A ferromagnetically coupled pseudo-calixarene [Co$_{16}$] wheel that self-assembles as a tubular network of capsules

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Abstract

Reaction of Co(OAc)$_2$·4H$_2$O and Hsal in a basic MeCN solution affords the hexadecanuclear wheel [Co$_{16}$(sal)$_{16}$(OAc)$_{16}$]·16MeCN (1·16MeCN) that displays ferromagnetic nearest neighbour exchange and has pseudo-calixarene character. Symmetry equivalent wheels self-assemble to form remarkable tubular networks of capsules in the extended structure.

Introduction

Molecular wheels attract continued attention, partly due to beautiful structural aesthetics, but also because some show fascinating and potentially useful physical properties. 1 In the field of molecular magnetism, molecular wheels of 3d transition metals came into prominence in the late 1980s and early 1990s with the publication of [Cr$_{II}$]$_8$ and [Fe$_{II}$]$_{10}$. 2 The former has inspired the development of a large family of homo- and heterometallic Cr wheels including the first examples of odd-numbered wheels that display topological frustration, with potential as quantum bits in information processing. 3 The latter, and other antiferromagnetically coupled even-membered wheels, are characterised by a diamagnetic spin ground state and display interesting quantum phenomena and spin dynamics, including tunneling of the Néel vector, 4 spin-multiplet mixing effects 5 and magnetic level repulsions. 6 The intervening years have witnessed the publication of wheels of all the 3d metals with nuclearities up to eighty four. 7 In Co$^{II}$ chemistry 8 early examples of wheels included a dodecanuclear cluster built with a substituted pyridine 9 and an heptanuclear Anderson wheel stabilised by tripodal alcohols, 10 both display ferromagnetic exchange interactions.

Results and discussion

The reaction between Co(OAc)$_2$·4H$_2$O and Hsal (salicylaldehyde) in a basic MeCN solution (see SI for full details) leads to the formation of pink single crystals after 3 days upon diffusion of Et$_2$O into the mother liquor. Crystals of [Co$_{16}$(sal)$_{16}$(OAc)$_{16}$]·16MeCN (1·16MeCN) were in a tetragonal cell and structure solution was performed in the $P4/ $n$/$ space group. The asymmetric unit (ASU) contains one quarter of the formula, and symmetry expansion affords the wheel shown in Fig. 1. The metallic skeleton (Fig. 2) describes a single-stranded, sinusoidal [Co$_{16}^{II}$] wheel of approximate diameter, Co1···Co1’ $\approx$ 14.5 Å. The ‘inside’ of the wheel is stabilised by sixteen $\mu_3$-, syn, syn, anti-OAc ligands. Eight lie in the metal plane, with four above and four below the plane. The sixteen $\mu$-sal ligands are arranged in a similar manner on the ‘outside’ of the wheel. Eight $\mu$-sal ligands are in a belt around the periphery of the wheel, whilst four are above the plane, and four below (Fig. 1). These out of plane $\mu$-sal ligands form an interesting arrangement that is reminiscent of calixarenes, 11 presenting a shallow hydrophobic pocket as a result. The magnetic unit between nearest neighbours contains one $\mu$-
O(alkoxide), one \(\mu\)-O(carboxylate) and one syn, syn-O-C-O(carboxylate). The interaction between next nearest neighbours is mediated by the syn, anti-O-C-O(carboxylate) bridge. The Co-O-Co angles subtended by the \(\mu\)-O atoms are in the range \(\sim 92.1\text{--}99.5^\circ\), with the Co\(^{II}\) ions all being in distorted octahedral \(\{\text{CoO}_6\}\) geometries.

**Fig 1.** Orthogonal views of the molecular structure of complex 1 viewed perpendicular (top) and parallel to the [Co\(_{16}\)] ‘plane’. Colour code: Co = pink, O = red, C = black, H = white. Solvent molecules of crystallisation omitted for clarity.

A search of the Cambridge Structural Database (CSD) reveals approximately twenty [Co\(_{16}\)] structures, with more than half being squares and tetrahedra stabilised by thia- and sulfonyl-calix[4]arenes.\(^{12}\) There are two other wheels, one comprising linked squares and cubes built with a bis-benzimidazole-diol ligand, and one incorporating four linear [Co\(_4\)] subunits constructed with polytriazolate ligands.\(^{13}\)

Further symmetry expansion of the new pseudo-calixarene structure presented by 1 reveals a remarkable arrangement in which symmetry equivalent (s.e.) wheels pack to form tubular networks of capsules, and channels between the tubules. Inspection of the ring structure of 1 in space filling representation (Fig. 3A, in the \(ab\) plane) shows a very small channel through the ring as a result of the syn, syn, anti-OAc ligands on the inside of the molecule. Symmetry expansion along the \(c\) axis gives rise to a dimer with the next s.e. wheel as shown in Fig. 3B (in the \(ac\) plane). These pseudo-calixarene wheels lock together in the solid state through inter-digitation of the \(\mu\)-sal ligands, with some OAc ligands also forming part of the space filling belt. This gives rise to an encapsulated space with a volume of \(\sim 272\ \text{Å}^3\) that is occupied by disordered solvent molecules (Fig. 3C).\(^{14}\) It was not possible to resolve this disorder given the high symmetry and diffuse nature of the electron density. Inter-digitation continues along the \(c\) axis, forming infinite tubular stacks of capsules, and these pack as
shown in Fig. 3D to form solvent filled channels that run parallel through the extended structure. Single crystals of 1 are solvent dependent, but the nature of the extended structure will be studied further with a view to forming more stable analogues that can be desolvated and explored for potential guest transport to the interior of the cages.

**Fig. 2** (A) The magnetic core of 1. (B) Close-up of the bridging between neighbouring Co$^{II}$ ions. The metallic core of viewed perpendicular (C) and parallel (D) to the [Co$_{16}$] ‘plane’. Colour code: Co = pink, O = red, C = black.
Fig. 3 Space filling representations of 1 (A, in the \textit{ab} plane) and two symmetry equivalents interdigitating to form a cage (B, in the \textit{ac} plane). C) Representation of the encapsulated space between [Co\textsubscript{16}] dimers with a volume of \textasciitilde 272 Å\textsuperscript{3} occupied by disordered solvent molecules. D) The extended structure showing the formation of channels by packing of infinite stacks of s.e. of 1 (in the \textit{ab} plane). Colour code: Co = pink, O = red, C = black, H = white.

Magnetic properties

DC magnetic susceptibility (\(\chi\)) and magnetisation (\(M\)) measurements of 1 were taken in the \(T = 300\text{-}\text{2.00 K}, B = 0.1\text{ T}\) and \(T = 2.0\text{-}10\text{ K}\) and \(B = 0.5\text{-}9.0\text{ T}\) temperature and field ranges, respectively. These are plotted as the \(\chi T\) product versus \(T\) and \(M\) versus \(B\) in Fig. 4. The \(T = 300\text{ K}\) value of \(\chi T = 43.2\text{ cm}^3\text{ K mol}^{-1}\) is equal to the value expected for sixteen non-interacting \(S = 3/2\) Co\textsuperscript{II} ions with \(g = 2.40\). Upon cooling the \(\chi T\) value decreases slowly to \(\textasciitilde 41.7\text{ cm}^3\text{ K mol}^{-1}\) at \(38\text{ K}\) before rising sharply to a maximum of \(\textasciitilde 52.8\text{ cm}^3\text{ K mol}^{-1}\) at \(T = 6\text{ K}\), and then falling to \(\textasciitilde 10.9\text{ cm}^3\text{ K mol}^{-1}\) at \(T = 2\text{ K}\). The initial drop in \(\chi T\) is due to the magnetic anisotropy of the octahedral Co\textsuperscript{II} ions,\textsuperscript{15} while the increase at low temperature is
due to weak ferromagnetic interactions. The drop in value between 6-2 K is most likely due to intermolecular antiferromagnetic interactions. This behaviour is similar to that observed for the pyridone-stabilised [Co12] wheel.9 The M vs B data is in agreement with this interpretation, with the magnetisation increasing rapidly with increasing field, not saturating and reaching a value of $M = 33.4 \mu_B$ at $T = 2$ K and $B = 9$ T. The ferromagnetic exchange in 1 is consistent with magneto-structural correlations developed for O-bridged CoIII clusters where the sign and magnitude of the interaction is dictated by the Co-O-Co angle, with the exchange becoming more ferromagnetic with decreasing angle.16 Here, the Co-O-Co angles are all $\leq 99.5^\circ$ and are therefore expected to mediate weak ferromagnetic exchange.

![Fig. 4. Plot of the $\chi T$ product versus $T$ in the range $T = 300$–$2$ K in an applied field, $B = 0.1$ T. Inset: plot of the $M$ versus $B$ data in the $T = 2.0$–$10$ K and $B = 0.5$–$9.0$ T temperature and field ranges, respectively.]

**Theoretical studies**

In order to probe the nature and magnitude of the magnetic exchange and anisotropy of the CoII ions further, we now turn to theory (see the computational details in the SI for full details).17 We have performed DFT calculations on a model of complex 1 (Model 1) based on its ASU, i.e. one [CoIV4] moiety plus one linking CoII ion (Fig. S3). Based on symmetry and structure there are four unique nearest neighbour magnetic exchange interactions with $J$ values ranging between $+1.7$ cm$^{-1} \leq J \leq +3.8$ cm$^{-1}$ (Table S2). The narrow range of ferromagnetic exchange interactions found can be attributed to the similarity of the structural parameters present, including the average Co-O-Co angles.16 We have also performed overlap integral calculations17 using the singly occupied molecular orbitals (SOMOs) of the CoII ions (Fig. S4). These help to elucidate the magnitude and sign of magnetic interactions since their magnitude is directly proportional to the magnitude of the antiferromagnetic interaction, i.e. the larger the overlap the larger the antiferromagnetic interaction and vice versa. For 1, there are three intermediate and six small overlap interactions, resulting in a small ferromagnetic interaction overall. Interestingly, replacement of the phenoxide group in Model 1 with a point charge changes the sign of the magnetic interaction from ferromagnetic to antiferromagnetic (4.2 cm$^{-1}$ to $-3.4$ cm$^{-1}$), highlighting the importance of this moiety for obtaining ferromagnetic exchange. We have also calculated the next-nearest neighbour exchange mediated via the syn, anti-O-C-O(carboxylate). These are weak and antiferromagnetic, with $J < -0.2$ cm$^{-1}$ (Fig. S5).

All the CoII ions in 1 are in distorted octahedral geometries (Table S3), with previous magneto-structural studies suggesting such ions would possess large easy-plane anisotropy.18 *Ab initio* NEVPT2
calculations on each Co\textsuperscript{II} ion in 1 confirms this, with values in the range $+41.2 \leq D \leq +87.1$ cm\textsuperscript{-1}. The dominant contribution to $D$ arises from the $d_{xy} \rightarrow d_{yz}$ electronic transition (Table S4, Fig. S5). Positive axial zero-field splitting can be attributed to electronic transitions between orbitals with different $m_L$ levels and the magnitude correlated to the energy separation between the orbitals involved in the electronic transition (Table S4, Fig. S6).\textsuperscript{19}

Conclusions

In summary, the reaction of Co(OAc)$_2$·4H$_2$O and Hsal affords the aesthetically pleasing [Co$_{16}$($\mu$-sal)$_{16}$($\mu_3$-OAc)$_{16}$] (1) wheel, which displays weak ferromagnetic nearest neighbour exchange interactions, in agreement with DFT calculations. Ab initio NEVPT2 studies suggest the presence of large single ion easy-plane anisotropy. In the extended structure the wheels form dimeric capsules via inter-digitation of the sal/acetate ions and this extends to form infinite tubular stacks of capsules upon symmetry expansion. Attempts to make analogues of 1 with different M\textsuperscript{III} ions, different carboxylates and derivatised salicylaldehyde ligands are in progress, with a view to also examining guest transport to the interior of the cages.

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**Supporting Information**

**Synthesis**

All reagents and solvents were obtained from commercial sources and used without further treatment. Hsal (122 mg, 1.0 mmol) and NEt$_3$ (0.2 ml, 1.0 mmol) were added to MeCN (20 ml) and the solution kept under stirring for 10 minutes, followed by addition of Co(OAc)$_2$·4H$_2$O (249 mg, 1.0 mmol). The resultant pink solution was left under stirring for 30 minutes during which time no colour change was observed. The solution was then filtered and layered with Et$_2$O (40 ml). Pink crystals of 1·16MeCN formed over 3 days in ~30% yield. Anal. Calcd (found) for 1: C, 45.21; H, 3.37. Found: C, 44.93, H, 3.23.

**Physical Measurements**

Elemental analyses (C, H, N) were performed by the University of Ioannina microanalysis service.

**X-ray diffraction**

Single crystal X-ray diffraction data were collected on a Bruker D8 VENTURE diffractometer (University of Crete), equipped with a PHOTION II CPAD detector. Crystal data for 1 (CCDC 2178060): C$_{176}$Co$_{16}$H$_{208}$O$_{72}$, $M = 4418.29$ g/mol, tetragonal, space group $P4/n$ (no. 85), $a = 29.9250(6)$ Å, $c = 11.2727(3)$ Å, $V = 10094.8(5)$ Å$^3$, $Z = 2$, $T = 200(2)$ K, $\mu$(CuKα) = 10.704 mm$^{-1}$, $D_{calc} = 1.454$ g/cm$^3$, 28843 reflections measured (4.176° ≤ 2Θ ≤ 136.522°), 9197 unique ($R_{int} = 0.0378$, $R_{sigma} = 0.0405$) which were used in all calculations. The final $R_1$ was 0.0435 ($I > 2\sigma(I)$) and $wR_2$ was 0.1257 (all data).

Powder X-ray diffraction data for 1 were collected using a Bruker D8 ADVANCE with copper radiation at 40 kV, 40 mA and a Johansson monochromator, 2 mm divergence slit and 2.5 degree Soller slits on the incident beam side. LynxEye detector and Bruker DIFFRAC software. Diffraction measured from $2\theta = 3°$ - 30°; step size, 0.0101°. Samples were loaded into quartz capillaries with a 1 mm inside diameter and measured while spinning.

**Magnetic Measurements**

Magnetic susceptibility data were collected on a polycrystalline sample of 1 on a Quantum Design Dynacool PPMS equipped with a 9 T magnet in the temperature range 300 - 2.00 K. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal’s constants.
Computational Details

To estimate the intramolecular magnetic exchange interactions in 1 we have employed Density Functional Theory (DFT) in Gaussian 09 on a model complex (Model 1) created from the ASU of 1. We have performed pairwise exchange interaction calculations by keeping only the two paramagnetic centres of interest in Model 1, replacing the remaining CoII ions with diamagnetic ZnII ions. This method is known to reproduce experimental magnetic exchange values for systems with weak intramolecular magnetic exchange interactions \( J \leq 10 \text{ cm}^{-1} \). The hybrid B3LYP functional has been used together with the TZV basis set for Co, SVP basis set for Zn, O and SV basis set for C and H atoms. We have employed Noodleman’s broken symmetry methodology.

To calculate the zero field splitting (zfs) parameters for each CoII centre in the ASU we have used the ORCA software suite (version ORCA 4.0). The zeroth-order regular approximation (ZORA) method in combination with the ZORA contracted version of basis set (ZORA-def2-TZVP for Co and ZORA-def-SVP for rest of the elements) is known to be a reliable methodology to estimate zfs parameters. We have used the resolution of identity (RI) approximation. During state-average complete active space self-consistent field (SA-CASSCF) calculations we have considered seven electrons in five d-orbitals (CAS (7 electrons / 5 3d-orbitals)) in the active space with ten triplet and fifteen singlet roots. We have used 2nd order N-electron valence perturbation theory to estimate the zero-field splitting parameter as well as to consider the dynamic correlation. We have used integration Grid 6 for Co, Grid 5 for O and Zn, and Grid 4 for the remaining elements.
Fig. S1. Powder diffraction data for compound 1 (top). Refinement of the experimental diffraction data of 1 collected at room temperature by using the Pawley method and the single-crystal structural model as starting parameters (bottom). Experimental (black circles), calculated (red line), difference plot [(lobs–Icalc)] (blue line) and Bragg positions (black ticks). Tetragonal, $P_4/n$; $a = 30.0816$ Å; $c = 11.7914$ Å; $\alpha = \beta = \gamma = 90^\circ$; $R_{exp} = 0.85\%$, $R_{wp} = 1.06\%$, GoF = 1.25.
Fig. S2. FT-ATIR spectrum of 1

Table S1. Bond Valence Sum (BVS) calculations for the metal ions in 1.

|    | Co(II) | Co(III) |
|----|--------|---------|
| Co1 | 2.16   | 2.20    |
| Co2 | 1.94   | 1.97    |
| Co3 | 2.12   | 2.16    |
| Co4 | 1.96   | 2.00    |
Fig. S3. (A) metal-oxygen core of complex 1, highlighting the ASU. The full structure (B) and metal-oxygen core (C) of Model 1. The latter is the ASU of complex 1. Colour code: Co = pink, O = red, Zn = silver and C = black. H atoms are removed for clarity.

Table S2. Pertinent structural parameters for 1 alongside the DFT computed magnetic exchange interactions.

|       | Average Co-O-Co angle (°) | Average Co-O distance (Å) | Average Co-O-Co-O angle (°) | Average Co···Co distance (Å) | J (cm⁻¹) nearest neighbour |
|-------|---------------------------|---------------------------|-----------------------------|-----------------------------|---------------------------|
| Co1-Co2 | 95.2                      | 2.100                     | 21.1                        | 3.100                       | +3.2                      |
| Co2-Co3 | 96.4                      | 2.089                     | 22.1                        | 3.113                       | +1.7                      |
| Co3-Co4 | 95.7                      | 2.096                     | 22.2                        | 3.104                       | +2.5                      |
| Co4-Co1 | 96.8                      | 2.084                     | 22.4                        | 3.114                       | +3.8                      |
\[ <\text{Co}(\alpha)d_{yz}||\text{Co}(\beta)d_{yz}> = 0.012 \]

\[ <\text{Co}(\alpha)d_{yz}||\text{Co}(\beta)d_{x^2-y^2}> = 0.020 \]

\[ <\text{Co}(\alpha)d_{yz}||\text{Co}(\beta)d_{z^2}> = 0.068 \]

\[ <\text{Co}(\alpha)d_{x^2-y^2}||\text{Co}(\beta)d_{x^2-y^2}> = 0.000 \]

\[ <\text{Co}(\alpha)d_{x^2-y^2}||\text{Co}(\beta)d_{z^2}> = 0.017 \]

\[ <\text{Co}(\alpha)d_{x^2-y^2}||\text{Co}(\beta)d_{x^2-y^2}> = 0.044 \]
Three intermediate (green text) and six small (black text) overlap interactions are computed.

\[<\text{Co}(\alpha)d_z^2 | \text{Co}(\beta)d_y^2> = 0.003\]

\[<\text{Co}(\alpha)d_x^2 - y^2 | \text{Co}(\beta)d_z^2> = 0.053\]

\[<\text{Co}(\alpha)d_z^2 | \text{Co}(\beta)d_x^2 - y^2> = 0.075\]

**Fig. S4.** DFT computed overlap integral values together with the representative MO diagram. Three intermediate (green text) and six small (black text) overlap interactions are computed.
Table S3. SHAPE analysis\(^9\) performed on each Co\(^{II}\) ion in the ASU of 1.

| Structure | HP-6 | PPy-6 | OC-6 | TPR-6 | JPPY-6 |
|-----------|------|-------|------|-------|--------|
| Co1-Co16  | 30.213, 24.549, 1.059 | 13.315 | 27.817 |
| Co2-Co16  | 29.535, 23.730, 0.969  | 12.691 | 27.326 |
| Co3-Co16  | 29.945, 24.306, 1.095  | 13.051 | 27.604 |
| Co4-Co16  | 29.227, 24.258, 0.878  | 13.275 | 27.290 |

Table S4. *Ab initio* NEVPT2 estimated anisotropy parameters (\(g, D\) and \(E/D\)) for each Co\(^{II}\) ion in the ASU of 1. We include the d orbital energies, \(d_{yz}\) = grey, \(d_{xz}\) = pink, \(d_{xy}\) = blue, \(d_{z^2}\) = red and \(d_{x^2-y^2}\) = black.

|          | \(g_{xx}, g_{yy}, g_{zz} (g_{iso})\) | \(D (\text{cm}^{-1})\) | \(E / D\) | NEVPT2 computed d orbital energies (\(\text{cm}^{-1}\)) |
|----------|--------------------------------------|------------------------|-----------|---------------------------------------------------|
| Co1      | 1.902, 2.439, 2.930 (2.424)          | 87.1                   | 0.24      | 0.0, 294.3, 842.8, 6467.4, 8226.7                |
| Co2      | 2.057, 2.408, 2.562 (2.342)          | 41.2                   | 0.23      | 0.0, 75.1, 1135.2, 7159.2, 9955.8                |
| Co3      | 1.880, 2.471, 2.928 (2.426)          | 88.5                   | 0.22      | 0.0, 287.4, 892.4, 6356.9, 8275.0                |
| Co4      | 2.050, 2.437, 2.576 (2.354)          | 44.6                   | 0.20      | 0.0, 105.5, 1001.4, 7256.7, 10037.3              |
Fig. S5. The trimetallic Co-Zn-Co models employed to estimate the two unique next-nearest neighbour magnetic interactions present in 1. a) **Model 2** where both next-nearest neighbour magnetic centres are not directly bridged by any functional group, and (b) **Model 3** where both centres are bridged via two syn-anti-O-C-O(carboxylate) groups. (c-d) Spin density plots for models **Model 2** and **Model 3**, respectively. Analysis further supports the presence of little/no magnetic interaction for the former and a very small interaction through the syn-anti-O-C-O(carboxylate) pathway for the latter.
Ab initio NEVPT2 computed d-orbital splitting for each Co\textsuperscript{II} ion in the ASU of 1. Easy-plane anisotropy (+D) can be attributed to the electronic transitions between orbitals with different m\textsubscript{L} levels (d\textsubscript{xz/yz} \rightarrow d\textsubscript{xy/x\textsuperscript{2}-y\textsuperscript{2}}). Note that two electronic transitions d\textsubscript{xz/yz} \rightarrow d\textsubscript{xy} (cyan curly arrow) and d\textsubscript{xz/yz} \rightarrow d\textsubscript{x\textsuperscript{2}-y\textsuperscript{2}} (light green straight arrow) give positive D values with the dominant contribution arising from the d\textsubscript{xz/yz} \rightarrow d\textsubscript{xy} electronic transition. The magnitude of D is correlated to the energy separation between the orbitals involved in the electronic transition (i.e. between d\textsubscript{yz/xz} and d\textsubscript{xy/x\textsuperscript{2}-y\textsuperscript{2}}).
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