Bridging different Co_{4}–calix[4]arene building blocks into grids, cages and 2D polymers with chiral camphoronic acid

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The employment of three different kinds of Co_{4}–calix[4]arene molecular building blocks (MBBs) generated in situ with (1R,3S)-(+)-camphoric acid has resulted in different architectures ranging from a grid, to a chiral cage, to a 2D polymer. The sorption behaviors and magnetic properties of these have been investigated.

Thiacalixarenes, a kind of multidentate ligands with sulfur-bridging phenolic groups, have been documented to be good candidates for the synthesis of polynuclear coordination compounds. It is found that one thiacalix[4]arene molecule or one molecule of its oxidized derivative sulfonylcalix[4]arene (Fig. 1a) prefers to coordinate to four divalent transition metal (TM) ions by its four lower-rim phenolic oxygen atoms and four bridging sulfur/sulfonyl oxygen atoms. By bridging with a μ_{3}/μ_{4}-X it forms shuttlecock-like cationic [TM_{4}(calix[4]arene)-μ_{3}/μ_{4}-X]^+ molecular building blocks (MBBs). These hold suitable curvature to be further linked into polynuclear coordination compounds with well-defined shapes and sizes or extended into 1D/2D structures, especially with the inclusion of anionic species (including anionic clusters, carboxylates, tetrazoles, carbonates and phosphates/phosphonates) for charge balance. For instance, they can be bridged into discrete Co_{32} nanospheres with Co^{III}O_{x} clusters, octahedral M_{24} (M = Mg, Co and Ni) coordination cages with ditri-carboxylates, high-nuclearity M_{4n} (M = Co or Ni, n = 2–6) nanocages with phosphate/phosphonate ligands, tetragonal-prismatic Co_{12} cages by in situ generated bitetrazoles and two-dimensional metal–calixarene polymers comprising pre-designed M_{12} (M = Fe, Co) cages bridged with isonicotinates.

In spite of the fact that it is facile to construct polymetallic complexes with different linkers from TM_{4}-calix[4]arene MBBs, there is no report on calixarene-based coordination complexes linked by chiral ligands, even though these are extensively used in the synthesis of homochiral metal–organic polymeric assemblies and frameworks with potential applications including heterogeneous asymmetric catalysis or enantioselective recognition/separation. Among these chiral ligands, the readily available (1R,3S)-(+)-camphoric acid (abbreviated as H_{2}CAM, Fig. 1a) is particularly appealing, since it possesses two carboxylic acid groups located in a suitable geometry to act as an excellent bent, divergent linker between metal cations. With a detailed search of the literature, there is a plethora of camphorate-based coordination complexes with intriguing structures and various nuclearities. However, coordination complexes based on MBBs and chiral ligands have rarely been described. In this work, we present three novel calix[4]arene-based coordination complexes utilizing (1R,3S)-(+)–camphoric acid (H_{2}CAM) as the linker, formed under solvothermal conditions. The molecular formulas for these three complexes are as follows: [Co_{6}(BSC4A)]_{2}(CAM)_{6}[μ_{4}-H_{2}O]_{4}Cl_{2}·9CH_{3}OH (1), [Co_{6}(BTC4A)]_{2}(CAM)_{6}[μ_{4}-Cl]_{2}(CH_{3}OH)_{2}·(dma)_{2}·0.5DMA·3CH_{3}OH (2), [Co_{6}(PTC4A)](CAM)[μ-HCOO]_{6}[μ_{4}-Cl]_{2}·H_{2}O]·[CH_{3}OH]_{1.7}(DMF) (3) (H_{2}BTC4A = p-tert-butylsulfonylcalix[4]arene; H_{4}BTC4A = p-tetra-butylicalix[4]arene; H_{4}PTC4A = p-phenylthiacalix[4]arene; DMA = N,N'-dimethylacetamide; DMF = N,N'-dimethylformamide; dma = dimethylamine). Complex 1 features a window frame-like rhombus grid, and 2 presents the first chiral calixarene coordination nanocage, while 3 features a 2D polymer structure, novel in a metal–calixarene system. To the best of our knowledge, these coordination complexes give the first examples of complexes based on Co_{4}–calix[4]arene and chiral ligands. Herein, the preparations, crystal structures, magnetic properties and
The reaction of $\text{H}_2\text{BTC4A}$ and $\text{H}_2\text{CAM}$ with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in an acidic DMA–CH$_3$OH mixed solution resulted in the isolation of a chiral Co$_8$ coordination nanocage (2). Complex 2 is the only one in this series with a chiral space group $I2$ and a Flack parameter of $0.06(2)$, suggesting each single crystal is homochiral. Structural study revealed that it contains a Co$_8$ core, which is built by two Co$_4$-BTC4A MBBs as vertices and three CAM$_2$ ligands as linkers (Fig. 1c). Complex 2 has a crystallographic two-fold axis, so its asymmetric unit contains one BTC4A$^{4-}$ ligand, one and a half CAM$_2$ ligands, one Cl$^-$ anion, one $\text{in situ}$ generated dma molecule, one CH$_3$OH molecule and four crystallographically unique Co(u) ions. All Co(u) sites are six-coordinated in a distorted octahedral environment and coordinated by two phenoxyl O atoms, one S atom, one $\mu_2$-Cl, one carboxylic O atom and one other component (a carboxylic O atom for Co1 and Co2, a CH$_3$OH for Co3 and a dma molecule for Co4). It should be noted that one CAM$_2$ ligand is in a general position, while the other one lies with some minor disorder about a twofold axis in this structure. Moreover, the CAM$_2$ ligands adopt two different kinds of coordination modes (Fig. S1†). Different from the reported Co$_{16}$ coordination nanocage with di/tri-carboxylates,$^5,10$ this coordination nanocage contains a small inner cavity and has rather small ports, which hinder us from further studying its chiral encapsulation and recognition behavior.

Replacing the $\text{H}_4\text{PTCA4}$ ligand with the $\text{H}_4\text{BTC4A}$ ligand in a similar reaction to that for the preparation of 2 affords red block crystals of 3. Complex 3 crystallizes in an orthorhombic system with the space group $Cmca$ and shows a novel calixarene-based 2D polymer structure (Fig. 1d). This reveals that the substituent of the upper-rim groups of the thiacalix[4]arene has an important influence on the resulting structure of the coordination complexes. Within the structure of 3, there are two crystallographically different cobalt sites, and both are six-coordinated and distorted octahedral in geometry. Except for two phenoxyl O atoms, two carboxyl O atoms, one S atom and one $\mu_2$-Cl, the Co1 site is still bound by one O from the formate ligand, which originates from the $\text{in situ}$ decarbonylation of the DMF solvent, while the Co2 site is still coordinated by a disordered combination of DMF and CH$_3$OH, refined in a ratio of 65 : 35 (Fig. S2†). Co1, Co2, CoA and Co2A (generated by the mirror symmetry operation through the (010) plane) are capped by a PTC4A$^{4-}$ ligand adopting a cone conformation to form a shuttlecock-like Co$_4$-PTCA4 MBB. Then each MBB is connected by two CAM$_2$ ligands with some minor disorder and two HCOO$^-$ anions, to form a calixarene-based 2D motif (Fig. S3†). The Co$_4$-PTCA4 MBBs can be thought as four-connected nodes while the bridging CAM$_2$ and HCOO$^-$ ligands act as two-connected linkers. Moreover, these HCOO$^-$ anions are generated from the decarbonylation of DMF in a solvothermal environment.
As can be seen from Fig. 2, the N2 sorption isotherm of complexes 1–3 shows a pseudo-type I isotherm with a saturated uptake of 127 cm$^3$ g$^{-1}$ at 77 K and 1.0 bar, characteristic of materials with permanent microporosity. The corresponding Langmuir isotherm values for complexes 1–3 are significantly higher than the expected values: observed 22.09, 21.68 and 11.88 cm$^3$ K mol$^{-1}$ for 1–3, respectively (calculated values of 15, 15 and 7.5 cm$^3$ K mol$^{-1}$ for 8, 8 and 4 uncoupled Co(n) ions, respectively). This can be attributed to the orbital moment as a consequence of spin–orbital coupling of the Co(n) ions, which is known to be significant in an octahedral field.11 Upon cooling, the $X_mT$ products for all three complexes continuously decrease to 0.31, 0.44 and 0.51 cm$^3$ K mol$^{-1}$ at 2 K, respectively, characteristic of intramolecular antiferromagnetic interactions. The magnetic behaviors of complexes 1–3 are similar to those reported for calix[4]arene-based cobalt complexes.3a,b,3c,4 Moreover, the magnetic data of complex 1 above 100 K obey the Curie–Weiss law ($1/X_m = T/C - \theta/\chi_C$), giving a Curie constant $C = 28.01$ cm$^3$ mol$^{-1}$ K and a Weiss constant $\theta = -95.24$ K, and fitting those of 2 and 3 above 50 K give $C = 24.10$ and 13.29 cm$^3$ mol$^{-1}$ K and $\theta = -32.92$ and -36.41 K for 2 and 3 (Fig. S5–S7), respectively. The negative Weiss constants also indicate the presence of antiferromagnetic behavior between the spin carriers, and/or the spin–orbit coupling effect of Co(n) ions.

In summary, by employing three different kinds of Co4–calix[4]arene MBBs with chiral H2CAM ligands, we have obtained grids, chiral cages and 2D polymer structures. Complex 1 features a window frame-like rhombus and 2 presents the first chiral calixarene coordination nanocage, while 3 features a 2D polymer structure, novel in a metal–calixarene system. It is obvious that the introduction of chiral dicarboxylic acids leads to the formation of these fascinating structures. Moreover this work also presents a possible way to build metal–calixarene assemblies with chiral ligands, and efforts with other chiral ligands are also ongoing.

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**Notes and references**

† Crystal data for complex 1: C$_{109}$H$_{156}$O$_{43}$Cl$_4$S$_8$Co$_8$, $M_r = 3024.21$, triclinic, space group $P1$, $a = 12.6110(3)$, $b = 13.0901(6)$, $c = 23.1314(11)$ Å, $\alpha = 86.751(4)$, $\beta = 89.366(3)$, $\gamma = 66.489(4)$, $V = 4955.7(2)$ Å$^3$, $Z = 1$, $F(000) = 1566$, $\lambda = 1.54184$ Å, $T = 100(2)$ K, $\beta_{\text{max}} = 135.0$, reflections collected/unique 26 472/12 438 ($R_{\text{int}} = 0.0592$), final $R_1 = 0.0629$, $wR_2 = 0.1564$, GoF = 0.978. Crystal data for complex 2: C$_{117}$H$_{170}$O$_{45}$Cl$_6$S$_8$Co$_8$, $M_r = 3865.06$, monoclinic, space group $I2$, $a = 11.7307(5)$, $b = 21.710(11)$, $c = 27.720(13)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90$, $V = 7072.4(6)$ Å$^3$, $Z = 2$, $F(000) = 2988$, $\lambda = 1.54184$ Å, $T = 100(2)$ K, $\beta_{\text{max}} = 140.0$, reflections collected/unique 14 926/10 287 ($R_{\text{int}} = 0.0645$), final $R_1 = 0.0771$, $wR_2 = 0.1564$.

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0.2223, GoFo = 1.095. Crystal data for complex 3: C_{62.6}H_{69.9}N_{1.3}O_{12}Cl_{4}S_{4}Co_{4}, \( M_r = 1431.89 \), orthorhombic, space group Cmca, \( a = 20.4878(9), b = 15.1811(6), c = 39.3306(11) \). \( \alpha = 90, \beta = 90, \gamma = 90, V = 12.232.98(8) \), \( Z = 8, F(000) = 5702, \lambda = 1.54184 \AA, T = 100(2) \) K, \( 2\theta_{max} = 140.0 \), reflections collected/unique 15 591/6003 \( (R_{int} = 0.0327), \) final \( R_I = 0.0869, wR_R = 0.2359, GoFo = 1.071. \) The diffraction data of 1 and 2 were treated by the "SQUEEZE" method routine in PLATON to subtract diffuse electron density. This had the effect of dramatically improving the agreement indices.


