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Steric Control of a Bridging Ligand for High-Nuclearity Metallamacrocycle Formation: A Highly Puckered 60-Membered Icosanuclear Metalladiazamacrocycle

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A novel S_4-symmetric icosanuclear manganese metalladiazamacrocycle was synthesized using a pentadentate ligand, *N*-3-phenyl-*trans*-2-propenoylsalicylhydrazide (H_3L), that has a rigid and bulky terminal *N*-acyl group. A 20 cyclic repeat of an –(Mn–N–N)– linkage resulted in a highly puckered diaza-bridged 60-membered icosanuclear metallamacrocycle. The steric interaction between the ligands in the cyclic system leads to five consecutive Mn^{III} centers in a chemically different $-(Mn_AMn_BMn_CMn_DMn_E)-$ environment, with the chiralities of the metal centers being in a rather complicated –(ΛΛΔΛΛ)(ΔΔΛΔΔ)– sequence.

Metallamacrocycles such as molecular squares[1] and rectangles,[2] molecular wheels,[3] metallacrowns,[4] metalladiazamacrocycles,[5−7] and cyclic polyoxometalates[8] that contain metal ions as ring constituents are an interesting class of compounds because these types of molecules could be used as building blocks for diverse molecular architectures,[9] molecular magnets,[10] sensor materials,[11] and host systems for various guest recognition chemistries.[12] The size of the

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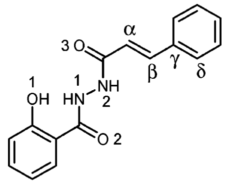
Chart 1. Schematic Diagram of Ligand H_3L with Partial Labeling



metallamacrocycles could be determined by the nature of the bridging ligands and metal ions involved, such as the length of a bridging group between the metal centers, the coordination geometries of the metal ions, or the number of repeating units in the cyclic structure.[1a,2a,c,3a,13]

Diaza-bridged metallamacrocycles,[5−7] termed metalla*diaza*macrocycles,[5a] have received considerable interest because of their potential to be used as secondary building blocks for the construction of two- or three-dimensional network structures.[14] These compounds can be readily assembled using a trianionic pentadentate ligand, *N*-acylsalicylhydrazide, with trivalent octahedral metal ions.[5,6] The ring size of the metalladiazamacrocycle can be controlled by modifying the close-contact interactions between the residues of the ligands that are directed to the inner core of the cyclic structure.[5b] With flexible linear or β-substituted *N*-acyl groups, the 18-membered hexanuclear metallamacrocycles are preferred as the most stable geometry, regardless of the length of the chain or the size of the β substituents.[5b−d,6c] With sterically demanding α substituents at the *N*-acyl groups, 24-[5b,6b] or 30-membered[5b,6a] metallamacrocycles could be generated depending on the size and numbers of α substituents on the *N*-acyl group. The introduction of a rigid-rod-shaped *N*-acyl group such as a *trans*-2-pentenoyl group with a double bond led to a puckered 36-membered dodecanuclear metallamacrocycle.[5a] Even though the size of the N substituent is comparable to those of linear acyl groups, the rigid *trans*-2-pentene group with a restricted rotational degree of freedom results in the ring expansion of the metallamacrocycle to a puckered dodecanuclear system.

In this study, we tried to observe the effect of a bulkier group along with rigidity at the *N*-acyl position of the ligand upon complexation with an octahedral metal ion such as Mn. In connection with this, we report the synthesis of a new pentadentate ligand, 3-phenyl-*trans*-2-propenoylsalicylhydrazide (H_3L), that has a rigid-rod-shaped terminal *N*-acyl residue with a sterically bulky phenyl end (Chart 1) and the preparation of its Mn complex: a 60-membered icosanuclear metalladiazamacrocycle (see the Supporting Information).

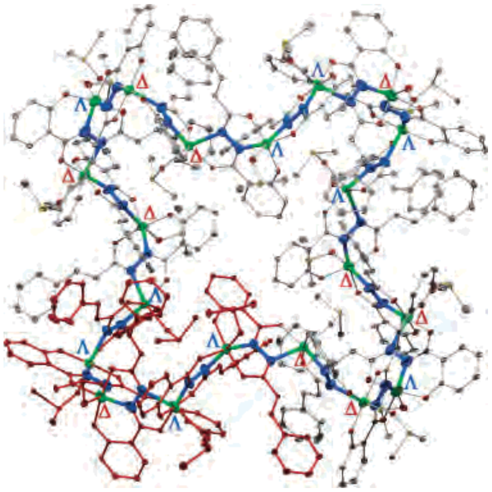


Figure 1. ORTEP diagram of complex **1** (top view) drawn with Mn and N atoms having 50% probability ellipsoids and the others having 10% probability ellipsoids. Mn atoms are represented by green, and N atoms are represented by blue. The $(\mathrm{Mn{-}N{-}N})_n{-}$ linkages are highlighted with thickened bonds, and the chiralities of the metal centers are shown in a −(ΛΛΔΛΛ)(ΔΔΛΔΔ)− sequence. The red part represents an asymmetric unit in the crystal structure.

Dark-brown needle-shaped single crystals[15] of $[\mathrm{Mn_{20}L_{20}(DMSO)_{18}(H_2O)_2}]$ were obtained by slow diffusion of ethanol into a dimethyl sulfoxide (DMSO) solution of manganese(II) acetate and the ligand. The ligand has three replaceable protons and hence coordinates as a trianion via three O atoms and two hydrazinic N atoms. The ligand not only bridges the ring metal ions using a hydrazide N−N group but also directs the stereochemistry of the metal ions into a Λ or Δ configuration (Figure S1 in the Supporting Information). The O1, N1, and O3 atoms bind to one Mn atom, and O2 and N2 bind to the adjacent Mn in a back-to-back fashion (Figure S2 in the Supporting Information), leading to a highly puckered S_4-symmetric 60-membered cyclic structure consisting of 20 Mn metal ions and 20 ligands (Figures 1 and 2). The Mn ions in complex **1** are in five different chemical environments that can be designated as $\mathrm{Mn_A}$, $\mathrm{Mn_B}$, $\mathrm{Mn_C}$, $\mathrm{Mn_D}$, and $\mathrm{Mn_E}$ and represented as a cycle of $-(\mathrm{Mn_AMn_BMn_CMn_DMn_E})-$ repeating units (Figure S1 in the Supporting Information and Figure 1). Each metal center has a distorted octahedral geometry with five donors from two ligands, with the remaining coordination site being occupied by a DMSO or water molecule. Only 8 N-terminal 3-phenyl-*trans*-2-propenoyl groups out of 20 are directed to the inner core of the metallamacrocycle, while the remaining 12 N-terminal groups are directed outward (Figure 1). While all phenoxy parts of the ligands are located at the outer side of the macrocycles in all previous instances, four phenoxy groups

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(15) Crystal structure determination for $[\mathrm{Mn_{20}L_{20}(DMSO)_{18}(H_2O)_2}]$: Crystal data: $\mathrm{C_{356}H_{332}N_{40}O_{80}S_{18}Mn_{20}}$, MW = 8126.61 g mol^{-1}, tetragonal, space group = $P4_2/n$, $a = b = 39.305(6)$ Å, $c = 17.810(4)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 27515(8)$ Å^3, $T = 100(2)$ K, $Z = 2$, μ(synchrotron, $\lambda = 0.749\,99$ Å) = 0.564 mm^{-1}, 87 844 reflections were collected, 23 775 were unique [$R_{\mathrm{int}} = 0.0582$]. The final R1 was 0.0686 for the observed data with $I > 2\sigma(I)$.

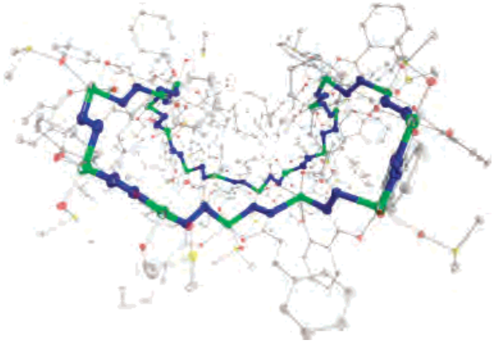

Figure 2. Perspective side view of complex **1** showing the ring puckering in the S_4-symmetric metallamacrocycle. Mn atoms are represented by green, and N atoms are represented by blue. The $(\mathrm{Mn{-}N{-}N})_n{-}$ linkages are highlighted with thickened bonds.

can be viewed as "inverted" to the inner side in this icosanuclear system. The sequence of the chiral configuration of Mn centers in the metalladiazamacrocycle was also found to be different from that of previous reports.[5,6] The five Mn centers $\mathrm{Mn_A}$, $\mathrm{Mn_B}$, $\mathrm{Mn_C}$, $\mathrm{Mn_D}$, and $\mathrm{Mn_E}$ of the asymmetric unit possess a rather complicated ΛΛΔΛΛ chiral sequence (Figure S2 in the Supporting Information and Figure 1). The observed chiral configuration after a ΔΔ (or ΛΛ) sequence is Λ (or Δ). The Mn centers in the S_4-symmetric icosanuclear metallamacrocycle can be identified as possessing a −(ΛΛΔΛΛ)(ΔΔΛΔΔ)− chiral configuration sequence. The change of the chirality of the metal center induces a bending in the puckered cyclic folding. While the change of the chirality from Λ to Δ (or vice versa) produces a wide turn in the folding, two consecutive changes of the chiralities, such as ΛΔΛ (or ΔΛΔ), produce a sharp turn (Figure 1). The combination of the wide and sharp turns leads to a puckered cyclic structure. The ΛΛΛ or ΔΔΔ consecutive configurations were not observed. This chiral sequence might lead to a helical structural segment that may make it difficult for ring closure of the folded chain. The neighboring Mn−Mn interatomic distances are in the narrow range of 4.820−4.911 Å. However, the Mn−Mn−Mn interatomic angles in the puckered 60-membered ring are in the range from 102.45° to 132.20° with an average value of 121.53°, which is much smaller than the value in the ideal planar cycloicosane structure (162°).

The magnetic behavior of complex **1** is illustrated in Figure 3. The effective magnetic moment (μ_{eff}) decreased slightly with decreasing temperature from 4.46 μ_B at 300 K to 4.07 μ_B at 50 K. Below 50 K, it rapidly decreased and reached 1.71 μ_B at 2 K. This behavior is typical for a weakly coupled antiferromagnetic system. Thus, by fitting the magnetic susceptibility data at high temperatures, $T > 50$ K, to the Curie−Weiss expression $\chi^{-1}(T) = C/(T + \Theta)$, we obtained an effective coupling constant J_{eff} (−1.99 K) and an effective magnetic moment per metal ion μ_{eff} (4.5 μ_B) for the metallamacrocycle **1**. This behavior is similar to that reported for other similar metalladiazamacrocycles.[5,6]

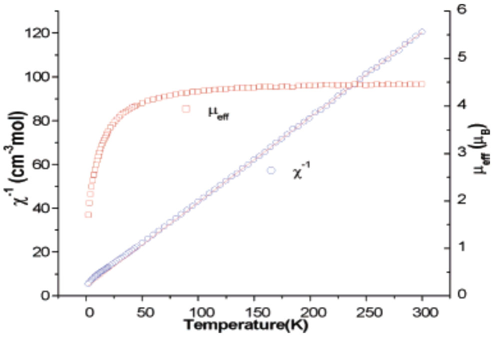

Figure 3. Plots of the effective magnetic moment (μ_{eff}) and the inverse magnetic susceptibility (χ^{-1}) as a function of temperature for complex **1**.

In this study, we prepared a 60-membered manganese metalladiazamacrocycle using 20 ring Mn ions and 20 3-phenyl-*trans*-2-propenoylsalicylhydrazides as diaza bridging ligands, where a 3-phenyl-*trans*-2-propenoyl group serves as a sterically rigid and bulky N-terminal residue. Steric repulsion between the N-terminal groups resulted in the inverted arrangement of some of the phenoxy parts of the ligands to the inner core of the macrocyclic ring system with some of the terminal *N*-acyl groups on the outer side. The inverted positioning of the phenoxy or *N*-acyl groups in the cyclic system resulted in a highly puckered S_4-symmetric icosanuclear metalladiazamacrocycle with a new type of −(ΛΛΔΛΛ)(ΔΔΛΔΔ)− chiral sequence.

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

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Supporting Information Available: X-ray crystallographic data (CIF format), synthesis and characterization of the ligand and complex **1**, details of crystal structure analysis, a schematic diagram showing the Λ and Δ configurations of the Mn ion, and an ORTEP diagram of complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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