Inorg. Chem. **2008**, *47*, 8807−8812

Inorganic Chemistry
Article

Novel 48-Membered Hexadecanuclear and 60-Membered Icosanuclear Manganese Metallamacrocycles

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Received April 20, 2008

Either an S_8 symmetrical 48-membered hexadecanuclear or an S_{10} symmetrical 60-membered icosanuclear manganese metallamacrocycle was self-assembled using a manganese ion and a ditopic pentadentate ligand. This was either *N*-4-phenylbenzoylsalicylhydrazide (H_3pbshz) containing a rigid rod-shaped, bulky biphenyl residue as a terminal *N*-acyl group or *N*-3,3-diphenylpropionylsalicylhydrazide (H_3dppshz) containing a flexible β-branched *N*-acyl group, but with two sterically bulky phenyl residues at the Cβ position. The backbone of these metal−organic assemblies is a repeating unit consisting of a −[Mn−N−N−] link that extends to complete either the 48-membered cyclic structure involving 16 manganese(III) centers and 16 ditopic linker ligands or the 60-membered cyclic structure involving 20 manganese(III) centers and 20 ditopic linker ligands (depending on the ligand used). Even though the nuclearity of the metallamacrocycles was different, the successive manganese centers were in the same chiral sequence, $\cdots(\Lambda\Lambda\Delta\Delta)(\Lambda\Lambda\Delta\Delta)\cdots$.

Introduction

Metallamacrocycles are important compounds due to their interesting molecular architectures,[1] magnetic properties,[2] and selective recognition.[3] Even though the topology of metallamacrocycles is simple, controlling their size, nuclearity, and physio-chemical properties is still a substantial challenge. It is also synthetically challenging to achieve stable metallamacrocycles with a high nuclearity, especially when forming large hydrophobic or hydrophilic inner cavities.

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10.1021/ic800708z CCC: $40.75

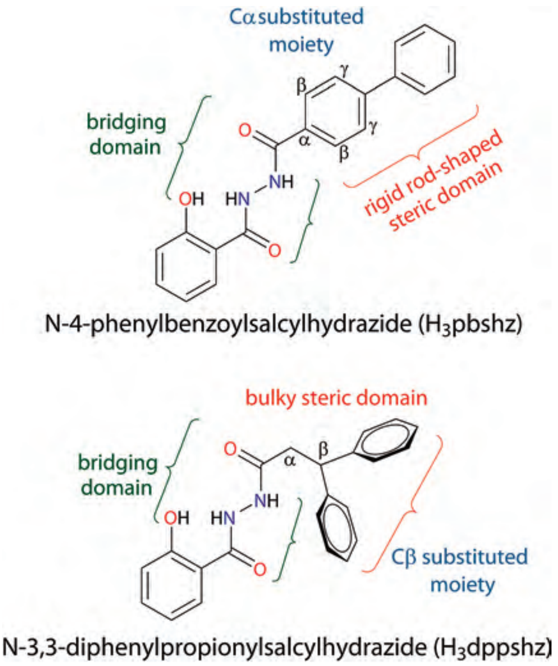
Diaza-bridged metallamacrocycles,[4−6] known as metalla*di-aza*macrocycles,[5] have received considerable interest because of their potential as host systems for various guest molecules' inclusion chemistry[7] and as supramolecular building blocks for the construction of extended metal−organic frameworks.[8]

These compounds can be readily assembled using a trianionic pentadentate ligand, *N*-acylsalicylhydrazide, having a trivalent octahedral metal ion.[4−7] The size of the ring of the metalladiazamacrocycle can be controlled by modifying the close-contact interactions between the *N*-acyl residues of the ligands that are directed toward the inner core of the cyclic structure. The formation of a metalladiazamacrocycle structure with a higher nuclearity is closely related to the number and size of the Cα substituents, as well as the rigidity of the *N*-acyl group. Although the introduction of a C*β* substituent at the *N*-acyl site of the ligand does not affect the nuclearity of the metallamacrocycle, probably because of a flexible Cα−C*β* bond,[4a,b] a Cα substituent at the *N*-acyl site results in an expansion of metalladiazamacrocycles with different nuclearities, depending on the steric volume of the Cα substituent.[4−7]

The metal centers of the metalladiazamacrocycles are always in a ···(ΛΔ)(ΛΔ)··· chiral sequence, regardless of the nuclearity, as is observed in 18-membered hexanuclear metallamacrocycles, and the metallamacrocycle is in the least puckered ring conformation. However, the introduction of a rigid, rod-shaped *N*-acyl group, such as a 2-pentenoyl group, leads to a slightly puckered metalladiazamacrocycle with a ···(ΛΛΔΔ)(ΛΛΔΔ)··· chiral sequence.[5] Recently, we reported on a 60-membered icosanuclear manganese metallamacrocycle with a pentadentate ligand, 3-phenyl-*trans*-2-propenoylsalicylhydrazide, that could offer a rigid rod-shaped terminal *N*-acyl residue with a sterically bulky phenyl end.[6] The metalladiazamacrocycle of this 60-membered ring system is severely puckered, with a complicated ···(ΛΛΔΔΛΔΔΛΛΔ)(ΛΛΔΔΛΔΔΛΛΔΛΔ)··· chiral sequence. The preparation of a 48-membered hexadecanuclear manganese metallamacrocycle using N^2-*trans*-cinnamoyl-2-hydroxy-3-naphthoylhydrazide has also been reported, where the phenoxyl part of the ligand was replaced by a naphthoyl group to prevent the *inverted* conformation in the resulting metalladiazamacrocycle.[4d]

Other possible approaches to prepare metalladiazamacrocycles with a high nuclearity are the use of a rigid and bulky *N*-acyl residue or the use of a flexible, but extremely bulky, *N*-acyl residue. Considering these approaches, we designed two new *N*-acyl salicylhydrazides. One is a ligand containing a biphenyl group at the *N*-acyl site as a Cα-substituted, rigid rod-shaped and bulky residue, and the other is a ligand containing a flexible *β*-branched *N*-acyl group, but with two sterically bulky phenyl residues at the C*β* position (Scheme 1), which could lead to a metalladiazamacrocycle with an extended and more or less planar ring conformation.

Scheme 1. A Schematic Diagram of the H_3pbshz and H_3dppshz Ligands



Experimental Section

Materials. All of the reagents and solvents used in the syntheses were purchased from commercial sources and were used as received.

Instrumentation. Elemental analysis of C, H, and N was performed at the Elemental Analysis Laboratory of the Korean Basic Science Institute using a CE Flash EA 1112 series elemental analyzer. Infrared spectra were recorded using KBr pellets in the range 4000−600 cm^{-1} employing a BioRad FT-IR spectrometer. Electrospray ionization mass spectra were obtained using an HP Agilent 1100 MSD mass spectrometer. NMR spectra were obtained using a Varian-300 spectrometer. Temperature-dependent magnetic susceptibility measurements were carried out on powdered samples between 3 and 300 K using a Quantum Design MPMS-7XL SQUID magnetometer. Field-cooled magnetization data were collected at $H = 1000$ Oe. Thermogravimetric analysis was performed on a Scinco Simultaneous Thermal Analyzer S-1000 thermal analyzer in the air with a heating rate of 10 °C/min between ambient temperature and 500 °C.

Ligand Synthesis. ***N*-4-Phenylbenzoylsalicylhydrazide (H_3-pbshz).** A 1.08 g (5.00 mmol) sample of biphenyl-4-carbonyl chloride was added to 50 mL of chloroform at 0 °C containing 0.77 mL (5.50 mmol) of triethylamine and 0.99 g (5.00 mmol) of biphenyl-4-carboxylic acid, while stirring. After stirring for a period of 20 min, the solution was slowly warmed to room temperature. Then, 0.75 g (4.95 mmol) of salicylhydrazide was added to the solution, which was then stirred for a period of 30 min. A white suspension began to appear, and stirring was continued for a further

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day to allow for the completion of the reaction. The white product formed was filtered and washed with small aliquots of cold chloroform, and then with water and ether, followed by drying in a vacuum. Yield = 1.51 g (91.1%). HRMS (FAB) *m/z* calcd for $C_{20}H_{17}N_2O_3$, $[M + H]^+$: 333.1239. Found: 333.1236. Elem anal. calcd: C, 72.28; H, 4.85; N, 8.43%. Found: C, 71.88; H, 4.68; N, 8.06%. IR spectrum: see Figure S1 (Supporting Information). ^1H NMR (300 MHz, dmso-d_6, ppm): 11.89 (bs, 1H, −NH), 10.76 (bs, 1H, −NH and 1H, −OH), 8.05∼7.75 (d, 7H, Ar−H), 7.53∼7.40 (t, 4H, Ar−H), 7.02∼6.94 (m, 2H, Ar−H). ^{13}C NMR (75 MHz, dmso-d_6, ppm): 168.43(C8), 165.90(C7), 160.03(C1), 144.16(C12), 139.72(C15), 131.80(C5), 129.75(C10), 129.00(C3), 128.89(C17, C9), 127.61(C16, C11), 127.43(C18), 119.73(C2), 118.11(C4), 115.32(C6).

***N*-3,3-Diphenylpropionylsalicylhydrazide (H_3dppshz).** H_3dppshz was prepared using a similar procedure described for the synthesis of H_3pbshz, where trimethylacetyl chloride (0.62 g, 5.00 mmol) and 3,3-diphenylpropionic acid (1.13 g, 5.00 mmol) were used instead of biphenyl-4-carbonyl chloride and biphenyl-4-carboxylic acid, respectively. Yield: 1.30 g, 71.9%. HRMS (FAB) *m/z* calcd for $C_{20}H_{21}N_2O_3$ $[M + H]^+$: 337.1552. Found: 337.1552. Elem anal. calcd: C, 73.11; H, 5.86; N, 7.75%. Found: C, 73.01; H, 5.89; N, 7.96%. IR spectrum: see Figure S2 (Supporting Information). ^1H NMR (300 MHz, dmso-d_6, ppm): 11.91 (bs, 1H, −NH), 10.62 (bs, 1H, −NH), 10.43(bs, 1H, −OH), 7.87 (d, 1H, Ar−H), 7.41 (t, 1H, Ar−H), 7.30∼7.26 (m, 8H, Ar−H), 7.19∼7.17 (m, 2H, Ar−H), 6.95∼6.87 (m, 2H, Ar−H), 4.54 (t, 1H, −CH), 3.03∼3.01 (d, 2H, $-CH_2$). ^{13}C NMR (75 MHz, dmso-d_6, ppm): 169.28, 166.75, 159.54, 144.83, 134.66, 129.12, 128.25, 126.91, 119.70, 117.92, 115.29, 46.98.

Preparation of the Metalladiazamacrocycle. $[Mn_{16}(pbshz)_{16}(DMF)_6(H_2O)_{10}]$, 1. A 16.6 mg (0.050 mmol) sample of H_3pbshz was dissolved in 2 mL of *N,N*-dimethylformamide (DMF) in a 15 mL vial, and 12.3 mg (0.050 mmol) of $Mn(OAc)_2\cdot 4H_2O$ was added to the solution and allowed to mix for a period of 15 min. A volume of 10 mL of ethanol was slowly added through the vial wall. After being allowed to stand for a period of 15 days, dark brown block crystals were obtained (14.9 mg, yield = 64.5%). Elem anal. calcd for $[Mn_{16}(pbshz)_{16}(DMF)_6(H_2O)_{10}]$ ($C_{338}H_{270}Mn_{16}N_{38}O_{64}$, fw = 6767.09 g mol^{-1}): C, 59.99; H, 4.02; N, 7.87%. Found: C, 60.08; H, 3.92; N, 8.03%. (*Note: Even though the crystal structure analysis suggested that the crystals contained at least 10 DMF molecules, 17 water molecules, and 23 ethanol molecules, as either ligating or structural solvents per molecule of complex **1**, the elemental analysis was not consistent with the original content of the crystals, despite several attempts. The compounds were found to lose coordinated ethanol during freeze-drying and exposure to the air. The ethanol molecules were subsequently replaced by either the structural solvent DMF or water molecules. This result is consistent with the thermogravimetric analysis (TGA) data.*) IR spectrum: see Figure S3 (Supporting Information).

$[Mn_{20}(dppshz)_{20}(EtOH)_{19}(DMF)]\cdot DMF\cdot 4EtOH$, 2. A 9.0 mg (0.025 mmol) sample of H_3dppshz was dissolved in 1 mL of DMF, and 7.4 mg (0.030 mmol) of $Mn(OAc)_2\cdot 4H_2O$ was dissolved in 10 mL of EtOH in another vial. The two solutions were mixed for a period of 15 min, and the combined solution was sealed in a 15 mL vial and allowed to stand for 5 days, when dark brown block crystals were obtained (4.9 mg, 41.5% yield). Elem anal. calcd for $[Mn_{20}(dppshz)_{20}(EtOH)_5(H_2O)_{15}]\cdot 13H_2O$, **2** ($Mn_{20}C_{450}H_{426}N_{40}O_{93}$, fw = 8975.74 g mol^{-1}): C, 60.16; H, 4.78; N, 6.24%. Found: C, 60.52; H, 4.30; N, 6.11%. (*Note: As in complex **1**, some solvent molecules in the crystal structure of **2** have been replaced by the water molecules in the air.*) IR spectrum: see Figure S4 (Supporting Information).

Crystallographic Data Collection and Refinements of the Structure. The crystals were coated with paratone oil because they lost their crystallinity upon exposure to the air. The diffraction data were measured using synchrotron radiation employing a 4AMXW ADSC Quantum-210 detector with a Pt-coated Si double-crystal monochromator located at the Pohang Accelerator Laboratory, Korea. The HKL2000 software program (v.0.98.694)[9] was used for data collection, cell refinement, reduction, and absorption correction. The structures were solved using direct methods and refined using either block diagonalized-matrix or full-matrix least-squares calculations using the SHELXTL-PLUS software package.[10] All non-hydrogen atoms, except those of the disordered coordinating solvent, some of the noncoordinating structural solvent molecules, and aromatic carbon atoms of the diphenylpropionyl tail, were refined anisotropically. Hydrogen atoms, except those attached to the solvent molecules, were assigned isotropic displacement coefficients of U(H) = 1.2U (C), and their coordinates were allowed to ride on their respective atoms.

Crystal Structure Determination. $[Mn_{16}(pbshz)_{16}(EtOH)_{13}(DMF)_{1.5}(H_2O)_{1.5}]\cdot 9DMF\cdot 11EtOH\cdot 15.5H_2O$, 1. A hexadecanuclear metallamacrocycle and at least 36 noncoordinating structural solvent sites were identified as the asymmetric unit. Five coordinating ethanol molecules, two noncoordinating ethanol molecules, two coordinating DMF molecules, and four noncoordinating DMF molecules with a poor geometry were refined with geometry restraints during the least-squares refinement. The solvent coordination sites of the manganese ions were occupied by ethanol, DMF, water, or statically disordered DMF/water molecules. In addition, nine DMF molecules, 11 ethanol molecules, and 16 water sites per asymmetric unit were observed in the lattice. The refinement converged to final values of R1 = 0.1058 and wR2 = 0.3030 for 31 361 reflections with $I > 2\sigma(I)$. Structural refinement was further performed after modification of the data for the noncoordinate lattice solvent molecules (7222.9 Å^3, 33.7% of the crystal volume) using the SQUEEZE routine of the PLATON software package,[11] which led to a better refinement and data convergence. Refinement of the structure converged at final values of R1 = 0.0723 and wR2 = 0.2018 for 30 724 reflections with $I > 2\sigma(I)$ and R1 = 0.1157 and wR2 = 0.2258 for all 55 652 reflections. The largest difference peak and hole were 1.132 and −0.535 $e\cdot$Å^{-3}, respectively.

$[Mn_{20}(dppshz)_{20}(EtOH)_{19}(DMF)]\cdot DMF\cdot 4EtOH$, 2. An icosanuclear macrocycle and at least five noncoordinating structural solvent sites were identified as an asymmetric unit in the crystal structure. The geometry of all the phenyl rings of the ligands was restrained as an ideal hexagon during the least-squares refinement. While the six aromatic carbon atoms of the salicyl moiety were refined anisotropically, 12 aromatic carbon atoms in the diphenylpropionyl tail were refined isotropically. In addition, some bad geometries in ligand units and the coordinating solvent molecules were refined using ideal geometry restraints during the least-squares refinement. The refinement converged to a final R1 = 0.1569 and wR2 = 0.3855 for 26 038 reflections of $I > 2\sigma(I)$. The structural refinement was further performed after modification of the data for the noncoordinate lattice solvent molecules (11 478 Å^3, 38.6% of the crystal volume) using the *SQUEEZE* routine of PLATON (after

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Table 1. Crystal Data and Structure Refinements for **1** and **2**

	1	**2**
empirical formula	$Mn_{16}C_{350.5}H_{299.5}N_{33.5}O_{64}$	$Mn_{20}C_{481}H_{460}N_{41}O_{80}$
fw, g mol^{-1}	6883.78	9193.70
T, K	100(2)	89(2)
λ, Å	0.70000	0.77000
cryst syst	triclinic	monoclinic
space group	P-1 (No. 2)	$P2_1$ (No. 4)
a, Å	26.669(5)	35.376(7)
b, Å	28.258(6))	24.484(5)
c, Å	30.076(6)	36.769(7)
α, deg	92.10(3)	90
β, deg	94.25(3)	110.87(3)
γ, deg	108.33(3)	90
V, Å^3	21414(7)	29759(10)
Z	2	2
μ, mm^{-1}	0.516	0.468
R^a ($I > 2\sigma(I)$, all data)	0.0723, 0.1157	0.1030, 0.1750
$R_w{}^a$ ($I > 2\sigma(I)$, all data)	0.2018, 0.2258	0.2684, 0.3080

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

removing lattice solvent molecules),[11] which led to a better refinement and data convergence. Refinement of the structure converged at a final R1 = 0.1030 and wR2 = 0.2684 for 24 805 reflections with $I > 2\sigma(I)$ and R1 = 0.1750 and wR2 = 0.3080 for all 64 272 reflections. The flack parameter (0.53(2)) suggests that **2** is racemic twined. The largest difference peak and hole were 0.501 and −0.302 $e \cdot$Å^{-3}, respectively.

A summary of the crystal and intensity data is given in Table 1.

Results and Discussion

H_3pbshz and H_3dppshz (Scheme 1) were prepared using a procedure similar to that reported in the literature.[4] Dark brown single crystals of [Mn_{16}(pbshz)$_{16}$(EtOH)$_{13}$(DMF)$_{1.5}$-(H_2O)$_{1.5}$], **1**, were obtained by the slow diffusion of ethanol into a DMF solution of manganese(II) acetate tetrahydrate and H_3pbshz over a period of 15 days. Single-crystal X-ray analysis showed that the asymmetric unit of complex **1** contains 16 manganese(III) ions, 16 ligands, and 16 solvent molecules. The structure exhibits a hexadecanuclear 48-membered ring in the manganese metalladiazamacrocycle core, with a conformation having S_8 symmetry (Figure 1). The deprotonated ligand, pbshz^{3-}, acts as a trianionic pentadentate ditopic bridging ligand and coordinates to manganese(III) cations *via* three oxygen atoms and two hydrazine nitrogen atoms in the bridging domain. A phenolate oxygen atom, O1; a hydrazide nitrogen atom, N1; and a carbonyl oxygen atom, O3, of the chosen ligand were each bound to a manganese atom. The other carbonyl oxygen atom, O2, and the other hydrazide nitrogen atom, N2, were bound to the adjacent manganese atom in a back-to-back fashion, leading to a cyclic structure consisting of 16 manganese metal ions (Figure S5, Supporting Information). The oxygen atom of a solvent ethanol molecule, water molecule, or a solvent DMF molecule filled the remaining coordination site of the manganese atom. The eight terminal biphenyl groups out of 16 ligands were directed to the inner core of the cyclic structure, while the remainder were directed to the outside of the metalladiazamacrocycle. All of the manganese ions in **1** were in a typical Jahn−Teller elongated octahedral coordination geometry, as in the other high-spin d^4 manganese(III) complexes. The average axial bond distance was about 0.34 Å longer than the average basal bond distance (Table S1, Supporting Information). All of the ring metal ions exhibited the propeller configurations, despite the Jahn−Teller distortion. Successive Mn centers in the S_8 symmetric metalladiazamacrocycle were identified as possessing a ···(ΛΛΔΔ)(ΛΛΔΔ)··· chiral sequence. Such a chiral sequence leads to the small difference in the interatomic Mn−Mn atom separations, but a significant difference in the two types of Mn−Mn−Mn interatomic angles.

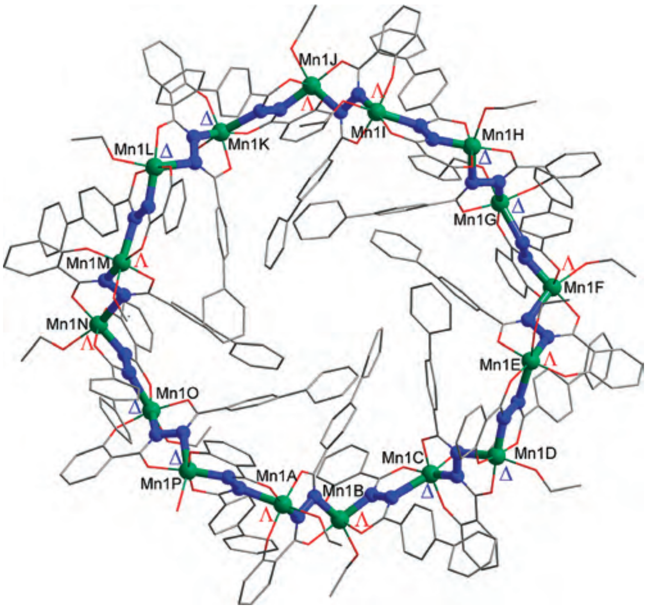

Figure 1. Top view of the 48-membered hexadecanuclear metallamacrocycle, **1**. The −[Mn−N−N−]$_{16}$ linkages are highlighted by the thicker bonds, and the chirality of the metal centers is shown in a ···(ΛΛΔΔ)(ΛΛΔΔ)··· sequence. Key: Mn (green), N (blue), O (red), C (gray).

The 48-membered ring is a −[Mn−N−N−]$_{16}$ ring, with neighboring Mn−Mn interatomic distances ranging from 4.824(1) Å to 4.931(2) Å. The Mn−Mn−Mn interatomic angles in the 48-membered ring were alternately in the range from 113.24 to 118.95° (with an average value of 116.19°) and 133.45 to 137.67° (with an average value of 135.57°), which is much smaller than the value of the ideal planar cyclohexadecane-like structure (157.5°). The 48-membered hexadecanuclear manganese metalladiazamacrocycle was in a slightly puckered conformation, similar to that of the dodecanuclear metalladiazamacrocycle with the same ···(ΛΛΔΔ)(ΛΛΔΔ)··· chiral sequence, which was prepared using a ligand with a 2-pentenoyl group as the *N*-acyl group. The hexadecanuclear metalladiazamacrocycle can be considered as a donut-shaped disk (Figure 1 and Figure S6, Supporting Information). The peripheral diameter of the core ring, measured between the opposite carbon atoms (C4C−C4K), together with an allowance for 1.55 Å for the van der Waals radius of the carbon atoms, was 32.7 Å. The approximate internal diameter at the entrance of the oval-shaped cavity was 3.7 Å, measured between the opposite carbon atoms of the biphenyl groups of the pbshz^{3-} ligands (C17A−C17I), and 19.6 Å in diameter at its widest point, as measured between the opposite manganese atoms (Mn1A−Mn1I, Mn1B−Mn1J, Mn1C−Mn1K, Mn1D−Mn1L, Mn1E−Mn1M, Mn1F−Mn1N, Mn1G−Mn1O, and Mn1H−Mn1P; Figure 1).

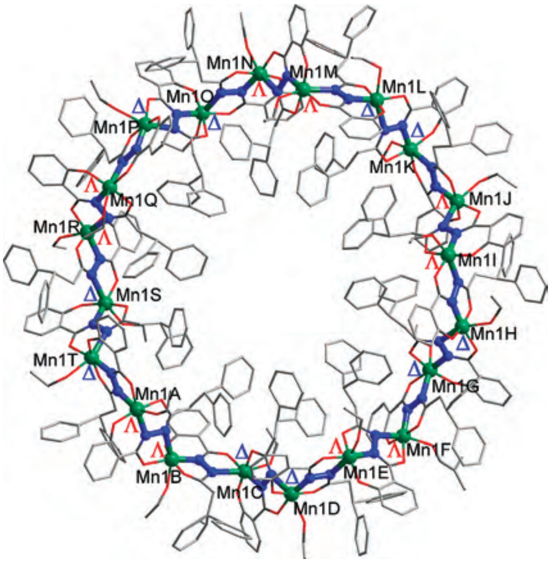

Figure 2. Top view of the 60-membered icosanuclear metallamacrocycle, **2**. The -[Mn−N−N-]$_{20}$ linkages are highlighted by the thicker bonds, and the chirality of the metal centers is shown in a $\cdots(\Lambda\Lambda\Delta\Delta)(\Lambda\Lambda\Delta\Delta)\cdots$ sequence. Key: Mn (green), N (blue), O (red), C (gray).

Dark brown block single crystals of [$Mn_{20}(dppshz)_{20}(EtOH)_{19}(DMF)$], **2**, were obtained by mixing the solution of H_3dppshz in DMF with a solution of manganese(II) acetate in methanol, then allowing the mixture to stand for a period of 5 days. The deprotonated ligand dppshz^{3-} again acts as a trianionic pentadentate ditopic bridging ligand and coordinates to manganese(III) cations *via* three oxygen atoms and two hydrazine nitrogen atoms in the bridging domain. The similar bridging mode of the ligand, dppshz^{3-}, leads to a cyclic structure consisting of 20 manganese metal ions, 20 ligands, and 20 solvent ligands (Figure 2 and Figure S7, Supporting Information). The terminal biphenylethyl groups of 10 ligands are directed to the inner core of the cyclic structure, while the remainders are directed to the outside of the metalladiazamacrocycle. The successive manganese centers in the S_{10} symmetric icosanuclear 60-membered metalladiazamacrocycle are identified as possessing a $\cdots(\Lambda\Lambda\Delta\Delta)(\Lambda\Lambda\Delta\Delta)\cdots$ chiral sequence. Such a chiral configuration is identical to that of metalladiazamacrocycles with rigid rod-shaped *N*-acyl substituents[4d,5] including the hexadecanuclear complex **1**. However, it is different from complexes with Cα- or Cβ-branched *N*-alkyl tails that have been reported so far, which have a $\cdots(\Lambda\Delta)(\Lambda\Delta)\cdots$ chiral sequence.[4a,b,6]

The diphenylethyl group at the *N*-acyl position can be considered as being a combination of two aryl β substitutions with four γ branches (Scheme 1). The freedom of rotation about the Cα−Cβ bond was restricted by introducing two bulky and rigid phenyl groups at the Cβ position, which leads to the formation of the 60-membered icosanuclear metallamacrocycle. This expansion of the nuclearity of the metallamacrocycle contrasts to the fact that a ligand having an *N*-acyl residue of a single aryl substituent at a flexible Cβ position was found to favor the formation of hexanuclear metalladiazamacrocycles with no ring expansion.[4a,b]

The 60-membered ring with 20 −[Mn−N−N−] repeat units is characterized by two different sets of torsion angles, the Mn−N−N−Mn torsion angle in the range 169.84(3)−179.52(4)° and the N−Mn−N−N torsion angles from 86.63(5) to 101.15(5)°. The neighboring Mn−Mn interatomic distances in the 60-membered ring are in the range 4.804(1)−4.911(1) Å, while the Mn−Mn−Mn interatomic angles are in the range 117.03(2)−131.94(1)° with an average value of 125.3°, which is much smaller than the value in the ideal planar cycloicosane structure (162°). The average value of the Mn−Mn−Mn angles in complex **2** is comparable with that of octanuclear metalladiazamacrocycle (127.2) with a $\cdots(\Lambda\Delta)(\Lambda\Delta)\cdots$ chiral sequence,[4b] but is smaller than those observed for decanuclear (139.8°)[4b] and dodecanuclear (134.0°)[7a] metalladiazamacrocycles with a $\cdots(\Lambda\Delta)(\Lambda\Delta)\cdots$ chiral sequence. The icosanuclear metalladiazamacrocycle can be considered a donut-shaped disk with a large enough hydrophobic inner cavity (Figure 2 and Figure S8, Supporting Information). The peripheral diameter of the core ring, measured between the opposite carbon atoms (C20B−C14L), is 40.1 Å (Figure S7, Supporting Information). The internal diameter of the cavity at the entrance in the 60-membered ring, measured between the opposite carbon atoms in the β-substitution phenyl groups of the dppshz^{3-} ligands at its widest point (C21C−C21M), was about 10.0 Å; the largest diameter at the center of the cavity, measured between the opposite manganese atoms (Mn1D−Mn1N), was about 26.9 Å, and the depth was approximately 16.4 Å.

When the extent of the ring puckering was represented using the average displacement of the ring metal ions from the best plane of the metalladiazamacrocycle, the ring puckering in the hexadecanuclear and icosanuclear manganese metalladiazamacrocycles with the $\cdots(\Lambda\Lambda\Delta\Delta)(\Lambda\Lambda\Delta\Delta)\cdots$ chiral sequence was larger than that in the metallamacrocycles with the $\cdots(\Lambda\Delta)(\Lambda\Delta)\cdots$ chiral sequence, but it was smaller than that in the severely puckered icosanuclear metallamacrocycle with the $\cdots(\Lambda\Lambda\Delta\Delta\Lambda\Delta\Delta\Lambda\Lambda\Delta)(\Lambda\Lambda\Delta\Delta\Lambda\Delta\Delta\Lambda\Lambda\Delta)\cdots$ chiral sequence and was comparable with that of the dodecanuclear metalladiazamacrocycle with the $\cdots(\Lambda\Lambda\Delta\Delta)(\Lambda\Lambda\Delta\Delta)\cdots$ chiral sequence (Table 2). This suggests that the chiral sequence of the metalladiazamacrocycle determines the extent of the ring puckering.

To assess the thermal stability of the metallamacrocycles, thermogravimetric analyses were carried out using a heating rate of 10 °C/min in the air. As shown in Figure S9 (Supporting Information), the TGA curve of complex **1** exhibited two significant weight losses. The first weight loss occurred between 50 and 250 °C, which was attributed to the loss of solvent molecules. The observed weight loss of 9.0% is in good agreement with the calculated value of 9.1% for six DMF and 10 water molecules. In the temperature range 340−450 °C, the observed weight loss of 67.6% suggests the decomposition of complex **1**. The desolvated compound remained stable up to 340 °C without any weight loss, showing that the metalladiazamacrocycle retained structural integrity to ∼340 °C.

Complex **2** exhibited a similar TGA characteristic, two-step weight loss (Figure S10, Supporting Information). The

Table 2. The Extent of the Ring Puckering in the Manganese Metalladiazamacrocycles

	metallamacrocycles in $-(\Lambda\Delta)(\Lambda\Delta)-$ chiral sequence				
	$[Mn_6(fshz)_6]$[b]	$[Mn_6(ashz)_6]$[c]	$[Mn_8(2\text{-mpshz})_8]$[d]	$[Mn_{10}(2\text{-dmpshz})_{10}]$[e]	$[Mn_{12}(chxshz)_{12}]$[f]
avg. displacement (Å)[a] (standard deviation)	0.74(3)	0.58(1)	0.56(11)	0.48(17)	0.73(28)

	metallamacrocycles in $-(\Lambda\Lambda\Delta\Delta)(\Lambda\Lambda\Delta\Delta)-$ chiral sequence		
	$[Mn_{12}(tpeshz)_{12}]$[g]	$[Mn_{16}(pbshz)_{16}]$[h]	$[Mn_{20}(dppshz)_{20}]$[h]
avg. displacement (Å) (standard deviation)	1.7(8)	1.8(2)	1.6(7)

	metallamacrocycle in $-(\Lambda\Lambda\Delta\Delta\Lambda\Lambda\Delta\Delta\Lambda\Delta)(\Lambda\Lambda\Delta\Delta\Lambda\Lambda\Delta\Delta\Lambda\Delta)-$ chiral sequence
	$[Mn_{20}(L)_{20}]$[i]
avg. displacement (Å) (standard deviation)	3.1(1.5)

[a] The extent of the ring puckering is represented as the average displacement of the ring metal ions from the best plane calculated using the ring metal ions of the metalladiazamacrocycles. [b] $fshz^{3-}$ = *N*-formylsalicylhydrazidate: *Inorg. Chem.* **1998**, *37*, 3599. [c] $ashz^{3-}$ = *N*-acetylsalicylhydrazidate: *Polyhedron* **2000**, *19*, 1985. [d] 2-mpshz^{3-} = *N*-(2-methylpropanoyl)salicylhydrazidate: *Inorg. Chem.* **2005**, *44*, 7109. [e] 2-dmpshz^{3-} = *N*-(2,2-dimethylpropanoyl)salicylhydrazidate: *Inorg. Chem.* **2005**, *44*, 7109. [f] $chxshz^{3-}$ = *N*-cyclohexanoylsalicylhydrazidate: *Chem. Commun.* **2006**, 3699. [g] $tpeshz^{3-}$ = *N*-2-pentenoylsalicylhydrazidate: *Chem. Commun.* **2004**, 2660. [h] $pbshz^{3-}$ = *N*-4-phenylbenzoylsalicylhydrazidate: $dppshz^{3-}$ = *N*-3,3-diphenylpropioylsalicylhydrazidate, this work. [i] L^{3-} = *N*-3-phenyl-*trans*-2-propenoylsalicylhydrazidate: *Inorg. Chem.* **2006**, *45*, 7991.

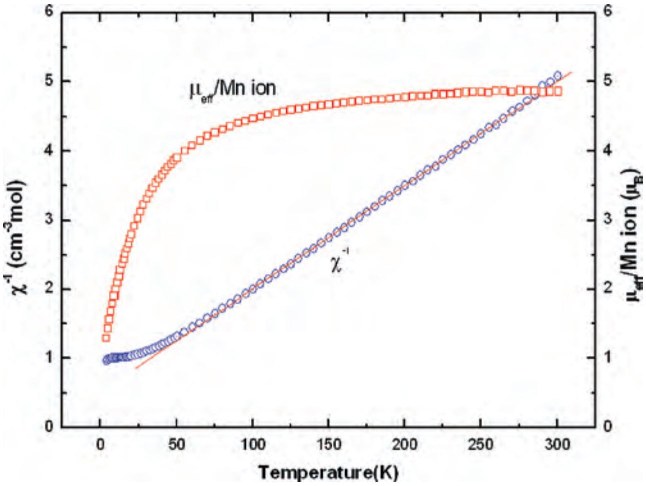

Figure 3. Temperature dependence of the effective magnetic moment per Mn ion (μ_{eff}), the inverse magnetic susceptibility (χ^{-1}), and its best fit (red solid line) for **2**.

observed weight loss was between 16 and 194 °C (8.2%), which is in good agreement with the calculated value of 8.2% for five ethanol and 28 water molecules. The decomposition of complex **2** occurs in the temperature range 255−450 °C.

Magnetic Properties. The magnetic behavior of **2** is shown in Figure 3 in the temperature range 4−300 K. The effective magnetic moment (μ_{eff}) decreases slightly with decreasing temperature from 4.87 μ_B at 300 K to 4.08 μ_B at 60 K. Below 60 K, it rapidly decreases and reaches 1.29 μ_B at 4 K. This behavior is typical for a weakly coupled antiferromagnetic system. Thus, by fitting the magnetic susceptibility data at temperatures $T > 60$ K to a Curie−Weiss expression $\chi(T) = C/[T + \Theta]$, we obtained an effective coupling constant J_{eff} (−5.12 K) and an effective magnetic moment per metal ion μ_{eff} (5.15 μ_B) for **2**. This behavior is similar to that reported for other, similar metalladiazamacrocycles.[4d,6]

Conclusions

In summary, when a pentadentate ligand, H_3pbshz, possessing a rigid rod-shaped biphenyl residue with a Cα substituted moiety as the *N*-acyl terminal group is self-assembled with manganese(III) ions, then an S_8 symmetric 48-membered hexadecanuclear metalladiazamacrocycle, $[Mn_{16}(pbshz)_{16}(EtOH)_{13}(DMF)_{1.5}(H_2O)_{1.5}]$, **1**, with alternating $\cdots(\Lambda\Lambda\Delta\Delta)(\Lambda\Lambda\Delta\Delta)\cdots$ stereochemistry can be constructed. The introduction of a rigid, rod-shaped *N*-acyl group with a bulky phenyl end leads to an expansion of the macrocyclic ring up to a 48-membered system, and the presence of the Cα substituted moiety moderates the ring puckering of the metallamacrocycle. When a 3,3-diphenylpropionylsalicylhydrazide was self-assembled with manganese(III) ions, a 60-membered icosanuclear manganese metalladiazamacrocycle was obtained. The introduction of two sterically bulky phenyl groups at the Cβ position of the ligand resulted in an expansion of the metalladiazamacrocycle ring to an S_{10} symmetric 60-membered icosanuclear metalladiazamacrocycle, $[Mn_{20}(dppshz)_{20}(EtOH)_{19}(DMF)]$, **2**, with the same $\cdots(\Lambda\Lambda\Delta\Delta)(\Lambda\Lambda\Delta\Delta)\cdots$ chiral configuration. The icosanuclear manganese metalladiazamacrocycle has a remarkable toroidlike shape with a relatively large internal hydrophobic cavity. Hence, **2** can be considered as a new donut-shaped host to accommodate small organic molecules.

Further effort to understand the factors that govern the sequence of the stereochemistry of the metal center; the nuclearity, size, and planarity of the macrocycle; and the final architecture of this type of macrocyclic assembly is in progress in our laboratory.

Acknowledgment. We gratefully acknowledge the financial assistance offered by KRF (KRF-2005-070-C00068), KOSEF (R01-2007-000-10167-0), and CBMH (R11-2008-8-0106). The authors also acknowledge PAL for beam line use (2008-2041-03).

Supporting Information Available: X-ray crystallographic data (CIF format) and the TGA data of **1** and **2**. IR spectra of the ligands, **1**, and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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