The largest single-strand molecular wheel: Ga_{20} from a targeted, diolate-induced size modification of the Ga_{10} 'gallic wheel'†

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A Ga_{20} single-strand wheel has been prepared by a targeted, propane-1,3-diolate-induced size modification of the known Ga_{10} 'gallic wheel'; the Ga_{20} reverts back to Ga_{10} on treatment with an excess of MeOH.

Polynuclear metal complexes with a single-strand wheel structure continue to attract a lot of interest from many groups. The prototypes were $[Cr_8F_8(O_2CBu^t)_{16}]$[1] and $[Fe_{10}(OMe)_{20}(O_2CCH_2Cl)_{10}]$,[2] the latter dubbed the 'ferric wheel'. Many other single-strand wheels are also now known, for Fe[3] as well as other metals such as Co,[4] Cr,[5] Cu,[6] Dy,[7] Mn,[8] Ni,[9] and V.[10] More recently, we reported the Ga analogue of the 'ferric wheel', *i.e.*, $[Ga_{10}(OMe)_{20}(O_2CMe)_{10}]$ (**1**), which we called the 'gallic wheel';[3] the analogous wheel with a different carboxylate was reported by Zafiropoulos and co-workers.[11] Single-strand molecular wheels almost always contain an even number of metal ions, and with very few exceptions possess metal nuclearities of 12 or less; these exceptions include Mn_{16},[8b] and three M_{18} (M = Fe, Ga) wheels.[3,12] Multiple-strand wheels are also known, such as Mn_{24}[13] and the giant torus-shaped complexes Mn_{84},[14] Mo_{154},[14] and Mo_{176}.[15]

Wheel complexes are of interest for a number of reasons. For paramagnetic 3d metal atoms, even-membered antiferromagnetic wheels represent model systems for one-dimensional antiferromagnetism, magnetic anisotropy, and quantum effects such as coherent tunnelling of the Néel vector.[16] However, there are also many wheels with large *S* values, such as Ni_{12},[9c] Mn_{12},[8c] Mn_{16},[8b] and Mn_{84}[14] that in addition are single-molecule magnets (SMMs).

Our recent interest in this area has been targeted at developing new synthetic routes to large M_x ($x > 12$) wheels, particularly methods that might also allow some level of control of the metal nuclearity (*i.e.* the wheel size). Our main interest, apart from the inherent synthetic challenge, is to achieve a range of wheel sizes to allow a study of progressive changes to their properties as they approach the 1-D limit, *i.e.*, a chain. This requires expanding the wheel size, and effectively rules out using a template approach,[5c,17] which is much less feasible for larger wheels since it requires a correspondingly larger template. Instead we have been exploring the substitution of diolates for two adjacent MeO^- groups of the M_{10} wheels. Since the MeO^- groups in the latter lie above and below the central cavity, their substitution by diolates such as propane-1,3-diolate (pd^{2-}) would likely affect the wheel curvature and yield a bigger wheel. A smaller one is unlikely, given the steric congestion that would result in the central hole. A previous use of pdH_2 in Ga chemistry had provided the wheel compound $[Ga_{18}(O_2CR)_6(pd)_{12}(pdH)_{12}(NO_3)_6](NO_3)_6$ (**3**)[3] but the presence of both pd^{2-} and pdH^-, as well as the additional presence of coordinated NO_3^- ligands, complicated matters by making unclear the exact effect of the pd^{2-}. This initial study thus could not answer the important question at hand, namely what happens to the Ga_{10} wheel size if pairs of MeO^- ligands are replaced by pd^{2-} groups? We have now answered this question, and in doing so have discovered a complex with a record size for a single-strand wheel.

Complex **1** was slowly dissolved with stirring in pdH_2/MeCN (1 : 7, v/v) to give a colourless solution, and this was filtered and layered with Et_2O/Me_2CO (1 : 1, v/v). Colourless crystals of $[Ga_{20}(pd)_{20}(O_2CMe)_{20}]\cdot 25MeCN$ (**2**·25MeCN) grew slowly over several days and were isolated by filtration; the yield was 20%.† Complex **2** was also obtained, and in higher yields of ~40%, from the reaction of $GaCl_3$ with 3 equivs of $NaO_2CMe\cdot 3H_2O$ in pdH_2/MeCN (1 : 7, v/v), followed by filtration and layering of the clear solution with Et_2O/Me_2CO (1 : 1, v/v). The structure‡ of **2** (Fig. 1) comprises twenty Ga^{III} ions linked through $MeCO_2^-$ and pd^{2-} bridges to form a puckered, single-strand wheel of virtual D_5 point group symmetry. It can be conveniently described as a pentagon of $\{Ga_4(O_2CMe)_4(pd)_4\}$ units (Ga20-Ga1-Ga2-Ga3, Ga3-Ga4-Ga5-Ga6, *etc.*) linked at each end by the O atoms of an acetate and two pd^{2-} groups (Fig. 1, bottom). The resulting complex can also be described as constructed of five linear $\{Ga_3(\eta^1:\eta^1:\mu\text{-}O_2CMe)_2(\eta^2:\eta^2:\mu_3\text{-}pd)_2\}$ 'edge' units (Ga–Ga–Ga = 177.25–179.42°) held together by five $\{Ga(\eta^1:\eta^1:\mu\text{-}O_2CMe)_2(\eta^2:\eta^2:\mu_3\text{-}pd)_2\}$ 'hinge' units (Fig. 2, top); note that every Ga_2 pair in the molecule is thus bridged by two pd^{2-} O atoms and an $MeCO_2^-$ group. As in **1**, the Ga atoms are six-coordinate and near-octahedral; unlike **1**, however, the Ga_{20} wheel **2** is not planar. The Ga–Ga distances and Ga–O(pd)–Ga angles lie in the 2.902–2.950 Å and 94.78–101.25° ranges, respectively.

A space-filling representation (Fig. 2, bottom) shows that **2** has a diameter of 25.5 Å, with a central hole of 10.0 Å diameter; the corresponding values for **1** are 16.7 Å and 8.1 Å, respectively. In both complexes, there is no residual electron density in the central hole, and the wheels stack to form nanotubular channels.

Consideration of the formulas of **1** and **2** shows that they both belong to a family of 'gallic wheels' of general formula $[Ga_n(OR)_{2n}(O_2CMe)_n]$, which is not the case for

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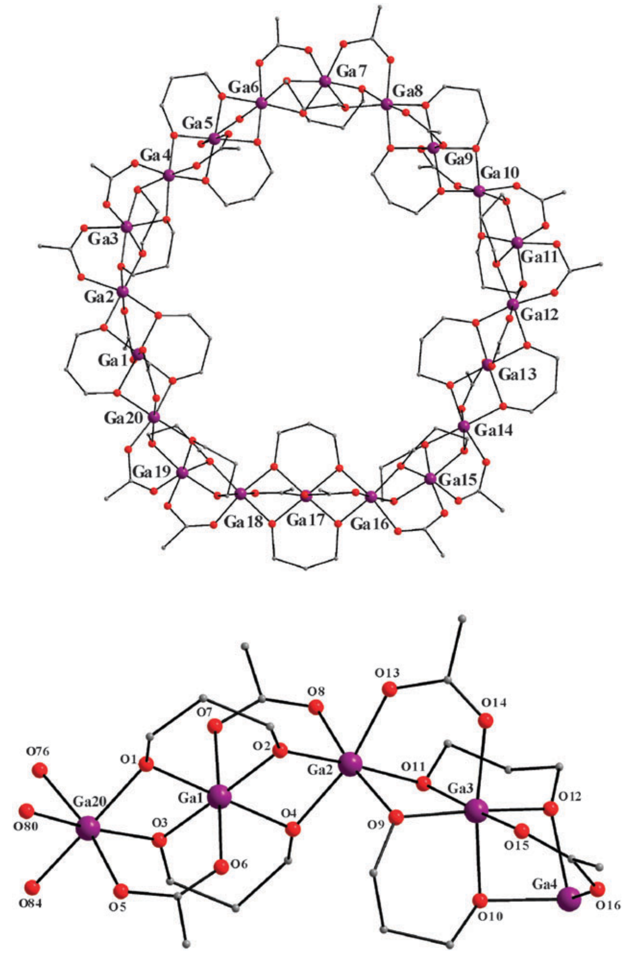

Fig. 1 The structure of the Ga_{20} wheel **2**: (top) the complete molecule with Ga atom labels; (bottom) the repeating $\{Ga_4(O_2CMe)_4(pd)_4\}$ unit (Ga20–Ga1–Ga2–Ga3) and the means of attachment to Ga4 of an adjacent unit. Hydrogen atoms have been omitted for clarity. Colour code: Ga purple, O red, C grey.

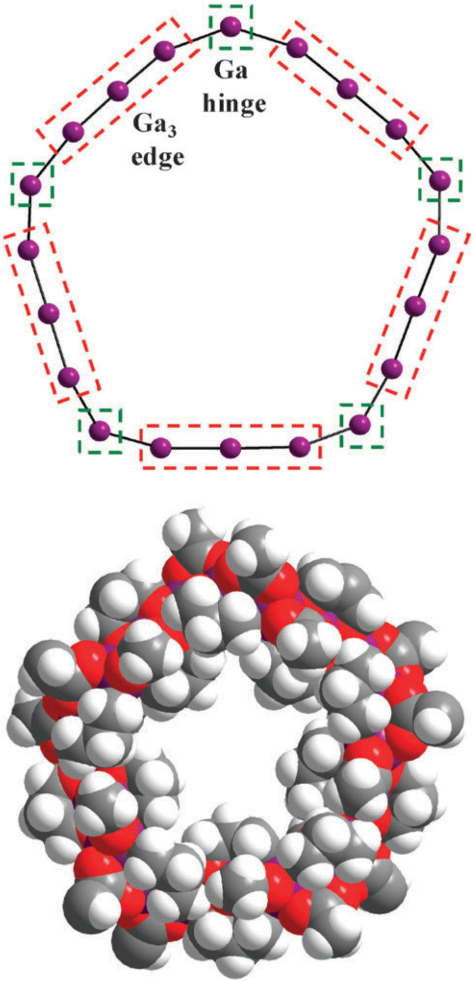

Fig. 2 The five-fold symmetric Ga_{20} structure: (top) the linkage of Ga_3 'edge' units by Ga 'hinge' atoms. Black thick lines indicate the Ga–Ga vectors; (bottom) a space-filling representation. Colour code: Ga purple, O red, C grey, H white.

3: for **1**, $n = 10$ and $RO^- = MeO^-$; for **2**, $n = 20$ and $(OR)_2 = pd^{2-}$. As for **2**, every Ga_2 pair in **1** is bridged by two alkoxide O atoms and one $MeCO_2^-$ group. Thus, the complexes differ only in the identity of the alkoxide, and the resulting *n* value, and we can therefore answer the question posed: the replacement of two adjacent MeO^- groups of the Ga_{10} wheel **1** with the diolate pd^{2-} has caused a doubling of the wheel size to give the Ga_{20} wheel **2**. No doubt several factors contribute to this, including diolate bite and torsion angle restrictions, steric repulsion that would result between the pd^{2-} $-CH_2CH_2CH_2-$ backbones in the central cavity for smaller wheels, and others; all these require careful analysis and modelling.

The conversion of **1** to **2** by treatment with pdH_2 can be reversed by dissolution of **2** in MeOH, which leads to an alcohol substitution reaction and the isolation in 75% yield of colourless complex **1**; the latter was confirmed by X-ray crystallography. The bi-directional interconversion between **1** and **2** is summarized in eqn (1).

$$2[Ga_{10}(OMe)_{20}(O_2CMe)_{10}]\ (\mathbf{1}) + 20\ pdH_2 \rightarrow [Ga_{20}(pd)_{20}(O_2CMe)_{20}]\ (\mathbf{2}) + 40\ MeOH \qquad (1)$$

To probe solution species and conversions further, an ^1H NMR spectroscopic investigation was carried out. The NMR spectrum of **1** in $CDCl_3$ exhibited the three resonances expected for an intact Ga_{10} wheel retaining the D_{5d} symmetry of the solid state: the signals are at 2.13 (singlet, 3H), 3.36 (singlet, 3H), and 3.51 ppm (singlet, 3H), corresponding to one acetate and two symmetry-inequivalent methoxide sets of ligands, respectively. The ^1H NMR of **2** in $CDCl_3$ shows two resonances at 1.95 (singlet, 3H) and 2.12 ppm (singlet, 3H) assignable to the two symmetry-inequivalent sets of acetates under D_5 symmetry, but is otherwise very complicated as expected for the many inequivalent pd^{2-} CH_2 groups, and diastereotopic H nuclei of CH_2 pairs at the 1 and 3 positions of pd^{2-}. The preliminary conclusion is that **2** also retains its solid-state structure in $CDCl_3$. Dissolution of **2** in CD_3OD, however, causes conversion to **1**, as indicated by a white precipitate identified as **1** by IR spectral comparison with authentic material, and the presence in the NMR spectrum now of only the two resonances due to free pdD_2, a quintet at 1.75 ppm and a triplet at 3.66 ppm.

In conclusion, we have successfully converted $[Ga_{10}(OMe)_{20}(O_2CMe)_{10}]$ (**1**) to the analogue in which pairs of MeO$^-$ groups have been replaced by the diolate pd^{2-} and found that the resulting wheel has doubled in nuclearity to [$Ga_{20}(pd)_{20}(O_2CMe)_{20}$] (**2**). This interesting result also provides the largest single-strand molecular wheel to date, and augurs well for further wheel size modifications being possible as a function of the diolate employed; such studies are currently in progress. There are also magnetic implications of this work, even though Ga(III) is diamagnetic: extension to large M_{20} wheels for paramagnetic metals such as Cr(III), Fe(III), *etc.* would provide larger analogues of the known wheels for these metals and thus provide a greater range of wheel sizes for the study of magnetic properties *vs.* size, and the relationship to the 1-D spin chain limit. Note that Cr_{20} and Fe_{20} analogues of **2** would contain essentially only one type (or at least very similar types) of pairwise exchange parameters, since all M_2 pairs have the same bridging ligands, as mentioned earlier. In effect, crystals of such materials would represent a collection of single-size (monodisperse) spin chains in which the magnetic properties would be specific for that chain length rather than represent the average for a distribution of chain lengths, as is the usual case in the study of spin chains.

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Notes and references

‡ Vacuum-dried solid analysed as **2**·2MeCN. Calcd. (found): C, 30.18 (30.06); H, 4.53 (4.45); N, 0.68 (0.67%). Crystal data for **2**·25MeCN: $C_{150}H_{255}Ga_{20}N_{25}O_{80}$, M_w = 5083.22, monoclinic, space group $P2/n$ with a = 22.768(5) Å, b = 33.543(7) Å, c = 29.161(7) Å, β = 97.201(4), V = 22095(9) Å^3, T = 173(2) K, Z = 4, 89990 reflections collected, 28911 unique (R_{int} = 0.2296), $R1$ [$I > 2\sigma(I)$] = 0.1007, $wR2$ = 0.2210 (F^2, all data). Many crystals from multiple preparations were screened and all were found to be weak diffractors of X-rays, no doubt due to the large amount of disordered solvent in the crystal. This limited the usable data collected, and thus only the Ga atoms were refined anisotropically. CCDC 692717.

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