Steric control of the nuclearity of metallamacrocycles: formation of a hexanuclear gallium metalladiazamacrocycle and a hexadecanuclear manganese metalladiazamacrocycle†‡

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An S_6-symmetric hexanuclear gallium metalladiazamacrocycle, $[Ga^{III}_6L^2_6S_6]$ with a $-(\Lambda\Delta)(\Lambda\Delta)-$ chiral sequence and an S_8-symmetric hexadecanuclear manganese metalladiazamacrocycle, $[Mn^{III}_{16}L^2_{16}S_{16}]$ with a $-(\Lambda\Lambda\Delta\Delta)(\Lambda\Lambda\Delta\Delta)-$ chiral sequence were prepared using the same N^2-*trans*-cinnamoyl-2-hydroxy-3-naphthoylhydrazide (H_3L^2) as a bridging pentadentate ligand between the metal centers for the formation of a macrocyclic system.

Introduction

Metallamacrocycles that contain metal ions as ring constituents have received attention from researchers over the past decade because of their interesting molecular architectures,[1] and their potential applications for magnetic materials,[2] electroluminescence materials[3] and sensors for small molecules.[4] In addition, metallamacrocycles could be used as supramolecular building blocks for the construction of diverse metal–organic frameworks.[5]

Even though the metallamacrocycles usually formed *via* a cyclic repeat of a ditopic metal node and a ditopic ligand node are simple from a topological point of view, the control of the size and nuclearity of macrocyclic ring systems is still challenging. The size and nuclearity of a metallamacrocycle depend on the properties of the metal ion and the linker ligand between the metal ions.[6]

As potential pentadentate ligands, *N*-acyl salicylhydrazides have led to various metalladiazamacrocycles depending on the *N*-acyl side chains used, in which the pentadentate ligand serves as a ditopic linker *via* a tridentate binding mode and a bidentate binding mode on each side of the ligand.[7–13] The nuclearity and ring size were controlled through the steric modulation of the *N*-acyl side chains. With flexible linear or β-branched *N*-alkyl groups, only 18-membered hexanuclear metalladiazamacrocycles have been obtained regardless of the metal ions and the solvents used.[7,8] When the ligands of α-branched *N*-alkyl groups were used, metalladiazamacrocycles with extended nuclearity have been prepared.[7,8] Metallamacrocycles of an octanuclear system have been obtained with the least sterically bulky *N*-acyl group, the *N*-isopropyl group.[9] Increases in the steric volume of the *N*-acyl group have led to either decanuclear[10] or dodecanuclear metalladiazamacrocycles.[11] The chirality induced from the biden-

tate and tridentate binding modes around the metal center of the ring alternates Λ and Δ, which leads to a $-(\Lambda\Delta)(\Lambda\Delta)-$ chiral sequence.[7–11] However, when a rigid but less sterically demanding *N*-acyl side chain such as the 2-pentenoyl group was introduced, the expanded dodecanuclear metalladiazamacrocycle, $[Mn_{12}(tpeshz)_{12}(DMF)_{12}]$ (in which $tpeshz^{3-}$ is *N-trans*-2-pentenoylsalicylhydrazidate), with $-(\Lambda\Lambda\Delta\Delta)(\Lambda\Lambda\Delta\Delta)-$ chiral sequence was prepared,[12] and this chiral sequence has led to a more puckered macrocyclic ring conformation than that of the metalladiazamacrocycles with the $-(\Lambda\Delta)(\Lambda\Delta)-$ chiral sequence. Half of the *N*-acyl chains were directed to the outer region of the ring cavity and the remaining half to the inner cavity region. When a rigid *N*-acyl group with a sterically bulky phenyl end such as the cinnamoyl group (H_3L^1) was introduced (Scheme 1), the resulting icosanuclear metalladiazamacrocycle, $[Mn_{20}L^1_{20}(DMSO)_{18}(H_2O)_2]$, was severely puckered and the corresponding chiral sequence of the metal center was somewhat complicated, forming the $-\{(\Lambda\Lambda\Lambda\Delta\Lambda)(\Delta\Delta\Lambda\Lambda\Delta)\}\{(\Lambda\Lambda\Lambda\Delta\Lambda)(\Delta\Delta\Lambda\Lambda\Delta)\}-$ chiral sequence.[13] Four out of 20 ligands are in *inverted* conformation in the macrocycle. The less sterically-demanding phenoxyl part of the
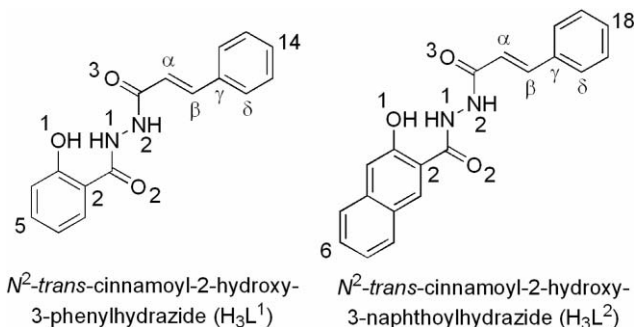
Scheme 1 Schematic drawings of two pentadentate ditopic linker ligands with partial numbering schemes. The tridentate and bidentate groups serve as a bridging domain that links two metal centers: an N^2-*trans*-cinnamoyl group serves as a primary steric domain that controls the nuclearity and size of the metallamacrocycle formed. An aroyl group of the ligand, either a phenoxyl or a naphthoyl group, serves as a secondary steric domain that is related to the ligand conformation in the macrocyclic ring system.

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ligand is directed towards the inner side of the macrocycle and the more sterically-demanding cinnamoyl part towards the outer side of the macrocycle, to reduce the excessive steric repulsion around the inner-core region of the cavity, which might be caused by the bulky phenyl end of the N-acyl side chain.[13]

In this study, we tried to modify the steric effect of the phenoxyl group on the orientation of the ligand in the metallamacrocycle on complexation with an octahedral metal ion such as manganese or gallium.

Results and discussion

We prepared a new pentadentate ligand, N^2-*trans*-cinnamoyl-3-hydroxy-2-naphthoylhydrazide (H_3L^2), in which the phenoxyl part of the ligand is replaced by the bulkier naphthoyl group to prevent the *inverted* conformation in the metalladiazamacrocycle formed (Scheme 1). Dark-brown needle-shaped crystals were obtained by layering et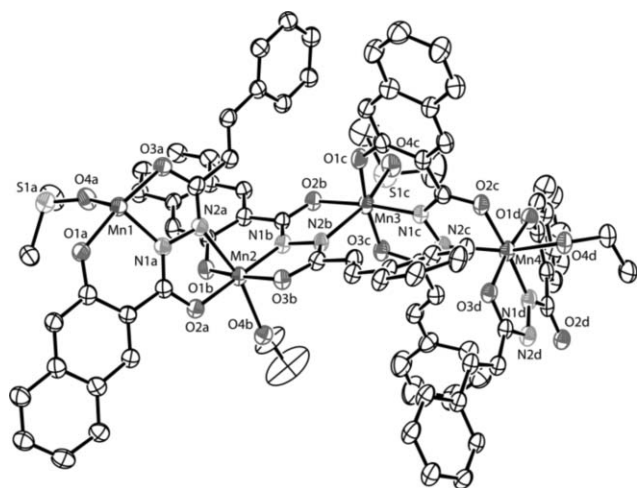hanol with the solution of equivalent amounts of the ligand and manganese acetate tetrahydrate in dimethyl sulfoxide (DMSO). The O1, N1, and O3 atoms bind to one manganese atom, while O2 and N2 bind to the adjacent manganese in a back-to-back fashion (Fig. 1), leading to a puckered S_8-symmetric 48-membered cyclic structure, $[Mn_{16}L^2{}_{16}(DMSO)_8(EtOH)_8]\cdot2(DMSO)$, **1**, consisting of 16 manganese metal ions and 16 ligands (Fig. 2a). The complex with $-(\Lambda\Lambda\Lambda\Delta)(\Lambda\Lambda\Lambda\Delta)-$ chiral sequence resembles puckered dodecanuclear manganese metalladiazamacrocycle, $[Mn_{12}(tpeshz)_{12}(DMF)_{12}]$, but extended further to a hexadecanuclear system. The Mn–Mn distances between the neighboring manganese centers alternate between 4.869(5) and 4.906(5): however, the Mn–Mn–Mn interatomic angles are in the range from 121.65(2)° to 124.92(2)° with an average value of 123.11(1)°, which is much smaller than the value in the ideal planar cyclohexadecane structure (157.5°) while closer to that for a puckered dodecanuclear metalladiazamacrocycle (117.7°).

Eight of the 16 ligands are directed toward the inner side of the macrocycle and the remaining ligands towards the outer side, but none of the ligands are in the *inverted* conformation, contrary to the case of the highly puckered icosanuclear manganese metalladiazamacrocycle, $[Mn_{20}L^1{}_{20}(DMSO)_{18}(H_2O)_2]$,[13] in which four out of 20 ligands are in the *inverted* conformation. The total steric volume of the eight cinnamoyl groups directed to the inner cavity region is not large enough to fill the cavity of the hexadecanuclear metalladiazamacrocycle, thereby leading to the formation of solvent pockets around the central cavity. Eight solvent DMSO molecules are observed in these pockets, four in each face of the macrocycle (Fig. 2b). The two different sets of ligand orientations in the hexadecanuclear manganese metallamacrocycle, resulting from the $-(\Lambda\Lambda\Lambda\Delta)(\Lambda\Lambda\Lambda\Delta)-$ chiral sequence, lead to slightly different sets of coordination geometries around the metal center, while only one type of ligand orientation in the hexanuclear gallium metallamacrocycle of $-(\Lambda\Delta)(\Lambda\Delta)-$ chiral sequence leads to one set of coordination geometry. There are two sets of dihedral angles between the plane of the tridentate-binding moiety and that of the bidentate-binding moiety of the ligand in the hexadecanuclear manganese metallamacrocycle.[14] One set of angles are in the range from 80.18(7) to 85.79(7)° with

Fig. 1 An ORTEP diagram of the asymmetric unit of the 48-membered hexadecanuclear manganese complex **1** drawn with 20%-probability ellipsoids.
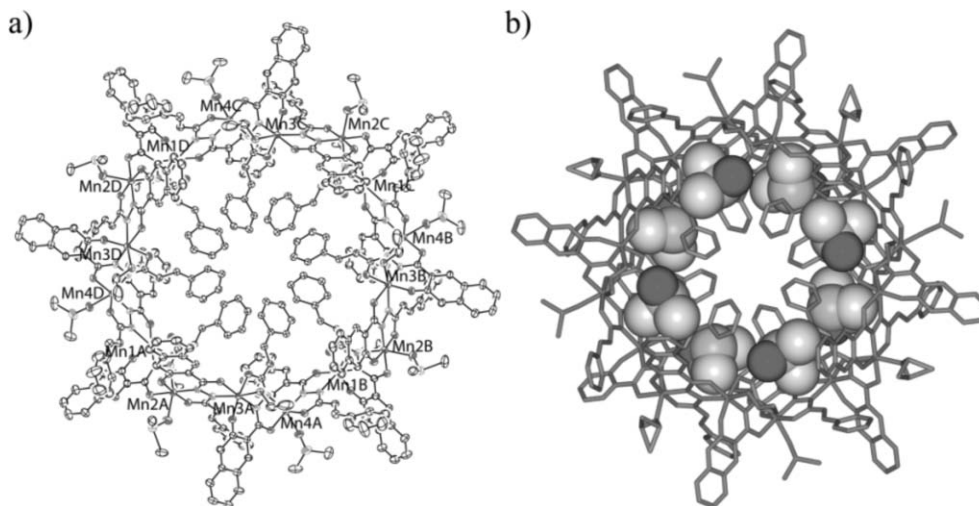

Fig. 2 (a) An ORTEP diagram of the 48-membered hexadecanuclear manganese complex **1**. (b) Eight DMSO molecules reside at the solvent pockets around the inner cavity region. The metallamacrocycle was presented using the green-stick model and the solvent DMSO molecules using the Corey–Pauling–Koltun model.

an average value of 82.87°, and the other set of angles are in the range from 88.90(7) to 89.64(6)° with an average value of 89.03°. However, only one set of dihedral angles were observed in the hexanuclear gallium metallamacrocycle, ranging from 82.81(5) to 86.16(5)° with an average value of 84.85°.

Allowing the mixed solution of the ligand and two equivalent amounts of gallium nitrate hexahydrate in ethanol to stand led to colorless block-shaped crystals. Fig. 3 shows the ORTEP diagram of hexanuclear gallium metalladiazamacrocycle **2**, [$Ga_6L^2_6$-$(EtOH)_6$], in which the chiral sequence of the metallamacrocycle is $-(\Lambda\Delta)(\Lambda\Delta)-$. Compound **2** is isostructural with other hexanuclear metallamacrocycles of S_6 symmetry with all N-terminal groups directed to the inner core of the macrocycle. The neighboring Ga–Ga interatomic distances are in the narrow range of 4.723(2)–4.739(1) Å, while the Ga–Ga–Ga angles in the 18-membered ring are in the range from 114.05(1) to 124.06(1)° with an average value of 117.39(6)°. These values are slightly bigger than that for a manganese hexanuclear metalladiazamacrocycle (115.2°).

Fig. 4 Ligand geometries showing the extent of bending in two different viewing directions. The top drawings are parallel to the ligand plane and the bottom drawings are perpendicular to the plane. a) The ligands of the hexadecanuclear manganese metalladiazamacrocycle in the environment of the least steric repulsion are planar. b) The ligands directed to the inner-core region show some degree of bending caused by the repulsion between the N-cinnamoyl groups. c) One of three ligands in the hexanuclear gallium complex shows the largest deviation from the ideal planar conformation.
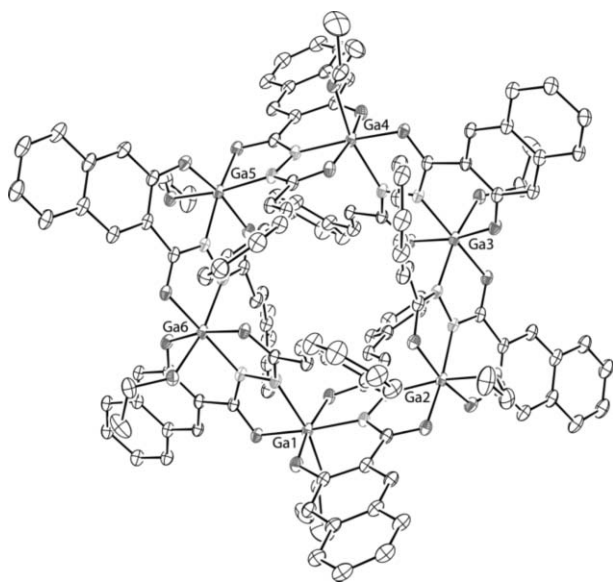

Fig. 3 An ORTEP diagram of 18-membered hexanuclear gallium complex **2**.

It appears that the ligands in each metallamacrocycle were bent from an ideal planar geometry to a different extent depending on the environment of the ligands, even though all bonds are conjugated (Fig. 4). In the manganese metallamacrocycle the ligands with the N-acyl moiety directed to the inner side of the macrocycle were bent more than the ligands with the N-acyl moiety directed to the outer side. The bending angles for the ligands[15] in the more sterically strained environment (17.72 and 16.44°; see Fig. 4b) are ~12° larger than those for the ligands in less sterically strained or unstrained environments (3.23 and 6.17°; see Fig. 4a). The average bending angle of the ligands in the hexanuclear gallium complex (15.81°) in the more sterically strained environment is slightly larger than that of the hexadecanuclear manganese complex (10.89°). Interestingly, the bending angles are found to be in a wide range, 6.79–26.63°, even though there are no distinctive differences in the environment of the three ligands of the crystallographic asymmetric unit. This variation indicates some degree of ligand flexibility, which provides
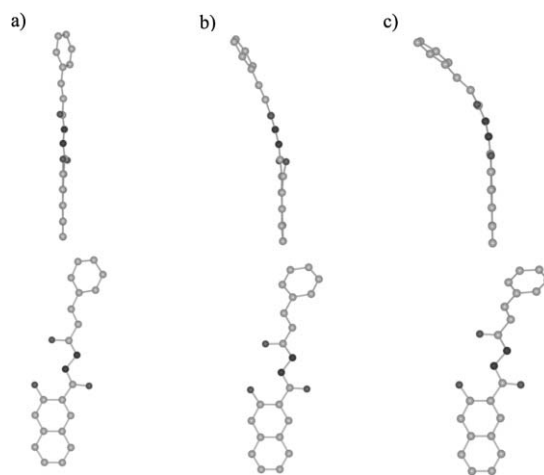
an alternative way to reduce excessive steric repulsion in the metalladiazamacrocycle. The local geometry of the Jahn–Teller distorted manganese(III) ion in the metalladiazamacrocycle might be distorted to extend its nuclearity without severe destabilization of the system when combined with the small bending of the ligands to reduce the steric repulsion. Though gallium of d^{10} configuration is known to have only a little geometry preference, it does not prefer greater distortion in the dihedral angle between the planes formed by the tridentate and bidentate chelation modes because of short metal–ligand distance. The restriction in the dihedral angles at the gallium center leads to a more regular octahedral geometry, and results in a hexanuclear system of $-(\Lambda\Delta)(\Lambda\Delta)-$ chiral sequence, in which the ligands are bent to a larger extent to reduce the severe steric repulsion between the bulky N-acyl groups. The severe bending (26.63°) of one ligand observed in the gallium metallamacrocycle (Fig. 4c) could be a consequence of the rigid coordination environment of gallium(III) centers of the bidentate and tridentate chelation modes that prefer a hexanuclear system.

The magnetic behavior of **1** is illustrated in Fig. 5 for the range 3–300 K. The effective magnetic moment (μ_{eff}) decreases slightly with decreasing temperature from 4.71 μ_B at 300 K to 4.07 μ_B at 60 K. Below 60 K, it rapidly decreases and reaches 1.51 μ_B at 3 K. This behavior is typical for a weakly coupled antiferromagnetic system. Thus, by fitting the magnetic susceptibility data at high temperatures, $T > 60$ K, to Curie–Weiss expression, $\chi(T) = C/[T + \Theta]$, we obtained an effective coupling constant J_{eff} (-1.85 K) and an effective magnetic moment per metal ion μ_{eff} (4.9 μ_B) for **1**. This behavior is similar to those reported for the other similar metalladiazamacrocycles.[9a,13]

Conclusions

We have prepared a hexanuclear gallium metallamacrocycle and a hexadecanuclear manganese metallamacrocycle using
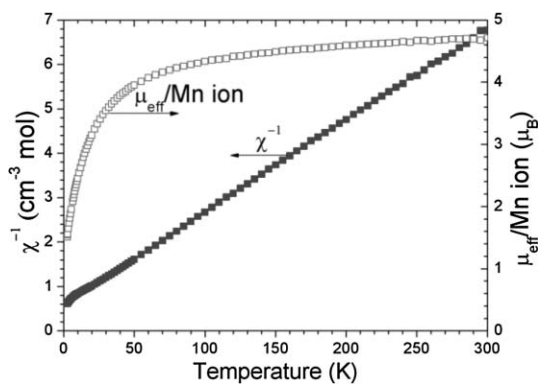
Fig. 5 Temperature dependence of the effective magnetic moment per Mn ion (μ_{eff}) and the inverse magnetic susceptibility (χ^{-1}) for **1**.

N^2-*trans*-cinnamoyl-2-hydroxy-3-naphthoylhydrazide (H_3L^2) as a diaza-bridging ditopic ligand in both compounds, where the phenoxyl part of the ligand has been replaced by a naphthoyl group to prevent the *inverted* conformation occurring in the metalladiazamacrocycle formed. The size and nuclearity of the metallamacrocycles were controlled *via* the modulation of the steric repulsion between the ligands in the macrocyclic ring system. The size and shape modulation of two domains of *N*-acyl-aroylhydrazide, an *N*-acyl domain and an aroyl domain, that are involved in the steric repulsion have led to an extremely large 48-membered hexadecanuclear metalladiazamacrocycle with a manganese ion and an 18-membered hexanuclear metalladiaza-macrocycle with a gallium ion. With a metal ion of soft coordination geometry such as Jahn–Teller distorted manganese(III) the steric repulsion between the ligands could be reduced mainly through the expansion of the ring system to hexadecanuclear metallamacrocycle with –(ΛΛΛΔ)(ΛΛΛΔ)– chiral sequence. With a gallium(III) ion of a relatively rigid coordination preference caused by the two chelating binding modes around the metal center, a hexanuclear metallamacrocyclic system with –(ΛΔ)(ΛΔ)– chiral sequence was obtained in which steric repulsion between the ligands was reduced *via* distortion of the ligand conformation.

Experimental

Materials

All reagents and solvents for syntheses were purchased from the commercial sources and used as received.

Instrumentation

Elemental analyses (C, H, N and S) 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 with KBr pellets in the range 4000–600 cm^{-1} on a BioRad FT-IR 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.

Ligand synthesis

N^2-***trans*-Cinnamoyl-2-hydroxy-3-naphthoylhydrazide (H$_3$L^2).** 0.62 mL (5.0 mmol) of trimethylacetyl chloride was added to 50 mL of chloroform solution at 0 °C, containing 0.77 mL (5.5 mmol) of triethylamine and 0.78 g (5.25 mmol) of *trans*-cinnamic acid, over a period of 15 minutes with stirring. The solution was slowly brought to ambient temperature. An equivalent amount of 3-hydroxy-2-naphthoic hydrazide (1.01 g, 5 mmol) was added to the solution and refluxed for a day. The white precipitate obtained was filtered and washed with small quantities of cold chloroform followed by water. Yield = 1.04 g (62.9%). Mp = 280–281 °C. Anal. calc. for C$_{20}$H$_{16}$N$_2$O$_3$: C 72.28, H 4.85, N 8.43; Found: C 71.97, H 4.82, N 8.39%; ^{1}H-NMR (DMSO-d_6, δ (ppm): 11.57 (s, 1H, O$\underline{H}$), 11.09 (d, 1H, N$\underline{H}$), 10.98 (d, 1H, N$\underline{H}$), 8.57 (s, 1H, Ar$\underline{H}$), 7.94 (d, 1H, Ar$\underline{H}$), 7.78 (d, 1H, Ar$\underline{H}$), 7.34–7.62 (m, 9H, Ar$\underline{H}$, –C$\underline{H}$=CHPh), 6.85 (d, 1H, –CH=C$\underline{H}$Ph); ^{13}C-NMR (DMSO-d_6, δ ppm): 164.3, 163.2, 154.3, 141.0, 136.6, 135.3, 131.7, 130.6, 129.7, 129.6, 129.1, 128.4, 127.5, 126.5, 124.6, 119.8, 119.4, 111.4; IR (KBr, cm^{-1}): 3171(br), 1669(w), 1640(s), 1587(s), 1557(s), 1484(s), 1394(w), 1358(m), 1209(m), 1019(w), 976(m), 912(w), 872(w), 852(w), 758(m), 690(m), 647(m), 600(w), 518(w), 475(w), 446(w).

Preparation of metallamacrocycles

[Mn$_{16}$L$^2_{16}$(DMSO)$_2$(EtOH)$_6$(H$_2$O)$_8$]. **1**: 16.6 mg (0.05 mmol) of H$_3$L^2 was dissolved in 1.0 mL of DMSO in a 1.5 mL microtube and 12.3 mg (0.05 mmol) of Mn(OAc)$_2$·4H$_2$O was dissolved in 1 mL of DMSO in another 1.5 mL microtube. The two solutions were mixed in a 15 mL vial and 10 mL of ethanol was slowly added through the vial wall. The solution was allowed to stand for 10 days, after which dark-brown needle-shaped crystals were obtained. The product was filtered, washed with methanol and ethanol successively and was freeze-dried before elemental analysis. (14.2 mg, 67.6% yield). Elemental analysis data for [Mn$_{16}$L$^2_{16}$(DMSO)$_2$(EtOH)$_6$(H$_2$O)$_8$] (C$_{336}$H$_{272}$N$_{32}$O$_{64}$Mn$_{16}$S$_2$, fw = 6725.16). Calc.: C 60.01, H 4.08, N 6.66, S 0.95%. Found: C 60.43, H 3.63, N 6.91, S 1.12%. IR (KBr pellet, cm^{-1}): 3428(br), 3056(br), 1631(s), 1593(s), 1513(s), 1453(s), 1400(s), 1367(s), 1261(m), 1171(w), 1108(w), 971(w), 914(w), 867(w), 802(w), 756(m), 680(w), 592(w), 551(w), 474(w), 429(w).

[Note: Even though the crystal-structure analysis suggests that the crystals contained at least 16 DMSO molecules, 16 water molecules and 22 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 some of the coordinated solvent molecules during freeze-drying and exposure to air and these were subsequently replaced by water molecules in air.]

[Ga$_6$L$^2_6$(EtOH)$_4$(H$_2$O)$_2$]. **2**: 8.3 mg (0.025 mmol) of H$_3$L^2 was added to 10 mL of ethanol in a 15 mL vial and was sonicated for 5 minutes to form a suspension. In another vial 12.8 mg (0.05 mmol) of Ga(NO$_3$)$_3$·6H$_2$O was sonicated for 30 minutes with 5 mL of ethanol to form a suspension. The contents of the two vials

were mixed in a 30 mL vial. When it was allowed to stand, it became clear and yielded colorless block crystals. The product was filtered, washed with small quantities of ethanol and freeze-dried before elemental analysis. (6.5 mg, 59.2% yield). Elemental analysis data for $[Ga_6L^2_6(EtOH)_4(H_2O)_2]$ $(C_{128}H_{106}N_{12}O_{24}Ga_6,$ fw = 2614.64). Calc.: C 58.80, H 4.09, N 6.43%. Found: C 59.20, H 3.85, N 6.87%. IR (KBr pellet, cm^{-1}): 3390(br), 3054(br), 1634(s), 1597(s), 1525(s), 1502(s), 1455(s), 1413(s), 1327(m), 1262(m), 1228(m), 1176(w), 1151(w), 1038(w), 970(w), 915(w), 866(w), 807(w), 754(w), 665(w), 579(w), 479(w).

[Note: Even though the crystal-structure analysis suggests that the crystals contained at least 15 ethanol molecules as either ligating or structural solvents per molecule of complex **2**, the elemental analysis was not consistent with the original content of the crystals, despite several attempts. The compounds were found to lose some of the coordinated solvent molecules during freeze-drying and exposure to air and these were subsequently replaced by water molecules in air.]

Crystallographic studies

The crystals were coated with paratone oil because they lose crystallinity on exposure to air. The diffraction data were measured with synchrotron radiation (λ = 0.70000 Å) on a 4AMXW ADSC Quantum-210 detector with a Pt-coated Si double-crystal monochromator at the Pohang Accelerator Laboratory, Korea. The HKL2000 (Ver. 0.98.694)[16] was used for data collection, cell refinement, reduction and absorption correction. Both the crystal structures were solved by direct methods and refined by full-matrix least-squares calculations with the SHELXTL-PLUS software package.[17]

Crystal structure determination for $[Mn_{16}L^2_{16}(DMSO)_8(EtOH)_8]\cdot8DMSO\cdot14EtOH\cdot16H_2O,$ 1

An asymmetric unit of hexadecanuclear metallamacrocycle consists of four manganese and four ligand units with two DMSO and two ethanol molecules coordinated to the available solvent coordination sites. Among the coordinated solvents one ethanol and one DMSO are disordered. The asymmetric unit also contains two DMSO molecules, one of which is disordered, four ethanol sites (three of them fully occupied, two of which are disordered and one half occupied) contributing three and a half ethanol molecules, and six partial-occupancy water sites with an overall contribution of four molecules. All non-hydrogen atoms except those of the non-coordinating structural solvent molecules were refined anisotropically and those of the remaining structural solvents were refined isotropically with the exception of two DMSO molecules. Hydrogen atoms of the main macrocyclic structural unit 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. One of the ethanol sites with severe disorder was refined with geometry restraints during the least-squares refinement. The refinement converged to a final $R1 = 0.0979$, and $wR2 = 0.2785$ for 10 238 reflections of $I > 2\sigma(I)$. The structure refinement was further performed after modification of the data for electron density, except for the two well-defined DMSO molecules of the free solvent region (6754.1 Å^3, 30.3%)

Table 1 Crystal data and structure refinement for **1** and **2**

	1	**2**
Empirical formula	$Mn_{16}C_{368}H_{344}N_{32}O_{72}S_{16}$	$Ga_6C_{150}H_{169}N_{12}O_{33.5}$
Formula weight/gmol^{-1}	7758.75	3094.29
Temperature/K	103(2)	99(2)
Wavelength/Å	0.70000	0.70000
Crystal system	Tetragonal	Monoclinic
Space group	$P4/n$	$P2_1/n$
Unit cell dimensions (length/Å, angle/°)	$a = 39.134(6), \alpha = 90$	$a = 16.918(3), \alpha = 90$
	$b = 39.134(6), \beta = 90$	$b = 27.325(6), \beta = 107.05(3)$
	$c = 14.553(3), \gamma = 90$	$c = 16.928(3), \gamma = 90$
Volume/Å^3	22 288(6)	7482(3)
Z	2	2
Density$_{calcd}$/mg m^{-3}	1.156	1.374
Absorption coefficient/mm^{-1}	0.577	1.143
$F(000)$	8016	3214
Crystal size/mm^3	0.20 × 0.10 × 0.10	0.20 × 0.20 × 0.10
θ range for data collection/°	1.56 to 30.42	1.47 to 30.44
Index ranges	$-56 \le h \le 56, -56 \le k \le 56,$	$0 \le h \le 24, -39 \le k \le 39,$
	$-21 \le l \le 0$	$-24 \le l \le 23$
Reflections collected	125 699	41 821
Independent reflections	35 175 [R(int) = 0.0685]	23 484 [R(int) = 0.0511]
Completeness to $\theta = 30.42°$ (%)	99.5	98.8
Absorption correction	Empirical	Empirical
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	35 175/0/1169	23 484/3/959
Goodness-of-fit on F^2	0.794	1.024
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0737, wR2 = 0.2024$	$R1 = 0.0589, wR2 = 0.1717$
R indices (all data)	$R1 = 0.1872, wR2 = 0.2437$	$R1 = 0.0905, wR2 = 0.1924$
Largest diff. peak and hole (e Å^{-3})	0.609 and -0.553	1.114 and -0.935

with the *SQUEEZE* routine of PLATON,[18] which led to better refinement and data convergence.

Crystal structure determination for [Ga₆L²₆(EtOH)₆]· 9EtOH·0.5H₂O, 2

Crystal structure determination for $[Ga_6L^2_6(EtOH)_6]\cdot 9EtOH\cdot 0.5H_2O$, **2**

An asymmetric unit of hexanuclear metallamacrocycle consists of three gallium and three ligand units with three ethanol molecules coordinated to the available solvent coordination sites. Among the coordinated solvents, one ethanol is disordered. The asymmetric unit also contains five ethanol sites (three of them fully occupied, one of which is disordered and the other two sites are partially occupied) with an overall contribution of four and a half ethanol molecules, and one partial-occupancy water site. All non-hydrogen atoms except one carbon from the ethanol solvent and one partially-occupied water molecule were refined anisotropically. The hydrogen atoms attached to the coordinated ethanol molecules were identified from difference Fourier analysis and were assigned isotropic displacement coefficients $U(H) = 1.5U(O_{hydroxyl})$. The rest of the hydrogen atoms were assigned isotropic displacement coefficients $U(H) = 1.2U(C)$ or $1.5U(C_{methyl}/O_{hydroxyl})$, and their coordinates were allowed to ride on their respective atoms. One free ethanol site is disordered and was refined with geometry restraints during the least-squares refinement.

A summary of the crystal and intensity data for **1** and **2** is given in Table 1.

CCDC 644811–644812.†

Notes and references

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