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Novel 36-membered dodecanuclear manganese metalladiazamacrocycle†

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A novel dodecanuclear manganese metalladiazamacrocycle was synthesized employing a new pentadentate ligand *N*-2-pentenoylsalicylhydrazide (H_3tpeshz) by supramolecular self-assembly. The backbone of this metal-organic assembly is a repeating unit of an M–N–N–M linkage that extends to complete a 36-membered cyclic structure involving 12 manganese(III) centers. Successive manganese centers are in a chemically different ···ABABAB···-type environment while the chirality varies as ···ΛΛΔΔΛΛ···. The unique arrangement of manganese centers results in a highly puckered metalladiazamacrocycle with an S_6-point group symmetry.

Metallamacrocycles have become important in recent years because of their interesting molecular architecture,[1] multinuclear structures[2] and magnetic properties.[3] They have also been used as building blocks for the construction of two- or three-dimensional network structures.[4] A variety of metallamacrocycles and cages were found to form interesting host–guest systems with different metal ions of varying coordination and symmetry.[5] High nuclearity metal clusters and metallamacrocycles containing copper,[6] nickel[7] and platinum[8] have raised interest in the engineering of large structures containing various metals. Metal ions such as Ga, Co, Fe and Mn that can easily form stable octahedral coordination, are found to yield hexanuclear metallamacrocycles with trianionic pentadentate ligands.[9] However manganese and iron have received special attention because of their ease of formation of metallamacrocycles and interesting magnetic properties.[10–13]

Controlling the size and nuclearity of metallamacrocycles and their properties has quite recently become of interest. Although there have been reports of metallamacrocycles and metallacrowns of high nuclearity containing iron and manganese, formation of stable cyclic high nuclearity structures has been an uphill task. Only a few examples including ferric wheels,[10] a {Mn_{84}} torus[11] and 30-membered decanuclear metalladiazamacrocycles‡ have so far been reported.[12] We report here a puckered cyclic high-nuclearity structure – a 36-membered dodecanuclear manganese metalladiazamacrocycle, employing a trianionic pentadentate ligand.

The ligand *N*-*trans*-2-pentenoylsalicylhydrazide (H_3tpeshz) (Fig. 1) was prepared using a procedure reported previously.[14] Dark brown single crystals§ of [Mn_{12}(tpeshz)$_{12}$(dmf)$_{12}$] were obtained by slow diffusion of manganese(II) acetate into a solution of H_3tpeshz in dmf over a period of 30 days.¶ The ligand H_3tpeshz that exists in solution in its enol form has three replaceable protons and hence coordinates as a trianion *via* three oxygen atoms and two hydrazinic nitrogen atoms. The asymmetric unit of the complex contains two unique manganese(III) cations, two ligands and two solvent molecules (Fig. 2). Each manganese ion is in a distorted octahedral environment. While the O1, N1 and O3 atoms of a given ligand bind to one manganese atom, O2 and N2 bind to the adjacent manganese in a back-to-back fashion leading to a cyclic structure consisting of 12 manganese metal ions (Fig. 3). The remaining coordination site of manganese is satisfied by the oxygen atom of the dmf solvent molecule. Half of the solvent molecules in the complex are directed away from the ring and half inward. The terminal alkyl groups of the tails of six ligands (green) are directed to the inner core of the cyclic structure, while the rest of them (blue) are directed outside the metalladiazamacrocycle. The Cγ carbon atoms at the C_3 equivalent positions on either side of the cyclic system are in close contact. Alternate manganese ions in complex **1** are in two different chemical environments that can be designated as A and B (Fig. 3), resulting in a cycle of ···ABABAB··· type. However, the chiral configuration (Figure S1†)[15] of manganese centers in the metalladiazamacrocycle was found to be in a different mode from previous reports. The two manganese centers A and B of the asymmetric unit possess the same chirality, ΛΛ. (Fig. 2) Because the whole molecule is of S_6-point group symmetry, the successive manganese centers can be identified as possessing a ···ΛΛΔΔΛΛΔΔ··· chiral configuration. This kind of chiral configuration of the manganese is different from complexes with similar ligating groups so far reported that had a combination of ···AAAA··· environment and ···ΛΔΛΔ··· chiral configuration.[9,12–14]

It appears that geometric restraints play a significant role in addition to steric influence. The freedom of rotation about the Cα–Cβ bond that has led to the formation of hexanuclear metalladiazamacrocycles[9] was restricted by introducing a double bond between Cα and Cβ which led to the formation of the dodecanuclear species. The previously reported decanuclear structure bears a phenyl at the *N*-acyl position, which can be considered as a combination of an α-substitution with geometric restriction along the Cα–Cβ bond, and the presense of directionally rigid γ and δ carbon atoms. It is likely that the presence of '*two β carbon atoms with* directionally rigid γ and δ carbon atoms' at the *N*-acyl position in decanuclear metalladiazamacrocycle[12] offers steric hindrance against the formation of a more stable

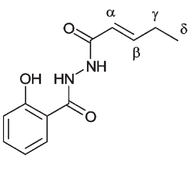

Fig. 1 Schematic diagram of the ligand H_3tpeshz with carbon atom labeling.

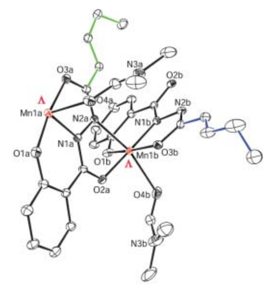

Fig. 2 ORTEP diagram of the asymmetric unit of complex **1** drawn at 20% probability ellipsoids.

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† Electronic supplementary information (ESI) available: synthesis and characterisation of the ligand, details of crystal refinement, and schematic diagram showing the Λ configuration of Mn ion. See http://www.rsc.org/suppdata/cc/b4/b407668k/

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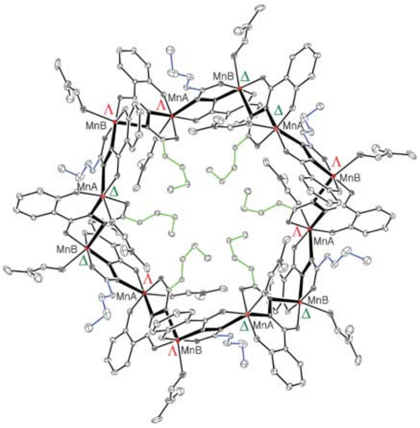

Fig. 3 ORTEP diagram of complex **1** (top view) drawn at 20% probability ellipsoids indicating manganese A and B centers. *N*-acyl groups are highlighted in blue and green colors.

dodecanuclear structure that requires puckering of the ring. However, the presence of '*just two β carbon atoms*' at the *N*-acyl group was found to favor the formation of an octanuclear iron(III) metalladiazamacrocycle.[13] In the present case the ligand can be considered as bearing an *N*-acyl group that differs from the previous case in the non-rigid orientation of the δ carbon atom.

The Mn···Mn distances between the neighboring manganese centers alternate between 4.90 and 4.91 Å, while the Mn···Mn···Mn angles are 111.90° and 123.50°. These values are much smaller than those expected (150°) for a *planar* cyclododeca structure, while closer to those for a *puckered* cyclododeca structure (113.5°). The average value of 117.7° for Mn···Mn···Mn angles in complex **1** is closer to that of a hexanuclear metalladiazamacrocycle (115.2°),[16] compared to that observed for the octanuclear (131°)[13] or decanuclear (139.8°)[12] metalladiazamacrocycles. The average deviation of each manganese metal ion from the least square plane in complex **1** is far greater than that observed for hexanuclear, octanuclear or decanuclear systems. Dodecanuclear metalladiazamacrocycle is in a puckered conformation (Fig. 4). The possible ring strain in a planar conformation can be released by the puckering of the macrocyclic ring. In short, complex **1** prefers the relaxed puckered conformation, which can be considered as a thermodynamically more stable structure than the strained planar conformation.

The molecule as a whole can be considered as a disc with the dimensions 14 × 28 Å. The presence of aliphatic groups at the core of the molecular disc and its outer areas provides a non-polar nature to this neutral molecule.

Further attempts to optimize the factors that govern nuclearity and size of metalladiazamacrocycles and their magnetic behavior are being pursued in our laboratory, and will be communicated later as a full paper.

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Notes and references

‡ This type of complex was termed "azametallacrowns". However, this terminology cannot be justified because all donor atoms involved in the coordination are coordinatively saturated and may not be able to function as a metallamacrocycle resembling an azacrown ether. Therefore we propose a more reasonable terminology for this class of compounds as "metalladiazamacrocycles", because a metal and two nitrogens constitute the repeating unit in the macrocyclic ring system.

§ Crystal structure determination for $[Mn_{12}(tpeshz)_{12}(dmf)_{12}]\cdot 2dmf$: *Crystal data*: $C_{216}H_{348}N_{48}O_{60}Mn_{12}$, MW = 5236.70 g mol^{-1}, rhombohedral, space group = $R\bar{3}$, $a = b = 23.7142(16)$, $c = 38.246(5)$ Å, $\alpha = \beta = 90$, $\gamma = 120°$, $V = 18626(3)$ Å^3, $T = 173(2)$ K, $Z = 3$, μ(Mo–K$_\alpha$) 0.674 mm^{-1}, 32464 reflections were collected, 9717 were unique [$R_{int} = 0.0913$]. The final $R1$ was 0.0591 for the observed data with $I > 2\sigma(I)$. CCDC for complex **1** is 240740. See http://www.rsc.org/suppdata/cc/b4/b407668k/ for crystallographic data in .cif or other electronic format.

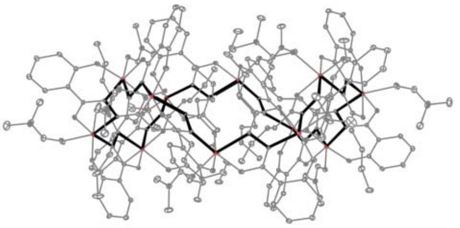

Fig. 4 A side view of the compound showing the puckered nature of the metalladiazamacrocycle. Red spheres represent manganese ions.

¶ *Preparation of complex* **1**: In a 20 mL vial 23.4 mg of the H_3tpeshz ligand was dissolved in 10 mL of dmf and 24.5 mg of $Mn(OAc)_2\cdot 4H_2O$ was added in the solid form. The resulting solution was allowed to stand for over a month. *Elemental data* for $Mn_{12}(tpeshz)_{12}(dmf)_9(H_2O)_3$ ($C_{171}H_{190}N_{33}O_{48}Mn_{12}$)[17] Calc: C 49.67, H 4.63, N 11.18%; Found: C 49.80, H 4.95, N 10.86%. IR (KBr disc, cm^{-1}): 1655, 1601, 1493, 1407, 1361, 1108, 863.

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