Making a [Co₂₄] metallamacrocycle from the shuttlecock-like tetranuclear cobalt-calixarene building blocks[†]

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A $[Co_{24}]$ metallamacrocycle with a $[36\text{-MC}_{Co}\text{-}12]$ periphery and an inner $[24\text{-MC}_{Co}\text{-}6]$ rim is constructed by linking six Co_4 -thiacalixarene shuttlecock-like SBUs with twelve 1,2,4triazole molecules.

Metallamacrocycles (MMCs), a class of ring-like coordination compounds with organic fragments and at least one ring metal center, have attracted extensive attention due to their wonderful architectures and potential applications as recognition agents for cations, anions or molecules, catalysts, sensors and so on.¹ A "periodic table" of such materials involves transition metals,^{2–6} lanthanides^{7,8} or mixed metals.⁹ However, relatively little progress has been made for the MMCs with cobalt cations while the [Co₁₂] units are the largest cobalt MMCs reported.⁴ Moreover, almost all these MMCs are composed of mononuclear bridge metallic centers and there are few metallamacrocyclic compounds with polynuclear bridge building blocks.^{2*a*,10} It is still a big challenge to build up polymetalliccluster-based MMCs.

p-tert-Butylthiacalix[4]arene (H₄TC4A, Scheme S1), possessing four phenoxy groups and four sulfur bridge atoms, has been proved to be a better multidentate ligand in constructing polynuclear complexes with the featured M_x core (commonly, x = 1-4).¹¹ We recently reported a TC4A-supported Co₃₂ nanosphere composed of six Co^{II}₄-TC4A shuttlecocks linked by eight Co^{III} cations.¹² It seems possible that a hollow nanosphere or a polymetallic-cluster-based MMC species can be obtained if the Co^{II}₄-TC4A subunits are taken as secondary building units (SBUs) and the Co^{III} cations are replaced by some bridging ligands. Herein we present a [Co₂₄] metallamacrocycle with six shuttlecock-like Co₄-TC4A SBUs linked by twelve 1,2,4-triazole (trz) molecules, {[Co₄(TC4A)(trz)₂Cl₂(CH₃OH)(H₂O)]₆}(CHCl₃)₁₃(CH₃OH)₂ (1). The crystal structure, magnetic property and pyrolysis of **1** were studied.

Red block crystals of 1 were obtained with good yields by the solvothermal reaction of Co(CH₃COO)₂·4H₂O, H₄TC4A, and 1,2,4-triazole in a 1:1(v/v) CH₃OH–CHCl₃ mixed solvent at 130 °C. Single-crystal X-ray diffraction determination‡ reveals that the Co₄-TC4A SBUs are linked by 1,2,4-triazole to form some nanosized MMCs in which a [24-MC_{Co}-6] ring is encased in a [36-MC_{Co}-12] structural motif (Fig. 1).

Compound 1 crystallizes in a trigonal system with space group $R\bar{3}$. There are four cobalt cations, one TC4A ligand adopting a cone conformation, two μ_3 -trz ligands, two chloride anions, one coordinated water and one methanol molecule in an asymmetric unit (Fig S1). All the four cobalt cations are bonded to the lower-rim phenoxy oxygens and bridge sulfur atoms of TC4A to form an approximate planar square and can be divided into two groups, one five-coordinated such as Co1 and Co4, and the other six-coordinated such as Co2 and Co3. The five-coordinated cobalt sites (Co1 and Co4) are bonded by two phenoxy μ_2 -O atoms, one sulfur, one nitrogen and one chloride anion, resulting in a distorted pyramidal coordination environment. Six-coordinated cobalt sites (Co2 and Co3) have an approximately octahedral coordination environment with two phenoxy μ_2 -O atoms, one sulfur, two nitrogen atoms from two different trz ligands, and one oxygen atom of the bonded water-methanol molecule. All the Co-N and Co-O bond distances are located in the normal bond length range (2.08-2.12 Å for Co-N bond and 2.02-2.15 Å for Co-O bond). Analysis of the bond lengths (Table S1), charge balance and bond valence sum calculations (BVS) suggest all cobalt cations in the title compound to be of Co^{II} nature. The Co-Co distances for the edge (linked by Ophenoxy) and the cross



Fig. 1 A [Co₂₄] metallamacrocycle assembled by six Co₄-TC4A SBUs viewed along the *c* (a) and *a* (b) axis and its [36-MC_{Co}-12] periphery and inner [24-MC_{Co}-6] rim (c). For clarity, all hydrogen atoms and the chloride anion, water and methanol molecules bonded to the metals are omitted and two SBUs generated through an inversion center are shown in the same color. The cobalt atoms in the rims are shown in purple and the rest shown in blue.

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Fig. 2 Polyhedral representation (a) and scheme (b) for the metal arrangement. Polyhedrons are highlighted in two colors for distinguishing those belonging to different SBUs. In (b), the blue and yellow lines stand for μ_2 -O atoms and trz molecules, respectively.

(free of linkers) of the Co₄ quadrangle are 3.46–3.53 and 4.69–5.18 Å, respectively, while those between the closest cobalt atoms from the adjacent Co₄ units are 6.11–6.24 Å. The arrangement of the cobalt atoms in a MMC can be schemed as a bigger [12-MC_{Co}-12] periphery (linked by both trz and μ_2 -O_{phenoxy} atoms) and an inner [6-MC_{Co}-6] rim (linked by only trz ligands) by macrocycle nomenclature if trz ligands and μ_2 -O atoms are schemed as the linkers (Fig. 2). These two rings are linked by the rest of the cobalt cations.

Four cobalt atoms are bonded to the same TC4A molecule to form a shuttlecock-like SBU.¹³ Six SBUs are interconnected by twelve 1,2,4-triazole molecules to form a [Co₂₄] MMC. Although there have been several reports on $\{Co_{32}\}$, $\{Cu_{24}\}$, or $\{Ga_{12/24}\}$ clusters with six capped calixarenes, ^{12,14} there are no cluster-based MMCs reported with calixarenes. The reported [Ln₈] and [Ho₁₂] MMCs supported by *p-tert*-butylsulfonylcalix[4]arenes also concerned mononuclear bridge metal centers.8 It is noted that the $[Co_{24}]$ metallamacrocycle is the largest MMC incorporating cobalt. As shown in Fig. 1, these six shuttlecocks are not located in a plane, that is, the dihedral angles between the planes through adjacent Co4 units are ca. 65.5°. But there is an inversion center for a $[Co_{24}]$ MMC. The thickness of a [Co₂₄] MMC is about 21.75 Å (the $C_{29} \cdots C_{29}^*$ distance) and the diameter of the MMC is about 29.94 Å (the $C_{37} \cdot \cdot \cdot C_{37}^*$ distance), larger than the diameter of a C_{032} nanosphere (23.4 Å).¹² With a close examination, one can find that a [Co₂₄] MMC involves two rings, one [36-MC_{Co}-12] periphery and the other [24-MC_{Co}-6] rim, which are bridged by some additional cobalt atoms. The repeat units for these two rings are -[Co-O-Co-N-C-N]- and -[Co-N-C-N]-, respectively. It is not common that the repeat unit for the larger ring, -[Co-O-Co-N-C-N]-, contains two metal ions and the repeat units for the outside and inner rings of a MMC are different. Although a copper MMC with two rings has been reported, the outside [36-MC_{Cu}-12] and inner [18-MC_{Cu}-6] of the MMC are built up by the same monometallic -[Cu-N-N]- repeat unit.5b

The extended structure of compound 1 was stacked by the $[Co_{24}]$ MMCs through supramolecular stacking interactions such as van der Waals' forces, $\pi \cdots \pi$ stacking interaction and hydrogen bonds. The interstices of the lattice are occupied by some solvent molecules. About ten CHCl₃ and two CH₃OH molecules can be located in the difference electron density map while three additional CHCl₃ molecules can be estimated from the result of *PLATON* squeeze¹⁵ and thermal gravimetric (TG) analysis. So the compound can be formulated as $\{[Co_4(TC4A)(trz)_2Cl_2(CH_3OH)(H_2O)]_6\}(CHCl_3)_{13}(CH_3OH)_2$.

Compound 1 can easily lose the solvent molecules involved in the lattice in air. Thermal gravimetric (TG) analysis of 1 is recorded with some fresh samples for which the surface solvents were wiped by filter paper. The result (Fig. S2) indicates that the onset of the solvent loss is at the very beginning of recording and the weight decreases sharply up to 120 °C corresponding to the release of the solvent CHCl₃ and the bonded/isolated CH₃OH molecules. The observed weight loss of 21.2% is close to the calculated value (20.4%). Further weight loss takes place without showing any distinct plateau before 200 °C and gives a total loss of 25.4% which indicated the loss of all coordinated waters. And then the compound began to decompose gradually and reached a stable weight at 900 °C. The residual black blocks have 20.35% weight of the feed, which is in good agreement with the calculated value of 20.26%. EDS analysis reveals the Co: O ratio (51.6:49.1) is comparable to the expected value for the pure CoO (1:1) (Fig. S3). To our great surprise, a systematic low-magnification scanning electron microscope (SEM) investigation showed that the black blocks are porous and constructed by some conglutinated small particles (Fig. 3). The particle size is mainly located in the range of 100-400 nm. The surface of the residual block is besprinkled with some slits and the body of the block is also not solid, which might be due to the expulsion of the generated gases during the decomposition of the ligands inside the lattice at high temperature. It is obvious that the nanoscaled [Co24] MMC structure plays a crucial role in the formation of this kind of porous block. So it might be an easy way to obtain novel porous metal oxides from the metal-organic precursors.¹⁶ Further characterizations and studies on the applications of this porous material are ongoing.

Magnetic susceptibility measurements were performed on the fresh samples with an applied magnetic field of 1 kOe and the plots of $\chi_{\rm M}T vs. T$ and $\chi_{\rm M}^{-1} vs. T$ (Fig. S4) showed that the $\chi_{\rm M}T$ value decreases gradually from 62.50 cm³ mol⁻¹ K at room temperature to 1.59 cm³ mol⁻¹ K at 2 K. When examining the coordination of cobalt cations, one can find that there are twelve five-coordinated Co^{II} ions and twelve six-coordinated Co^{II} ions in a metallamacrocycle. If the five-coordinated cobalt ions are assumed to be low-spin (s = 1/2) state and the six-coordinated ones are high-spin (s = 3/2) state,⁴ the $\chi_{\rm M}T$ value for twelve uncoupled low-spin Co^{II} ions at 300 K is 22.50 cm³ mol⁻¹ K and the experimental $\chi_{\rm M}T$ value per high-spin Co^{II} ion would be 3.33 cm³ mol⁻¹ K which is consistent with the typical value for Co^{II} ion in an octahedral



Fig. 3 Porous cobalt oxide (CoO) obtained from the pyrolysis of 1 in N₂.

field (${}^{4}T_{1g}$ ground state, the $\chi_{M}T$ value normally ranges from 2.7 to 3.4 cm³ mol⁻¹ K).^{4,12} However, the assumption of 24 high-spin Co^{II} centers would result in a lower $\chi_{M}T$ value of 2.60 cm³ mol⁻¹ K per Co^{II} ion, being out of the usual range. Fitting the experimental data ranging from 50–300 K to Curie–Weiss law gives a Curie constant (*C*) of 69.80 cm³ mol⁻¹ K and a Weiss constant (θ) of –35.10 K. No obvious hysteresis loop is observed for compound **1** (Fig. S5).

In conclusion, the largest metallamacrocycle $[Co_{24}]$ has been constructed by the Co₄-TC4A SBUs linked by 1,2,4-triazole. The MMC contains an unprecedented [36-MC_{Co}-12] periphery and an inner [24-MC_{Co}-6] rim which form with different –[Co–O–Co–N–C–N]– and –[Co–N–C–N]– repeat units, respectively. When heated in nitrogen flow, this compound was pyrolyzed into some porous metal oxides. This work would present a novel route to build functional MMCs with calixarene-supported cluster SBUs and a way to prepare porous metal oxides from metal–organic compounds.

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Notes and references

‡ Crystal data for 1: $C_{285}H_{345}Cl_{51}Co_{24}N_{36}O_{38}S_{24}$, $M = 8874.68 \text{ g mol}^{-1}$ trigonal, $R\bar{3}, a = b = 28.1842(3)$ Å, c = 46.3608(6) Å, V = 31892.8(6) Å³, $Z = 3, D_c = 1.386 \text{ g cm}^{-3}, \mu = 1.402 \text{ mm}^{-1}, T = 150(2) \text{ K}, \theta_{\text{max}} = 1.402 \text{ mm}^{-1}$ 25.0° , F(000) = 13530, reflections collected/unique, 92239/12498($R_{int} = 0.032$), final $R_1 = 0.0656$, $wR_2 = 0.2142$ [$I > 2\sigma(I)$], GooF = 1.006. The intensity data were recorded on a Bruker APEX-II CCD system with Mo-K α radiation ($\lambda = 0.71073$ Å). The crystal structures were solved by means of direct methods and refined employing full-matrix least squares on F^2 (SHELXTL-97).¹⁷ All nonhydrogen atoms were refined anisotropically except solvent molecules, and hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. Hydrogen atoms on methanol molecules can't be generated and were included in the molecular formula directly. Three additional $CHCl_3$ were estimated from $PLATON^{15}$ squeeze and thermal gravimetric (TG) analysis and included in the molecular formula directly. In addition, the high R_1 and wR_2 factor of compound 1 might be due to the weak high-angle diffractions and the disorder of tert-butyl atoms and solvent molecules.

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