2 + S_3)$, where S_1, S_2, S_3, and S_4 are the electron spins on Mn^{II}, Mn^{III}, Mn^{III}, and Mn^{II}, respectively ($S_1 = S_4 = {}^5/_2$; $S_2 = S_3 = 2$), J_1 and J_2 are the exchange interaction parameters, g_{II} and g_{III} are the g values of Mn^{II} and Mn^{III}, respectively, and the other symbols have their usual meanings. Here $g_{II} = g_{III}$ is assumed for simplicity.