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Encapsulation of a guest molecule in a strained form: An extended 36-membered dodecanuclear manganese metallamacrocycle that accommodates a cyclooctane in the S_4 symmetry conformation

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Ligand synthesis

H_3chxshz: The synthesis of the ligand was carried out by a slight modification of our previous reports.[1] 1.25 mL (10.0 mmol) of trimethylacetyl chloride was added to 20 mL chloroform solution of 1.31 mL (10.0 mmol) of cyclohexylcarboxylic acid at 0 ºC and triethylamine (1.54 mL, 11.0 mmol), and stirred for about 20 min slowly increasing to ambient temperature. To the above solution, 1.51 g (9.80 mmol) of salicylhydrazide was added and stirred for 30 min. A white suspension began to appear after a while. The product was refluxed for about an hour and then cooled to room temperature. The product formed was filtered, washed with cold chloroform followed by water and ether. The product was then dried under vacuum over P_2O_5. Yield 2.34 g, 90.7%. Elemental Analysis. Found: C, 63.92; H, 6.94; N, 10.71%. Calc. for $C_{14}H_{18}N_2O_3$; C, 64.11; H, 6.92; N, 10.68%. M^+ (mass spectrum), 263.1. IR (KBr pellet, ν/cm^{-1}): 3309(m), 3248(m), 2935(m,sh), 2858(m), 1652(m), 1618(s), 1607(s), 1565(m), 1519(m), 1491(s), 1455(m), 1388(m), 1313(m), 1243(m), 1218(w), 1103 (w), 972 (w), 894 (m), 805 (w), 757(m); δ_H (300 MHz, dmso-d_6 in ppm): 11.96 (bs, 1H, –NH), 10.53 (bs, 1H, –NH), 10.05 (bs, 1H, –OH) 7.87 (d, 1H, Ar–H), 7.43 (t, 1H, Ar–H), 6.94 (m, 2H Ar–H), 2.28 (m, 1H, $H_{cyclohexyl}$), 1.2–1.8 (m, 10H, $H_{cyclohexyl}$). δ_C (75.5 MHz, dmso-d_6 in ppm) 174.0(C_8), 167.0(C_7), 159.2 (C_1), 134.0 (C_5), 128.2 (C_3), 119.0 (C_4), 117.3 (C_2), 114.5 (C_6).

Preparation of metalladiazamacrocycles

$[Mn_{12}(chxshz)_{12}(MeOH)_{12}]\cdot 12(dmf)\cdot 2(H_2O)\cdot 4.5(MeOH)$, **1**: The complex was best grown as crystals on addition of solid manganese acetate tetrahydrate (24.5 mg, 0.100 mmol) to a 10.0 mL solution of H_3chxshz (26.3 mg, 0.100 mmol) in a mixture of *N*,*N*-dimethyl formamide (dmf) and methanol in the ratio 3 : 7 in a 25 mL vial over a period of five days. The crystals isolated were dried under vacuum over fused calcium chloride. Elemental Analysis. Found. C, 49.88; H, 5.88; N, 10.12%. Calc. for $[Mn_{12}(chxshz)_{12}(dmf)_{12}]\cdot 15(H_2O)$, $Mn_{12}C_{204}H_{294}N_{36}O_{63}$: C, 49.82; H, 6.03; N, 10.25%. (*Note: Even though the crystal structure analysis suggests that the crystals contain at least twelve dmf molecules, two water molecules and five molecules of methanol as structural solvents per molecule of complex **1**, due to the sensitivity of the compound to air the elemental analysis could never be consistent with the original contents of the crystals despite several attempts. The compounds were found to lose coordinated methanol during exposure to air. The methanol molecules are subsequently replaced by the structural solvent dmf.*) IR (KBr pellet, ν_{max}/cm^{-1}): 3455 (br), 1661 (m), 1602(m), 1565(m), 1498(s), 1409(m), 1365(m), 1355(m), 911(w), 757(m), 697(m), 687(m).

1⊃cyclohexane: Method A: The crystals of cyclohexane bound complex **1** were isolated by a similar procedure, except that the latter contained 11.0 μL (0.100 mmol) of cyclohexane and manganese acetate tetrahydrate (24.5 mg, 0.100 mmol) was layered as methanol solution over that of ligand. The dmf–methanol mixture ratio remained at 3 : 7. Diffraction quality crystals were obtained within 36 hours. Method B: Large crystals of dodecanuclear manganese metallamacrocycles were grown as described for complex **1** over a period of 5 days. During the diffusion of cyclohexane the preformed crystals remained intact in solution. To this vial about 20.0 μL (0.185 mmol) of cyclohexane were added to allow diffusion into the crystal. The X-ray diffraction data were collected after three days of guest addition. Elemental Analysis. Found. C, 51.49; H, 6.21; N, 11.41%. Calc. for $[Mn_{12}(chxshz)_{12}(dmf)_{12}]\cdot 3(dmf)\cdot 6(H_2O)$, $Mn_{12}C_{213}H_{297}N_{39}O_{57}$: C, 51.42; H, 6.02; N, 10.98%. (*Note: Even though the crystal structure analysis verifies the encapsulation of cyclohexane in the cavity of the metallamacrocycle, the elemental analysis suggests the decapsulation of the bound cyclohexane during the drying of the crystal in the desiccator under light vacuum. This may be due to weak binding of the symmetry mismatched guest in the hydrophobic cavity.*) IR (KBr pellet, ν_{max}/cm^{-1}) 3423(br), 2928(s), 2854(s), 1657(s), 1601, 1565, 1498, 1445, 1406, 1355, 1106, 1033, 910, 863, 756, 683, 601.

1⊃cyclooctane: Method A: The crystals of cyclooctane bound complex **1** were obtained by following the same procedure as above method A using 0.100 mmol of the reactants, except that 15.0 μL (0.110 mmol) of cyclooctane were added to the solution instead of cyclohexane. Method B, Crystals were grown as described in the procedure for compound **1** and 30.0 μL (0.224 mmol) of cyclooctane were added to the mother liquor to allow diffusion into the crystal. During the diffusion of cyclooctane the preformed crystals retained their crystal morphology in solution. The X-ray diffraction data were collected after four days of guest addition. Elemental Analysis. Found. C, 53.96; H, 6.08; N, 11.19%. Calc. for $[Mn_{12}(chxshz)_{12}(dmf)_{12}]\cdot(dmf)\cdot(C_8H_{16})$, $Mn_{12}C_{215}H_{287}N_{37}O_{49}$: C, 53.43; H, 5.99; N, 10.72%. (*Note: The elemental analysis suggests the encapsulated cyclooctane remained intact during drying under light vacuum. This might be due to the stronger binding of the symmetry matched cyclooctane guest in the cavity compared with the symmetry mismatched cyclohexane.*)

Crystallographic Data Collections and Refinements of Structures

$[Mn_{12}(chxshz)_{12}(MeOH)_{12}]\cdot12(dmf)\cdot2(H_2O)\cdot4.5(MeOH)$, **1**: The diffraction data were measured at −173 ˚C with synchrotron radiation (λ = 0.82657 Å) on a 6BX Bruker Proteum 300 CCD detector with a platinum coated double crystal monochromator at the Pohang Accelerator Laboratory, Korea. The Proteum 2 (*Ver*. 1.0.22)[2] was used for data collection, cell refinement, and reduction. Collected data were corrected for absorbance using SADABS[3] based upon Laue symmetry using equivalent reflections. All structures were solved by direct methods and refined by full-matrix least-squares calculations with the SHELXTL-PLUS software package.[4] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2 U (C, N), and their coordinates were allowed to ride on their respective atoms. Three dmf molecules per asymmetric unit were observed in the lattice. Additional two water sites and four methanol sites with partial occupancies were also observed. The solvent methanol in the inner cavity of the metallamacrocycle is disordered with total of half occupancy. The refinement converged to a final $R1 = 0.0874$, and $wR2 = 0.2573$ for 6969 reflections of $I > 2\sigma(I)$. The structure refinement was further performed after modification of the data for the disordered electron density except for the vicinity of the inner cavity with the *SQUEEZE* routine of PLATON (after removing free solvent molecules),[5] which led to better refinement and data convergence. Refinement of the structure converged at a final $R1 = 0.0548$, $wR2 = 0.1682$ for 6793 reflections with $I > 2\sigma(I)$, $R1 = 0.0598$, $wR2 = 0.1777$ for all 7500 reflections.

The largest difference peak and hole were 0.693 and –0.420 e·Å^{-3}, respectively. A summary of the crystal and intensity data is given in Table S1.

1⊃cyclohexane: Data collection was performed using a crystal obtained from the template reaction (Method A) at –100 °C with Mo Kα radiation (λ = 0.71073 Å) on a Bruker SMART CCD equipped with a graphite crystal, incident-beam monochromator. The SMART and SAINT software packages[6] were used for data collection and integration, respectively. Collected data were corrected for absorbance using SADABS based upon Laue symmetry using equivalent reflections. Since the crystals of **1** and **1**⊃cyclohexane were isomorphous, the coordinates of **1** were used as the basis for the refinement of **1**⊃cyclohexane structure. The difference Fourier synthesis and the subsequent least square refinement revealed remaining structural solvents. The crystal structure contains at least three dmf sites and one water site with partial occupancies per asymmetric unit. A disordered cyclohexane site was observed at the inner cavity of the metallamacrocycle. Refinement of the structure converged to a final $R1$ = 0.1403, and $wR2$ = 0.3431 for 13094 reflections with $I > 2\sigma(I)$. The structure was further refined after modification of disordered electron density except for the vicinity of the inner cavity using the *SQEEZE* option in PLATON (after removing free solvent molecules). The cyclohexane in chair conformation could be derived from the six cyclic carbon atoms of 0.25 site occupancies when their 1-2 and 1-3 carbon distances are restrained at 1.54 Å and 2.51 Å respectively, which mean four disordered cyclohexane sites in chair conformations at S_4 symmetric cavity of the metallamacrocycle. A final $R1$ = 0.0853, $wR2$ = 0.1957 for 12169 reflections with $I > 2\sigma(I)$, $R1$ = 0.1068, $wR2$ = 0.2049 for all 16082 reflections. The largest difference peak and hole were 0.796 and –0.617 e·Å^{-3}, respectively. A summary of the crystal and intensity data is given in Table S2. Data collection and refinement result of the crystal obtained from the batch into which cyclohexane was added after growth of the crystals of compound **1** showed similar cyclohexane encapsulation at the cavity of the metallamacrocycle.

1⊃cyclooctane: Data collection was performed using a crystal obtained from the template reaction (Method A) at –100 °C with Mo Kα radiation (λ = 0.71073 Å) on a Bruker SMART CCD equipped with a graphite crystal, incident-beam monochromator. The refinement was also performed using the coordinates of **1** as the basis for the refinement of **1**⊃cyclooctane structure as described for **1**⊃cyclohexane. The crystal lattice contains three dmf molecules per asymmetric unit and a statically disordered water/methanol site was observed. A cyclooctane site was again observed at the S_4 symmetric inner cavity of the metallamacrocycle. The data converged to an R value of $R1$ = 0.1438 and $wR2$ = 0.3768 for 13037 reflections with $I > 2\sigma(I)$. The free solvent molecules were then removed and the SQUEEZE routine was performed to modify the disordered electron density. The cyclooctane with prolate

ellipsoidal thermal factors could be resolved using two disordered cyclooctane molecules with half occupancy factors, where the 1-2 and 1-3 carbon distances of the cyclooctane are restrained at 1.54 Å and 2.51 Å respectively. Further refinement of the structure converged at a final R1 = 0.0948, wR2 = 0.2394 for 12152 reflections with $I > 2\sigma(I)$, R1 = 0.1174, wR2 = 0.2515 for all 16854 reflections. The largest difference peak and hole were 0.873 and –0.711 e·Å^{-3}, respectively. A summary of the crystal and intensity data is given in Table S3. Data collection and refinement result of the crystal obtained from the batch into which cyclooctane was added after growth of the crystals of compound **1** showed similar cyclooctane encapsulation at the cavity of the metallamacrocycle.

References

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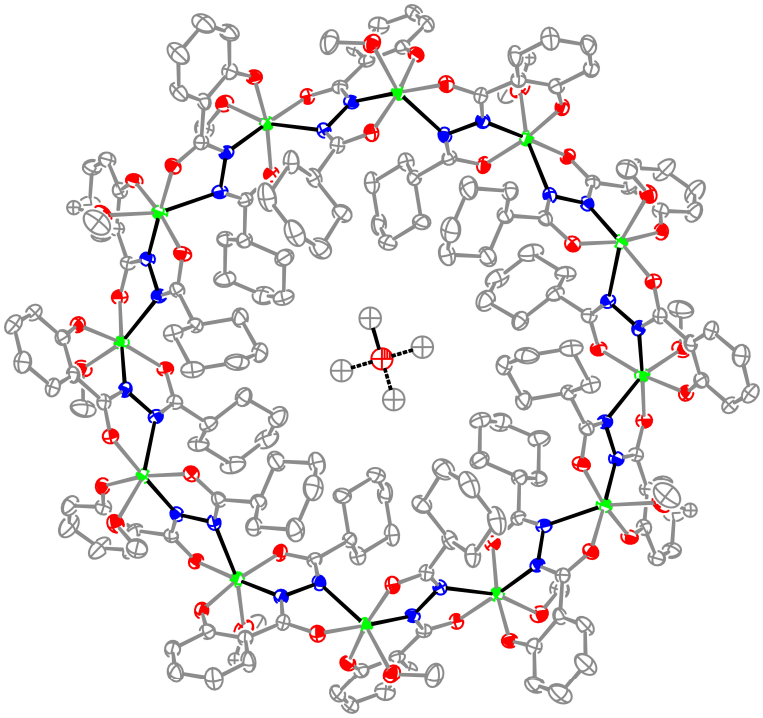

Fig. S1. Ortep diagram of complex **1** with a disordered methanol at the inner cavity of the metallamacrocycle. The carbon atoms connected by dashed bonds represent the locations of the carbon atoms in the disordered methanol. Mn (green), N (blue), O (red), C (gray).

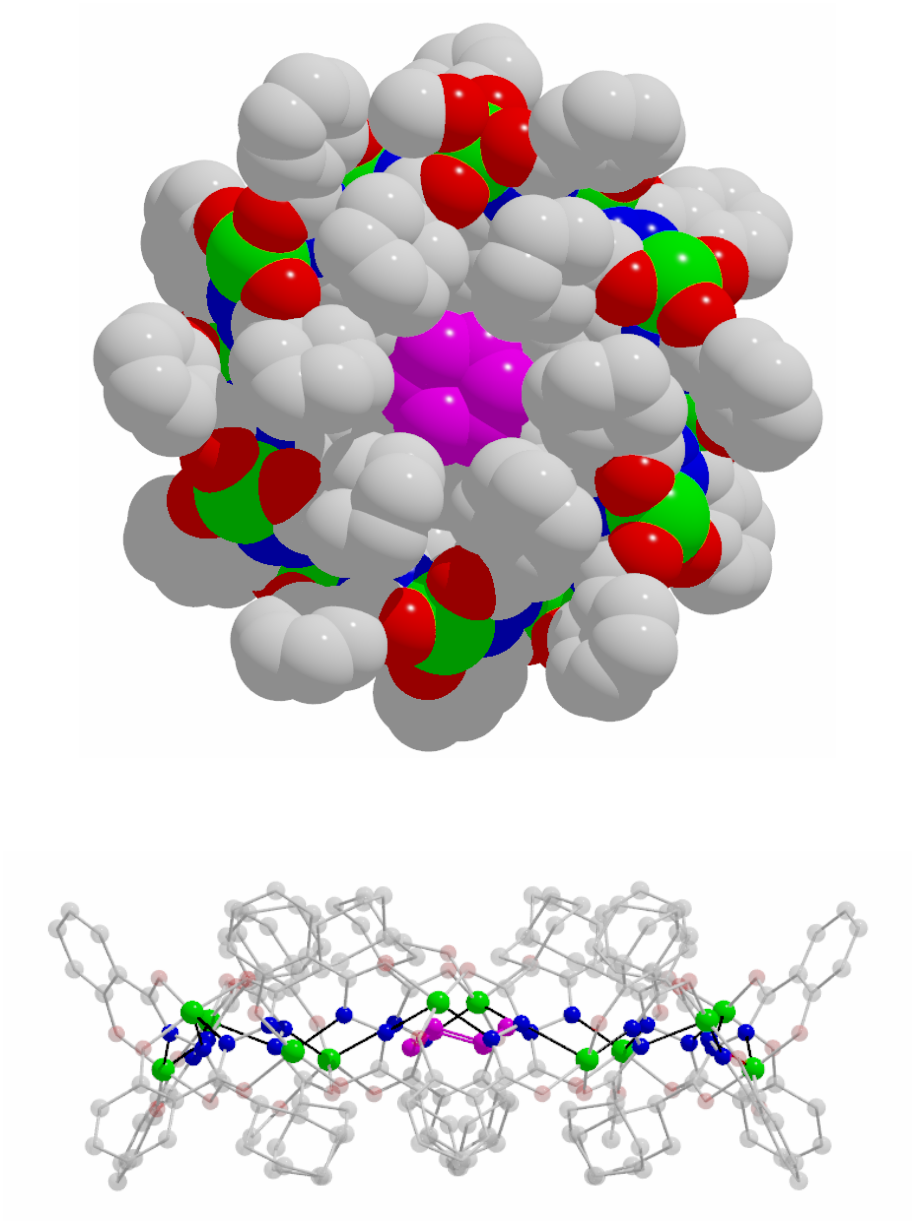

Fig. S2. (Top) The CPK diagram of $[Mn_{12}(chxshz)_{12}(MeOH)_{12}]\supset$cyclohexane in top view. The encapsulated cyclohexane is shown in purple. (Bottom) Side view of a ball and stick diagram of $1\supset$cyclohexane. The guest in purple represents one of four symmetry mismatched positions of a disordered cyclohexane at the center of the metallamacrocycle. Mn (green), N (blue), O (red), C (gray).

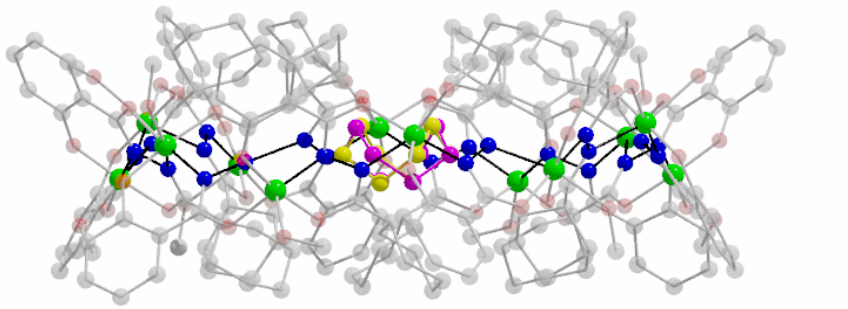

Fig. S3. The ball and stick diagram of $[Mn_{12}(chxshz)_{12}(MeOH)_{12}]\supset$cyclooctane in side view. The two encapsulated cyclooctane sites both in strained S_4 conformations are shown at the center of the metallamacrocycle in purple and yellow. Mn (green), N (blue), O (red), C (gray).

Table S1. Crystal data and structure refinement for **1**.

Empirical formula	$Mn_{12}\ C_{182}\ H_{238}\ N_{24}\ O_{51}$	
Formula weight	4237.24	
Temperature	100(2) K	
Wavelength	0.82657 Å	
Crystal system	Tetragonal	
Space group	$P4_2/n$	
Unit cell dimensions	a = 27.0406(3) Å	α= 90°.
	b = 27.0406(3) Å	β= 90°.
	c = 18.7658(3) Å	γ = 90°.
Volume	13721.4(3) $Å^3$	
Z	2	
Density (calculated)	1.022 Mg/m^3	
Absorption coefficient	0.592 mm^{-1}	
F(000)	4394	
Crystal size	0.50 x 0.30 x 0.20 mm^3	
Theta range for data collection	2.16 to 25.10°.	
Index ranges	-27<=h<=25, -26<=k<=27, -18<=l<=19	
Reflections collected	54175	
Independent reflections	7500 [R(int) = 0.0357]	
Completeness to theta = 25.10°	96.6 %	
Absorption correction	Empirical	
Max. and min. transmission	0.8908 and 0.7563	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7500 / 3 / 621	
Goodness-of-fit on F^2	1.091	
Final R indices [I>2sigma(I)]	R1 = 0.0548, wR2 = 0.1682	
R indices (all data)	R1 = 0.0598, wR2 = 0.1777	
Largest diff. peak and hole	0.693 and -0.420 $e.Å^{-3}$	

Table S2. Crystal data and structure refinement for **1**⊃cyclohexane.

Empirical formula	$Mn_{12}\ C_{186}\ H_{240}\ N_{24}\ O_{48}$	
Formula weight	4239.30	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	$P4_2/n$	
Unit cell dimensions	a = 27.189(3) Å	α= 90°
	b = 27.189(3) Å	β= 90°
	c = 18.904(4) Å	γ = 90°
Volume	13974(3) $Å^3$	
Z	2	
Density (calculated)	1.007 Mg/m^3	
Absorption coefficient	0.580 mm^{-1}	
F(000)	4416	
Crystal size	0.80 x 0.50 x 0.30 mm^3	
Theta range for data collection	1.51 to 28.39°	
Index ranges	–35<=h<=33, –36<=k<=18, –24<=l<=24	
Reflections collected	67612	
Independent reflections	16082 [R(int) = 0.0683]	
Completeness to theta = 28.39°	91.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8451 and 0.6538	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16082 / 11 / 628	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0853, wR2 = 0.1957	
R indices (all data)	R1 = 0.1068, wR2 = 0.2049	
Largest diff. peak and hole	0.796 and -0.617 $e.Å^{-3}$	

Table S3. Crystal data and structure refinement for **1**⊃cyclooctane.

Empirical formula	$Mn_{12}\ C_{188}\ H_{244}\ N_{24}\ O_{48}$	
Formula weight	4267.35	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	$P4_2/n$	
Unit cell dimensions	a = 27.073(2) Å	α= 90°
	b = 27.073(2) Å	β= 90°
	c = 18.909(3) Å	γ = 90°
Volume	13860(3) $Å^3$	
Z	2	
Density (calculated)	1.023 Mg/m^3	
Absorption coefficient	0.586 mm^{-1}	
F(000)	4448	
Crystal size	1.25 x 0.88 x 0.65 mm^3	
Theta range for data collection	1.51 to 28.36°	
Index ranges	–24<=h<=36, –34<=k<=35, –25<=l<=25	
Reflections collected	73193	
Independent reflections	16854 [R(int) = 0.0745]	
Completeness to theta = 28.36°	97.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7021 and 0.5280	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16854 / 14 / 620	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0948, wR2 = 0.2394	
R indices (all data)	R1 = 0.1174, wR2 = 0.2515	
Largest diff. peak and hole	0.873 and -0.711 $e.Å^{-3}$	

Table S4. Comparisons of bond distances (Å) and angles (˚) around the metal centers

	1	**1** ⊃ cyclohexane	**1** ⊃ cyclooctane
Mn(1)–O(1)	1.865(7)	1.869(2)	1.857(1)
Mn(1)–O(2)	1.971(4)	1.976(8)	1.966(3)
Mn(1)–O(3)	1.935(3)	1.938(3)	1.928(4)
Mn(1)–O(4)	2.25(1)	2.25(2)	2.24(3)
Mn(1)–N(1)	1.940(4)	1.949(5)	1.938(7)
Mn(1)–N(2)	2.26(1)	2.27(1)	2.255(8)
O(1)–Mn(1)–O(2)	92.6(7)	92.4(8)	92.8(7)
O(1)–Mn(1)–O(3)	170.0(4)	170.3(2)	169.9(3)
O(1)–Mn(1)–O(4)	90(2)	89(1)	89(2)
O(1)–Mn(1)–N(1)	90.2(4)	90.4(2)	90.4(4)
O(1)–Mn(1)–N(2)	90(1)	91(2)	90(2)
O(3)–Mn(1)–O(2)	97.2(6)	97.1(6)	97.0(6)
O(2)–Mn(1)–O(4)	85(2)	84(2)	84(2)
N(1)–Mn(1)–O(2)	177.1(4)	177.0(4)	176.7(3)
O(2)–Mn(1)–N(2)	74.4(2)	74.5(3)	74.3(1)
O(3)–Mn(1)–O(4)	90(1)	89(1)	89(1)
O(3)–Mn(1)–N(1)	80.0(3)	80.15(9)	79.8(3)
O(3)–Mn(1)–N(2)	94(1)	94(2)	95(2)
N(1)–Mn(1)–O(4)	95(3)	95(2)	95(2)
O(4)–Mn(1)–N(2)	159(2)	159(2)	159(2)
N(1)–Mn(1)–N(2)	106.1(3)	106.4(7)	106.6(4)
N(1)–N(2)–Mn(1)	107.5(6)	107.6(6)	107.8(7)
N(2)–N(1)–Mn(1)	114.6(3)	114.7(3)	114.9(7)