

Novel Mixed-Valence Manganese Cluster with Two Distinct Mn₃(II/III/II) and Mn₃(III/II/III) Trinuclear Units in a Pseudocubane-like Arrangement

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Received March 14, 2008

The reaction between Mn(ClO₄)₂ and di-(2-pyridyl)-ketone in the presence of the sodium salt of propanediol as a base in MeOH leads to the formation of a hexanuclear manganese cluster. This cluster has been characterized by the formula [Mn(II)₃Mn(III)₃O(OH)(CH₃pdol)₃(Hpdol)₃(pdol)](ClO₄)₄ (**1**). Molecular conductance measurements of a 10⁻³ M solution of compound **1** in CH₃CN, DMSO, or DMF give $\Lambda_m = 529, 135, \text{ or } 245 \mu\text{S/cm}$, respectively, which suggests a 1:4 cation/anion electrolyte. The crystal structure of hexanuclear manganese cluster **1** consists of two distinct trinuclear units with a pseudocubane-like arrangement. The trinuclear units show two different valence distributions, Mn(II)/Mn(III)/Mn(II) and Mn(III)/Mn(II)/Mn(III). Additional features of interest for the compound include the fact that (a) two of the Mn(III) ions show a Jahn–Teller elongation, whereas the third ion shows a Jahn–Teller compression; (b) one bridge between Mn(III) atoms is an oxo (O²⁻) ion, whereas the bridge between Mn(II) and Mn(III) is a hydroxyl (OH⁻) group; and (c) the di-(2-pyridyl)-ketone ligand that is methanolized to methyl-Hpdol and R₂pdol (R = CH₃, H) acts in three different modes: methyl-pdol(-1), Hpdol(-1), and pdol(-2). For magnetic behavior, the general Hamiltonian formalism considers that (a) all of the interactions inside the two “cubanes” between Mn(II) and Mn(III) ions are equal to the J_1 constant, those between Mn(II) ions are equal to the J_2 constant, and those between the Mn(III) ions are equal to the J_3 constant and (b) the interaction between the two cubanes is equal to the J_4 constant. The fitting results are $J_1 = J_2 = 0.7 \text{ cm}^{-1}$, $J_3 \approx 0.0$, $J_4 = -6.2 \text{ cm}^{-1}$, and $g = 2.0$ (fixed). According to these results, the ground state is $S = 1/2$, and the next excited states are $S = 3/2$ and $5/2$ at 0.7 and 1.8 cm⁻¹, respectively. The EPR spectra prove that the spin ground state at a low temperature is not purely $S = 1/2$ but is populated with the $S = 3/2$ state, which is in accordance with the susceptibility and magnetization measurements.

Introduction

The photosynthetic conversion of water to dioxygen occurs in the oxygen evolving complex (OEC) of photosystem II. Four manganese ions form the heart of the water oxidation machinery of this enzyme.¹ The recent crystal structure resolution of PS II of the cyanobacterium *Thermosynechococcus elongatus* at 3.5 Å revealed the presence of a heterometallic Mn₄CaO₄ cluster² consisting of a Mn₃CaO₄ cubane with a fourth Mn atom attached to one of its bridging O²⁻ ions. There are five resolvable enzyme oxidation levels, termed S states. The most reduced form is the S₀ level, and

the liberation of dioxygen occurs during the S₃→S₄→S₀ transition.³ Several homo- or mixed-valence trinuclear⁵ and homo-⁶ or mixed-valence tetranuclear⁷ manganese complexes

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have been prepared as potential models for the OEC of PS II. Reports of tetranuclear Mn complexes with average oxidation states of $2.5+/\text{Mn}$ ((II,III,II,III) or (II,II,II,IV) formulations),^{7b,d,e} $2.75+/\text{Mn}$ (represented by two valence distributions, Mn(II)Mn(III)_3 ^{8d} and $\text{Mn(II)}_2\text{Mn(III)Mn(IV)}$),^{7c} $3.0+/\text{Mn}$ (with only Mn(III)_4 oxidation states),^{6a,b} $3.25+/\text{Mn}$ and $3.50+/\text{Mn}$ (with valence distributions $\text{Mn(III)}_3\text{Mn(IV)}$ and $\text{Mn(III)}_2\text{Mn(IV)}_2$, respectively),^{6b,c,7f,g} $3.75+/\text{Mn}$ (with Mn(III)Mn(IV)_3 formulation), and $4.00+/\text{Mn}$ (with Mn(IV)_4 homovalence formulation) have been published.^{6c} The $3.25+/\text{Mn}$ and $3.50+/\text{Mn}$ oxidation states most resemble the S_1 state of the OEC, whereas the $3.75+/\text{Mn}$ state is the best model for the S_2 state.

Whereas there are examples of tetranuclear manganese clusters having cubane-like cores,⁸ there is only one⁹ currently known trinuclear compound in inorganic chemistry that has a pseudocubane-like arrangement. Trinuclear manganese clusters that interact with calcium ions forming a

CaMn_3O_4 cubane-like cluster remain largely elusive in inorganic chemistry and are reported as only a part of the structure of a $\text{Ca}_2\text{Mn}_{13}$ compound.¹⁰

The reported compound belongs to the family of hexanuclear compounds; therefore, a detailed discussion of this class of compounds is given below.

Our previous efforts have been centered on the preparation and characterization of trinuclear mixed-valence $\text{Mn(III)-Mn(II)Mn(III)(Schiff base)}_2(\text{carboxylato})_4(\text{solvent})_2$ and $\text{Mn(II)Mn(IV)Mn(II)(pko)}_2(\text{X})_4$ ($\text{X} = \text{SCN}^-$, Cl^- , NNN^- , NCO^-) complexes with predominantly oxygen-donor ligands in order to understand the fundamental coordination, structure, and magnetochemistry of complexes that are potentially relevant to the active site of the OEC.^{5a-g}

In this Article, we present the crystal structure of a hexanuclear manganese cluster $[\text{Mn(II)}_3\text{Mn(III)}_3\text{O(OH)-(CH}_3\text{pdol)}_3(\text{Hpdol})_3(\text{pdol})](\text{ClO}_4)_4$ (**1**) consisting of two distinct trinuclear units. This compound is the second reported example of a compound with trinuclear units in a pseudocubane-like arrangement. Furthermore, this is the first time a compound with two trinuclear units in different valence distributions, $\text{Mn(II)/Mn(III)/Mn(II)}$ and $\text{Mn(III)/Mn(II)/Mn(III)}$, is reported. Additional features of interest for the compound include the fact that (a) two of the Mn(III) ions show a Jahn–Teller elongation, whereas the third ion shows a Jahn–Teller compression; (b) one bridge between Mn(III) atoms is an oxo (O^{2-}) ion, whereas the bridge between Mn(II) and Mn(III) is a hydroxyl (OH^-) group; and (c) the di-(2-pyridyl)-ketone ligand methanolyzed to methyl-Hpdol and R_2pdol ($\text{R} = \text{CH}_3$, H) acts in three different modes: methyl-pdol(-1), Hpdol(-1), and pdol(-2). The synthesis and the detailed study of synthetic analogues of this cluster would greatly enhance our understanding of the spectroscopic, physical, and redox properties of the OEC. The reported compound should be a useful agent in our attempt to prepare CaMn_3 clusters with a cubane-like structure.

Experimental Section

Safety Note. Caution! Although no problems were experienced in the handling of perchlorate compounds, these salts are potentially explosive when combined with organic ligands and should be manipulated with care and used in only small quantities.

Materials. *N,N*-Dimethylformamide (DMF) was distilled from calcium hydride (CaH_2), and methanol was distilled from Mg. Both were stored over 3 Å molecular sieves. Di-(2-pyridyl)-ketone, Br_2 ,

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Table 1. Crystal Data and Structure Refinement for Mn(II)₃Mn(III)₃(CH₃pdol)₃(Hpdol)₃(pdol)(O)(OH)(ClO₄)₄·CH₃OH·2.3H₂O (1)

1	
empirical formula	C ₈₂ H _{79.6} Cl ₄ Mn ₆ N ₁₄ O _{35.3}
fw	2297.44
temp	180(2) K
cryst syst	triclinic
space group	<i>P</i> $\bar{1}$
<i>a</i> , (Å)	13.9501(5)
<i>b</i> , (Å)	16.3574(5)
<i>c</i> , (Å)	23.2809(9)
α , (deg)	84.437(1)
β , (deg)	78.913(1)
γ , (deg)	67.782(1)
<i>V</i> , (Å ³)	4824.5(3)
<i>Z</i>	2
<i>D</i> _{calcd} , mg·m ⁻³	1.582
μ (Mo K α), mm ⁻¹	0.964
<i>F</i> (000)	2340
θ range for data collection	3.03–25.00°
index ranges	–16 ≤ <i>h</i> ≤ 16, –19 ≤ <i>k</i> ≤ 18, –27 ≤ <i>l</i> ≤ 27
GOF on <i>F</i> ²	1.075
final <i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> 1 = 0.0724, <i>wR</i> 2 = 0.1899 ^a

^a For 13 371 reflections with *I* > 2 σ (*I*).

1,3-propanediol, and Mn(ClO₄)₂·6H₂O were purchased from Aldrich and used as received. All chemicals and solvents were reagent grade.

Physical Measurements. Infrared spectra (200–4000 cm⁻¹) were recorded on a Perkin-Elmer FT-IR 1650 spectrometer, and samples were prepared as KBr pellets. Ultraviolet/visible spectra were recorded on a Shimadzu-160A dual-beam spectrophotometer. Electron paramagnetic resonance spectra were recorded on a Bruker ESR 300 spectrometer equipped with a Varian variable-temperature controller. The external standard was *dpph*. Variable-temperature magnetic susceptibility measurements were carried out on powdered samples in the 3–300 K temperature range by the use of a Quantum Design SQUID susceptometer in 0.1 and 1.0 kG applied magnetic fields. Magnetization measurements were carried out at different temperatures in the range of 1.8–6 K and in the field range of 0–5 T. Carbon, hydrogen, and nitrogen elemental analyses were performed on a Perkin-Elmer 240B elemental analyzer. Electric conductance measurements were carried out with a WTW model LF 530 conductivity outfit and a type C cell, which had a cell constant of 0.996. This represents a mean value calibrated at 25 °C with potassium chloride. All temperatures were controlled to an accuracy of ±0.1 °C by the use of a Haake thermoelectric circulating system.

X-ray Crystal Structure Determination. Slow crystallization from MeOH yielded brown prismatic crystals. A crystal with approximate dimensions of 0.10 × 0.20 × 0.30 mm³ was taken directly from the mother liquor and immediately cooled to –93 °C. Diffraction measurements were made on a Rigaku R-AXIS SPIDER image plate diffractometer using graphite monochromated Mo K α radiation at –93 °C. The data collection (ω scans) and processing (cell refinement, data reduction, and empirical absorption correction) were performed using the CrystalClear program package.¹¹ The structure of compound **1** was solved by direct methods by the use of SHELXS-97^{12a} programs and was refined by full-matrix least-squares techniques on *F*² by SHELXL-97.^{12b} Important crystal data and structure refinement details are listed in Table 1. Additional experimental crystallographic details for compound **1** include $2\theta_{\max}$ = 50°; reflections collected/unique/used, 73 827/

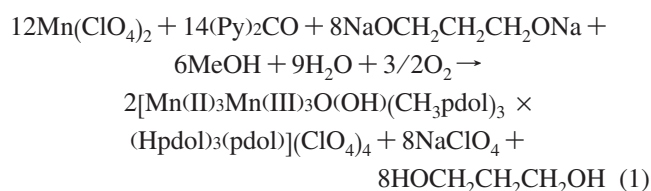
16 939 (*R*_{int} = 0.0655)/16 939; 1455 parameters refined; (Δ/σ)_{max} = 0.009; ($\Delta\rho$)_{max}/ $(\Delta\rho)$ _{min} = 1.592/–0.993 e/Å³; and *R*1/*wR*2 (for all data), 0.0882/0.2045. Hydrogen atoms were either located by difference maps and refined isotropically or introduced at calculated positions as riding on bonded atoms. No H atoms for the solvate molecules were included in the refinement. All nonhydrogen atoms were refined anisotropically.

CCDC 679815 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K.; fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Preparation of [Mn(II)₃Mn(III)₃O(OH)(CH₃pdol)₃(Hpdol)₃(pdol)](ClO₄)₄·CH₃OH·2.3H₂O (1). Compound **1** was synthesized by adding 10 mmol (1.842 g) of di-(2-pyridyl)-ketone to 10 mmol (3.62 g) of Mn(ClO₄)₂·6H₂O in 20 mL of methanol, and the mixture was stirred for 20 min; 30 mmol of Br₂ (1.53 mL) was added, and the yellow mixture became dark brown. After 30 min of stirring, 40 mmol (3.52 g) of the sodium salt of 1,3-propanediol in 10 mL of methanol was added. The solution was left to evaporate slowly, and after three days, brown crystals suitable for X-ray diffraction studies were deposited from the mother liquor. These crystals have been structurally characterized with the formula C₈₂H_{79.60}-Cl₄Mn₆N₁₄O_{35.30} (fw = 2297.44). The crystals were collected via filtration, and the resulting powder was analyzed as solvent-free. Anal. Calcd for C₈₁H₇₁Cl₄Mn₆N₁₄O₃₂: C, 43.75; H, 3.22; N, 8.82. Found: C, 43.50; H, 3.10; N, 8.50.

Results and Discussion

The preparation of complex **1** can be achieved by the reaction of a mixture of Mn(ClO₄)₂ with (Py)₂CO in MeOH at room temperature.



The reaction between Mn(ClO₄)₂ and di-(2-pyridyl)-ketone in the presence of the sodium salt of propanediol as a base in MeOH produces a deep-brown solution. By slow evaporation, brown crystals of compound **1**, which is soluble in DMF, CH₃CN, and DMSO, were deposited. Molecular conductance measurements of a 10⁻³ M solution of compound **1** in CH₃CN, DMSO, or DMF gives Λ_m = 529, 135, or 245 $\mu\text{S}/\text{cm}$, respectively, which suggests a 1:4 cation/anion electrolyte. The IR spectrum of compound **1** derived from the methanolysed form of Hdpk exhibits characteristic bands as a result of the ligand ($\nu(\text{O}-\text{H})_{\text{Hdiol}}$, $\nu(\text{C}=\text{N})_{\text{pyridyl}}$, and $\nu(\text{C}-\text{O})_{\text{diol}}$ at ~3507, 1602, and 1100 cm⁻¹, respectively) and the noncoordinated perchlorate anions ($\nu(\text{Cl}-\text{O})_{\text{assym}}$ at 1095 cm⁻¹, $\nu(\text{Cl}-\text{O})_{\text{sym}}$ at 1052 cm⁻¹, and $\delta(\text{O}-\text{Cl}-\text{O})$ at 623 cm⁻¹). The presence of two overlapping broad bands at ~3507 and 3350 cm⁻¹ reflects the extended H-bonding network between the O–H bridging ion and the unbound O–H groups of Hpdol ligands (Figure 1).

Description of the Structure. Selected bond distances and angles for complex **1** are listed in Table 2. The molecule consists of a discrete tetracationic hexamanganese unit, four

(11) CrystalClear; Rigaku/MSC Inc.: The Woodlands, TX, 2005.

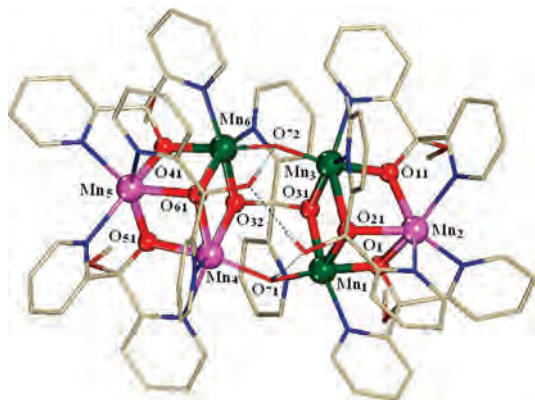


Figure 1. X-ray crystal structure of $[\text{Mn}(\text{II})_3\text{Mn}(\text{III})_3\text{-O}(\text{OH})(\text{CH}_3\text{pdol})_3(\text{Hpdol})_3(\text{pdol})](\text{ClO}_4)_4$ (**1**). The unbound ClO_4^- ions are omitted for clarity.

Table 2. Selected Bond Distances and Angles of **1**

bond distances (Å)			
Mn1–O71	1.859(3)	Mn4–O61	2.093(3)
Mn1–O1	1.906(3)	Mn4–O71	2.104(3)
Mn1–O31	2.018(3)	Mn4–O32	2.190(3)
Mn1–N1	2.084(4)	Mn4–O51	2.225(3)
Mn1–O21	2.166(3)	Mn4–N61	2.255(4)
Mn1–N31	2.213(4)	Mn4–N52	2.300(4)
Mn2–O11	2.082(3)	Mn5–O61	2.094(3)
Mn2–N2	2.195(4)	Mn5–O51	2.186(3)
Mn2–N22	2.221(5)	Mn5–O41	2.198(3)
Mn2–O21	2.225(3)	Mn5–N42	2.213(4)
Mn2–O1	2.240(3)	Mn5–N62	2.252(4)
Mn2–N11	2.269(4)	Mn5–N51	2.298(4)
Mn3–O72	1.849(3)	Mn6–O72	1.855(3)
Mn3–O11	1.953(3)	Mn6–O41	1.935(3)
Mn3–O31	2.022(3)	Mn6–O32	1.938(3)
Mn3–N12	2.187(4)	Mn6–N41	2.069(4)
Mn3–N21	2.204(4)	Mn6–O51	2.210(3)
Mn3–O21	2.301(3)	Mn6–N32	2.272(4)
Mn1···Mn2	3.249(2)	Mn3···Mn6	3.393(3)
Mn1···Mn3	3.365(2)	Mn4···Mn5	3.263(2)
Mn1···Mn4	3.583(3)	Mn4···Mn6	3.346(1)
Mn2···Mn3	3.321(3)	Mn5···Mn6	3.269(3)
angles (deg)			
Mn1–O1–Mn2	102.9(2)	Mn6–O41–Mn5	104.4(1)
Mn3–O11–Mn2	110.7(2)	Mn5–O51–Mn6	96.1(1)
Mn1–O21–Mn2	95.4(1)	Mn5–O51–Mn4	95.4(1)
Mn1–O21–Mn3	97.7(1)	Mn6–O51–Mn4	97.9(1)
Mn2–O21–Mn3	94.4(1)	Mn4–O61–Mn5	102.4(2)
Mn1–O31–Mn3	112.8(1)	Mn1–O71–Mn4	129.3(2)
Mn6–O32–Mn4	108.1(2)	Mn3–O72–Mn6	132.8(2)
O71–Mn1–O1	169.7(2)	O61–Mn4–O71	166.0(1)
O31–Mn1–N1	168.9(2)	O51–Mn4–N61	147.1(1)
O21–Mn1–N31	152.3(1)	O32–Mn4–N52	140.9(1)
O72–Mn6–O41	167.3(1)	O51–Mn5–N42	142.7(1)
O32–Mn6–N41	171.1(2)	O41–Mn5–N62	154.7(1)
O51–Mn6–N32	156.0(1)	O61–Mn5–N51	148.0(2)
O72–Mn3–O11	168.3(2)	O11–Mn2–N22	142.2(2)
O31–Mn3–N21	141.5(1)	N2–Mn2–O21	144.6(1)
N12–Mn3–O21	148.7(1)	O1–Mn2–N11	156.2(2)

coordinatively unbound perchlorate anions, CH_3OH , and 2.3 H_2O solvent molecules. The hexamanganese cation comprises two distinct $\text{Mn}_3(\text{II}/\text{III}/\text{II})$ and $\text{Mn}_3(\text{III}/\text{II}/\text{III})$ trinuclear units in a pseudocubane-like arrangement. Each trinuclear unit could be described as a strongly distorted cube with a missing edge, in which four corners are occupied by four oxygens and three corners are occupied by manganese atoms. The four oxygen atoms are derived from two methylpdol(–1) ligands, a Hpdol(–1) ligand, and a pdol(–2)

ligand. Each manganese atom is six-coordinated in an octahedral arrangement. All oxidation states have been assigned by using a combination of charge balance considerations, bond lengths, and bond valence sum (BVS) analyses.¹² BVS calculations lead to values of 3.1, 2.1, 2.9, 2.2, 2.1, and 3.1 for Mn(1)–Mn(6) centers, respectively, which suggests that Mn(1), Mn(3), and Mn(6) atoms are valence-trapped in oxidation state 3+, whereas Mn(2), Mn(4), and Mn(5) are in oxidation state 2+. BVS calculations also confirmed that the oxygen atoms connecting the two trinuclear subunits are a OH^- and an O^{2-} ion, giving values of 1.2 and 1.6 for O(71) and O(72), respectively. Mn(1), Mn(3), Mn(4), and Mn(6) possess an O_4N_2 coordination environment with Mn–O(N) average distances of 2.041, 2.086, 2.195, and 2.047 Å, respectively, whereas Mn(2) and Mn(5) have an O_3N_3 coordination environment with Mn–O(N) average distances of 2.205 and 2.207 Å, respectively. Mn(1) and Mn(6) in oxidation state 3+ show Jahn–Teller elongation with Mn–O/N average distances of 1.967 and 1.950 Å, respectively, for the equatorial plane and average elongated axes of 2.190 and 2.241 Å, respectively, whereas Mn(3), also in oxidation state 3+, shows a Jahn–Teller compression with a Mn(3)–O/N average distance for the equatorial plane of 2.179 Å and average compressed axes of 1.901 Å. For the bridging groups of the trinuclear species, the bridge between Mn(III)(3) and Mn(III)(6) may be assigned as an O^{2-} atom (Mn(3)–O(72) = 1.848 Å and Mn(6)–O(72) = 1.855 Å) and that between Mn(III)(1) and Mn(II)(4) may be assigned as a OH^- ion (Mn(1)–O(71) = 1.861(3) and Mn(4)–O(71) = 2.105(3)). The Mn(III)–O distances are comparable with those of $\mu\text{-O}$, $\mu_3\text{-O}$, and $\mu_4\text{-O}$ bridges of polynuclear Mn(III) compounds.^{7f,g}

The Mn–O–Mn angles within cubane-like trinuclear units vary between 94.4(1) and 112.8(1)° for the smaller angle Mn(2)–O(21)–Mn(3) and the larger angle Mn(1)–O(31)–Mn(3), respectively. The average Mn–O–Mn angles were 102.3 and 100.7° for each trinuclear unit, respectively. The angle between Mn(III) and the bridging oxo group (Mn(3)–O(72)–Mn(6)) is 132.8(2)°, and the angle for Mn(II), Mn(III), and the OH^- group (Mn(1)–O(71)–Mn(4)) is 129.3(2)°.

The separations within the pseudocubane cores, Mn(III)(1)···Mn(II)(2), Mn(III)(1)···Mn(III)(3), Mn(II)(4)···Mn(II)(5), and Mn(II)(4)···Mn(III)(6) (3.249, 3.364, 3.263, and 3.346 Å, respectively) are not related to the oxidation states of manganese atoms, which is obvious after comparing the separations between the trinuclear units Mn(III)(1)···Mn(II)(4) and Mn(III)(3)···Mn(III)(6) (3.583 and 3.393 Å, respectively). The two O–H groups of Hpdol ligands, the O–H bridging anion and the O^{2-} bridging atom, create a H-bonding network with $\text{O}\cdots\text{H}$ separations from 1.816 to 1.884 Å.

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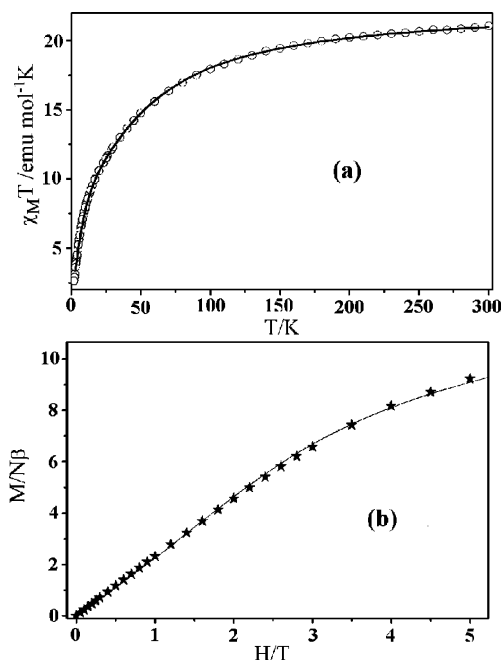


Figure 2. (a) Temperature dependence of the susceptibility data in the form of $\chi_M T$ at 0.1 T (○). The solid line represents the best fit according to eq 1; see the text for details. (b) Magnetization data of compound **1** at 2 K (★) and a theoretical model according to the fitting results of the susceptibility data (—).

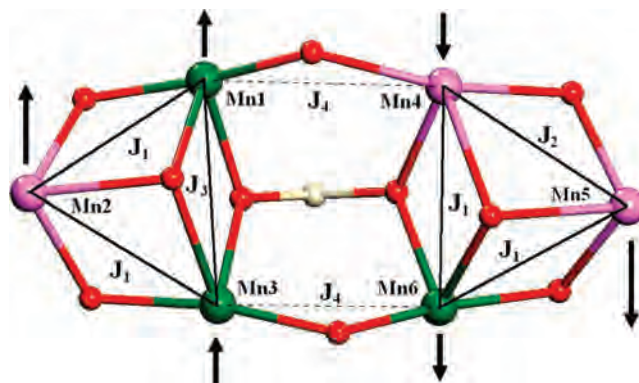
Magnetic Discussion. The temperature dependence of the susceptibility data in the form of $\chi_M T$ as well as the magnetization data are shown in Figure 2.

For the susceptibility data, the value of $\chi_M T$ at room temperature is $21.0 \text{ emu} \cdot \text{mol}^{-1} \cdot \text{K}$, which is close to the expected value for six-isolated ($3\text{Mn(III)} + 3\text{Mn(II)}$) ions. Until 50 K, there is a smooth decrease, whereas after 50 and until 2 K, a more pronounced decrease occurs and reaches $2.6 \text{ emu} \cdot \text{mol}^{-1} \cdot \text{K}$ at 2 K. Two different magnetic models (Supporting Information) were used to fit the magnetic susceptibility according to the crystallographic criteria: (a) the bond distances (Mn–Mn) and angles (Mn–O–Mn) and (b) the valences of the Mn ions (Table 2). A general Hamiltonian formalism is given in eq 2, according to which (a) all of the interactions inside the two cubanes between Mn(II)–Mn(III) ions are equal to the J_1 constant, between Mn(II) ions are equal to the J_2 constant, and between Mn(III) ions are equal to the J_3 constant and (b) the interaction between the two cubanes is equal to the J_4 constant (Scheme 1).

$$H = -2J_1(S_1S_2 + S_2S_3 + S_4S_6 + S_5S_6) - 2J_2(S_1S_3) - 2J_3(S_4S_5) - 2J_4(S_1S_4 + S_3S_6) \quad (2)$$

The pair of J_1 , J_2 interactions is expected to be small and ferromagnetic, whereas, the other two interactions are antiferromagnetic.^{13a} The fitting results ($J_1 = J_2 = 0.7$, $J_3 \approx 0.0$, $J_4 = -6.2 \text{ cm}^{-1}$ and $g = 2.0$ (fixed)), are shown in Figure 2a as a solid line. According to these results, the ground state is $S = 1/2$, and the next excited states are $S = 3/2$ and $5/2$ at 0.7 and 1.8 cm^{-1} , respectively. To verify the correctness of the fitting results, a simulation of the magnetization data was carried out with the values obtained and is shown in Figure 2b as a solid line along with the

Scheme 1. Magnetic Model Used in This Study



experimental data. The magnetic susceptibility and the magnetization of compound **1** were fitted by the use of the MAGPACK program^{13b} employed with a nonlinear least-squares curve-fitting DSTEPIT program.^{13c}

It is very difficult to extract a general magnetostructural correlation concerning the magnitude and the sign of the exchange interaction. The values (and signs) obtained in this fitting procedure are analogous to, or follow the same trend as, the other hexanuclear Mn(II)/(III) complexes discussed in the final part of the Article. The X-band EPR spectrum at various temperatures from 4 K to room temperature is shown in Figure 3. Apart from the central transition at $g = 2$ (Figure 3b) where hyperfine lines are observable (probably corresponding to an impurity of a Mn(II) ion), there are multiple transitions in the low-field region due to $m_S = \pm 1/2$ for an $S = 3/2$ ground state, Figure 3c. At higher temperatures, there is only a broad signal centered at $g \approx 2$. Thus, the EPR spectra provide proof that the spin ground state at a low temperature is not purely $S = 1/2$ but is populated with the $S = 3/2$ state, in accordance with the susceptibility and magnetization measurements.¹⁴

Relationship between Different Structures. Complex **1** is a valuable addition to the small but growing family of hexanuclear manganese complexes. The present work also extends to the body of results that emphasizes the ability of the

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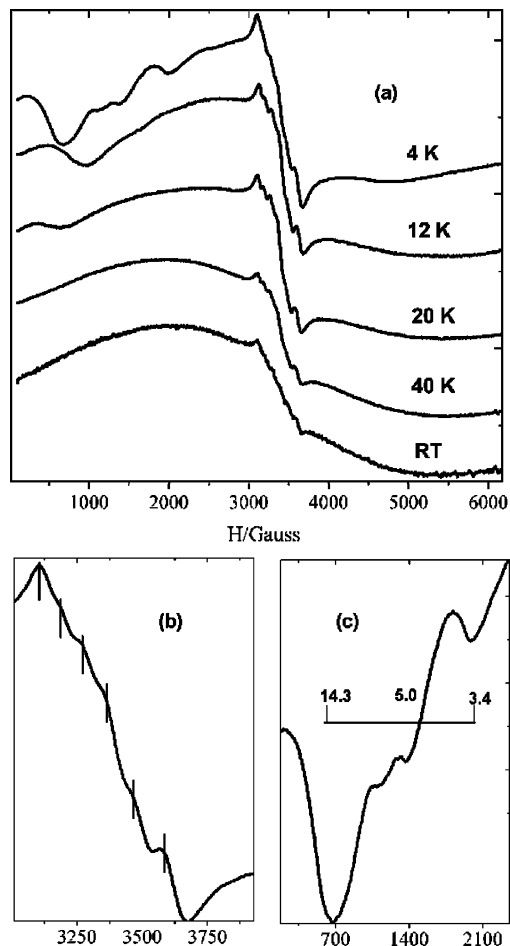


Figure 3. (a) X-band powder EPR spectra of the compound at various temperatures, (b) enlargement of the area around $g = 2$, and (c) enlargement of the low-field area in the range of the g values, which are also shown.

dpc ligand to form new structural types in 3d metal chemistry. Because most hexanuclear manganese complexes have been reported only recently, we felt that it was timely to collect all hexanuclear manganese complexes reported by different groups (Table 3).

An inspection of Table 3 clearly shows that there are 12 different cores and types 3 and 6 (Figure 4) are the most common.

Core type 1 can be described as a nonplanar $(\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_4(\mu_2\text{-OR})_2(\mu_3\text{-OR})_4)^{8+}$ unit or as a central planar $(\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2)$ rhombus with two peripheral Mn ions above and below the plane. Core type 2 consists of a rodlike $(\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_4(\mu_2\text{-OR})_6(\mu_3\text{-OR})_4)^{4+}$ unit comprising four edge-sharing triangles. Core type 3, similar to type 1, consists of a nonplanar $(\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_4(\mu_2\text{-OR})_4(\mu_3\text{-OR})_4)^{6+}$ unit and can be described as consisting of a central $(\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2)$ plane with two Mn ions located above and below the plane. Core type 4 consists of a hexanuclear motif in which two cuboidal (Mn_3O_4) units are fused together through a pair of T-shaped $\mu_3\text{-oxo}_4$ groups. Core type 5 contains a central planar Mn_4 rhombus, edge-bridging O atoms, and capping O atoms. Two additional Mn^{II} ions are each connected to the central

rhombus by an alkoxide O atom. Core type 6 contains a nonplanar $(\text{Mn}_6(\mu_3\text{-O}^{2-})_2(\mu_2\text{-OR})_2)^{n+}$ unit of two offset, stacked $(\text{Mn}_3(\mu_3\text{-O}^{2-}))^{n+}$ triangular subunits linked by two central O atoms. Core type 7 can be regarded as a face-sharing double-cubane cluster with a (Mn_6O_6) core. The centrosymmetric complex comprises two groups of Mn_3 clusters, and the core of the molecule can be regarded as a dimer of trimers joined together by O bridges. Core type 8 (the present compound) exhibits two independent trinuclear subunits bridged by two oxygen atoms that are not a part of the pseudocubane-like cores. Core type 9 consists of two $\text{Mn}(\text{III})$ ions surrounded by four $\text{Mn}(\text{II})$ ions to form two edge-sharing OMn_4 tetrahedra that give rise to the (Mn_6O_2) core. Core type 10 contains two $(\text{Mn}_3(\mu_3\text{-O}))^{n+}$ units linked by two RCO_2^- ligands and one $\mu_4\text{-CH}_2\text{O}_2^{2-}$ bridge. Core type 11 consists of six Mn atoms disposed in a distorted trigonal antiprismatic topology, and core type 12 consists of two trinuclear wheel-type subunits bridged by two $\mu_2\text{-O}$ units of two tridentate carboxylato ligands.

By a close examination of all core types reported, we may conclude that assuming that there are two trinuclear subunits they are sharing at least one oxygen atom; thus, compound **1** is unique in exhibiting two independent trinuclear subunits bridged by two oxygen atoms that are not part of the pseudocubane-like cores.

For the valence distribution of manganese atoms, $(\text{Mn}(\text{I-III})_6)$ and $(\text{Mn}(\text{III})_2\text{Mn}(\text{II})_4)$ seem to be the most popular, whereas the spin ground state is not related to the core type. It is obvious that $(\text{Mn}_6(\text{OAc})_8(\text{thme})_2(\text{py})_4)$, $(\text{Mn}_6((\text{CH}_3)_3\text{CCO}_2)_8(\text{tmp})_2(\text{py})_2)$, and $(\text{Mn}_6(\text{CH}_3\text{CO}_2)_6(\text{thme})_2(\text{H}_2\text{tea})_2)$, all of core type 3, show spin ground states of $S = 4, 3$, and 0 , respectively, and $(\text{Mn}_6\text{O}_2(\text{sao})_6(\text{O}_2\text{CH})_2(\text{MeOH})_4)$, $(\text{Mn}_6\text{O}_2\text{-}(\text{Etsao})_6(\text{O}_2\text{CCMe}_3)_2(\text{EtOH})_5)$, and $(\text{Mn}_6\text{O}_2(\text{Etsao})_6(\text{O}_2\text{CPh})_2\text{-}(\text{EtOH})_4(\text{H}_2\text{O})_2)$, all of core type 6, show spin ground states of $S = 4, 7$, and 12 , respectively. A general remark could be that the presence of multiple Mn^{2+} ions in the structure, which promotes weak exchange interactions and results in the presence of low-lying excited states, does not contribute to the enhancement of the spin ground state.

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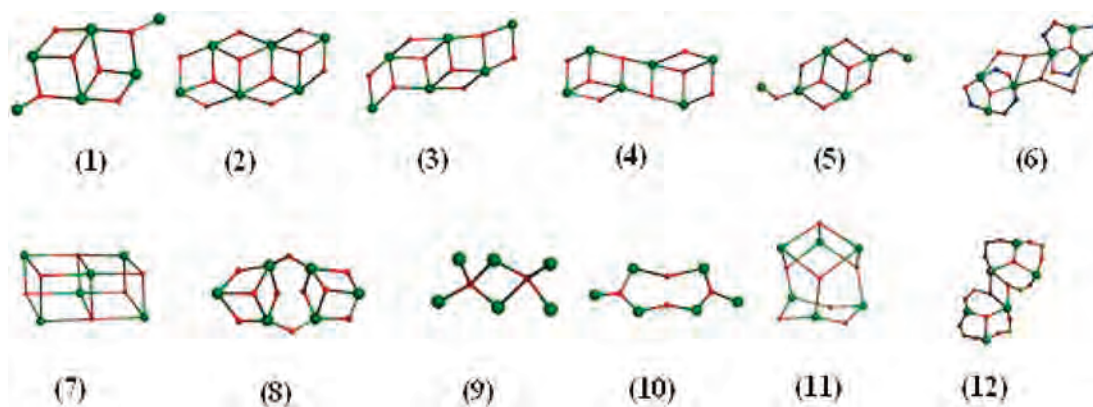
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Table 3. Structural and Magnetic Features of Hexanuclear Manganese Compounds Reported^a

	compound	ground state <i>S</i>	<i>D</i> (cm ⁻¹)	core type	ref
[Mn(III)₂Mn(II)₄]					
1	[Mn ₆ (OAc) ₆ (H ₂ tea) ₂ (tmp) ₂]	0		2	15
2	[Mn ₆ (acac) ₄ (OAc) ₂ (Htmp) ₂ (H ₂ N-ep) ₂]	0		2	15
3	[Mn ₆ (OAc) ₈ (tmp) ₂ (py) ₄]	4	-0.44	1	15
4	[Mn ₆ (OAc) ₈ (thme) ₂ (py) ₄]	4	-0.58	3	15
5	[Mn ₆ ((CH ₃) ₃ CCO ₂) ₈ (tmp) ₂ (py) ₂]	3	-0.75	3	16
6	[Mn ₆ (CH ₃ CO ₂) ₆ (thme) ₂ (H ₂ tea) ₂]	0		3	16
7	[Mn ₆ (teaH) ₂ (teaH ₂) ₂ (O ₂ CCHPh) ₂]	5	-0.20	5	17
8	[Mn ₆ O ₂ (O ₂ CR) ₁₀ (L ⁴) ₄]	0		9	18
9	[Mn ₆ O ₂ (O ₂ CPh) ₁₀ (S) ₄]	0		9	19
[Mn(III)₃Mn(II)₃]					
10	[Mn ₆ O ₂ (O ₂ CPh) ₈ (L ¹) ₃]	7/2	-0.56	3	20
11	Mn ₆ O ₂ (O ₂ CPh) ₈ (L ²) ₃]	7/2	-0.46	3	21
12	[Mn ₆ O(OH)(CH ₃ pdol) ₃ (Hpdol) ₃ (pdol)](ClO ₄) ₄	1/2		8	this work
[Mn(III)₆]					
13	[Mn ₆ O ₂ (L ³) ₄ (O ₂ CMe) ₂ (OMe) ₆]			2	22
14	[Mn ₆ O ₄ (OMe) ₂ (OAc) ₄ (Mesalim) ₄]	0		7	23
15	[Mn ₆ O ₂ (sao) ₆ (O ₂ CH) ₂ (MeOH) ₄]	4	-1.39	6	24
16	[Mn ₆ O ₂ (Etsao) ₆ (O ₂ CMe) ₂ (EtOH) ₅]	7	-0.75	6	24
17	[Mn ₆ O ₂ (Etsao) ₆ (O ₂ CPh) ₂ (EtOH) ₄ (H ₂ O) ₂]	12	-0.43	6	24
18	[Mn ₆ O ₂ (salox) ₆ (O ₂ CMe) ₂ (EtOH) ₄]	4	-1.22	6	25
19	[Mn ₆ O ₂ (salox) ₆ (O ₂ CPh) ₂ (EtOH) ₄]	4	-1.21	6	25
20	[Mn ₆ O ₂ (O ₂ CH ₂)(O ₂ CPet) ₁₁ (HO ₂ CPet) ₂ (O ₂ CMe) ₂]	<2		10	26
21	[Mn ₆ O ₂ (Etsao) ₆ (O ₂ CPh(Me) ₂)(EtOH) ₆]	12	-0.43	3	27
[Mn(III)₂Mn(IV)₄]					
22	[Mn ₆ O ₈ (O ₂ CAr ^{tol}) ₈ (dmb) ₆](OTf) ₃			4	28
[Mn(II)₂Mn(III)₄]					
23	[Mn ₆ O ₂ (O ₂ CPh) ₁₂ (py) ₂]	3	-1.1	12	29
[Mn(III)₃Mn(IV)₃]					
24	[Mn ₆ O ₈ (mpdp) ₃ (bpy) ₃](ClO ₄)	3/2	-0.79	11	30

^a H₃tea, triethanolamine; H₃tmp, 1,1,1-tris(hydroxymethyl)propane; H₂N-H₂ep, 2-amino-2-ethyl-1,3-propanediol; H₃thme, 1,1,1-tris(hydroxymethyl)ethane; HL¹, (L-phenyl-3-pyridin-2-yl)propane-1,3-dione; HL², 1-(2-pyridyl)-3-(*p*-tolyl)propane-1,3-dione; L³, *N*-(5-MeO-salicylidene)-*N,N*-bis(2-hydroxyethyl)-ethylenediamine; HMesalim, methyl salicylimidate; EtsaoH₂, 2-hydroxypropio-phenone oxime; dmb, 4,4'-dimethyl-2,2'-bipyridine; OTf, trifluoromethane-sulfonate; L⁴, H₂O, py, MeCN; mpdp, *m*-phenylenedipropionate; S, py, MeCN, DMF.

**Figure 4.** Structural cores observed in hexanuclear manganese compounds.

Conclusions

In this Article, we present the crystal structure of a hexanuclear manganese cluster [Mn(II)₃Mn(III)₃O(OH)-(CH₃pdol)₃(Hpdol)₃(pdol)](ClO₄)₄ (**1**) consisting of two distinct trinuclear units in different valence distributions, Mn(II)/Mn(III)/Mn(II) and Mn(III)/Mn(II)/Mn(III), and a unique core type among all hexanuclear compounds reported. The synthesis and detailed study of synthetic analogues of this cluster would greatly enhance our understanding of the spectroscopic, physical, and redox properties of the OEC. Trinuclear manganese clusters interacting with calcium ions forming a CaMn₃O₄ cubane-like cluster remain largely

elusive in inorganic chemistry and are reported as only a part of the structure of a Ca₂Mn₁₃ compound. The reported compound should be a useful agent in our attempt to prepare CaMn₃ clusters with cubane-like structures.

Acknowledgment. This project is cofunded by the European Union/European Social Fund, “Pythagoras II”.

Supporting Information Available: A crystal structure diagram with all of the heteroatoms labeled. Magnetic data showing the magnetic models used in this study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC800472C