A dodecanuclear metallamacrocycle having a multidentate bridging ligand in two different binding modes†

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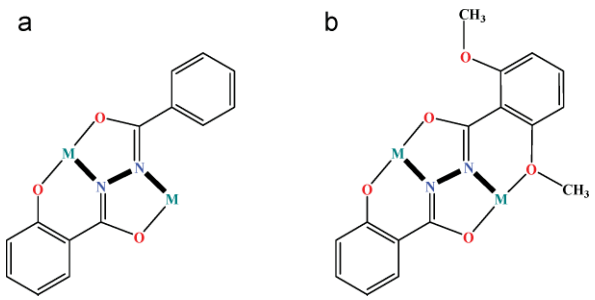
The reaction of $Mn(OAc)_2{\cdot}4H_2O$ with 2,6-dimethoxybenzoylsalicylhydrazide (H_3dmbshz) leads to a dodecanuclear manganese metallamacrocycle $[Mn_{12}(dmbshz)_{12}(EtOH)_6]$, **1**. The successive manganese centers are connected by the hydrazide N–N groups of the ligands in an alternating pentadentate binding mode, hexadentate binding mode. The alternation results in two alternating chelation modes around the metal centers, a tridentate–tridentate chelation mode and a bidentate–tridentate chelation mode. The metal ions in **1** are in a $\cdots(A_A\Delta_BC_A\Lambda_B)(A_A\Delta_BC_A\Lambda_B)\cdots$ chiral sequence, the alternation of the chiralities expanding the cyclic ring system to a 36-membered dodecanuclear manganese metallamacrocyclic ring system with S_6 point group symmetry.

Introduction

Ongoing efforts are being made in the designed formation of metallamacrocycles or metallacages with cavities of different sizes and shapes[1] because of their potential application in many areas such as molecular recognition, separation processes, and catalysis.[2] Metallamacrocycles are discrete, finite cyclic architectures composed of metal ions and ditopic organic linkers. The stoichiometry as well as the shape of the metallamacrocycle may be finely tuned through the coordination geometry of the metal center and the structural features of the organic linker. A small change in the ligand can produce a major effect on the self-assembled structure.[3] Therefore, controlling or tuning the structure, which gives an understanding of the self-assembly process and properties of the supramolecular species, is still a challenging goal.[4]

Metallamacrocycle can be synthesized on the basis of a rational ligand-directed approach. In diaza-bridged metallamacrocycles, that is, metalladiazamacrocycles,[4a,5–7] the primary organic species is an *N*-acylsalicylhydrazide. Our group has designed and synthesized a series of diaza-bridging linkers, *N*-acylsalicylhydrazides, that have three potential deprotonable sites and five potential donor atoms. The disposition of the donor atoms for tridentate coordination on one side and bidentate coordination on the other side enables its role as a ditopic linker between two metal centers, while a 'salicyl head domain' and '*N*-acyl tail domain' extends out of the 'bridging domain' for construction of the metalladiazamacrocycles (Scheme 1a). Considering the close-contact interactions caused by the *N*-acyl tails of the ligands that are directed towards the inner core of the cyclic structure, we can control the nuclearity and the shape of the metallamacrocycle.[4a,6]



Scheme 1 Two kinds of bridging modes: (a) a pentadentate binding mode forms 6,5,5-membered chelating rings; (b) a hexadentate binding mode forms 6,5,5,6-membered chelating rings.

Liu *et al.* have reported the decanuclear metalladiazamacrocycle of a 30-membered ring system, where *N*-phenylsalicylhydrazide (H_3bzshz) was used as a trianionic pentadentate bridging ligand.[8] In this contribution, as an attempt to perturb the coordination environment of the ring metal center of the metallamacrocycle by providing an additional coordination site at the bulky *N*-acyl residue without changing the charge of the ligand, we have synthesized a new multidentate bridging ligand, 2,6-dimethoxybenzoylsalicylhydrazide (H_3dmbshz), which has a 2,6-dimethoxybenzoyl residue as an *N*-acyl group. The triply deprotonated 2,6-dimethoxybenzoylsalicylhydrazidate ($dmbshz^{3-}$) having an additional potential donor group, a methoxy residue, can be involved in a different type of bridging mode. While in the metallamacrocyclic ring system of H_3bzshz only a pentadentate binding mode of a 6,5,5-membered chelation was observed, a hexadentate binding mode of a 6,5,5,6-membered chelation might also be possible with H_3dmbshz as shown in Scheme 1. The alteration of the ligand bridiging mode can lead to a metallamacrocycle of different stereochemistry and nuclearity.

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† Electronic supplementary information (ESI) available: Numbering scheme for the ligand, CIF file, a summary of the crystal and intensity data, TGA characterization, and some graphics of **1**. CCDC reference number 692608. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b810711d

Experimental

Materials

All reagents and solvents for syntheses were purchased from commercial sources and used as received with no further purification.

Instrumentation

Elemental analyses (C, H, and N) were performed at the Elemental Analysis Laboratory of the Korean Basic Science Institute on a CE Flash EA 1112 series elemental analyzer. Melting points of well-ground solid samples were measured using a SANYO Gallenkamp PLC melting point apparatus. Infrared spectra were recorded as KBr pellets in the range 4000–600 cm^{-1} on a Bio-Rad FT–IR spectrometer. The FAB mass spectrum was obtained using a JEOL JMS700 high-resolution mass spectrometer. Thermogravimetric analysis (TGA) experiments were carried out at a heating rate of 4 °C min^{-1} under an air atmosphere on a SCINCO STA S-1000 system. The UV spectra were recorded on a CARY 100 Conc UV–Visible spectrophotometer. NMR spectra were obtained using a Varian-500 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.

Ligand synthesis

2,6-Dimethoxybenzoylsalicylhydrazide (H_3dmbshz). The ligand was prepared using a procedure similar to that reported elsewhere.[7] 2,6-Dimethoxybenzoyl chloride (80%, tech, 1.25 g, 5.00 mmol) was added to a 50 mL chloroform solution containing triethylamine (0.77 mL, 5.5 mmol) and of 2,6-dimethoxybenzoic acid (0.91 g, 5.0 mmol) over a period of 15 min at 0 °C, while stirring. After stirring for about 1 h, the solution was slowly warmed to an ambient temperature. Then, salicylhydrazide (0.75 g, 5.0 mmol) was added to the solution in small portions, then stirred for a period of 30 min, when a white suspension began to appear, and stirring was continued for about 1 day. The white product formed was filtered and washed with small portions of cold chloroform, and ether, followed by drying in vacuum (0.804 g, 51% yield). Mp 222.1–224.8 °C. HRMS (FAB) m/z calcd for $C_{16}H_{16}N_2O_5$ $[M + H]^+$ 317.1137, found 317.1136. IR spectrum (KBr, cm^{-1}): 3103(m), 3022(w), 2715(w), 1675(m), 1601(s), 1574(s), 1486(s), 1476(s), 1433(w), 1386(w), 1304(w), 1255(s), 1111(s), 861(w), 782(w), 754(m), 703(w), 524(w); ^{1}H NMR spectrum (500 MHz, dmso-d_6, ppm): δ 12.13 (s, 1H), 10.79 (d, 1H, $J = 2$ Hz) (both amide NHs), 10.47 (d, 1H, $J = 1.5$ Hz, phenolic OH), 7.99 (dd, 1H, $J = 3.9$, 1.5 Hz, $H(3)_{salicyl}$), 7.46–7.42 (m, 1H, $H(5)_{salicyl}$), 7.35 (t, 1H, $J = 8.5$ Hz, $H(12)_{Ph}$), 7.00 (d, 1H, $J = 1.8$ Hz, $H(6)_{salicyl}$), 6.94 (m, 1H, $H(4)_{salicyl}$), 6.71 (d, 2H, $J = 4.3$ Hz, $H(11,13)_{Ph}$), 3.76 (s, 6H, $H(15,16)_{-CH3}$). ^{13}C NMR spectrum (126 MHz, dmso-d_6, ppm): δ 166.08(C8), 162.75(C7), 159.00(C10, C14), 157.34(C1), 133.94(C12), 130.84(C5), 128.59(C3), 119.04(C4), 117.27(C2), 114.73(C6), 114.05(C11, C13), 104.26(C9), 55.80(C15, C16). See Scheme S1 for the atom labeling of the ligand.†

Preparation of the metalladiazamacrocycle

$[Mn_{12}(dmbshz)_{12}(H_2O)_6]\cdot 3DMF\cdot 4H_2O$, 1. H_3dmbshz (15.8 mg, 0.050 mmol) and $Mn(OAc)_2\cdot 4H_2O$ (12.3 mg, 0.050 mmol) were dissolved in 4 mL DMF and allowed to mix for a period of 15 min. A 1 mL aliquot of this solution was transferred to a 6 mL tube, then 3 mL ethanol was slowly added through the tube wall. After being allowed to stand for 5 days, dark-brown rectangular crystals were obtained, freeze-dried (12.2 mg, 60.8% yield). Elemental analysis of $[Mn_{12}(dmbshz)_{12}(H_2O)_6]\cdot 3DMF\cdot 4H_2O$ ($C_{201}H_{197}Mn_{12}N_{27}O_{73}$, fw = 4815.51). Calc.: C 50.09, H 4.12, N 7.85%; found: C 49.94, H 3.99, N 7.78%.‡ IR (KBr pellet, cm^{-1}): 3443(br), 2936(w), 2840(w), 1654(w), 1601(s), 1564(m), 1497(s), 1453(m), 1405(m), 1348(s), 1245(w), 1150(w), 1105(m), 859(w), 756(w), 683(w), 646(w). UV–Vis (DMSO) [$\lambda_{max}(\varepsilon)$]: 256 nm (163000 $M^{-1}cm^{-1}$), 295 nm (120000 $M^{-1}cm^{-1}$), 370 nm (58300 $M^{-1}cm^{-1}$).

Crystallographic data collection and refinement of structure

The diffraction data were measured at 100 K with synchrotron radiation ($\lambda = 0.70000$ Å) on a 4AMXW ADSC Quantum-210 detector with a Pt-coated Si double crystal monochromator at the Pohang Accelerator Laboratory, Korea. HKL2000 (Ver. 0.98.694)[9] was used for data collection, cell refinement, reduction, and absorption correction.

Crystal structure determination for $[Mn_{12}(dmbshz)_{12}(EtOH)_6]\cdot 5EtOH\cdot 3H_2O$, **1**:† crystal data: $Mn_{12}C_{230}H_{294}N_{24}O_{82}$, fw = 5366.17, rhombohedral, space group $R\bar{3}$, $a = b = 29.040(4)$ Å, $c = 26.733(5)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 19524(5)$ Å^3, $T = 100(2)$ K, $Z = 3$, μ(synchrotron, $\lambda = 0.70000$ Å) = 0.648 mm^{-1}, 25 353 reflections were collected, 9406 were unique [$R_{int} = 0.0711$]. The structure was solved by a direct method and refined by full-matrix least-squares calculations with the SHELXTL-PLUS software package.[10] Two manganese atoms, two ligand units, a coordinating ethanol solvent molecule, and at least four non-coordinating structural solvent sites were identified as the asymmetric unit. A partially identified ethanol was observed in an S_6 symmetry site, and another ethanol site with a half occupancy and the other ethanol molecule in three disordered sites were also identified. An additional disordered water molecule was identified as a lattice solvent. All non-hydrogen atoms except those of the disordered coordinating solvent and non-coordinating structural solvent molecules were refined anisotropically; hydrogen atoms except those attached to the solvent molecules were assigned isotropic displacement coefficients $U(H) = 1.2U(C)$ or $1.5U(C_{methyl})$, and their coordinates were allowed to ride on their respective atoms. Solvent molecules of poorly defined geometry were refined with geometry restraints during the least-squares refinement. The refinement converged to a final $R1 = 0.0891$, and $wR2 = 0.2661$ for 4184 reflections with $I > 2\sigma(I)$. The structure refinement was further performed after modification of the data for the non-coordinate lattice solvent molecules (5741.3 Å^3, 29.4% of the crystal volume) with the *SQUEEZE* routine of PLATON (after removing lattice solvent molecules),[11] which led to better

‡ Even though the crystal structure analysis† did not show DMF molecules, but contained six water molecules and 16 ethanol molecules, as either ligating or structural solvents per molecule of complex **1**, the elemental analysis result was not consistent with the original content of the crystals. However, the IR spectrum showed the $\nu_{C=O}$ of DMF at 1654 cm^{-1}, which suggests the presence of some DMF molecules as disordered solvent although they were not identified in the crystal structure analysis. The compounds were found to lose coordinated ethanol during the freeze-drying process and on exposure to air. In addition, the structural solvent water molecules subsequently exchanged the coordinated ethanol molecules. This result is also consistent with the TGA data.

refinement and data convergence. Refinement of the structure converged at a final $R1 = 0.0656$, $wR2 = 0.1896$ for 4103 reflections with $I > 2\sigma(I)$, $R1 = 0.1299$, $wR2 = 0.2123$ for all 25 353 reflections. The largest difference peak and hole were 0.535 and –0.454 e Å^{-3} respectively. A summary of the crystal and intensity data is given in Table S1. CCDC 692608 contains the supplementary crystallographic data for this paper.†

Results and discussion

We have synthesized a new multidentate ligand, H_3dmbshz, by the coupling of a salicylhydrazide and a 2,6-dimethoxybenzoyl chloride in chloroform. The macrocyclic dodecanuclear metal cluster $[Mn^{III}_{12}(dmbshz)_{12}(EtOH)_6]$, **1**, was obtained by slow diffusion of ethanol into a DMF solution of manganese(II) acetate tetrahydrate and the ligand over a period of 5 days. Single-crystal X-ray analysis showed that compound **1** crystallized in the rhombohedral system with space group $R\bar{3}$ (Fig. 1). The asymmetric unit of the complex contains two unique manganese(III) cations, two ligands, and one solvent molecule (Fig. S1†). The deprotonated ligand, dmbshz^{3-} acts as a trianionic ditopic bridging ligand. The two ligands in the asymmetric unit are in different binding modes in **1**. One ligand is in a chelating pentadentate binding mode and coordinates to manganese(III) cations *via* three oxygen atoms and two hydrazine nitrogen atoms in the bridging domain (Fig. 2a). A phenolate oxygen atom, O1A, a hydrazide nitrogen atom, N1A, and a carbonyl oxygen atom, O3A, of the chosen ligand are each bound to a manganese atom in a tridentate chelation, the other carbonyl oxygen atom, O2A, and the other hydrazide nitrogen atom, N2A, are bound to the adjacent manganese atom in a bidentate chelation. The metal centers are connected through a hydrazide N–N linkage as the shortest path in this type of binding mode. The other ligand serves as a hexadentate bridging ligand containing three oxygen atoms and two hydrazine nitrogen atoms and the oxygen atom (O4B) from one methoxyl group occupying the sixth coordination site of the second manganese atom, Mn1A (Fig. 2b). Two tridentate chelations similarly bridge the metal centers through a hydrazide N–N linkage as the shortest path. The two meridional tridentate coordinations of the ligand to the metal ions make the overall conformation of the ligand more planar than that of the ligand in the bidentate-tridentate coordinations to the metal ions. The plane of the 2,6-dimethoxybenzoyl residue in a pentadentate binding mode is orthogonal to the plane formed by the residues in a bridging domain. The structure of metallamacrocycle **1** is unusual in that the ligands adopt two different bridging modes: a pentadentate binding mode of 6,5,5-membered chelation and a hexadentate binding mode of 6,5,5,6-membered chelation which emphasizes one of the methoxyl oxygen atoms participating in coordination. The alternation of these two different ligand binding modes generates two different coordination modes around the alternating metal centers: a bidentate–tridentate binding around the metal center, Mn1B, (Fig. S2a†) and a tridentate–tridentate binding around the metal center, Mn1A, (Fig. S2b†). The two different chemical environments of the manganese ions are bridged by the hydrazide N–N groups of the ligands leading to a cyclic $\cdots Mn_A Mn_B Mn_A Mn_B \cdots$-type structure consisting of 12 manganese metal ions and 36 member atoms. The multiple chelations on a metal center enforce the stereochemistry of the metal ion as a propeller configuration. The two manganese centers of the asymmetric unit possess different types of chiral configuration, *C* (clockwise) or *A* (anticlockwise)[12] for the tridentate–tridentate binding metal center A, and Δ or Λ for the bidentate–tridentate binding metal center B (Fig. 3).

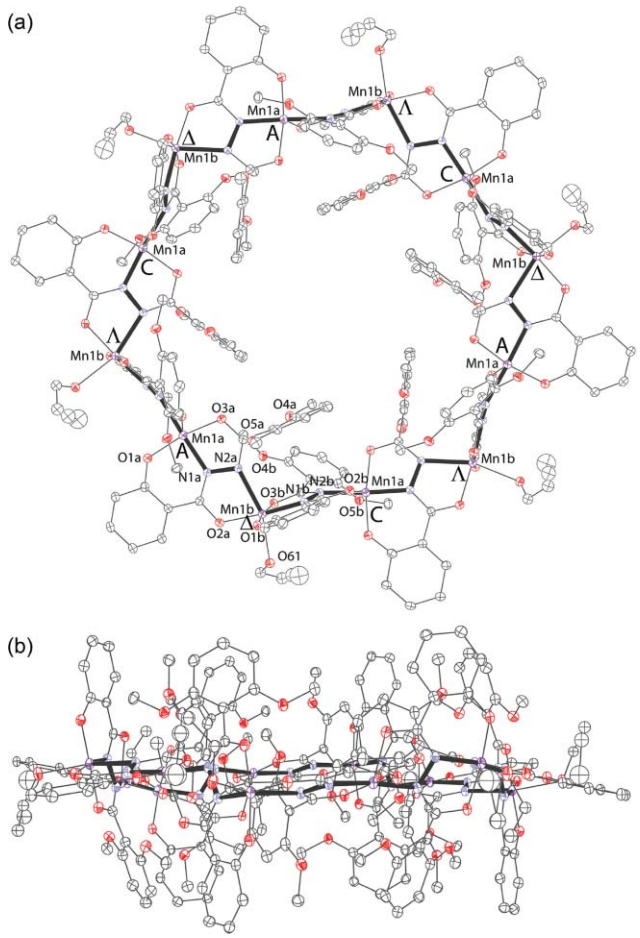

Fig. 1 (a) An ORTEP diagram of dodecanuclear metallamacrocycle **1** with $\cdots(A_A\Delta_B C_A\Lambda_B)(A_A\Delta_B C_A\Lambda_B)\cdots$ chiral sequence with 10% thermal ellipsoids. The 36-membered, 12-metal ring system is highlighted using thick bonds. (b) A side view of **1**. Key: Mn (purple), N (blue), O (red), C (gray).

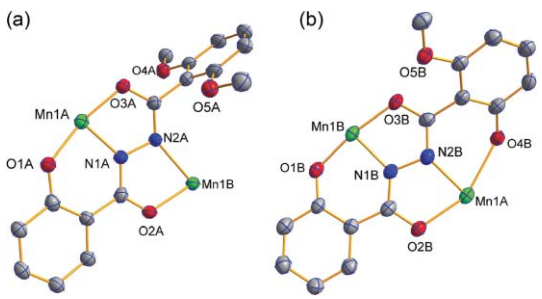

Fig. 2 The two different ligand binding modes observed in **1**. (a) A ligand bridges two metal centers in a pentadentate binding mode of 6,5,5-membered chelating rings. (b) The other ligand bridges two metal centers in a hexadentate binding mode of 6,5,5,6-membered chelating rings.

Therefore, this dodecanuclear macrocycle has a different configuration about the metal center in that the successive metal centers are in a $\cdots(A_A\Delta_B C_A\Lambda_B)(A_A\Delta_B C_A\Lambda_B)\cdots$ chiral sequence

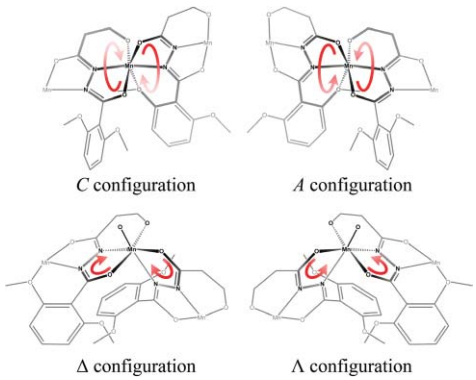

Fig. 3 Schematic diagrams for two different types of chiral configurations around the metal centers, *C*/*A* for the metal center of meridional tridentate–tridentate binding mode (top) and Δ/Λ for the metal center of the propeller bidentate–tridentate binding mode (bottom), observed in **1**.

(Fig. 1). This kind of chiral configuration of the manganese center is noticeably different from those of other reported dodecanuclear manganese(III) metallamacrocycles. In these metallamacrocycles, the all metal centers are in the same bidentate-tridentate chelation mode but the chiral sequence varies in the structures: a $\cdots\Lambda\Delta\Lambda\Delta\cdots$ chiral sequence[5g] or a $\cdots\Lambda\Lambda\Delta\Delta\Lambda\Lambda\Delta\Delta\cdots$ chiral sequence.[7] While the different chiral sequences in those metallamacrocycles are due to the different extents of ring puckering,[7,13] the tridentate–tridentate chelation mode caused by coordination of the substituent methoxyl group in **1** leads to a different stereochemistry and chiral sequence of the metal centers in the metallamacrocyclic ring system.

The successive Mn centers of the $\cdots(A_A\Delta_B C_A\Lambda_B)(A_A\Delta_B C_A\Lambda_B)\cdots$ chiral sequence lead to a small difference in Mn···Mn interatomic distances, but a significant difference between the Mn···Mn···Mn interatomic angles. The neighboring Mn···Mn interatomic distances in **1** alternate between 4.87 and 4.65 Å, while the Mn···Mn···Mn angles are 173.13°, associated with the tridentate–tridentate coordination mode, and 122.82°, associated with the bidentate–tridentate coordination mode. The average value of 148.0° for the Mn···Mn···Mn angles is very close to that expected (150°) for a planar cyclododecane structure (Fig. 4).

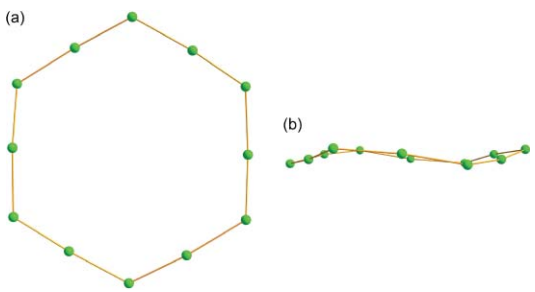

Fig. 4 (a) A top view and (b) a side view of the metallamacrocycle show that the ring system is very close to a planar cyclododecane structure. Green spheres represent manganese ions and brown sticks represent the interconnectivity between the manganese centers.

The tridentate–tridentate coordination mode can only generate an infinite chain structure rather than a finite cyclic structure, because the permitted Mn···Mn···Mn angle is close to 180°. The bidentate–tridentate coordination that allows an Mn···Mn···Mn angle smaller than 180° can provide the bend needed for the formation of a cyclic structure.

The six terminal 2,6-dimethoxyphenyl groups that are not involved in the ligation point toward the inner core of the macrocycle, while the remaining six 2,6-dimethoxyphenyl groups involved in the ligation are arranged vertically up and down relative to the metalladiazamacrocyclic ring plane (Fig. 1 and S3†). All the six solvent molecules ligated at the metal centers of the bidentate and tridentate chelations are oriented away from the ring.

The largest peripheral diameter of the metallamacrocycle, **1**, is ~3 nm. The metallamacrocycle has a hydrophobic cavity at the center (Fig. 5). Although, the largest diameter of the inner cavity measured between Mn1A and the symmetry-related Mn1A at the opposite position is ~14 Å, the size of the accessible hydrophobic core is ~6 Å in diameter at the center and 5.4 Å at the entrance (Fig. 5). A partially identified solvent ethanol was statically disordered in this cavity of S_6 symmetry.

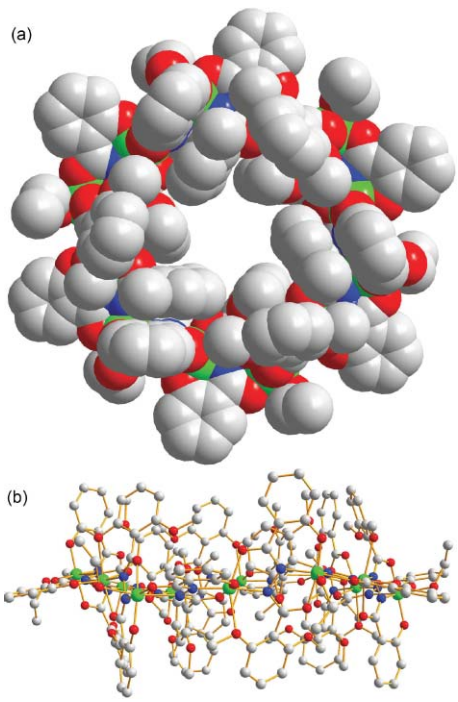

Fig. 5 (a) A CPK drawing of **1**. (b) A ball-and-stick side view of **1**. Key: Mn (green), N (blue), O (red), C (gray).

TGA experiments were performed to explore the thermal stability for compound **1** between ambient temperature and 500 °C. As shown in Fig. S4,† there are three weight losses exhibited on the curve. The first weight loss of 1.4% in the temperature range of 20–52 °C corresponds to the loss of four structural water molecules (calcd 1.5%). The loss of 6.9% in the temperature range of 90–200 °C is in good agreement with the calculated value of 6.8% for three solvent DMF molecules and six coordinated water molecules. No further weight loss was observed below 280 °C, at which temperature the decomposition of $[Mn_{12}(dmbshz)_{12}]$ occurred.

Magnetic properties

The inverse susceptibility for complex **1** is shown as a function of temperature in Fig. 6. The effective magnetic moment per Mn ion

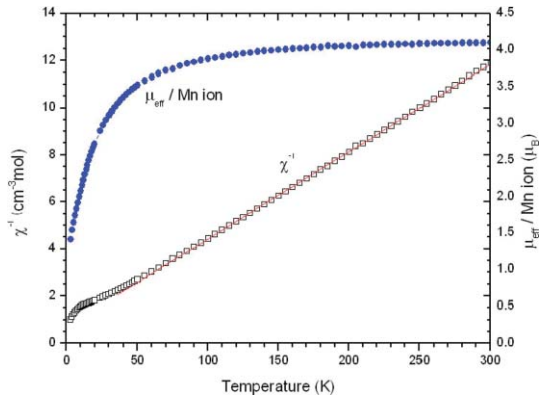

Fig. 6 Plot of the effective magnetic moment (μ_{eff}) and the inverse magnetic susceptibility (χ^{-1}) as a function of temperature for **1**.

(μ_{eff}/Mn ion) decreases first slightly with decreasing temperature from 4.1 μ_B at 300 K to 3.7 μ_B at 60 K. Below 60 K, μ_{eff}/Mn ion rapidly decreases and reaches 1.4 μ_B at 3 K. This behavior suggests a weakly coupled antiferromagnetism. At high temperatures, $T > 60$ K, the susceptibility follows the Curie–Weiss law $\chi = C/(T + \Theta)$. The best fit of the data using a Curie–Weiss expression gives rise to a Weiss constant $\Theta = -19.43$ K, an exchange parameter between the neighboring centers of $J/k_B = -2.43$ K, and an effective magnetic moment per metal ion μ_{eff} of 4.24 μ_B for complex **1**. The negative value of J/k_B indicates an antiferromagnetic coupling between the uncorrelated paramagnetic centers with $S = 2$.

Conclusions

A novel 36-membered dodecanuclear metallamacrocycle has been self-assembled using 12 Mn ions, 12 bridging ligands, and six solvent molecules as building components. In this assembly, the multidentate ligand, 2,6-dimethoxybenzoylsalicylhydrazide, adopts two bridging modes: a pentadentate binding mode of 6,5,5-membered chelating rings and a hexadentate binding mode of 6,5,5,6-membered chelating rings. The dodecanuclear metallamacrocycle having the ligands in two hetero-bridging modes is in a $\cdots(A_A\Delta_B C_A\Lambda_B)(A_A\Delta_B C_A\Lambda_B)\cdots$ chiral sequence and possesses a 36-membered ring system with an S_6 point group symmetry. The introduction of a potential donor at the *N*-acyl residue of the well-established bridging ligand can lead to an alteration of the coordination mode of the ring metal center and a subsequent modification of the stereochemistry and nuclearity of the resulting metalladiazamacrocycle.

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