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Tetranuclear Manganese(II) Complexes of Thiacalixarene Macrocycles with Trigonal Prismatic Six-Coordinate Geometries: Synthesis, Structure, and Magnetic Properties

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Two tetranuclear manganese(II) complexes $[Mn^{II}_4(thiaS)_2]$ (**1**) and $[Mn^{II}_4(thiaSO)_2]$ (**2**) have been synthesized under solvothermal conditions in methanol with *p*-*tert*-butylthiacalix[4]arene (thiaS) and *p*-*tert*-butylsulfinylthiacalix[4]arene (thiaSO). For both complexes, the structure has been established from single-crystal X-ray diffraction. $[Mn_4(thiaS)_2]\cdot H_2O$ (**1**) crystallizes in the orthorhombic *Immm* (No. 71) space group with the following parameters: $a = 18.213$ (5) Å, $b = 19.037$ (5) Å, $c = 29.159$ (5) Å, $V = 10110$ (4) Å^3, and $Z = 4$. $[Mn_4(thiaSO)_2]\cdot H_2O$ (**2**) crystallizes in the monoclinic *C*2/*m* (No. 12) space group with the following parameters: $a = 33.046(1)$ Å, $b = 19.5363$ (8) Å, $c = 15.7773$ (9) Å, $\beta = 115.176$ (2)°, $V = 9218.3$ (8) Å^3, and $Z = 4$. The two complexes are neutral and are best described as manganese squares sandwiched between two thiacalixarene macrocycles. In both complexes, each manganese center is six-coordinated in a trigonal prismatic geometry with four phenoxo oxygen atoms plus two sulfur atoms for **1** or two oxygen atoms from SO groups for **2**. The two tetranuclear complexes exhibit identical magnetic behaviors resulting from antiferromagnetic interactions between the four manganese centers. The simulation of the magnetic susceptibility was done considering a single exchange-coupling constant between the manganese(II) ions, J ($H = -J(S_1S_2 + S_2S_3 + S_3S_4 + S_1S_4)$). The best fits give the same result for the two complexes: $g = 1.94$ and $J = -5.57$ cm^{-1}.

Introduction

One prerequisite for the emerging nanotechnologies is in many cases the production of unique-size nanometric metal clusters in relation with size-dependent properties.[1] Current methods, such as grinding of bulk materials and wet chemistry,[2] always lead, to some extent, in dispersion of the particle size. In contrast, coordination chemistry is an elegant alternative to the design of tailored and functionalized nanosize metal-cluster molecules of identical size[3−19] Many coordination metal clusters have been obtained serendipitously, but as more examples are available, we may be expected to become more able to predict these structures.[11]

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Our work on metal clusters is done mainly in our area of interest, the field of molecular-based magnetism,[4,20−23] and in the study of magnetostructural relationships. The discovery that some polynuclear complexes may behave as single-molecule magnets (SMMs)[24] is particularly stimulating to us because it opens a new field with many challenges to answer. Indeed, SMMs are molecular entities which behave as single-domain magnetic particles below a so-called blocking temperature. For a metal cluster to have such a behavior requires it to have a high nuclearity and ground-state spin (S) with a large and negative magnetic anisotropy and weak intermolecular interactions. Despite numerous recent discoveries in this field,[25] the blocking temperatures are still very low. Therefore, there is a real need to discover new polynuclear systems and this is what prevailed to the present work.

When we look at coordination metal clusters there are always some bulky ligands on the rim of the central metal core. Indeed, these peripheral ligands are required to stop metal polycondensation. They may be also useful for further functionalization and cluster isolation. With this in mind, we revisited the coordination chemistry of the thiacalixarene macrocycles whose chemistry is well-known by some of us.[26−29] Our aim is to use the lower rim of the thiacalixarene to grow the metal clusters and the upper rim to further functionalize them.

Compared to that of the related calixarenes, the chemistry of the thiacalixarenes is recent. It is only since the late 90's that some facile synthesis of the thiacalixarene and their sulfinyl and sulfonyl derivatives have become known.[30−36] From early reports, the high complexation ability of the thiacalixarene macrocycles has been pointed out[33,34,37,38] and the crystal structures of some polynuclear complexes have further confirmed this ability either with the thiacalix[4]arene[34,39−46] or with the thiacalix[6]arene[47,48]with Cu(II),[42,48,49] Zn(II),[39] Co(II),[39−41,48] Ni(II),[40,41] UO_2,[44] Mn,[48] Nd,[45] or alkali metal.[46] The magnetic behaviors were also studied in the case of tetranuclear Cu(II),[42] trinuclear Co(II),[39] and decanuclear copper(II)[47] complexes, and the metal−metal interactions were found to be antiferromagnetic.

Despite these early results, thiacalixarene complexes have now become more scarce. This may be, in part, the result of crystallization difficulties because of the low solubility of the thiacalixarene and their complexes in convenient solvents. We found that under solvothermal conditions the *p-tert*-butylthiacalix[4]arene and the sulfonyl and sulfinyl derivatives give polynuclear complexes with most transition metal ions. We got polynuclear complexes with various nuclearities which depend in a reproductive way on the experimental conditions such as the solvent, deprotonating agent, metal salt, and temperature.

In this paper, we report the syntheses, crystal structures, and magnetic properties of two tetranuclear complexes, $[Mn_4(thiaS)_2]$ (**1**) and $[Mn_4(thiaSO)_2]$ (**2**), which were obtained with *p-tert*-butylthiacalix[4]arene (abbreviated thiaS) and *p-tert*-butylsulfinylthiacalix[4]arene (abbreviated thiaSO), respectively. These two compounds do not show

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any SMM behavior but should be considered as exploratory work aimed at finding a new family of magnetic metal clusters.

Experimental Section

All chemicals and solvents were used as received; all preparations and manipulations were performed under aerobic conditions. The ligands, *p-tert*-butylthiacalix[4]arene[30,31] and *p-tert*-butylsulfinylcalix[4]arene[40,42] were synthesized by the published procedures. FT-IR spectra were recorded on a Nicolet Magna-IR560 spectrometer.

Synthesis of $[Mn^{II}_4(thiaS)_2]\cdot H_2O$ (1) and $[Mn^{II}_4(thiaSO)_2]\cdot H_2O$ (2). Compounds **1** and **2** were both obtained in the form of colorless needle-shaped crystals from the reaction mixture of *p-tert*-butylthiacalix[4]arene (thiaS, **1**) (0.15 g, 0.2 mmol) or *p-tert*-butylsulfinylcalix[4]arene (thiaSO, **2**) (0.163 g, 0.2 mmol) with $MnCl_2$ (0.078 g, 0.6 mmol), pyridine (2 mL), and methanol (23 mL) in a 43 mL Teflon-lined autoclave under an autogenous pressure at 170 °C for 3 days. The crystals were isolated upon filtration; then they were washed with methanol and chloroform. Compounds **1** and **2** are insoluble in common organic solvents. Compound **1**. Yield: 72%. Anal. Calcd for $Mn_4C_{80}H_{88}S_8O_8$: C, 58.1; H, 5.36; S, 15.51; Mn, 13.29. Found: C, 58.5; H, 5.51, S, 15.7; Mn, 13.34. IR (cm^{-1}): 2952 (s), 1587, 1448 (s), 1392, 1360, 1308 (s), 1254 (s), 885, 834 (s), 751, 730 (s), 699 (s). Compound **2**. Yield: 84%. Anal. Calcd for $Mn_4C_{80}H_{88}S_8O16$: C, 53.93; H, 4.98; S, 14.4; Mn, 12.33. Found: C, 54.12; H, 5.21, S, 14.53; Mn, 12.47. IR (cm^{-1}): 2958 (s), 1594, 1449 (s), 1393, 1360, 1309 (s), 1256 (s), 1005 (s), 882, 833 (s), 750 (s), 729 (s), 700 (s).

X-ray Crystallography. Data Collection. The data were processed using the KappaCCD analysis programs.[50] The lattice constants were refined by least-squares refinement using 6426 reflections (1.0° $< \theta <$ 27.9°) and 7459 reflections (1.0° $< \theta <$ 26.7°) for compounds **1** and **2**, respectively. No absorption correction was applied to the data sets.

Structure Solution and Refinement. $[Mn^{II}_4(thiaS)_2]\cdot H_2O$ **(1)** crystallizes in the orthorhombic system. According to the observed systematic extinctions, the structure has been solved in the *Immm* space group (No. 71). $[Mn^{II}_4(thiaSO)_2]\cdot H_2O$ **(2)** crystallizes in the monoclinic system, and according to the observed systematic extinction, the structure has been solved in the *C*2/*m* space group (No. 12). Both structures have been solved by direct methods using the SIR97 program[51] combined with Fourier difference syntheses and refined against *F* using reflections with $[I/\sigma(I) > 3]$ using the CRYSTALS program.[52] All of the thermal atomic displacements for the non-hydrogen atoms have been refined anisotropically.

Crystallographic data and refinement details for compounds **1** and **2** are summarized in Table 1. Selected interatomic distances and angles are listed in Tables 2 and 3 for compound **1** and in Tables 4 and 5 for compound **2**.

Magnetic Measurements. The magnetic susceptibilities were measured on polycrystalline samples in the range of 2−300 K with a Quantum Design MPMS SQUID magnetometer operating at a field strength of 0.5 T. The data were corrected for the diamagnetism of the constituent atoms using the Pascal constants and measured diamagnetism for the thiacalixarene ligands.

Table 1. Crystal Data and Structure Refinement Parameters for Compounds **1** and **2**

	$Mn_4(thiaS)_2\cdot 1H_2O$ **1**	$Mn_4(thiaSO)_2\cdot 1H_2O$ **2**
formula	$C_{80}H_{82}Mn_4O_9S_8$	$C_{80}H_{82}Mn_4O_{17}S_8$
fw (g mol^{-1})	1647.8	1791.8
T (K)	293	293
λ(Mo Kα) (Å)	0.71069	0.71069
cryst syst	orthorhombic	monoclinic
space group	*Immm* (No. 71)	*C*2/*m* (No. 12)
a (Å)	18.213(5)	33.046(1)
b (Å)	19.037(5)	19.5363(8)
c (Å)	29.159(5)	15.7773(9)
β (deg)	−	115.176(2)
V ($Å^3$)	10110(4)	9218.3(8)
Z	4	4
D_{calcd} (g cm^{-3})	1.09	1.29
μ (mm^{-1})	0.696	0.775
$R(F)^a$ $I > 4\sigma(F_o)$	0.0992	0.1038
$R_w(F^2)^b$ all data	0.1853	0.0994

[a] $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $R_w(F^2) = \sum[w((F_o^2 - F_c^2)^2 / \sum w F_o^4]^{1/2}$.

Table 2. Selected Interatomic Distances (Å) for **1**[a]

	Mn1 and Mn2 environment		
Mn1−O11	2.095(6)	Mn1−O11(a)	2.095(6)
Mn1−O11(b)	2.095(6)	Mn1−O11(c)	2.095(6)
Mn1−S11(a)	2.702(3)	Mn1−S11	2.702(3)
Mn2−O11	2.116(6)	Mn2−O11(d)	2.116(6)
Mn2−O11(b)	2.116(6)	Mn2−O11(e)	2.116(6)
Mn2−S12	2.694(3)	Mn2−S12(b)	2.694(3)
Mn1− Mn2	3.307(2)		
S11− S11(a)	4.391(7)	O11−O11(b)	2.41(2)
O11−O11(c)	3.02(2)	O11−S11	2.990(6)
S12−S12(b)	4.403(6)	O11−O11(e)	3.06(2)
O11−S12	3.001(7)		
	Mn3 environment		
Mn3−O32	2.111(5)	Mn3−O32(e)	2.111(5)
Mn3−O31	2.123(5)	Mn3−O31(e)	2.123(5)
Mn3−S31	2.702(2)	Mn3−S31(e)	2.702(2)
Mn3−Mn3(a)	3.346(4)	Mn3−Mn3(f)	3.324(3)
S31−S31(e)	4.443(4)	O32−O32(e)	2.44(2)
O31−O32	3.03(1)	O31−S31	2.992(4)
O32−S31	3.001(4)		

[a] Symmetry transformations used to generate equivalent atoms: (a) $-x, -y, z$; (b) $-x, y, z$; (c) $x, -y, z$; (d) $-x, y, -z$; (e) $x, y, -z$; (f) $x, -y + 1, z$.

Results and Discussion

Synthesis. Most previously reported thiacalixarene complexes have been synthesized and crystallized under conventional conditions (in an open vessel and below the boiling point of the solvent).[39−48] The solvents were $CHCl_3$ or CH_2Cl_2 in which thiacalixarenes are very soluble,[32] but DMF and DMSO, where they dissolve quickly upon the addition of a base such as triethylamine, were also used. The problem is that the resulting complexes are also very soluble in those solvents. Therefore, it becomes tedious to get single crystals; this is generally done with help of a second solvent in which the thiacalixarenes are not or are only sparingly soluble such as CH_3CN, EtOH, and MeOH. After trials, we found that the conventional conditions and these solvents did not give strong control of the formation of the clusters and their crystallization. Therefore, we tried the solvothermal synthesis method using solvents in which thiacalixarenes and their complexes are sparingly soluble. Indeed, as the solvothermal

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Table 3. Selected Interatomic Angles (deg) for **1**[a]

Mn1 and Mn2 environment			
O11−Mn1−S11	75.9(2)	O11−Mn2−S12	76.2(2)
O11−Mn1−S11(a)	133.8(3)	O11−Mn2−S12(b)	133.8(3)
S11−Mn1−S11(a)	108.7(2)	S12−Mn2−S12(b)	109.6(1)
O11−Mn1−O11(a)	134.7(5)	O11−Mn2−O11(d)	133.8(4)
O11−Mn1−O11(b)	70.3(4)	O11−Mn2−O11(b)	69.5(4)
O11(a)−Mn1−O11(b)	92.3(6)	O11(d)−Mn2−O11(b)	92.5(6)
O11−Mn1−O11(c)	92.3(6)	O11(d)−Mn2−S11	76.2(2)
Mn1−O11−Mn2	103.5(3)		
O11−S11−O11c	59.2(2)	S11−O11(c)−O11	59.62)
O11−S12−O11(e)	59.5(2)	S12−O11(e)−O11	59.4(2)
O11(c)−O11−O11(e)	90.0	O11−O11(c)−O11(d)	90.0
Mn3 environment			
O32−Mn3−O31	91.4(5)	S31−Mn3−S31(e)	110.6(1)
O32−Mn3−S31	76.1(2)	O32−Mn3−O32e	70.5(4)
O31−Mn3−S31	75.6(2)	O31−Mn3−O32(e)	133.0(4)
O32−Mn3−S31(e)	135.1(3)	O31−Mn3−O31(e)	69.5(5)
O31−Mn3−S31(e)	133.5(4)		
Mn3(f)−O32−Mn3	103.9(3)	Mn3(d)−O31−Mn3	104.0(3)
O31−S31−O32	60.7(3)	S11−O32−O31	59.5(2)
O11−S12−O11(e)	61.2(3)	S12−O11(e)−O11	59.4(2)
O31−O32−O32(e)	89.8(3)		

[a] Symmetry transformations used to generate equivalent atoms: (a) $-x, -y, z$; (b) $-x, y, z$; (c) $x, -y, z$; (d) $-x, y, -z$; (e) $x, y, -z$; (f) $x, -y + 1, z$.

Table 4. Selected Interatomic Distances (Å) for **2**[a]

Mn1 and Mn2 environment			
Mn1−O15^b	2.08(2)	Mn2−O14^b	2.23(2)
Mn1−O12	2.17(1)	Mn2−O13^b	1.98(3)
Mn1−O11	2.153(9)	Mn2−O12	2.163(9)
Mn1−O15(a)^b	2.08(2)	Mn2−O11	2.17(1)
Mn1−O11(a)	2.153(9)	Mn2−O12(b)	2.163(9)
Mn1−O12(a)	2.17(1)	Mn2−O11(b)	2.17(1)
O15^b−O15(a)^b	2.19(4)	O11−O12	2.60(1)
O11−O15^b	3.05(2)	O15^b−O12(b)	2.98(2)
O13^b−O14^b	2.33(4)	O11−O13^b	2.99(2)
O14^b−O12	3.07(2)	O12−O11(a)	3.03(2)
O12−O12(b)	3.07(2)		
Mn3 environment			
Mn3−O35^b	2.20(2)	Mn3−O31	2.153(9)
Mn3−O33	2.14(1)	Mn3−O34^b	2.06(3)
Mn3−O32	2.16(1)	Mn3−O31(a)	2.19(1)
Mn1−Mn2	3.32(3)	Mn1−Mn2(a)	3.32(3)
O35^b−O34(a)^b	2.39(4)	O35^b−O31	3.06(2)
O32−O35^b	2.95(2)	O31−O32	3.03(2)
O32−O33	2.58(2)	O31−O31(a)	2.64(2)

[a] Symmetry transformations used to generate equivalent atoms: (a) $-x, y, -z$; (b) $x, -y + 1, z$; (c) $x, -y + 2, z$; (d) $x, -y, z$; (e) $-x, -y + 1,-z$.
[b] Oxygen atoms from SO groups.

Table 5. Selected Interatomic Angles (deg) for **2**[a]

Mn1 and Mn2 environment			
O15^b−Mn1−O12	131.5(6)	O12−Mn1−O15(a)^b	89.0(6)
O15^b−Mn1−O11	92.2(6)	O11−Mn1−O15(a)^b	128.5(5)
O12−Mn1−O11	73.9(4)	O11−Mn1−O11(a)	134.3(5)
O15^b−Mn1−O15(a)^b	63.6(1)	O12−Mn1−O12(a)	135.3(5)
O14−Mn2−O13	66.9(1)	O12−Mn2−O11	73.8(4)
O14−Mn2−O12	88.8(6)	O12−Mn2−O12b	90.2(5)
O13−Mn2−O12	129.9(4)	O11−Mn2−O12(b)	135.7(4)
O14−Mn2−O11	130.6(4)	O11−Mn2−O11(b)	89.2(6)
O13−Mn2−O11	89.3(6)	O33−Mn3−O34(a)	89.4(8)
Mn2−O12−Mn1	99.8(4)		
O11−O15^b−O12(a)	60.3(3)	O15−O12(a)−O11	61.0(5)
O11−O13^b−O11(b)	62.9(6)	O13^b−O11(b)−O11	58.6(3)
O12−O14^b−O12(b)	59.8(3)	O14^b−O12(b)−O12	60.1(3)
O11−O12−O11(a)	89.3(4)	O12(a)−O11−O11(b)	90.2(3)
Mn3 environment			
O35−Mn3−O33	131.0(7)	O32−Mn3−O34(a)	126.6(9)
O35−Mn3−O32	85.2(6)	O31−Mn3−O34a	133.6(7)
O33−Mn3−O32	73.7(5)	O35−Mn3−O31(a)	135.0(5)
O35−Mn3−O31	89.4(7)	O33−Mn3−O31(a)	86.7(5)
O33−Mn3−O31	132.7(5)	O32−Mn3−O31(a)	135.1(5)
O32−Mn3−O31	89.1(5)	O31−Mn3−O31(a)	75.0(4)
O35−Mn3−O34(a)	68.4(1)	O34(a)−Mn3−O31(a)	92.2(9)
O33−Mn3−O34(a)	89.4(8)	Mn3(c)−O32−Mn3	99.3(7)
Mn3−O31−Mn3(a)	100.4(4)	O31−O35^b−O32	60.5(4)
O35^b−O32−O31	61.5(4)	O31−O32−O33	89.6(4)
Mn2−O12−Mn1	99.8(4)		

[a] Symmetry transformations used to generate equivalent atoms: (a) $-x, y, -z$; (b) $x, -y + 1, z$; (c) $x, -y + 2, z$; (d) $x, -y, z$; (e) $-x, -y + 1, -z$.
[b] Oxygen atoms from SO groups.

syntheses are carried out in an autoclave, it allows the use of temperatures above the boiling point to modify the solvent properties in a manner that favors the reaction of even sparingly soluble materials which would be impossible under conventional conditions. Other advantages of the method are the control of the gas atmosphere inside the autoclave and the possibility to adjust the cooling rate to favor the growth of single crystals. The method has long been dominated by water (hydrothermal synthesis) and is widely used for the crystal growth of minerals.[53] However, during the past decade, a veritable renaissance, in particular with applications in mesoporous materials and the use of nonaqueous solvents, has occurred. The method has proven to be particularly efficient in coordination chemistry for the synthesis of polyoxometalates,[54,55] metal clusters,[56−61] and extended compounds.[62−65]

In the present case, we were unable to isolate any manganese(II) complexes of the thiacalixarene with conventional methods. In contrast, under solvothermal conditions using methanol as the solvent and pyridine as the deprotonating agent for the phenol groups, we were able to synthesize the two tetranuclear complexes reported in this paper in a good yield and in the form of single crystals using *p*-*tert*-butylthiacalix[4]arene (thiaS) and *p*-*tert*-butylsulfinylthiacalix[4]arene (thiaSO). Unfortunately, all our attempts to synthesize the tetranuclear analogue with the thiacalixarene sulfonyl derivative (SO_2 bridge) failed.

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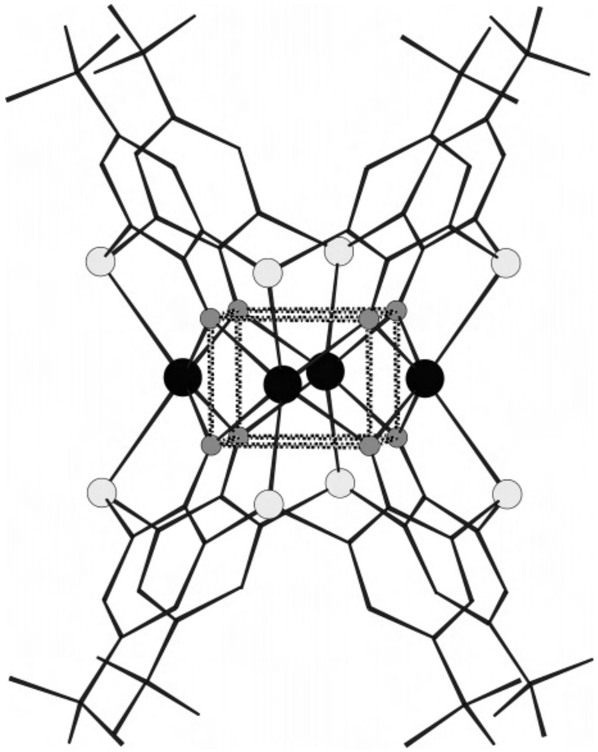

Figure 1. Molecular structure of one [Mn_4(thiaS)$_2$] tetranuclear manganese(II) entity (M1) for compound **1**.

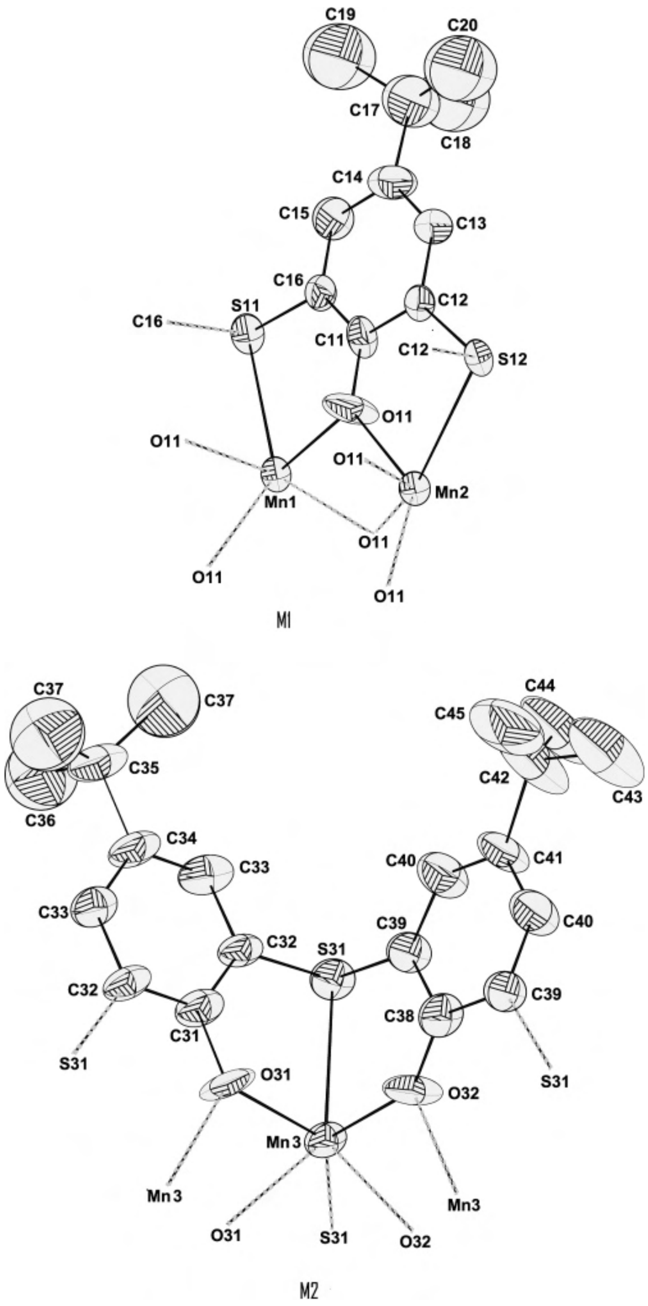

Figure 2. Representation of the two asymmetric units (M1 and M2) in compound **1**. The hydrogen atoms have been omitted for clarity.

Description of the Crystal Structures. [Mn^{II}_4(thiaS)$_2$]·H_2O (1). The structure of compound **1** is formed by two crystallographically independent and neutral entities called hereafter M1 and M2 and shown in Figure 1. Crystallization water molecules were also found in the crystal. A selection of interatomic distances and angles are given in Tables 2−3.

The M1 entity is built from two independent manganese(II) ions (Mn1 and Mn2), one *tert*-butylphenoxy group (O11, C11, C12, C13, C14, C15, C16, C17, C18, C19 and C20), and two sulfur atoms with half-occupation factors (S11 and S12) as shown in Figure 2. The latter play the role of linker between the phenoxy groups (four in the total) to form the thiacalixarene macrocycle (thiaS). The M2 entity is built from only one crystallographically independent manganese(II) ion (Mn3) and two independent *tert*-butylphenoxo groups (O31, C31, C32, C33, C34, C35, C36, and C37 and O32, C38, C39, C40, C41, C42, C43, C44, and C45) linked by one sulfur atom (S31) to form the thiacalixarene macrocycle as shown in Figure 2. Thus, each of the M1 and M2 entities is built from a manganese square sandwiched between two *p*-*tert*-butylthiacalix[4]arene macrocycles as exemplified for the M1 molecule in Figure 1. A similar structure was previously reported for a tetranuclear copper(II) complex.[39]

In both entities (M1 and M2), the eight phenoxo oxygen atoms lie at the corner of a compressed square-base parallelepiped (Figure 1). The edges of the parallelepiped are nearly orthogonal (89.83−90.73°). The parallelepiped is capped up and down by the two thiaclaixarene macrocycles (thiaS) on the square bases (Figure 1). The manganese(II) ions are located in the middle and above each of the four lateral faces of the parallelepiped (Figure 1). The deviations of the manganese(II) ions from the [O_4] mean plane made by the four phenoxo oxygen atoms are 0.81 (Mn1), 0.83 (Mn2), and 0.84 Å (Mn3).

Each manganese (II) ion exhibits the same six-coordinated [O_4S_2] environment (Figure 3a) made by four phenoxo oxygen atoms [Mn1−O11 = 2.095(6) Å, Mn2−O11 = 2.116(6) Å, Mn3−O32 = 2.111(5) Å, and Mn3−O31 = 2.123(5) Å] and two sulfur atoms [Mn1−S11 = 2.702(3) Å, Mn2−S12 = 2.694(3) Å, and Mn3−S31 = 2.702(2) Å). The Mn−O bond lengths are in agreement with those previously reported for Mn^{II}−O(phenoxo).[4,20,66−70] The Mn^{II}−S bond lengths are longer than the few previously reported for

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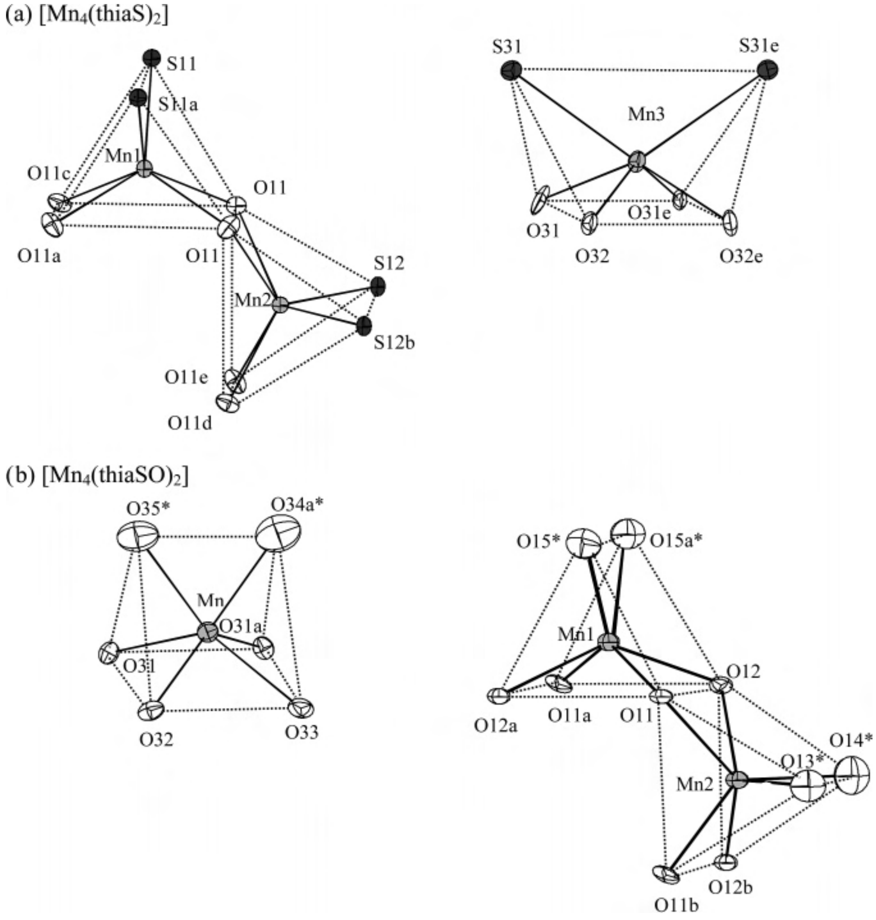

Figure 3. Representation of the manganese(II) coordination polyhedrons for in $[Mn_4(thiaS)_2]$ (**1**) and in $[Mn_4(thiaS)_2]$ (**2**) (the asterisk denotes oxygen atoms from the SO groups in **2**).

thioether complexes of high-spin manganese(II) (2.53−2.62 Å).[71−74] This may be attributed to the rigidity of the macrocycle which does not allow the sulfur atoms to come closer to the manganese(II) ions. Careful analysis of the interatomic distances and angles revealed that the coordination polyhedron is a distorted trigonal prism, as shown in Figure 3a. Such a geometry has already been reported for manganese(II), but it is quite rare.[75−77] The triangular faces of the trigonal prism are defined by two phenoxo oxygen atoms and one sulfur atom belonging to the same thiacalixarene macrocycle and are equilateral (Tables 2−3). The trigonal twist angles[78] are zero but the triangular faces are not parallel and make angles of 45.16° (Mn1), 45.40° (Mn2), and 45.86°(Mn3). The four coordination polyhedrons are orthogonal to each other. The Mn⋯Mn distances are in the range of 3.307(2)−3.346(4) Å (mean value = 3.326 Å) which is in agreement with those previously reported for the bis(phenoxo) bridge.[20,70] The Mn−O−Mn angles are in the range of 103.5−104.0° (Table 3).

In the crystal, the $[Mn_4(thiaS)_2]$ entities are packed in infinite chains running parallel to the *b* axis of the unit cell in such a manner that two successive molecules are rotated by 90° with respect to each other (Figure 4).

$[Mn_4(thiaSO)_2]$ (2). The crystal structure of **2** is also formed by two crystallographically independent and neutral entities hereafter called M3 and M4 (Figure 5). The M3 entity is built from two independent manganese atoms (Mn1 and Mn2), two *tert*-butylphenoxy groups (O12, C11, C12, C13, C14, C15, C16, C17, C18, C19, and C20 and O11, C21, C22, C23, C24, C25, C26, C27, C28, C29, and C30), and three SO groups (S11/O13, S12/O15, and S13/O14) as shown in Figure 5. As in compound **1**, the sulfur atoms of the SO groups play the role of linker between each phenol group (four in total) to form the thiacalixarene macrocycle (thiaSO). In this case, the oxygen atoms of the SO groups are coordinated to the manganese center, not the sulfur atom as

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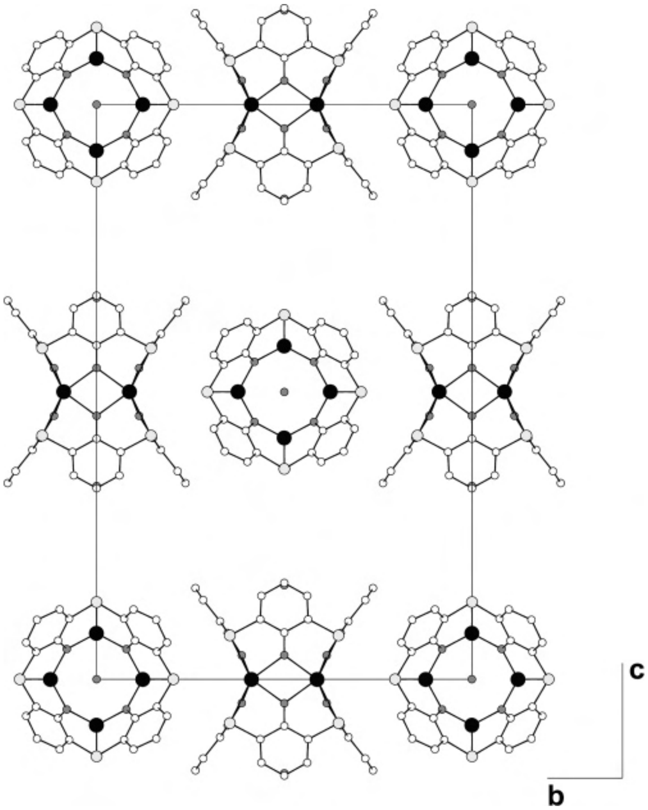

Figure 4. Projection of the crystal packing of compound **1** in the (*b*, *c*) plane. The hydrogen atoms and *tert*-butyl groups have been omitted for clarity.

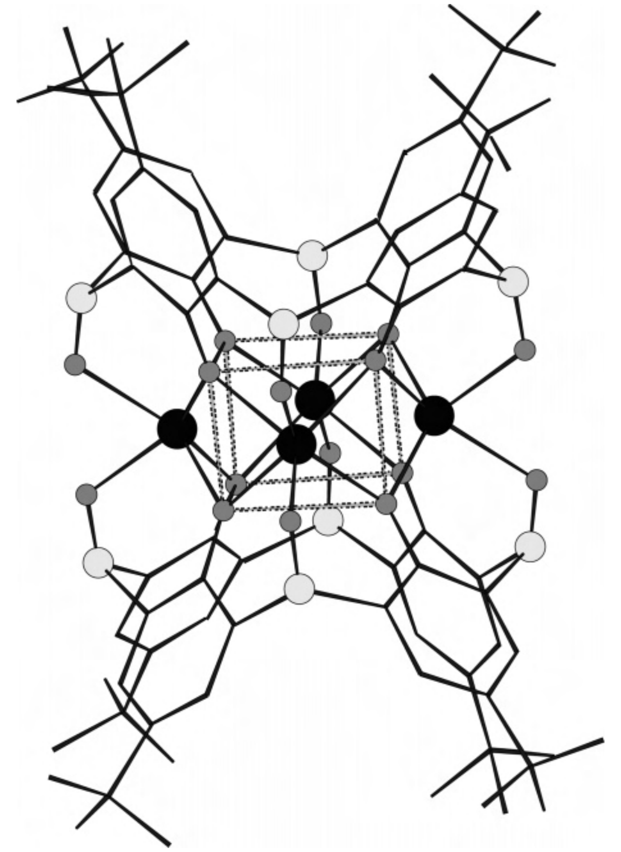

Figure 5. Molecular structure of one [Mn_4(thiaSO)$_2$] tetranuclear manganese(II) entity (M3) of compound **2**.

in **1**. The M4 entity is built from only one crystallographically independent manganese(II) ion (Mn3), three independent phenol groups (O31, C38, C39, C40, C41, C42, C43, C44, C45, C46, and C47; O32, C48, C49, C50, C51, C52, C53, and C54; and O33, C31, C32, C33, C34, C35, C36, and C37) as shown in Figure 6. They are linked by three sulfur atoms which belong to three SO groups (S11/O13, S12/O15, and S13/O14).

As observed for compound **1**, the M3 and M4 entities are composed of a square of four manganese(II) ions sandwiched between two *p-tert*-butylthiacalix[4]arene macrocycles as shown for the M4 molecule in Figure 5.

Again, as for compound **1**, in both entities (M3 and M4), the eight phenoxo oxygen atoms lie at the corner of a compressed square-base parallelepiped as shown in Figure 5. The edges of the parallelepiped are nearly orthogonal (90.00−90.73°). The parallelepiped is capped up and down by the two sulfinylccalixarene macrocycles (thiaSO) located on the square bases (Figure 5). The manganese(II) ions are located in the middle and above each of the four lateral faces of the parallelepiped (Figure 5). The deviations of the manganese(II) ions from the mean [O_4] plane made by the four phenoxo oxygen atoms are 0.83 (Mn1), 0.82 (Mn2), and 0.84 Å (Mn3)

The sulfur atoms, in compound **1**, have been replaced by SO groups, in compound **2**, so that each manganese center is surrounded by six oxygen atoms (Figure 4b). Two of these six atoms come from the SO groups and the others come from the phenoxo groups. All the Mn−O bond lengths are in the same range for the three environments (from 2.08(2) to 2.172(1) Å for Mn1, from 1.98(3) to 2.23(2) Å for Mn2, and from 2.06(3) to 2.20(2) Å for Mn3). The mean value for the Mn−O(phenoxo) bond length (2.16 Å) is slightly longer than that for **1** (2.11 Å). The coordination polyhedron is a compressed trigonal prism as shown in Figure 3b. The triangular faces are defined by two phenoxo oxygen atoms and one SO oxygen atom belonging to the same macrocycle and equilateral (Tables 4−5). The trigonal twist angles[78] are zero, and the triangular faces are nearly parallel making angles of 9.00° (Mn1), 6.31° (Mn2), and 4.80° (Mn3). The Mn···Mn distances are in the range of 3.317(3)−3.332(4) Å (mean value = 3.315 Å) which is close to those found in **1**. The Mn−O−Mn angles, considering only the oxygen atoms belonging to phenol groups, are in the range of 99.3−100.9°, also close to those found in **1**. Therefore, the nature of the ligand, (thiaS) or (thiaSO), seems to have no influence on the Mn···Mn distances or the Mn−O−Mn angles.

In compound **2**, the [Mn_4(thiaSO)$_2$] tetranuclear entities are also stacked in chains, but they are rotated 45° with respect to each other.

Magnetic Properties. Measurement of the thermal variation of the magnetic susceptibility for compounds **1** and **2** in the temperature range of 2−300 K revealed similar and almost superimposable behaviors. The results are displayed in the form of the magnetic susceptibility (χ) and its product with the temperature (χT) in Figure 7.

The χT products are 14.03 cm^3 K mol^{-1} for **1** and 14.12 cm^3 K mol^{-1} for **2** at 300 K. These values are smaller than

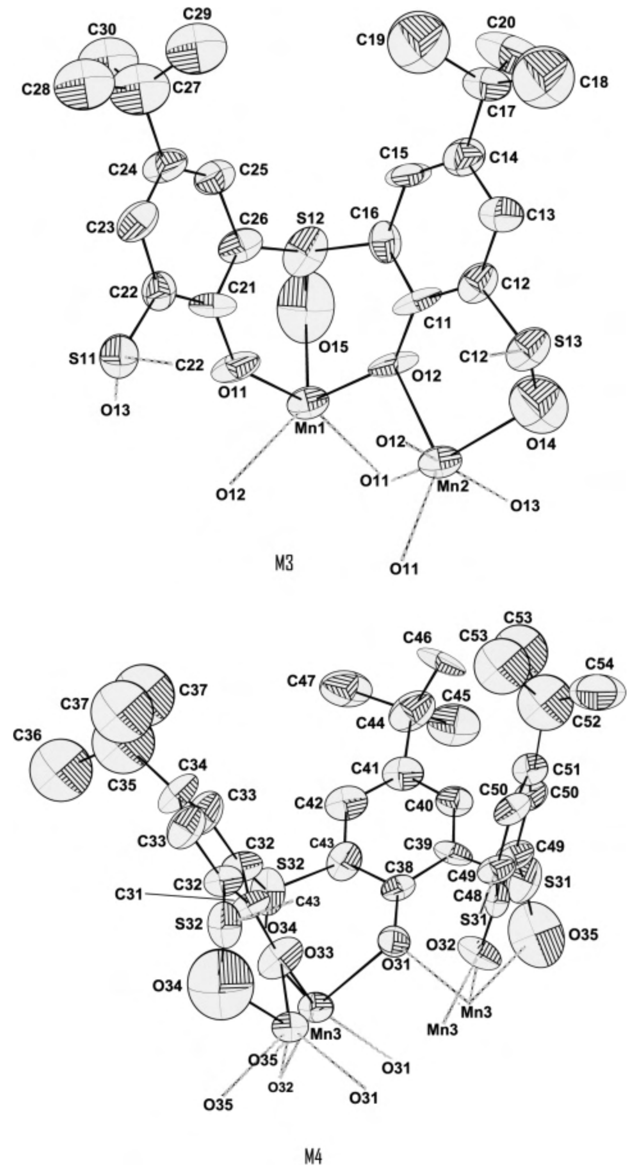

Figure 6. Representation of the two asymmetric units (M1 and M2) in compound **2**. The hydrogen atoms have been omitted for clarity.

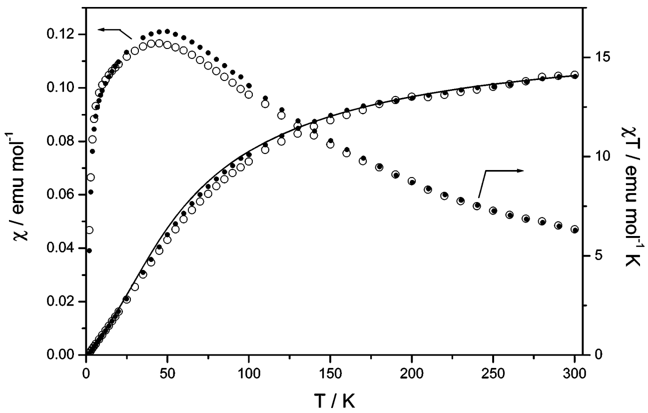

Figure 7. Temperature dependence of the molar magnetic susceptibility (χ) and the product with temperature (χT) for compound **1** (●) and compound **2** (○). The solid line shows the best fit of the data with the values in the text.

those expected for four uncoupled manganese(II) ions (17.5 cm^3 K mol^{-1}). Upon cooling, the χT values decrease continuously down to zero. The magnetic susceptibility shows a maximum at 45 K for both compounds**.** Linearization of the $1/\chi$ versus T curve in the range of 100−300 K shows Curie−Weiss regimes with Curie constants (C) of 17.3 cm^3 mol^{-1} K for **1** and 17.5 cm^3 mol^{-1} K for **2**. These Curie constants are exactly the value expected for four manganese(II) ions (17.5 cm^3 K mol^{-1}). These behaviors indicate that dominant antiferromagnetic interactions occur between the manganese(II) ions. Indeed, the intermolecular interactions are ruled out because the tetranuclear cores are well separated from each other because of screening by the bulky thiacalixarene ligands. The shorter intermolecular Mn−Mn distances are greater than 5.8 Å in **1** and **2**.

As shown in the structural section, in cluster **1** as well as in **2** the four manganese centers, independently of the entities M1 and M2 in **1** and M3 and M4 in **2**, have the same environment. Moreover the Mn−O(phenoxo) bond length and the Mn−O−Mn bond angles which are relevant to magnetic exchange couplings do not show any sticking differences in both compounds. This allows great simplification for the determination of the coupling exchange constant. Accordingly, the magnetic data of compound **1** and **2** have been analyzed by considering one manganese square with four equal exchange couplings ($J = J_{12} = J_{13} = J_{34} = J_{14}$) on the edges and no diagonal interactions ($J_{13} = J_{24} = 0$) on the base of the Heisenberg Hamiltonian, $H = -J(S_1S_2 + S_2S_3 + S_3S_4 + S_1S_4)$].

The energy levels of this Hamiltonian can be expressed as $E = -J[S(S + 1) - S_{13}(S_{13} + 1) - S_{24}(S_{24} + 1)]$, where S is the total spin and S_{13} and S_{24} are the intermediate spins. The S_{13} and S_{24} values vary from 0 to 5, and for each pair of intermediate spins, the total spin takes values from $|S_{13} - S_{24}|$ to $S_{13} + S_{24}$.

The best least-squares fitting of the χT versus T data with the van Vleck equation on the basis of the above energy levels give, as may be expected, identical results for **1** and **2** with a g factor value of 1.94 and an antiferromagnetic exchange parameter $J = -5.57$ cm^{-1} ($R = [\sum(\chi_M T_{\text{calcd}} - \chi_M T_{\text{obs}})^2/\sum(\chi_M T_{\text{obs}})^2]$ is in both cases on the order of 10^{-6}). Trials to include an intercluster magnetic interaction did not improve the fit qualities, and this was not taken in account in the final fittings. This is in agreement with the fact that the clusters are well separated by the bulky ligands.

The small value of the coupling constant found for the two tetramanganese is in agreement with those generally reported for dinuclear[20,66−69] or tetranuclear[70,79,80] manganese(II) complexes with phenoxo bridges. These coupling constants are generally antiferromagnetic and small ($J < 10$ cm^{-1}) [20,66−69] but in some case weak ferromagnetic interactions were also found.[20,70,79,80]

There is no generally accepted theoretical model of magnetostructural correlations in Mn(II) polynuclear clusters. One can assume that the exchange parameters are not very sensitive to the local symmetry of the metallic centers, as at

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any symmetry all five d orbitals are occupied. For isoelectronic Fe(III) ions, either Fe$-$O$_{\mathrm{bridge}}$ distances[81] or Fe$-$O$_{\mathrm{bridge}}$$-$Fe angles[82] were proposed as key geometric parameters. However, the exact similarity of the exchange coupling, *J*, for **1** and **2**, despite the small differences observed in Mn$-$O(phenoxo) distances and Mn$-$O$-$Mn angles, suggests that in our case the variation of *J* cannot be attributed to a one of these parameters. One can assume that the angle between two trigonal prisms, forming the Mn(II) environment and equal to 90° for both clusters, can also play a role.

Concluding Remarks

The two tetranuclear manganese(II) clusters reported here confirm the high coordination ability of the thiacalixarene macrocycles. The compounds were obtained via a solvothermal route. Compound **2** is the first example of complex with the sulfonyl derivative. In both clusters, the manganese geometry is a rare example of a trigonal prism. Both tetranuclear clusters exhibit intamolecular antiferromagnetic coupling consistent with other phenoxo-bridged Mn(II)-coupled systems.

We are now engaged in a program to synthesize clusters of higher nuclearities with mixed valence or heterometals.

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Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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