CrystEngComm

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/crystengcomm

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Constructing Calixarene-supported High Nuclearity Co_{27}, Co_{28} and $Ni_{18}Na_6$ Clusters with triazoles as the co-bridges

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Three nanosize flying saucer-like cobalt compounds, [Co_{28}(TC4A)$_6$(3-SH-trz)$_8$(di-S-trz)$_4$(SO_4)Cl_{10}(OH)$_4$(CH_3OH)$_4$(H_2O)$_6$] (**CIAC-210**), [Co_{27}(TC4A)$_6$(3-SH-trz)$_8$(di-S-trz)$_4$(CO_3)$_{0.25}$(SO_3)$_{0.75}$$Cl_{10}$(O H)$_2$($CH_3OH$)$_2$($H_2O$)$_4$] (**CIAC-211**) and [$Co_{28}$(TC4A)$_6(trz)_{16}$($CO_3$)$Cl_{11}(OH)_3$($CH_3OH$)$_2$($H_2O$)$_6$] (**CIAC-212**), and one ring-like mixed NiNa compound [$Ni_{18}Na_6$(TC4A)$_6$(3-S-trz)$_6$$Cl_6$($H_2O$)$_6$] (**CIAC-213**) were obtained by solvothermal reactions of the metal salts, *p-tert*-butyltetrathiacalix[4]arene (H_4TC4A) and 1H-1,2,4-triazole-3-thiol (1H-3-SH-trz) /1H-1,2,4-triazole-3-carboxylic acid (1H-3-COOH-trz). All these four compounds are feathered with some shuttlecock-like secondary building units (SBUs) which are constructed by four metal atoms capped by a calixarene molecule. In **CIAC-210**, **-211** and **-213**, the Co_4-TC4A SBUs are bridged together by 3-SH-trz and its dimmer into the high nuclearity clusters while in **CIAC-212**, the SBUs are bridged by 1H-1,2,4-triazole (trz). It is found that not only the kind of metals and the molar ratio of the reactants play important roles in the formation of the clusters, but also the mixed solvents and their ratio affect the final structures. Magnetic measurements suggested that the metal centers exhibit antiferromagnetic interactions for all these four compounds.

INTRODUCTION

Because of their intriguing structures and potential technological applications in magnetism,[1-2] catalysis,[3-5] nonlinear optical material[6] and gas adsorption and storage[7,8], the design and synthesis of high nuclearity polyhedral metal clusters have become one of the most active fields in coordination chemistry and material chemistry over the past few decades.[9-11] These structures are commonly constructed by mononuclear vertices or dinuclear paddle-wheel subunits and a diverse range of ligands[12-15]. An alternative approach is to link metal clusters with ancillary ligands or groups.[16]

Calixarenes, a kind of macrocyclic ligands with methylene/heteroatom-bridging phenolic groups, have been documented to be effective multidentate ligands to build polynuclear clusters and cages.[17-23] Recently, a large number of polymetallic clusters based on calixarenes, especially thiacalix[4]arene, with interesting geometries and novel properties have been reported.[24,25] Such compounds can be constructed by simple calixarene assembly or combination of metal-calixarene units and small molecules. Typically, thiacalix[4]arenes adopt cone conformation and bond the metal centers by their four phenolic oxygens and four sulfur bridge atoms to form a shuttlecock-like cationic $\{M^{II}_x(\text{thiacalix[4]arene})\}^{n+}$ (M = Mn, Fe, Co, Ni ; n = 2, 3 or 4) second building units (SBUs).[25] It is more likely to get high nuclearity polyhedral metal clusters by linking metal-calixarene SUBs with deliberately introduced ancillary ligands. For instance, our group firstly designed a strategy to construct a series of calixarene-based octahedral $\{Co_{24}\}$coordination nanocages by a [6 + 8] condensation using Co_4-TC4A or Co_4-(SC4A-SO_2) SBUs (H_4TC4A = *p*-tert-butylthiacalix[4]arene; H_4SC4A-SO_2= *p*-tert-butylsulfonylcalix[4]arene) as vertices and tripodal aromatic tricarboxylic acids as linkers.[26,27] Wang[28-31] and Hong[32] also reported some supercontainers incorporating M_4-(SC4A-SO_2) or M_4-TC4A (M = Mg, Co, Ni) and ancillary aromatic acids. Recently, ancillary azole liangds showed particular advantage in constructing high nuclearity polyhedral metal clusters. A [Co_{24}] metallamacrocycle compound and a $\{Co_{32}\}$ nanocage were obtained by [6 + 12] and [8 + 4] condensation strategy using Co_4-TC4A SBUs and azole ligands by us.[33,34] Hong[35] and Liu[36-37] also reported several examples of metal clusters based on metal-calixarene SUBs and azole ligands. However, up to date, there are only a few examples with nuclearity higher than 24 for calixarene-based compounds.[24-39]

As our continuous investigations, two small azole linkers, 3-SH-trz and 1H-1,2,4-triazole-3-carboxylic acid, were selected as ancillary ligands to construct higher nuclearity clusters with M_4-TC4A SUBs as the vertices. It is gratifying that four new polynuclear clusters were obtained. Herein, we present crystal structures, and magnetic property of these four high nuclearity clusters based on calixarenes, [Co_{28}(TC4A)$_6$(3-SH-trz)$_8$(di-S-trz)$_4$(SO_4)Cl_{10}(OH)$_4$(CH_3OH)$_4$(H_2O)$_6$] (**CIAC-210**), [Co_{27}(TC4A)$_6$(3-SH-trz)$_8$(di-S-trz)$_4$(CO_3)$_{0.25}$(SO_3)$_{0.75}$$Cl_{10}(OH)_2$($CH_3OH$)$_2$($H_2O$)$_4$](**CIAC-211**), [$Co_{28}$(TC4A)$_6(trz)_{16}$($CO_3$)$Cl_{11}(OH)_3$($CH_3OH$)$_2$($H_2O$)$_6$] (**CIAC-212**), and [$Ni_{18}Na_6$(TC4A)$_6$(3-S-trz)$_6Cl_6$(H$_2$O)$_6$] (**CIAC-213**). This work may shed the light on constructing calixarene-based high nuclearity clusters with ancillary azole ligands.

Experimental Section

Materials, Syntheses and Characterization:

p-tert-Butyltetra-thiacalix[4]arene (H$_4$TC4A) was synthesized by literature method[40] and other chemicals were purchased commercially and used without further purification. Elemental analysis for C, H, N was recorded on a VarioEL instrument. The powder X-ray diffraction (XRD) data (Fig. S16 - S18) were recorded on a Bruker D8 Advance diffractometer. TGA measurement (Fig. S19) was performed on a NETZSCH STA 449F3. FT-IR spectra (KBr pellets, Fig. S20) were taken on a Bruker Vertex 70 spectrometer. Magnetic susceptibility measurement for **CIAC-210--213** was performed on a Quantum Design MPMS XL-5 SQUID system in the temperature range of 2-300 K. Diamagnetic corrections for the sample and sample holder were applied to the data.

Synthesis of CIAC-210:

Celadon single crystal blocks of **CIAC-210** were obtained from the reaction of the mixture of *p-tert*-butylthiacalix[4]arene (0.072 g, 0.1 mmol), Co(CH$_3$COO)$_2$·4H$_2$O (0.11 g, 0.44 mmol), Na$_2$SO$_4$ (0.007 g, 0.05 mmol), 1H-3-SH-trz (0.020 g, 0.2 mmol), CH$_3$OH (8 ml) and CHCl$_3$ (2 ml), in a 20 ml Teflon-lined autoclave which was kept at 130 °C for 3 days and then slowly cooled to room temperature at about 4 °C/h. The crystals were isolated by filtration and then washed with 8:2 methanol-chloroform and dried in air. Yield (0.10 g): ca. 72 % with respect to H$_4$TC4A. Elemental analysis: calculated (%) for $C_{276}H_{320}Cl_{10}Co_{28}N_{48}O_{42}S_{41}$ (excluding the disordered solvents), C 39.90, H 3.86, N 8.10; found (after dried in vacuum): C 39.62, H 3.67, N 7.88. FT-IR (cm^{-1}): 3345(m), 2963(s), 2906(w), 2871 (w), 1593(w), 1454(s), 1362(m), 1260(s), 1195(m), 1088(m), 1044(w), 880(w), 836(s), 745(s), 677(w), 549(w), 460(m), 439(m)

Synthesis of CIAC-211:

Celadon single crystal diamonds of **CIAC-211** were obtained from the reaction of the mixture of *p-tert*-butylthiacalix[4]arene (0.10 g, 0.14 mmol), Co(CH$_3$COO)$_2$·4H$_2$O (0.10 g, 0.4 mmol), 1H-3-SH-trz (0.020 g, 0.2 mmol), CH$_3$OH (8 ml) and CHCl$_3$ (2 ml) in a 20 ml Teflon-lined autoclave which was kept at 130 °C for 3 days and then slowly cooled to room temperature at about 4 °C/h. The crystals were isolated by filtration and then washed with 1:1 methanol-chloroform and dried in air. Yield (0.10 g): ca. 56 % with respect to H$_4$TC4A. Elemental analysis: calculated (%) for $C_{274.25}H_{306}Cl_{10}Co_{27}N_{48}O_{35}S_{40.75}$(excluding the disordered solvents), C 40.70, H 3.78, N 8.31; found (after dried in vacuum): C 40.30, H 3.41, N 8.53. FT-IR (cm^{-1}): 3274(m), 2963(s), 2870 (w), 1593(w), 1454(s), 1363(m), 1260(s), 1195(m) 1087(m), 880(w), 836(s), 744(s), 676(w), 542(w), 499(w), 460(m).

Synthesis of CIAC-212:

Celadon single crystal blocks of **CIAC-212** were obtained from the reaction of the mixture of *p-tert*-butylthiacalix[4]arene (0.10 g, 0.14 mmol), Co(CH$_3$COO)$_2$·4H$_2$O (0.10 g, 0.4 mmol), Dy(NO$_3$)$_3$ (0.08 g, 0.1 mmol), 1H-1,2,4-Triazole-3-carboxylic acid (0.023 g, 0.2 mmol) and CH$_3$OH (10 ml), in a 20 ml Teflon-lined autoclave which was kept at 130 °C for 3 days and then slowly cooled to room temperature at about 4 °C/h. The crystals were isolated by filtration and then washed with 8:2 methanol-chloroform and dried in air. Yield (0.028 g): ca. 15 % with respect to H$_4$TC4A. Elemental analysis: calculated (%) for $C_{275}H_{319}Cl_{11}Co_{28}N_{48}O_{38}S_{24}$ (excluding the disordered solvents), C 42.78, H 4.13, N 8.71; found (after dried in vacuum): C 42.20, H 3.84, N 9.25. FT-IR (cm^{-1}): 3410(m), 2963(s), 2870 (w), 1621(w), 1453(s), 1363(m), 1259(s), 1156(m), 1086(m), 1003(m) 880(m), 835(s), 734(m), 663(s), 543(w), 455(m).

Synthesis of CIAC-213:

Green single crystal blocks of **CIAC-213** were obtained from the reaction of the mixture of *p*-tert-butylthiacalix[4]arene (0.10 g, 0.14 mmol), Ni(CH$_3$COO)$_2$·4H$_2$O (0.10 g, 0.4 mmol), Na$_2$SO$_4$ (0.007 g, 0.05 mmol), CH$_3$OH (3 ml) and CHCl$_3$ (3 ml) in a 20 ml Teflon-lined autoclave which was kept at 130 °C for 3 days and then slowly cooled to room temperature at about 4 °C/h. The crystals were isolated by filtration and then washed with 1:1 methanol-chloroform and dried in air. Yield (0.060 g): ca. 40 % with respect to H$_4$TC4A. Elemental analysis: calculated (%) for $C_{252}H_{282}Cl_6N_{18}Na_6Ni_{18}O_{30}S_{30}$(excluding the disordered solvents), C 47.16, H 4.40, N 3.93; found (after dried in vacuum): C 46.54, H 4.28, N 3.95. FT-IR (cm^{-1}): 3136(m), 2963(s), 2869 (w), 1593(m), 1469(s), 1362(s), 1320(m), 1259(s), 1088(w), 884(m), 840(s), 750(s), 666(w), 542(w), 457(w).

Table 1. Crystal data and structure refinement for **CIAC-210--213**

	CIAC-210	**CIAC-211**	**CIAC-212**	**CIAC-213**
formula	$C_{283}H_{348}Cl_{10}Co_{28}N_{48}O_{49}S_{41}$	$C_{284.25}H_{322}Cl_{34}Co_{27}N_{48}O_{37}S_{40.75}$	$C_{283}H_{351}Cl_{11}Co_{28}N_{48}O_{46}S_{24}$	$C_{258}H_{294}Cl_{18}N_{18}Na_6Ni_{18}O_{32}S_{30}$
formula wt.	8525.09	9105.75	7970.55	6953.73
T/K	150	192	150	192
Cryst. syst	monoclinic	orthorhombic	orthorhombic	trigonal
space group	P2(1)/m	Pnma	Pnma	R-3
a (Å)	20.9882(3)	37.682(3)	37.033(7)	23.340(3)
b (Å)	43.6525(6)	45.190(3)	45.290(9)	23.340(3)
c (Å)	24.5435(3)	24.5650(17)	24.166(5)	55.409(11)
α (°)	90	90	90	90
β (°)	111.6710	90	90	90
γ (°)	90	90	90	120
V (Å^3)	20897.1(5)	41831(5)	40532(14)	26140(10)
Z	2	4	4	3
D_c/g cm^{-3}	1.355	1.446	1.306	1.325
μ/mm^{-1}	1.406	1.517	1.366	1.327
F(000)	8712	18474	16320	10740
Tot. Data	24900	13315	28471	3479
Uniq. Data	15910	10632	18759	2494
R_{int}	0.0980	0.0827	0.0969	0.0911
GOF	1.074	1.057	1.032	1.181
$R1^a$ [I>2σ(I)]	0.0823	0.0946	0.0654	0.1047
$wR2^b$(all data)	0.2600	0.2744	0.1919	0.3015

^{a}R1=Σ||F$_o$|-|F$_c$||/Σ|F$_o$|; ^{b}wR2={Σ[w(F$_o$^{2}-F$_c$^{2})2]/Σ[w(F$_o$^{2})^2]}$^{1/2}$

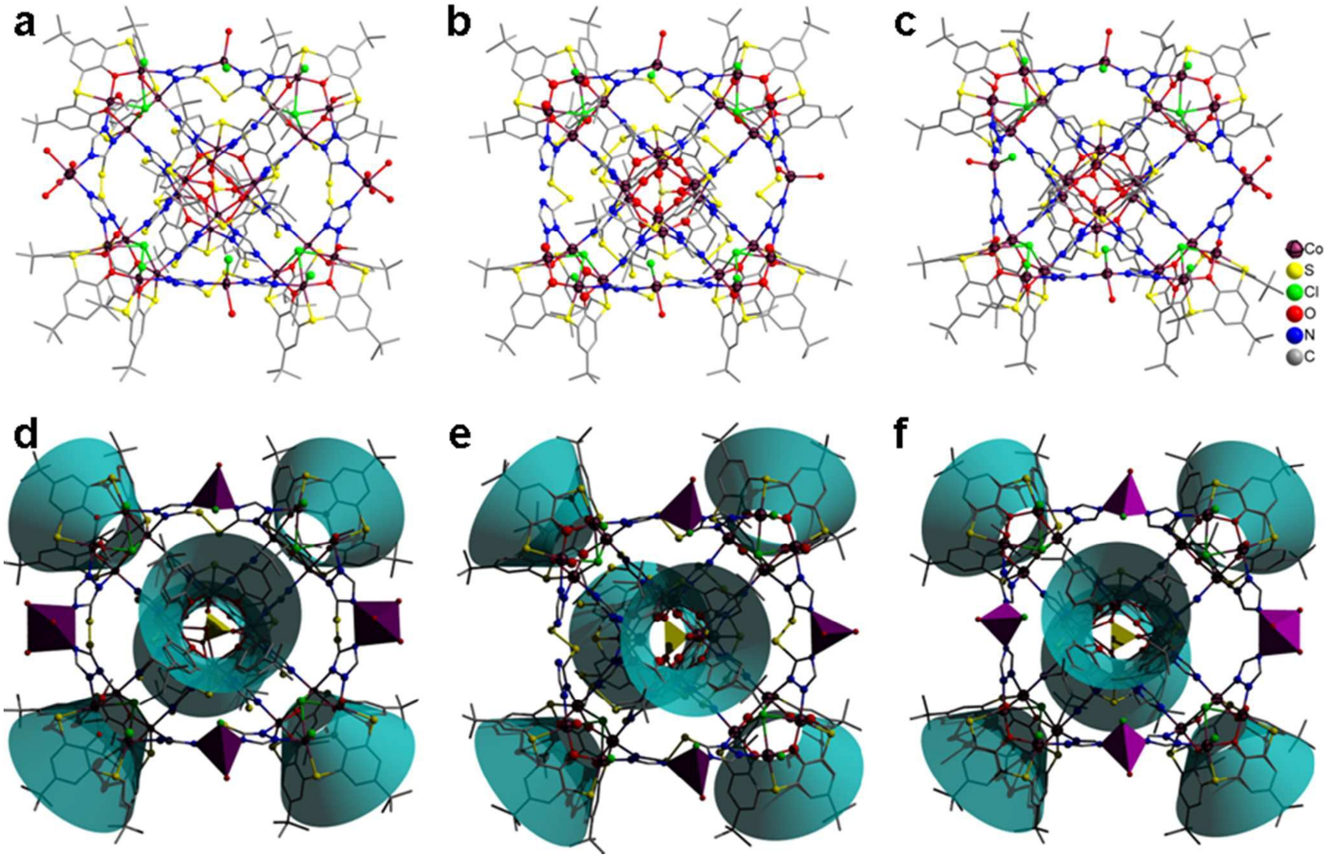

Fig. 1 Molecular structure (**a**-**c**) of Compounds **CIAC-210--212** showing the arrangement of six Co_4-TC4A SBUs (**d**-**f**).

Single Crystal X-ray Diffraction:

The intensity data were recorded on a Bruker APEX-II CCD system with Mo-Kα radiation (λ = 0.71073 Å). The crystal structures were solved by means of Direct Methods and refined employing full-matrix least squares on F2 (SHELXTL-97).[41] The high R1 and wR2 factor of compounds CIAC-210--213 might be due to the weak high-angle diffractions and the disorder of p-tert-butyl atoms. It was not possible to model the disordered solvent molecules appropriately even with low temperature data obtained at about 150K. The diffraction data were treated by the "SQUEEZE" method[42] as implemented in PLATON. Based on the void_volume/count_electrons results, for example, seven CH_3OH molecules per formula unit were removed by the SQUEEZE process. That is, the tentative formulas are $[Co_{28}(TC4A)_6(3\text{-}SH\text{-}trz)_8(di\text{-}S\text{-}trz)_4(SO_4)Cl_{10}(OH)_4(CH_3OH)_4(H_2O)_6] \cdot (CH_3OH)_7$ for **CIAC-210**, $[Co_{27}(TC4A)_6(3\text{-}SH\text{-}trz)_8(di\text{-}S\text{-}trz)_4(CO_3)_{0.25}(SO_3)_{0.75}Cl_{10}(OH)_2(CH_3OH)_2(H_2O)_4] \cdot (CH_3OH)_2(CHCl_3)_8$ for **CIAC-211**, $[Co_{28}(TC4A)_6(trz)_{16}(CO_3)Cl_{11}(OH)_3(CH_3OH)_2(H_2O)_6] \cdot (CH_3OH)_8$ for **CIAC-212**, and $[Ni_{18}Na_6(TC4A)_6(3\text{-}S\text{-}trz)_6Cl_6(H_2O)_6] \cdot (CH_3OH)_2(CHCl_3)_4$ for **CIAC-213**, respectively. Non-hydrogen atoms except some disordered and *p-tert*-butyl carbon atoms were refined anisotropically, and hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. CCDC 1043696-1043699 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

Syntheses of compounds CIAC-210--213

Compounds **CIAC-210--213** were obtained by similar solvothermal reactions. The ratio of the metal salt and H_4TC4A was crucial to the formation of different structures of **CIAC-210 and CIAC-211**. Compound **CIAC-212** was synthesized with in situ decarboxylation of 1H-1,2,4-triazole-3-carboxylic acid, which was also observed in the synthesis of MOFs.[43] The addition of $Dy(NO_3)_3$ was essential to the formation of **CIAC-212**. If $Dy(NO_3)_3$ was not added, **CIAC-212** cannot be obtained. Even if a little $Dy(NO_3)_3$ (eg. 0.025 mmol) was added in the synthesis system, **CIAC-212** can be obtained. It would be due to the catalysis of $Dy(NO_3)_3$ to the decarboxylation of 1H-1,2,4-triazole-3-carboxylic acid. In the structures of **CIAC-211** and **CIAC-212**, carbonate anions were observed, which might come from carbon dioxide in the air. Deliberate addition of Na_2CO_3 can promote the yields of **CIAC-211** and **-212** indeed.

Structures of Compounds CIAC-210--212.

The essential feature of compounds **CIAC-210--212** were given by the flying saucer like structures which result from six Co_4-TC4A SBUs (with two tail-to-tail in the center and four hanging

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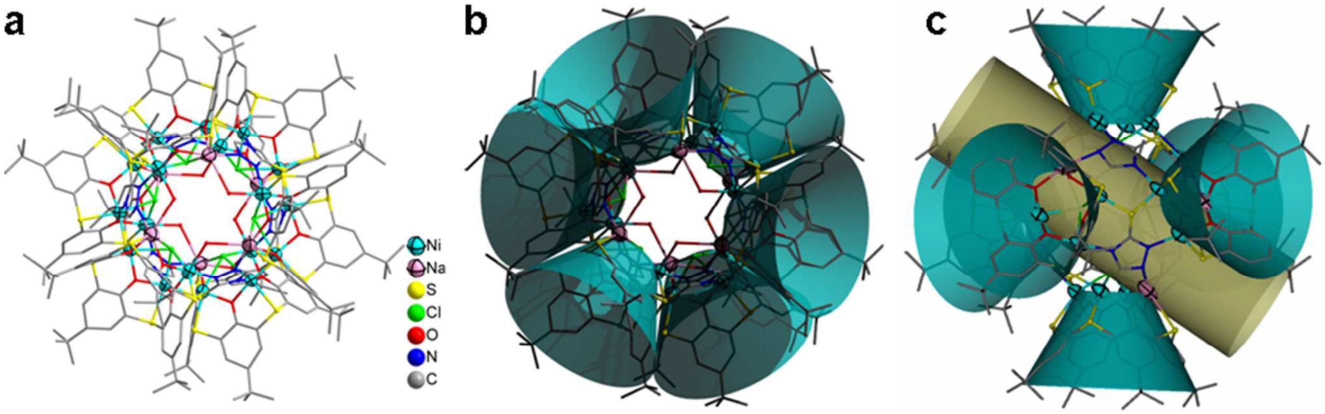

Fig. 2 Molecular structure of **CIAC-213** showing arrangement of six Ni_3Na-TC4A SBUs.

outside), sixteen 3-SH-trz (including eight condensed into di-S-trz) or 1H-1,2,4-triazole ligands and three or four cobalt four links (Fig. 1, Fig. S2-S4, ESI). Single-crystal X-ray diffraction determination reveals that the differences among these three structures are the center anions and the number of the cobalt links on the out edge. A sulphate, a disordered bisulfite/carbonate **2** and a carbonate anion are found in between two central tail-to-tail Co_4-TC4A SBUs for **CIAC-210**, **CIAC-211** and **CIAC-212**, respectively, which would act as the template as that in the reported Mn_{24} nanocage.[44] For the cobalt links on the outside edges, there are just different numbers for these three compounds (e. g. four in **CIAC-210** and **-212**, three in **CIAC-211**). Furthermore, slight different coordination of the metal sites does not affect the shape of the clusters. Therefore **CIAC-210** was mainly described as an example.

Compound **CIAC-210** crystallizes in the monoclinic system with space group $P2(1)/m$, which possesses crystallographically imposed 2/m symmetry. An asymmetric unit contains a half of the $\{Co_{28}\}$ entity. There are seventeen crystallographically independent cobalt sites (Co1-Co17). A TC4A molecule adopting a cone conformation bonds a tetranuclear Co_4 square through its four phenolic oxygen atoms and four sulfur atoms to form a shuttlecock-like Co_4-TC4A SBU. As shown in Fig. S5a, the outside Co_4-TC4A SBU bonds two 3-SH-trz molecules and two in situ generated di-S-trz molecules[45], one μ_4-Cl, one Cl and one methanol molecule while the central tail-to-tail SUB is coordinated by eight different 3-SH-trz molecules and one sulfate anion. In the outside Co_4-TC4A SBUs, Co1, Co4, Co5 and Co8 are six-coordinated by two phenoxy μ_2-O atoms, one sulfur, one μ_4-chloride and two nitrogen atoms from two 3-SH-trz molecules while Co2, Co3, Co6 and Co7 are bonded by two phenoxy μ_2-O atoms, one sulfur, one nitrogen, one μ_4-chloride and one chloride anion or one oxygen from methanol molecule, resulting in an approximately octahedral coordination environment. In the tail-to-tail SUBs, all the cobalt cations also have an approximately octahedral coordination environment bonded by two phenoxy μ_2-O atoms, one sulfur, two nitrogen atoms from two different 3-SH-trz ligands, and one oxygen atom from sulfate ion (Fig. S5b). Six SBUs act as the metal vertexes which are supported by eight 3-SH-trz brackets to form a 24 nuclear entity. Furthermore, four SBUs at the edge are linked into a ring by four in situ generated di-S-trz molecules. Four additional Co(II) cations adhere to the di-S-trz linkers. The Co15 site is four-coordinated by two Cl atoms and two nitrogen atoms from a di-S-trz molecule while Co16 and Co17 are six-coordinated by two Cl atoms, two nitrogen atoms from di-S-trz ligand and two O atoms of the bonded water molecules (Fig. S2a, S3a).

It should be noted that the inner anions such as sulphate, bisulfite and carbonate in these three structures show different coordination mode. In **CIAC-210**, the sulphate anion exhibits a μ_8 mode and bonds all the cobalt cations of two tail-to-tail Co_4-TC4A SBUs in the center. In **CIAC-211** and **-212**, the bisulfite or carbonate anions show a μ_6 mode contacting six cobalt cations (Fig. S5b, S8b, S11b). The different coordination mode of the center anions results in different coordination of the cobalt cations in the tail-to-tail Co_4-TC4A SBUs, that is, six of eight cobalt cations are six-coordinated and other two are five-coordinated in the latter two structures while all the cobalts are six-coordinated in the former one (Fig. 1, Fig. S4, S7, S10).

Structure of Compound CIAC-213.

Compound **CIAC-213** crystallizes in the trigonal system with space group R-3, which possesses crystallographically imposed -3 symmetry. There are three Ni atoms, one Na atom, one TC4A ligand, one μ_5-3-SH-trz ligand, one μ_4-chloride anion and one bonded water molecule in an asymmetric unit (Fig. S14a). In Compound **CIAC-213**, a TC4A molecule adopting a cone conformation bonds three nickel atoms and one sodium atom by four phenolic oxygen atoms and four sulfur atoms to form a shuttlecock-like Ni_3Na-TC4A SBU. The Ni_3Na-TC4A SBU is different from the usual M_4-TC4A SBU with six-coordinated metals. In the Ni_3Na-TC4A SBU, the nickel cations are six-coordinated by two phenoxy μ_2-O atoms, one μ_4-Cl, one nitrogen from 3-SH-trz, one sulfur atom from TC4A, and one sulfur of 3-SH-trz or one oxygen from the bonded water molecule, while the Na atom is five-coordinated by two phenoxy μ_2-O atoms, one μ_4-chloride anion, one sulfur of TC4A and one oxygen atom from the bonded water molecule (Fig. S14a). In this structure, each 3-SH-trz molecule is bonded by three Ni_3Na-TC4A SBUs and each $NaNi_3$-TC4A SBU is linked by three 3-SH-trz ligands (Fig. S14). The SBUs acting as the metal vertexes are bridged by 3-SH-trz linkers into a $\{Ni_{18}Na_6\}$ entity through a [6 + 6] condensation (Fig. 2). Viewed along the c axis, this $\{Ni_{18}Na_6\}$ entity looks like a metallocycle ring. However, different from those triazoles in the reported $\{Co_{24}\}$ metallamacrocycle [33] which are perpendicular to the ring axis, all the azole planes are parallel to the ring axis. On the other hand, the $\{Ni_{18}Na_6\}$ entity can also be thought by bridging six SBUs arranged in an octahedral mode with six 3-SH-trz ligands located on the octahedral faces and leaving two opposite octahedral faces uncovered to form two portals (Fig. 2c).

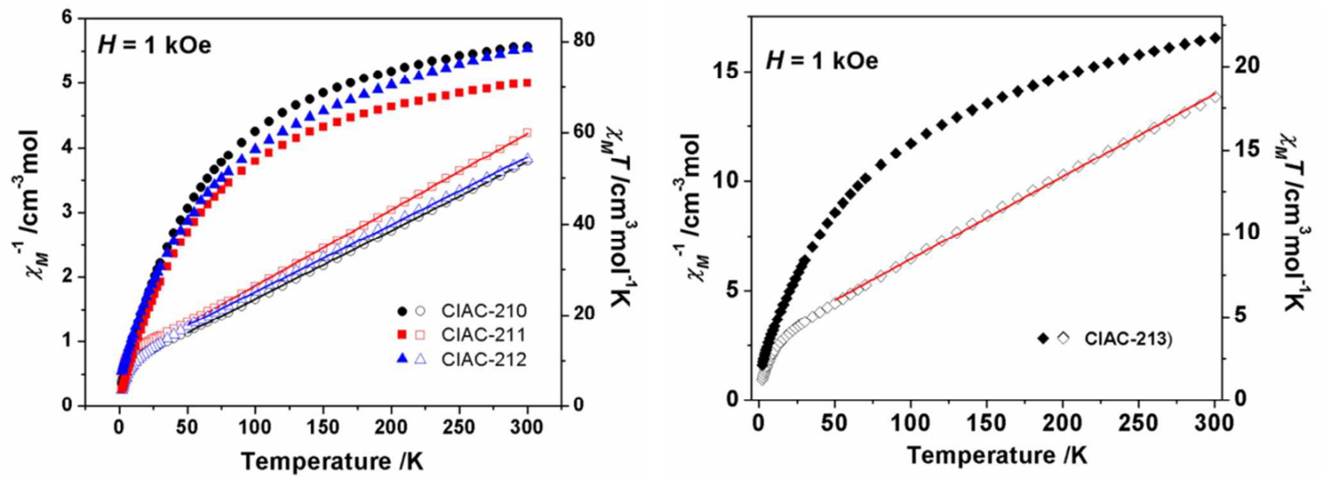

Fig. 3 Plots of $\chi_M T$ vs T and $1/\chi_M$ vs T for **CIAC-210--213** in a 1K Oe field.

Different from those in an octahedral or wheel-like arrangement in the reported $\{Co^{II}{}_{24}Co^{III}{}_8\}$,[38] $\{Co_{24}Mo_8\}$ and $\{Co_{24}W_8\}$[39] nanospheres, $\{Co_{24}\}$ nanocages[26-28, 32] and $\{Co_{24}\}$ metallamacrocycle (MMC),[33] the Co_4-TC4A SBUs in **CIAC-210--212** are stacked into a flying saucer-like structure. The sizes of these structures are ca. ϕ28.7 Å × 17.5 Å (with the $C_{butyl}\cdots C_{butyl}$ distance), which are comparable with that for the $\{Co_{24}\}$ metallamacrocycle (ϕ29.9 Å × 21.8 Å)[33] but smaller than those for the octahedral $\{Co^{II}{}_{24}\}$ nanocages linked by aromatic carboxylic acids.[26-28, 32] Differently, the M_4-TC4A SBUs in **CIAC-213** are stacked in an octahedral method and the dimension is ca. 25.2 × 25.2 × 25.2 Å^3, which is comparable with those for the $\{Co^{II}{}_{24}Co^{III}{}_8\}$, $\{Co_{24}Mo_8\}$ or $\{Co_{24}W_8\}$ nanospheres but is still smaller than those for the $\{Co^{II}{}_{24}\}$ nanocages linked by aromatic carboxylic acids.[26-28, 32, 38, 39] There is also a small spherical cavity (with the diameter being of 7.48 Å, measured with the distance of two opposite μ_4-chlorides) which communicates with the outside by two triangle portals on the opposite octahedral faces.

Magnetic measurements.

Magnetic susceptibility measurements were carried out on polycrystalline samples of compounds **CIAC-210--213** in 2-300 K with a 1000 Oe applied field (Fig. 3). The $\chi_M T$ values at 300 K are 78.98, 70.78 and 78.40 cm^3 mol^{-1}K for compounds **CIAC-210--212**, respectively, which are much larger than the spin-only value of twenty-eight (**CIAC-210** and **-212**) (52.50 cm^{3}mol^{-1}K) or twenty-seven (**CIAC-211**) (50.63 cm^{3}mol^{-1}K) isolated high-spin d^7 ions. Based on the structure determination, the $\chi_M T$ values at 300 K can be attributed to twenty-six octahedrally coordinated Co^{II} cations and two tetrahedrally coordinated Co^{II} cations for **CIAC-210**, twenty-two octahedrally coordinated Co^{II} cations and five tetrahedrally coordinated Co^{II} cations for **CIAC-211,** twenty-three octahedrally coordinated Co^{II} cations and five tetrahedrally coordinated Co^{II} cations for **CIAC-212**, respectively. For each octahedrally coordinated Co^{II} center, the experimental $\chi_M T$ value at room temperature is 2.91, 2.80 and 3.03 cm^3 mol^{-1}K, respectively, which is consistent with the typical value of the Co^{II} ion (for Co^{II}, the $\chi_M T$ value normally ranges from 2.7 to 3.4 cm^3 mol^{-1}K).[38] The $\chi_M T$ values decrease continuously with lowering temperature and fall rapidly in the lower temperature region to the minimums of 4.96, 3.88 and 7.79 cm^{3}mol^{-1}K for compounds **CIAC-210--212**, respectively. For all three compounds, fitting the experimental data in the range of 50~300 K to Curie-Weiss law $1/\chi_M = (T-\theta)/C$ gives Curie constants (C) being of 94.34, 84.96, and 95.88 cm^{3}mol^{-1}K and Weiss constants (θ) of -56.97, -58.82, and -70.02 K for **CIAC-210--212**, respectively. The negative Weiss constants (θ) suggest antiferromagnetic interactions between the metal centers and/or the spin-orbit coupling effect of Co^{II}.[33,38,39] For **CIAC-213**, the χ_MT value at 300 K is 21.73 cm^{3}mol^{-1}K, which is also larger than the expected value 18.00 cm^{3}mol^{-1}K for eighteen uncoupled nickel(II) atoms (g = 2.0).[46,47] As temperature is lowered, the $\chi_M T$ value decreases continuously and falls rapidly in the lower temperature region to 2.11 cm^{3}mol^{-1}K at 2 K. The reciprocal molar susceptibility in 50-300 K follows the Curie-Weiss law with C = 26.67 cm^{3}mol^{-1}K and θ = -72.14 K. The large negative Weiss constant (θ) value suggests an antiferromagnetic interaction between the nickel(II) centers.

Conclusions

In summary, we successfully obtained four calixarene-based high nuclearity nanostructures by introducing 3-SH-trz or 1H-1,2,4-triazole linker into the M_4-thiacalix[4]arene system. Three cobalt compounds are featured with some flying saucer-like structures while the $Ni_{18}Na_6$ compound can be thought as a ring-like metallocycle compound or an octahedral coordination nanocage with two opposite triangular faces uncovered. The sulfur atoms of 3-SH-trz ligands are also involved into the coordination of the metals to stabilize the cluster. Furthermore, some in situ generated di-S-trz ligands were also found to stabilize these clusters. It would be possible to design and synthesize a series of high nuclearity clusters by moving the bridging cobalt(II) cations at the peirphery or extended structures by linking them with deliberately chosen ligands or entities.

Acknowledgements

This work was supported by National Natural Science Foundation of China (No. 21221061, 21301170 and 51222404). We thank Mr. Kuiyue Yang for TGA analyses.

Notes and references

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† Electronic Supplementary Information (ESI) available: X-ray crystallographic data in CIF format, coordination modes of M_4-TC4A, 3-SH-trz and trz ligands, additional structural figures, TGA, IR and X-ray powder diffraction patterns of **CIAC-210--213**. See DOI: 10.1039/b000000x/

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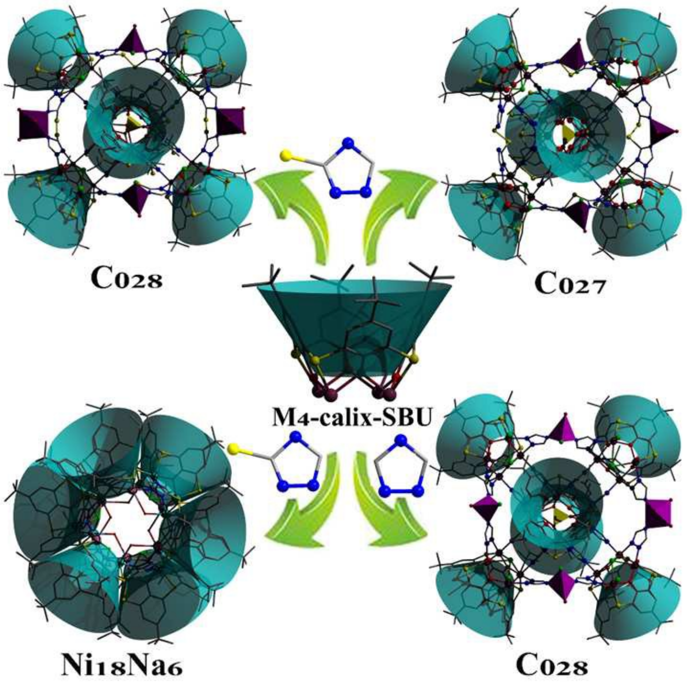

Four high nuclearity compounds are constructed by the M_4-calixarene SBUs and triazole co-bridges.