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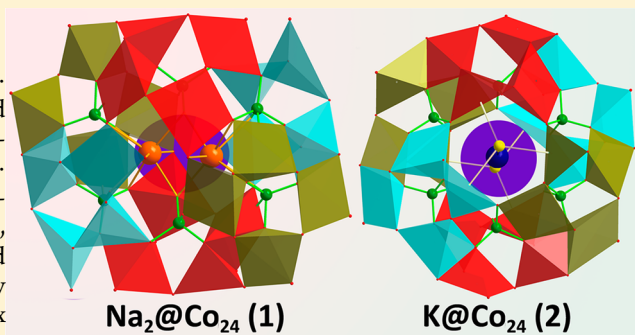
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Alkali-Metal-Templated Assembly of Two High-Nuclearity Cobalt Clusters Based on Thiacalix[4]arene

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S Supporting Information

ABSTRACT: Two novel thiacalix[4]arene-based high-nuclearity cobalt clusters, $[\text{Na}_2\text{Co}_{24}(\text{BTC4A})_6(\text{PO}_4)_6(\text{HCOO})_6(\text{DMC})_2(\text{DMF})_2(\text{dma})_4] \cdot 5\text{DMF} \cdot 9\text{CH}_3\text{OH}$ (denoted as $\text{Na}_2@\text{Co}_{24}$, **1**) and $[\text{KCo}_{24}(\text{BTC4A})_6(\text{PO}_4)_6(\text{Cl})_2(\text{HCOO})_4(\text{DMF})_8] \cdot [\text{KCo}_{24}(\text{BTC4A})_6(\text{PO}_4)_6(\text{Cl})_2(\text{HCOO})_6(\text{DMF})_4(\text{CH}_3\text{OH})_2] \cdot 8\text{DMF} \cdot 23\text{CH}_3\text{OH}$ (denoted as $\text{K}@\text{Co}_{24}$, **2**) ($\text{H}_4\text{BTC4A}$ = *p*-tert-butylthiacalix[4]arene, DMC = *N,N'*-dimethylcarbamic acid anion, dma = dimethylamine), have been solvothermally prepared and structurally characterized. Compounds **1** and **2** are each capped by six Co_4 -BTC4A molecular building blocks (MBBs) and six phosphate linkers and other different auxiliary anions, possessing an eicositranuclear Co_{24} core templated by alkali-metal cations. In essence, compound **1** is templated by two Na^+ cations with an attractive interaction in the center of the core, while **2** is templated by one K^+ with a larger radius. Such differences “convert” an oval-shaped Co_{24} disklike core in **1** to a circular core in **2**. Interestingly, **2** contains both anionic and cationic KCo_{24} cores, representing the largest cobalt aggregate salt reported, to the best of our knowledge. In addition, magnetic measurements of **1** and **2** were investigated, revealing the existence of antiferromagnetic interactions between the magnetic Co^{II} centers.



■ INTRODUCTION

Owing to their potential applications in magnetism,¹ optics,² conductivity,³ catalysis⁴ and so forth,⁵ as well as the additional benefit of architectural beauty, high-nuclearity transition-metal (TM) coordination clusters have been receiving remarkable interest in chemistry and physics nowadays. Although reports on new polynuclear TM metal clusters with fascinating geometries and novel properties continue to appear,⁶ the synthesis of such giant clusters still remains a great challenge.⁷ Furthermore, the assembly of coordination complexes induced by different stimuli, such as anions, cations, pH value, temperature, solvent, light, and electric and magnetic fields, has been a hot topic, because such stimuli can have a large influence on the nuclearity and arrangement of metals in the resulting compounds, which may further lead to their structurally related physiochemical properties.⁸

On the other hand, one of the strategies to construct high-nuclearity clusters is to adopt large macrocyclic ligands with several coordination sites. *p*-tert-Butylthiacalix[4]arene ($\text{H}_4\text{BTC4A}$), a multidentate ligand bridged by four sulfur atoms and possessing four lower-rim phenolic oxygen atoms, has been documented as an excellent molecule in the

construction of polymetallic compounds.⁹ It is found that each $\text{H}_4\text{BTC4A}$ molecule tends to bind to four divalent TM cations to form a $\text{TM}^{\text{II}}_4\text{-BTC4A}$ entity acting as an molecular building block (MBB), which can be linked into fascinating coordination complexes with high nuclearity by different kinds of linkers, such as complementary ligands and bridging ions. For example, they can be extended into discrete giant spherical Co_{32} clusters with $\text{Co}^{\text{III}}\text{O}_6$ tetrahedrons,¹⁰ elongated octahedral M_{24} ($\text{M} = \text{Co}, \text{Fe}$) coordination cages with 2,2'-bipyridine-4,4'-dicarboxylate,¹¹ large Co_{24} metallamacrocycles by 1,2,4-triazole ligands,¹² and tetragonal-prismatic Co_{32} nanoscale cages by in situ generated ditetrazolate ligands.¹³ Moreover, its oxidized derivatives (*p*-tert-butylsulfonylcalix[4]arene and *p*-tert-butylsulfonylthiacalix[4]arene) with additional oxygen donor atoms around the sulfur bridges as well as methylene-bridged calix[4]arenes have also been widely utilized in the syntheses of polymetallic compounds.¹⁴

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Our research group has been dedicated to using calixarene ligands in constructing new high-nuclearity polymetallic clusters that may exhibit interesting magnetic properties.¹⁵ Very recently, by using phosphate and phosphonate ligands that have different anionic species and can take diverse binding modes as linkers, we have obtained several novel calix[4]arene-based high-nuclearity compounds with interesting properties.^{15a,b} Moreover, our group has also reported a chlorine-templated assembly of a cationic Mn_{24} coordination cluster based on $\text{H}_4\text{BTC4A}$ ligands.^{15d} However, no cation-templated clusters based on calixarene ligands have been reported so far. Herein, we present the syntheses, structures, and magnetic behavior of two high-nuclearity cobalt compounds: $[\text{Na}_2\text{Co}_{24}(\text{BTC4A})_6(\text{PO}_4)_6(\text{HCOO})_6(\text{DMC})_2(\text{DMF})_2(\text{dma})_4]\cdot 5\text{DMF}\cdot 9\text{CH}_3\text{OH}$ (denoted $\text{Na}_2\text{@Co}_{24}$, **1**) and $[\text{KCo}_{24}(\text{BTC4A})_6(\text{PO}_4)_6(\text{Cl})_2(\text{HCOO})_4(\text{DMF})_8][\text{KCo}_{24}(\text{BTC4A})_6(\text{PO}_4)_6(\text{Cl})_2(\text{HCOO})_6(\text{DMF})_4(\text{CH}_3\text{OH})_2]\cdot 8\text{DMF}\cdot 23\text{CH}_3\text{OH}$ (denoted K@Co_{24} , **2**) ($\text{DMF} = N,N'$ -dimethylformamide, $\text{DMC} = N,N'$ -dimethylcarbamic acid anion, $\text{dma} = \text{dimethylamine}$). Structural analyses reveal that compounds **1** and **2** are each capped by six Co_4 -BTC4A MBBs, where phosphate anions perform as the cork bases (Figure 1), possessing a disklike

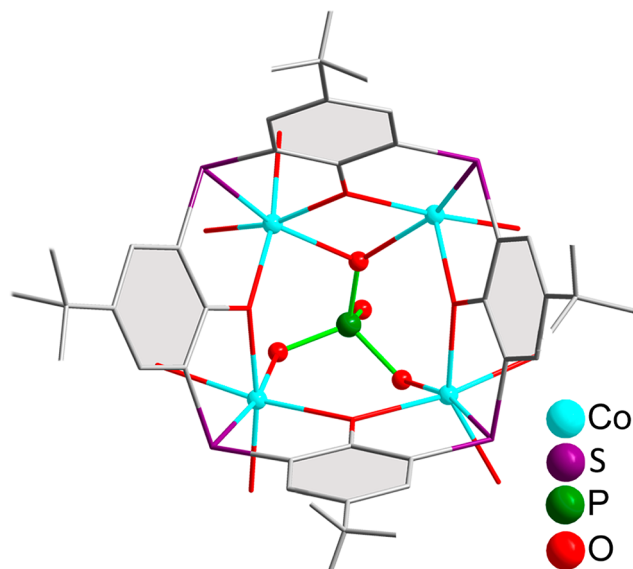


Figure 1. Shuttlecock-like MBB of Co_4 -BTC4A, whose base is capped by a phosphate anion.

arrangement of the Co^{II} ions templated by alkali-metal cations, but with two sodium cations in the central core of **1** and with one larger potassium ion in the core of **2**. This change “converts” an oval-shaped disklike core (**1**) to a circular core (**2**).

EXPERIMENTAL SECTION

Materials and Physical Measurements. *p*-tert-Butylthiacalix[4]-arene was synthesized by a literature procedure,¹⁶ while other reagent-grade chemicals from commercial sources were employed without further purification. Elemental analyses were performed on a Elementar Vario EL III analyzer. The powder X-ray diffraction patterns (PXRD) were taken on a Rigaku MiniFlex 600 diffractometer. Infrared spectra (KBr pellets) were recorded in the region 400–4000 cm^{-1} using a VERTEX70 FT-IR spectrometer. Thermogravimetric measurements (TG) were recorded under a flowing N_2 atmosphere on a NETZSCH STA 449C instrument. Magnetic measurements for compounds **1** and **2** were collected with PPMS-9T and MPMS-XL

magnetometers made by Quantum Design. The magnetic susceptibilities were obtained on polycrystalline samples. All experimental magnetic data were corrected with respect to the sample holder as well as the diamagnetic contribution of all atoms using Pascal's constants.

Synthesis Procedures. **Compound 1.** $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.40 mmol, 120 mg), Na_2HPO_4 (0.10 mmol, 14 mg), and $\text{H}_4\text{BTC4A}\cdot\text{CHCl}_3$ (0.10 mmol, 82 mg) were added to DMF (5 mL) and CH_3OH (5 mL). The mixture was placed in a 25 mL Teflon-lined stainless steel autoclave, which was heated at 120 $^\circ\text{C}$ for 3 days, and cooled to 30 $^\circ\text{C}$ for 1 day. After they were washed with fresh DMF/ CH_3OH (v/v 1/1), the red crystals of **1** were collected in 69% yield with respect to $\text{H}_4\text{BTC4A}\cdot\text{CHCl}_3$. Anal. Calcd for $\text{C}_{302}\text{H}_{423}\text{N}_{17}\text{O}_{84}\text{P}_6\text{S}_{24}\text{Na}_2\text{Co}_{24}$ ($M_r = 8051.51$): C, 45.05; H, 5.29; N, 2.96. Found: C, 44.69; H, 5.10; N, 2.77. IR (KBr pellet, cm^{-1}): 3851 (w), 3753 (w), 3655 (w), 2962 (s), 2865 (m), 1682 (s), 1648 (s), 1462 (s), 1388 (m), 1355 (m), 1290 (m), 1257 (s), 1110 (s), 1061 (s), 881 (w), 835 (m), 752 (w), 611 (w), 629 (w), 548 (w), 458 (w). The phase purity of the sample was determined by PXRD (Figure S14a in the Supporting Information).

Compound 2. $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.40 mmol, 120 mg), K_2HPO_4 (0.10 mmol, 17.5 mg), and $\text{H}_4\text{BTC4A}\cdot\text{CHCl}_3$ (0.10 mmol, 82 mg) were added to DMF (5 mL) and CH_3OH (5 mL). The mixture was placed in a 25 mL Teflon-lined stainless steel autoclave, which was heated to 120 $^\circ\text{C}$ for 3 days and cooled to 30 $^\circ\text{C}$ for 1 day. However, the yield was low (5% based on the $\text{H}_4\text{BTC4A}\cdot\text{CHCl}_3$). Enhancement of the synthetic yield can be achieved by directly adding KCl (0.10 mmol, 7.5 mg) to the above mixture, and thus the yield of **2** was subsequently raised to 48%. Anal. Calcd for $\text{C}_{575}\text{H}_{774}\text{N}_{20}\text{O}_{161}\text{P}_{12}\text{S}_{48}\text{Cl}_2\text{K}_2\text{Co}_{48}$ ($M_r = 15502.09$): C, 44.55; H, 5.03; N, 1.81. Found: C, 44.82; H, 4.92; N, 1.95. IR (KBr pellet, cm^{-1}): 3859 (w), 3746 (w), 3655 (w), 2962 (s), 2864 (m), 1682 (s), 1649 (s), 1467 (s), 1388 (m), 1355 (m), 1291 (m), 1260 (s), 1086 (s), 1063 (s), 966 (m), 883 (w), 834 (m), 755 (w), 637 (w), 589 (w), 556 (w), 459 (w). The phase purity of the sample was determined by PXRD (Figure S14b in the Supporting Information).

Single-Crystal X-ray Crystallography. Intensity data for compounds **1** and **2** were measured on a SuperNova diffractometer which was equipped with a copper microfocus X-ray source ($\lambda = 1.5406 \text{ \AA}$) at 100(2) K. The crystal structures were resolved by direct methods, and all calculations were performed on the SHELXTL-97 program package.¹⁷ All non-hydrogen atoms were refined anisotropically, except for several highly disordered *t*-Bu carbon atoms and the isolated solvent molecules. Hydrogen atoms of the organic ligands were added in the riding model and refined with isotropic thermal parameters. Moreover, several free lattice solvent molecules were badly disordered, and assignment and refinement of the solvent peaks failed for the structures of **1** and **2**. The diffraction data were treated by the SQUEEZE program as implemented in PLATON to subtract the diffuse electron density with respect to the disordered solvent molecules.¹⁸ The final formulas of the title compounds were determined by the SQUEEZE results together with TG data as well as elemental analysis. The detailed crystal data and cell parameters for both compounds are summarized in Table 1. CCDC-1011952 (**1**) and CCDC-1011953 (**2**) give supplementary crystallographic data for this paper. These data can be obtained free of charge through www.ccdc.cam.ac.uk/conts/retrieving.html.

RESULTS AND DISCUSSION

Crystal Structures. Single-crystal X-ray diffraction analysis shows that compound **1** crystallizes in the triclinic space group $P\bar{1}$ and contains a neutral oval-shaped $\text{Na}_2\text{Co}_{24}$ cluster (Figure 2a and Figure S1 in the Supporting Information), which is constructed by six Co_4 -BTC4A MBBs, six PO_4^{3-} anions, two sodium ions, and other different auxiliary anions, including HCOO^- and DMC^- anions. There are 12 crystallographically unique cobalt ions and 1 sodium ion in its asymmetry unit. The latter sodium ion is eight-coordinated in an O_8 coordination environment with Na–O distances in the region 2.301–2.682 \AA . Among the cobalt ions ($\text{Co1}–\text{Co12}$), Co5 is five-

Table 1. Crystallographic Data and Structure Refinement Details for 1 and 2

	1	2
chem formula	C ₃₀₂ H ₄₂₃ N ₁₇ O ₈₄ P ₆ S ₂₄ Na ₂ Co ₂₄	C ₅₇₅ H ₇₇₄ N ₂₀ O ₁₆₁ P ₁₂ S ₄₈ Cl ₂ K ₂ Co ₄₈
formula mass (amu)	8051.51	15502.09
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	21.6989(3)	22.8996(4)
<i>b</i> (Å)	22.0322(5)	24.2213(3)
<i>c</i> (Å)	23.5087(4)	34.9910(5)
α (deg)	105.718(2)	78.6500(10)
β (deg)	103.2130(10)	75.7330(10)
γ (deg)	115.237(2)	70.7830(10)
<i>V</i> (Å ³)	8989.6(3)	17618.9(5)
<i>Z</i>	1	1
temp (K)	100(2)	100(2)
wavelength (Å)	1.54184	1.54184
<i>D_c</i> (Mg/m ³)	1.4870	1.4608
<i>R_{int}</i>	0.0481	0.0947
no. of data collected	99627	123955
no. of unique data	33982	62870
no. of params	1656	3594
GOF	1.081	0.983
<i>R</i> 1 (<i>I</i> > 2σ(<i>I</i>)) ^a	0.0508	0.0866
<i>wR</i> 2 ^b	0.1313	0.2180

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

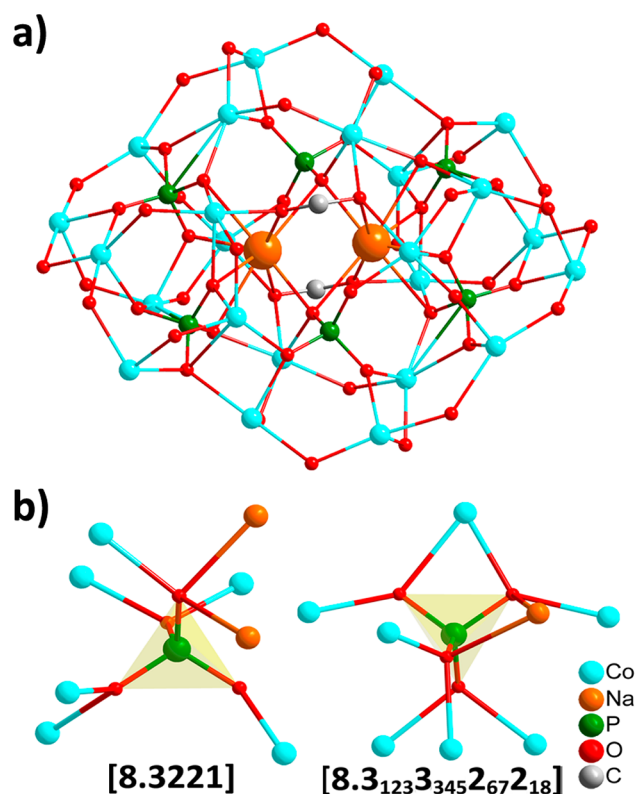


Figure 2. (a) Na@Co₂₄ cluster. For clarity, only the bridge atoms and Co^{II} and Na⁺ cations are shown. (b) Coordination modes of phosphate anions within 1 indicated by the Harris notation.

coordinated in a distorted-trigonal-bipyramidal SO₄ coordination environment, Co1 and Co6 are six-coordinated in a distorted-octahedral NSO₄ environment, and the nine remaining cobalt centers are also six-coordinated but are in a distorted-octahedral SO₅ environment (Figures S2 and S3 in the

Supporting Information). Notably, six PO₄^{3−} anions in 1 show two kinds of modes: two with a [8.3221] coordination mode, while the remaining anions have the [8.3₁₂₃3₃₄₅2₆₇2₁₈] mode according to the Harris notation (Figure 2b).¹⁹ Moreover, the dma molecules and HCOO[−] and DMC[−] anions in this structure are generated from in situ reactions of DMF molecules under the solvothermal conditions.^{15h,20} In the crystal packing, compound 1 shows a skewed bilayer structure packed up by Na₂Co₂₄ clusters via supramolecular stacking interactions, including van der Waals, C–H⋯π, and hydrogen bond interactions (Figure S4, Supporting Information). The voids of the lattice are occupied with isolated CH₃OH and DMF molecules.

For compound 2, structural analysis reveals that there is an obvious geometrical change in the arrangement of cobalt ions on moving from an oval-shaped disklike core in 1 to a circular core in 2, because the two template Na⁺ ions have been replaced by one K⁺ (Figure 3a and Figure S5 (Supporting Information)). An X-ray diffraction study of 2 shows that it is also in the triclinic crystal space group $P\bar{1}$ but in a larger unit cell, and there are 24 crystallographically independent cobalt and 2 potassium ions in its asymmetric unit. However, different from the case for compound 1 containing only neutral Na₂Co₂₄ clusters, compound 2 contains both anionic and cationic KCo₂₄ clusters. These two clusters are structurally analogous, and the primary differences are in the number of ligated HCOO[−] anions; thus only the cationic cluster is described as a representative henceforth. Within the cationic KCo₂₄ part, 2 chlorine anions and 12 oxygen atoms from 6 different PO₄^{3−} anions form the coordination sphere of the potassium ion, with the Cl–K distance being 2.871 Å and K⋯O distances ranging from 3.256 to 3.347 Å. All of the cobalt ions (Co1–Co12) are six-coordinated in a distorted-octahedral coordination environment, and they can be divided into two different types with Co1, Co4, and Co9 being in ClO₅ spheres, whereas the nine remaining cobalt centers are in O₆ spheres (Figures S6 and S7,

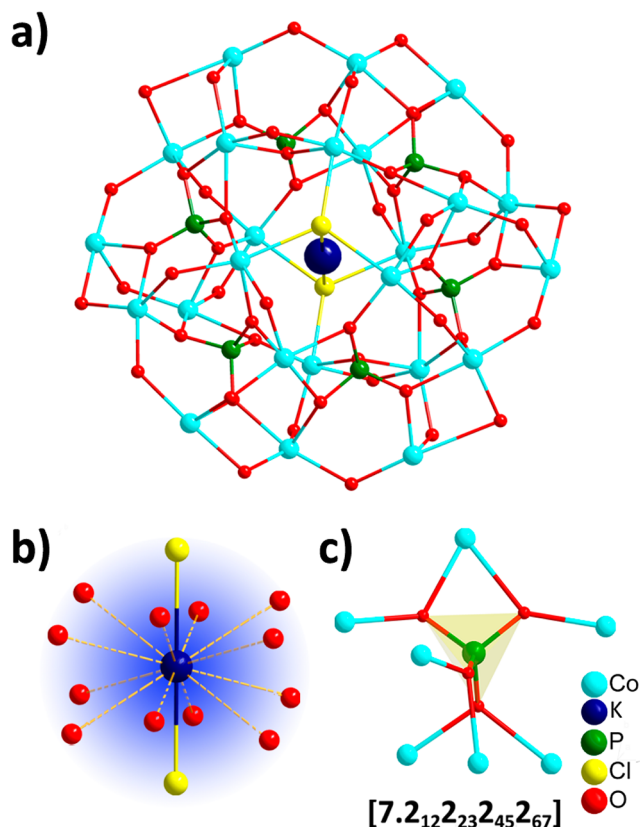


Figure 3. (a) K@Co_{24} cluster. $[\text{K@Co}_{24}]^+$ and $[\text{K@Co}_{24}]^-$ are structurally analogous; for clarity, here only $[\text{K@Co}_{24}]^+$ is provided as a generic description and only the bridge atoms and Co^{II} , Na^+ , and K^+ cations are shown. (b) Coordination environments of potassium and cobalt ions in **2**. (c) Coordination modes of phosphate anions within **2**.

Supporting Information). It should be noted that the yield we found of **2** was extremely low in the beginning, which may arise from unexpected chloride anions in this cluster resulting from the decomposition of chloroform under solvothermal situations.^{9a} However, enhancement of the synthetic yield can be obtained by directly employing KCl as the source of chloride anions. Moreover, all of the PO_4^{3-} anions bind to seven cobalt cations in a chelating mode [7.21223245267] (Figure 3c), which are distinct from those in **1**. Very recently, a polynuclear cobalt salt, $[\{\text{Co}_{14}(\text{ThiaSO}_2)_3(\mu_4\text{-OH})_3(\mu_6\text{-O})_3(\text{OCH}_3)_6\}^+\{\text{Co}_4(\text{ThiaSO}_2)_2(\mu_4\text{-OH})\}^-]$, based on *p*-tert-butylsulfonycalix[4]arene ($\text{H}_4\text{ThiaSO}_2$) was obtained, representing the first example of a cobalt aggregate salt reported in a one-pot reaction.^{14f} However, compound **2** comprises both cationic and anionic KCo_{24} clusters, and thus it represents the largest cobalt aggregate salt. Examination of the extended structure reveals that compound **2** exhibits a layer structure constructed by KCo_{24} entities in an ABAB... fashion through supramolecular interactions (Figure S8, Supporting Information), which is distinct from the skewed bilayer arrangement of **1** for the coexistence of two kinds of KCo_{24} cores.

To further analyze the influence of the templated alkali metal on eicositetranuclear Co_{24} core configurations, a closer observation of the environments of templated cations as can be seen from Figure 4. In the center core of **1**, the distinctly shorter $\text{Na}\cdots\text{Na}$ distance (Na1 and its symmetry equivalent Na1A) of 3.059 Å reveals an attractive interaction (3.82 Å in

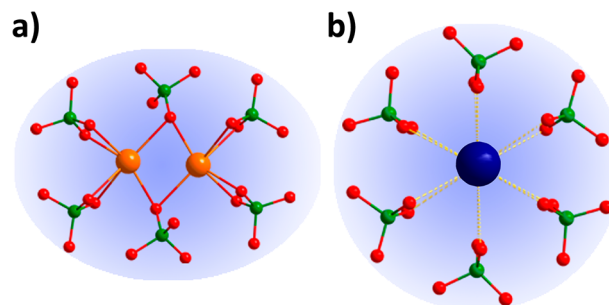


Figure 4. Environment of alkali-metal cations with phosphate ligands in **1** (a) and in **2** (b).

elemental Na),²¹ and six PO_4^{3-} anions with two different chelating modes bridge to these two sodium ions and are arranged in an oval shape. Unlike the case for **1**, six PO_4^{3-} anions with the same coordination mode connect to one larger radius potassium ion via weak interactions and are arranged in a circular shape in **2**. In addition, each PO_4^{3-} anion acts as a cork base of a $\text{Co}_4\text{-BTC4A}$ MBB, which further leads to differences between the geometries of the Co_{24} cores in compounds **1** and **2**. To sum up, the alkali-metal ions affect the arrangements of phosphonate ligands, which further influence the geometries of the Co_{24} cores. Moreover, the $\text{Co}_4\text{-BTC4A}$ MBB whose cork base is capped by one PO_4^{3-} anion in compound **1** and **2** is distinct from the reported $\text{TM}_4\text{-calix[4]arene}$ MBBs, in which OH^- , Cl^- , and CO_3^{2-} anions act as the cork base.^{15a,c} Very recently, our group has reported a anionic octahedral Co_{24} nanocage also constructed by $\text{Co}_4\text{-TBC4A}$ MBBs and PO_4^{3-} linkers, but it comprises eight PO_4^{3-} anions which bind to six cobalt cations by three donor oxygen atoms and adopt the [6.2220] coordination mode.^{15a} It should be noted that these two Co_{24} clusters encapsulate alkali-metal ions within their centers and have no ports, which are different from the reported Co_{24} nanocages linked by ditopic or tritopic aromatic carboxylic acids with larger inner cavities and ports.²² In addition, they also differ from the large Co_{24} metallamacrocycle with triazole ligands.¹²

Magnetic Properties. Magnetic susceptibilities data for compounds **1** and **2** have been measured over 2–300 K with an applied 1000 Oe direct current magnetic field, as depicted in Figure 5. At 300 K, the $\chi_{\text{M}}T$ values for **1** and **2** are 67.63 and 129.62 $\text{cm}^3 \text{K mol}^{-1}$, respectively, which are much higher than

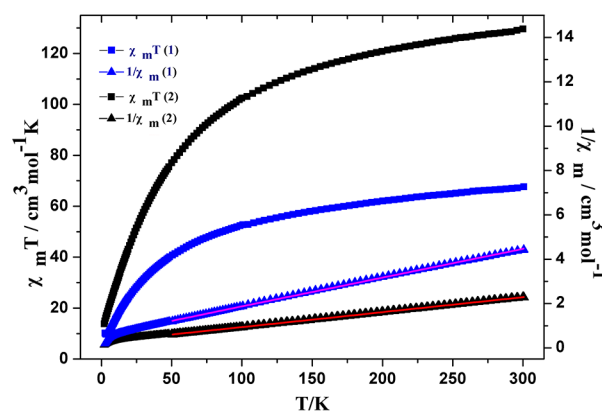


Figure 5. Temperature dependence of $\chi_{\text{M}}T$ and χ_{M}^{-1} for compounds **1** and **2** in a 1 kOe field. The solid purple and red lines represent the best fits of the experimental data of **1** and **2**, respectively.

the expected values (calculated values of 45.00 and 90.00 cm³ K mol⁻¹ for 24 and 48 uncoupled Co(II) ions, respectively), suggesting significant orbital contributions of the Co^{II} centers in an octahedral field.²³ Upon cooling, both of the $\chi_M T$ curves continuously decrease from 300 to 50 K and then fall rapidly to 10.18 and 13.82 cm³ K mol⁻¹ at 2 K for **1** and **2**, respectively. The reciprocal molar magnetic susceptibility (χ_M^{-1}) data above 50 K versus temperature obeys the Curie–Weiss law, giving the Curie constant $C = 77.04$ and 148.80 cm³ mol⁻¹ K and Weiss constants $\Theta = -46.80$ and -46.09 for **1** and **2**, respectively. The negative Weiss constants as well as the trend of $\chi_M T$ vs T data may be due to the intracluster antiferromagnetic interactions and/or the spin–orbit coupling effect of Co^{II} spin carriers within the Co₂₄ cores. Moreover, there is no obvious hysteresis loop as well as frequency-dependent peaks of out-of-phase susceptibility signals for both title compounds (Figures S9–S12, Supporting Information). These results reveal that neither compound shows single-molecule magnet behavior. Moreover, it is not possible to further evaluate the coupling parameters between the Co^{II} ions, because of the complicated structures of both compounds.

CONCLUSION

In conclusion, we have successfully obtained and structurally characterized two novel thiacalix[4]arene-based high-nuclearity cobalt clusters, both of which are templated by alkali-metal ions. Specifically, compound **1** is templated by two Na⁺ cations with an attractive interaction in the center of the core, while **2** is templated by the larger radius cation K⁺. This leads to obvious structural changes in the magnetic cores, moving from an oval-shaped disklike core in **1** to a circular core in **2**. Moreover, compound **2** consists of both anionic and cationic KCo₂₄ cores, representing the largest cobalt aggregate salt reported to the best of our knowledge. Studies exploring other multiply charged metal cations as structure-directing templates are under way.

ASSOCIATED CONTENT

Supporting Information

Figures and CIF files giving field dependences of magnetization data, ac susceptibility magnetic data, TGA curves, PXRD and X-ray crystallographic data for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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