Two octanuclear gallium metallamacrocycles of topologically different connectivities†‡

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Two topologically different metallamacrocycles—$S_8$ symmetric octanuclear gallium(III) metalladiazamacrocycle and pseudo-$D_4$ symmetric octanuclear gallium(III) metalladiazamacrocycle—could be prepared using two similar heteroditopic bridging ligands having asymmetrical tridentate–bidentate binding residues.

Introduction

Self-assembled metal–organic architectures are of interest because of their potential as functional materials in areas such as molecular recognition,1 delivery,2 catalysis3 and storage.4 To prepare architectures with the desired structures and properties, it is important to understand the delicate factors influencing the formation of those systems. Even though metallamacrocycles belong to one of the simplest forms of metal–organic clusters, there are still many difficulties in predicting the self-assembled products from the building blocks. The metallamacrocycles can be self-assembled using diverse metal ions and rationally designed organic ligands in an appropriate solvent, where the organic ligands serve as ditopic linkers between ditopic metal centers.5 The connectivity, nuclearity, and size of the final macrocyclic system could be determined depending on the characteristics of the ring components such as length, rigidity and bending angle of the ligands, and the coordination geometry of the metal ions.

We have recently reported the preparation of metalladiazamacrocycles—diaza-bridged metallamacrocycles—via a combination of a distorted octahedral manganese(III) ion and an asymmetrical bridging ligand, $N$-acyl salicylhydrazide, where the size and nuclearity of the metalladiazamacrocycle could be modulated by controlling the steric repulsions between the ligands in the macrocyclic ring system.6 The metal ions and the ligands serve as bent ditopic nodes and linear ditopic linkers, respectively. Modification of the ligand part involved in the steric repulsion by an introduction of sterically more demanding groups has led to metallamacrocycles with diverse nuclearities ranging from 6 to 20 metal ions.5,7 Regardless of the size, nuclearity or stereochemistry of the metalladiazamacrocycles, the binding mode of the ligands around the metal centers and the connectivity of the ligands between the metal centers are the same. This happens despite the possibility of the formation of several different linkage isomers arising out of the asymmetrical nature of the bridging ligands (Scheme 1).5,7

Two topologically different metallamacrocycles—$S_8$ symmetric octanuclear gallium(III) metalladiazamacrocycle and pseudo-$D_4$ symmetric octanuclear gallium(III) metalladiazamacrocycle—could be prepared using two similar heteroditopic bridging ligands having asymmetrical tridentate–bidentate binding residues.

Results and discussion

$N^1$-Cyclopentylcarbonyl-2-hydroxybenzoylhydrazide (H,L) and $N^1$-cyclopentylcarbonyl-2-aminobenzoylhydrazide (H,L) were prepared using similar procedures to those reported previously.8 The reaction of $\text{Ga(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O}$ with H,L was carried out with a metal to ligand ratio of 1 : 1 in MeOH–EtOH mixed solvent. Slow diffusion of acetonitrile into the solution produced colorless crystals suitable for single-crystal X-ray diffraction study.† The crystallographic analysis revealed that the complex is a 24-membered...
octanuclear metallamacrocycle, [Ga₈(L¹₃)(H₂O)₆(MeOH)₆] ¹, which is isostructural with other octanuclear manganese or iron metalladiazamacrocycle (Fig. 1a and Fig. S1 in the ESI†). The pentadentate ligand bridges the metal ions using the diaza group via simultaneous tridentate and bidentate bindings on both sides of the bridging domain. The 24-membered macrocyclic ring system is formed by eight cyclic repeats of the -[Ga(III)–N–N]- unit, where the ligand serves as a trianion and the resulting macrocycle is neutral with the tricationic gallium(III) ion as a ring metal. This kind of back-to-back binding mode results in an S₈ symmetric octanuclear metalladiazamacrocycle, ¹ with metal centers in an alternating ··· DK(−) DK ··· chiral sequence, where the Δ or Δ chirality of the metal center was induced by simultaneous tridentate and bidentate bindings around the metal center (Fig. 2). The sixth coordination site of the octahedral gallium ion in the metallamacrocycle is occupied by a solvent molecule. The formation of an octanuclear gallium(III) metallamacrocycle is not expected, because other similar ligands having Cα-substituted steric domains of comparable or even smaller steric volumes lead to metalladiazamacrocycles with higher nuclearity on combination with manganese(III) ions. The strain caused by the repulsive interaction between the steric domains of the ligands in the metalladiazamacrocycles could be released by an expansion of the macrocyclic ring system with the expense of the increased strain around the metal center caused by the ring expansion. The lower nuclearity in the gallium(III) metallamacrocycle than in the corresponding manganese(III) metallamacrocycle might be caused by the larger force constants in the bond distances and angles around the regular octahedral gallium(III) metal centers than those around the Jahn–Teller elongated hexa-coordinate manganese(III) centers.

The substitution of the hydroxyl group attached to the aromatic ring of the ligand by an amino group while keeping all other parts of the ligand the same may change the protonation state of the ligand in the complex because of the difference in the pKₐ values of the residues. It may also alter the binding mode around the metal center, which might lead to the formation of a cationic metallamacrocycle in different binding modes around the metal centers. To test this, we prepared another ligand (H₄L₂), in which the hydroxyl group in the bridging domain is replaced by an amino group. Colorless crystals of 2/3 were obtained from methanol with 1 : 1 ratio of ligand to metal. The crystals are in two different morphologies, the major form in a block-shaped morphology and the minor form in a plate-like morphology. The crystallographic analysis† revealed that the block-shaped crystal is [Ga₈(H₂L₂)₈(MeOH)₈(H₂O)₁₂](NO₃)₈, ² (Fig. 1b and Fig. S2 in the ESI†), and the plate-shaped crystal is [Ga₈(H₂L₂)₈(MeOH)₈(H₂O)₁₂][Ga₈(H₂L₂)₈(MeOH)₈(H₂O)₈][Ga₈(H₂L₂)₈(MeOH)₈(NO₃)₂][NO₃]₂·24MeOH·2H₂O, ³ (Fig. S3 in the ESI†). All five crystallographically different macrocyclic complexes in both crystals are very similar to each other. The binding modes of the ligands in metallamacrocycle 2/3 are exactly the same; the only difference is in the kinds and number of the

![Fig. 1](image1.png)
Fig. 1 (a) An ORTEP diagram of the S₈ symmetric 24-membered octanuclear gallium(III) metallamacrocycle ¹. (b) An ORTEP diagram of the D₄ symmetric 24-membered octanuclear gallium(III) metallamacrocycle ².

![Fig. 2](image2.png)
Fig. 2 A schematic diagram showing the Δ and Δ configurations for the metal center of the propeller bidentate/tridentate binding mode, observed in ¹.
solvent molecules or anions coordinated to the macrocycles.\(^5\) The ligand is in a doubly deprotonated dianionic state, \([\text{H}_2\text{L}_2]^-\), in contrast to the other ligand, which is in a triply deprotonated trianionic state, \([\text{L}_1]^-\). The ligand, \([\text{H}_2\text{L}_2]^-\), still behaves as a bridging pentadentate ligand. The tridentate coordination on one side and bidentate coordination on the other side bridge two metal centers as \([\text{L}_1]^-\) in complex 1. The eight successions of the diaza bridged -[Ga(III)-N-N]- unit lead to a metallamacroyclic structure. However, two different kinds of metal centers are observed in 2/3, in contrast to one kind of metal center in complex 1. The difference occurs because of the two different binding modes of the dianionic \([\text{H}_2\text{L}_2]^-\) ligand around the metal centers, meridional tridentate–tridentate coordination and propeller bidentate–bidentate coordination, which originate from the asymmetric nature of the bridging ligand (Fig. 3). The average M···M distance in metallamacrocycle 2/3 is very similar to that in 1. However, the M···M···M angles in 2/3 are quite different from those in 1. All angles in 1 are in the narrow range, 127–133°, with the average value of about 131(2)° and hence the overall shape of metallamacrocycle 1 is like a circular disc. However, two different binding modes around the metal centers in 2/3 led to two different M···M···M angles, 158(2)° associated with meridional tridentate–tridentate coordination mode, and 111(2)° associated with a propeller bidentate–bidentate coordination mode; hence the overall shape of metallamacrocycle 1 is like a square disc. Both the meridional tridentate–tridentate binding mode around the metal center and the propeller bidentate–bidentate binding mode around the other metal center (Fig. 3) induce a chirality in the metal center, as in the metal center with tridentate–bidentate binding mode in complex 1 (Fig. 2). These two binding modes result in a chiral pseudo-D₃ symmetric octanuclear metalladiazamacrocycle, 2 and 3. The metallamacrocyces have two chemically different metal centers with different kinds of chiral configurations, C (clockwise)\(^4\) for the meridional tridentate–tridentate binding metal center and \(\Delta\) for the propeller bidentate–bidentate binding metal center, where the metal centers are in the \(\cdots(C_\Delta A_\Delta)(C_\Delta A_\Delta)\cdots\) chiral sequence.

Having the same bridging mode between the metal centers but different binding modes around the metal centers led to metalladiazamacrocyces with two topologically different connectivities. While the ligand connectivity in metallamacrocycle 1 can be represented as a cyclic \(\gamma_1\text{L}_4M\gamma_1\text{L}_4M\gamma_1\text{L}_4\cdots\) linkage (Fig. 4a), that in 2 and 3 can be represented as alternating \(\gamma_1\text{L}_4M\gamma_1\text{L}_4M\gamma_1\text{L}_4\gamma_1\text{L}_4\gamma_1\text{L}_4\cdots\) linkages (Fig. 4b).\(^5\) These different connectivities of the heteroditopic bridging ligands around the metal centers have led to two topologically different octanuclear gallium(III) metallamacrocyce systems.

\(^5\) In complex 2, the solvent coordination sites of the gallium ions are occupied by methanol, water, or statistically disordered methanol/water molecules. In complex 3, three crystallographically independent octanuclear metallamacrocyces, and a half of one octanuclear metallamacrocycle in the crystallographic \(C_2\) axis were identified. As in 2, the solvent coordination sites of the gallium ions are occupied by either methanol or water molecules; however, in the metallamacrocycle in the crystallographic \(C_2\) axis, a nitrate anion is ligated at the sixth coordination site of the gallium ion per crystallographic asymmetric unit (Fig. S2 and S3 in the ESI).\(^\¶\)

\(^4\) For convenience of representation, the asymmetric bridging ligand in the macrocycle was symbolized as \(\gamma_1\text{L}_4\) and the connectivity was represented as an arrow, where the bidentate binding region of the ligand designated using the subscript \(B\) is the head part of an arrow and the tridentate binding region designated using the subscript \(T\) is the tail part (Fig. 4).

Fig. 3 Schematic diagrams for two different types of chiral configurations around the metal centers: \(C/A\) for metal center of meridional tridentate–tridentate binding mode and \(\Delta/A\) for the metal center of propeller bidentate–bidentate binding mode, observed in 2.
Conclusions

We were able to synthesize two topologically different gallium(III) metalladiazamacrocycles via a controlled modification of the building blocks. The minimal modification in the bridging domain of the potential pentadentate ligand, while keeping all the remaining part of the ligand the same, has led to different chelation modes around the macrocyclic ring metal centers. When trianionic ligand $[L^1]^-$ was used as a bridging ligand between the metal centers, the cyclic repeat of the same tridentate–bidentate chelation mode at the metal center led to an achiral $S_8$ symmetric octanuclear metalladiazamacrocycle, which has the same topological connectivity as that reported in other metalladiazamacrocycles prepared using the same types of ligands. However, when dianionic ligand $[H_2L^2]^-$ was used as a bridging ligand between the metal centers, the occurrence of alternate tridentate–tridentate and bidentate–bidentate chelation modes at the metal centers led to a chiral pseudo-$D_4$ symmetric octanuclear metalladiazamacrocycle with a different connection topology. The different connectivities around the metal centers come from the asymmetric nature of the tridentate and bidentate binding modes of the heteroditopic bridging ligands.

Experimental

Materials

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

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 BioRad FT-IR spectrometer. ESI mass spectra were obtained using an HP Agilent 1100 MSD mass spectrometer. NMR spectra were obtained using a Varian-300 spectrometer.

Ligand synthesis

$N^2$-Cyclopentylcarbonyl-2-hydroxybenzohydrazide ($H_2L^1$).

2.51 mL (20.2 mmol) of trimethylacetyl chloride was added
to 30 mL of chloroform solution at 0 °C, containing 2.95 mL (21.0 mmol) of triethylamine and 2.25 g (20.4 mmol) of cyclopentanecarboxylic acid, over a 5 min period with stirring. The solution was slowly brought to ambient temperature. An equivalent amount of salicylhydrazide (3.08 g, 20.0 mmol) was added to the solution and refluxed for a day. The white precipitate was filtered and washed with chloroform followed by water. Yield 3.78 g (75.9%). Mp 188–191 °C.

The solution was slowly brought to ambient temperature. An equivalent amount of 2-aminobenzhydrazide (1.53 g, 10.0 mmol) over a 5 min period with stirring. Acetonitrile was added to the solution and refluxed for a day. The white precipitate obtained was filtered and washed with chloroform and mixture of 1.5 mL of methanol and 0.5 mL of ethanol, which became a clear solution in 15 min on stirring. Elemental data for [Ga8(L1)8(H2O)8]

C13H17N3O2: C 63.14, H 6.93, N 16.97%, found C 63.41, H 6.89, N 16.97%. IR spectrum (KBr, cm−1): 3419(br), 28660(10), 28621, 2860(m), 1602(m), 1518(m), 1499(w), 1384(s), 1086(m), 1048(w), 1004, 993, 967, 934, 877, 828(m), 756(m), 570(m), 530(m), 490(m).

\[ \text{N}^3\text{-Cyclopentylcarbonyl-2-aminoazobenzohydrazide (H}_{1}\text{L}^2\text{).} \]

1.27 mL (10.2 mmol) of trimethylacetyl chloride was added to 40 mL of chloroform solution at 0 °C, containing 1.48 mL (10.5 mmol) of triethylamine and 1.12 mL (10.2 mmol) of cyclopentanecarboxylic acid, over a 5 min period with stirring. The solution was slowly brought to ambient temperature. An equivalent amount of 2-aminoazobenzohydrazide (1.53 g, 10.0 mmol) was added to the solution and refluxed for a day. The white precipitate obtained was filtered and washed with chloroform and water. Yield 1.47 g (61.2%). Mp = 188–190 °C.

Crystallographic studies†

The crystals were coated with paratone oil because they lose crystallinity on exposure to air. The diffraction data were measured at 100 K with synchrotron radiation (λ = 0.7000 Å) on a 4AXM ADSC Quantum-210 detector with a Pt-coated Si double crystal monochromator at the Pohang Accelerator Laboratory, Korea. The HKL2000 (Ver. 0.98.694) was used for data collection, cell refinement, and absorption correction.

Crystal structure determination for [Ga4(L1)L(HMeOH)2(MeOH)2]·5.75ETOH·12MEOH. 1. Crystal data: Ga4(C3H53O80N13)·M = 6260.26 g mol−1, monoclinic, space group Cc, a = 49.314(10), b = 19.934(4), c = 36.5547(4) Å, β = 127.10(3)°, V = 28660(10) Å3, T = 90(2) K, Z = 4, μ(synchrotron, λ = 0.7000 Å) = 1.563 mm−1. 74658 reflections were collected, 74658 were unique. The structure of complex 1 was solved by direct methods as the noncentrosymmetric space group Cc and could be refined by full-matrix least-squares calculations with racemic twin option using the SHELXTL-PLUS software package. All attempts to solve the structure as the centrosymmetric space

The crystals were found to lose the solvent molecules during freeze-drying and exposure to air and were subsequently replaced by water molecules in air. These results are also consistent with the TGA data of complex 1 and mixture of complex 2 and 3.
group C2/c failed. Two octanuclear metallamacrocycles and at least 16 non-coordinating structural solvent sites were identified as an asymmetric unit. All non-hydrogen atoms except the atoms of disordered groups were refined anisotropically; hydrogen atoms except those attached to some of the disordered solvent molecules were assigned isotropic displacement coefficients U(H) = 1.2U(C, N), and their coordinates were allowed to ride on their respective atoms. Several cyclopentyl parts of the ligands are statically disordered and were refined with geometry restraints during the least squares refinement. The solvent coordination sites of the gallium ions are occupied by methanol, water, or statistically disordered methanol/water molecules. In addition, seven methanol and five water (or partially identified methanol) sites per asymmetric unit were identified and included in the least-squares refinement. The refinement converged to a final R1 = 0.0677 and wR2 = 0.1860 for 22816 reflections of I > 2σ(I). Further structure refinement was performed after modification of the data for the non-coordinate lattice solvent molecules with the SQUEEZE routine of PLATON (after removing lattice solvent molecules), which led to better refinement and data convergence. Refinement of the structure converged at a final R1 = 0.0437, wR2 = 0.1036 for 22670 reflections with I > 2σ(I), R1 = 0.0653, wR2 = 0.1098, GOF = 0.936 for all 31273 reflections. The largest difference peak and hole were 0.564 and −0.547 e Å⁻³, respectively. A summary of the crystal and intensity data is given in Table 1.

Crystal structure determination for [Ga₈(H₂L₂)₈(MeOH)₆·(H₂O)₂]·[Ga₄(H₂L₄)₄(NO₃)₂]·(NO₃)₂·24MeOH·2H₂O, 3. Crystal data: Ga₄$_{20}$H₄₀N$_{37}$O$_{115}$, M = 12114.25 g mol⁻¹, monoclinic, space group C2/c, a = 73.383(15), b = 37.082(7), c = 40.988(8) Å, β = 110.56(3)°, V = 104279(36) Å³, T = 100(2) K, Z = 8, μ(synchrotron, λ = 0.70000 Å) 1.522 mm⁻¹, 186273 reflections were collected. 105910 were unique [Rint = 0.0480]. The crystal structure of complex 3 was solved by direct methods and refined by full-matrix least-squares calculations with the SHELXTL-PLUS software package.38 Three crystallographically independent octanuclear metallamacrocycles, half of one octanuclear metallamacrocycle in the crystallographic C₃ axis, one nitrate except those attached to the solvent molecules were assigned isotropic displacement coefficients U(H) = 1.2U(C, N), and their coordinates were allowed to ride on their respective atoms. One cyclopentyl group of bad geometry was refined with geometry restraints during the least squares refinement. The solvent coordination sites of the gallium ions are occupied by methanol, water, or statistically disordered methanol/water molecules. In addition, seven methanol and five water (or partially identified methanol) sites per asymmetric unit were identified and included in the least-squares refinement. The refinement converged to a final R1 = 0.0677 and wR2 = 0.1860 for 22816 reflections of I > 2σ(I). Further structure refinement was performed after modification of the data for the non-coordinate lattice solvent molecules with the SQUEEZE routine of PLATON (after removing lattice solvent molecules), which led to better refinement and data convergence. Refinement of the structure converged at a final R1 = 0.0437, wR2 = 0.1036 for 22670 reflections with I > 2σ(I), R1 = 0.0653, wR2 = 0.1098, GOF = 0.936 for all 31273 reflections. The largest difference peak and hole were 0.564 and −0.547 e Å⁻³, respectively. A summary of the crystal and intensity data is given in Table 1.

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### Table 1 Crystallographic data for complexes 1–3

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<th>2</th>
<th>3</th>
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<td>Ga₈C₄₆H₇₀N₂₅O₁₃₅</td>
<td>Ga₄C₃₆H₆₄N₁₃O₆₂</td>
<td>Ga₅C₃₅H₇₁N₁₅O₉₀</td>
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<td>3174.33</td>
<td>12114.25</td>
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<tr>
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<td>100(2)</td>
<td>90(2)</td>
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<td>0.70000</td>
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<td>Monoclinic</td>
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<td>C2/c</td>
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<td>73.383(15)</td>
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<td>b/Å</td>
<td>19.934(4)</td>
<td>26.951(5)</td>
<td>37.082(7)</td>
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<td>c/Å</td>
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<td>β/°</td>
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<td>110.56(3)</td>
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<td>8</td>
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<td>Final R indices [I &gt; 2σ(I)]</td>
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<td>R1 = 0.0653, wR2 = 0.1098</td>
<td>R1 = 0.1061, wR2 = 0.1984</td>
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<td>Largest diff. peak and hole/e Å⁻³</td>
<td>1.386 and −1.127</td>
<td>0.564 and −0.547</td>
<td>2.539 and −1.652</td>
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* R1 = [Σ ||Fo|−|Fc||/Σ |Fo|]. b wR2 = ([Σ w(Fo²−Fc²)]/[Σ w(Fo²)])¹/².

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anion as coordinate ligand. 27 nitrate counter anions including one partially identified, 27 coordinating solvent molecules, and at least 26 additional non-coordinating structural solvent sites were identified as an asymmetric unit. All non-hydrogen atoms except those of the solvent molecules were refined anisotropically; hydrogen atoms except those attached to the solvent molecules were assigned isotropic displacement coefficients U(H) = 1.2U(C, N), and their coordinates were allowed to ride on their respective atoms. Several cyclopyridyl parts of the ligands were refined with statically disordered models. The solvent coordination sites of the gallium ions are occupied by methanol, water, or nitrate anions. An additional 24 methanol molecules, and two water (or partially identified methanol), per asymmetric unit were identified as an asymmetric unit. All non-hydrogen atoms except those of the solvent molecules were refined anisotropically; hydrogen atoms except those attached to the solvent molecules were refined with geometry identified and included in the least-squares refinement. A couple of water (or partially identified methanol), per asymmetric unit were assigned isotropic displacement coefficients U(H) = 1.2U(C, N), and their coordinates were allowed to ride on their respective atoms. Several cyclopyridyl parts of the ligands were refined with statically disordered models. The solvent coordination sites of the gallium ions are occupied by methanol, water, or nitrate anions. An additional 24 methanol molecules, and two water (or partially identified methanol), per asymmetric unit were identified and included in the least-squares refinement. A couple of nitrate anions and methanol molecules were refined with geometry restraints during the least-squares refinement. Refinement of the structure converged at a final R1 = 0.0614, wR2 = 0.1745 for 67823 reflections with I > 2σ(I), R1 = 0.1061, wR2 = 0.1984, GOF = 1.083 for all 105910 reflections. The largest difference peak and hole, 2.539 and −1.652 e Å⁻³ respectively, were observed in the vicinities of the metal centers. A summary of the crystal and intensity data is given in Table 1.†

Acknowledgements

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Notes and references