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Three *p-tert*-Butylthiacalix[4]arene-Supported Cobalt Compounds Obtained in One Pot Involving In Situ Formation of N_6H_2 Ligand

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Three *p-tert*-butylthiacalix[4]arene (H_4TC4A)-supported Co^{II} compounds, $[Co_4(TC4A)(N_3)_4(N_6H_2)(CH_3OH)](CH_3OH)_2$ (**1**), $[Co_8(TC4A)_2(N_3)_2(N_6H_2)_2(CH_3COO)_4(CH_3OH)_4](OH)_2(CH_3OH)_4$ (**2**), and $[Co_{10}(TC4A)_4(N_3)_4](CH_3OH)_4$ (**3**), have been solvothermally obtained in one pot and structurally characterized by single-crystal X-ray diffraction analyses, powder XRD, and IR spectroscopy. This work presents the first one-dimensional (**1**) cobalt cluster for the calixarene complexes and another two octanuclear (**2**) or decanuclear (**3**) cobalt clusters. In the structures of compounds **1** and **2**, a novel N_6H_2 ligand formed by the in situ (2 + 3) cycloaddition of two azides was observed. Density functional theory (DFT) calculations give the heat of formation ($2N_3^- + 2H^+ \rightarrow N_6H_2$) and decomposition energy ($N_6H_2 \rightarrow 3N_2 + H_2$) of 677.47 and 124.85 kcal/mol, respectively. Furthermore, an intergradation was determined at the B3LYP/6-311++g(d,p) level for the formation of the N_6H_2 ligand. In addition, one TC4A ligand of a sandwich unit adopts a cone conformation, while the other adopts a pinched cone conformation in **3**. The magnetic properties of these three compounds were influenced mainly by the orbital contributions of the distorted octahedral Co^{II} ions.

Introduction

High-nuclearity metal cluster magnets have become one of the most active fields in coordination chemistry and materials chemistry.[1−3] Notedly, the metal cluster compounds with both magnetism and other properties, such as optical/nonlinear optical property,[4] porosity,[5] and conductivity,[6] have attracted increasing interest. Such complexes can be rationally synthesized by using the multidentate ligands, and the synthetic strategies can be further ameliorated by the judiciously chosen ancillary ligands.[7] *p-tert*-Butylthiacalix[4]arene (H_4TC4A, Scheme 1), as a macrocyclic multidentate ligand[8] possessing four phenoxyl groups and four bridge sulfur atoms, has been proven to be a good candidate for constructing polynuclear complexes.[9] Recently, a series of low-nuclearity complexes with the featured M_x cores (commonly, $x = 1-4$) bonded at the lower rim of calixarene or sandwiched between two calixarenes have been reported by us and others.[9−13] In these structures, some small molecules or anions, such as

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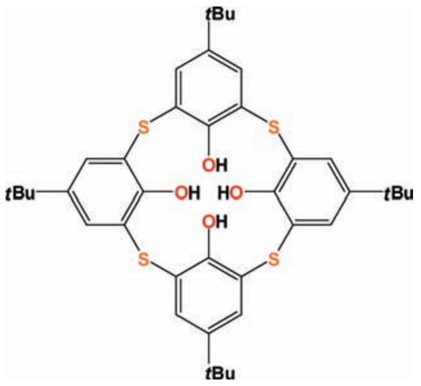
Scheme 1



water, methanol, μ−OH$^-$, chloride anion, acetate, and so on, were found to act as the terminal ligands. It is possible that the structurally well-defined high-nuclearity species might be obtained if these terminal ligands were substituted by some bridging ligands. As recently reviewed by Gao and Bu,[14] azide exhibits diverse coordination mode (terminal or bridge) to the metals and provides superexchange pathways for magnetic couplings among metal spin centers. So azide might be a proper ancillary ligand in constructing high-nuclearity compounds involving *p-tert*-butylthiacalix[4]arene-based low-nuclearity clusters. Furthermore, azide would process in situ (2 + 3) cycloaddition with organic nitriles in the presence of transition-metal ions under solvothermal or hydrothermal conditions to form novel coordination compounds that are inaccessible or not easily obtainable by conventional methods,[15,16] which arouses more experimental and theoretical interests in nitrogen-rich compounds termed as high-energy density materials (HEDM).[17]

Recently, we successfully synthesized a series of polynuclear compounds such as tetranuclear $\{Mn^{II}{}_2Gd^{III}{}_2\}$,[13b] hexanuclear $\{Mn^{II}{}_2Ln^{III}{}_4\}$ (Ln = Gd, Eu),[18] and two-dimensional Cu(I)[13c] complexes with H_4TC4A or its derivatives. We also obtained three isomers of a $\{Co_{24}{}^{II}Co^{III}{}_8\}$ nanosphere compound with H_4TC4A.[13a] As an extension of our previous work on constructing the metal clusters with calixarenes, we present herein the preparation, structures, and magnetic properties of three Co^{II} compounds, namely, $[Co_4(TC4A)(N_3)_4(N_6H_2)(CH_3OH)](CH_3OH)_2$ (**1**), $[Co_8(TC4A)_2(N_3)_2(N_6H_2)_2(CH_3COO)_4(CH_3OH)_4](OH)_2(CH_3OH)_4$ (**2**), and $[Co_{10}(TC4A)_4(N_3)_4](CH_3OH)_4$ (**3**). The formation of **1** and **2** involves in situ N_6H_2 ligand formation, which was confirmed by X-ray diffraction analysis, charge balance consideration, and IR spectra. Density functional theory (DFT) calculation was also performed on the N_6H_2 ligand, indicating that N_6H_2 molecule might be a potential high-energy density material.

Experimental Section

Materials and Measurements. *p-tert*-Butyltetrathiacalix[4]arene was synthesized by literature method,[19] and other reagents were purchased from commercial sources and used as received. IR spectra (KBr pellets) were taken on a Bruker Vertex 70 spectrometer. The powder X-ray diffraction (XRD) data were recorded on a Bruker D8 Advance diffractometer. TG measurement was performed on a NETZSCH STA449-F3 JUPITER. Magnetic susceptibility measurements for **1**−**3** were performed on a Quantum Design MPMS XL-7 SQUID system in the temperature range of 2−300 K. Diamagnetic corrections for the sample and sample holder were applied to the data.

Preparation of Compounds 1−**3.** ***Caution!*** *Although we did not experience any problems in the present work, azide complexes are potentially explosive. Only a small amount of material should be prepared and handled with care. All experiments were performed in an isolated room and guarded with protective equipments.*

Single crystals of **1**−**3** were obtained from a reaction of the mixture of *p-tert*-butylthiacalix[4]arene (0.09 g, 0.13 mmol), $Co(CH_3COO)_2\cdot 4H_2O$ (0.1 g, 0.4 mmol), NaN_3 (0.065 g, 1 mmol), CH_3OH (10 mL), and several drops of water in a 20 mL Teflon-lined autoclave which was kept at 130 °C for 3 days and then slowly cooled to 20 °C at about 4 °C/h. The crystals were isolated by filtration and then washed with methanol and chloroform. Compounds **1**−**3** are separated manually in methanol solution under a microscope for experiments. Yield: ca. 25% for **1** (red, prism), 5% for **2** (orange, cuboid), and 45% for **3** (celadon, block) with respect to H_4TC4A (based on a successful trial). All three compounds are stable in methanol and/or chloroform solutions. They can lose solvent molecules easily in air but remain crystalline according to the results of TG and XRD measurements. The result of the elemental analysis for these three compounds deviated much from the calculated values due to easy loss of the involved solvent molecules in the lattices.

The powder XRD patterns were recorded for **1** and **3** to confirm the purity of the obtained samples. Thermal gravimetric analyses (TGA) were also carried out to examine the thermal stability of **1** and **3** (see Supporting Information). EDS analysis of Co and S reveals that the molar ratios of Co/S are 5.55:5.48 for **1**, 10.01:10.10 for **2**, and 7.73:12.60 for **3**, comparable to the expected 4: 4, 8:8, and 10:16 obtained by X-ray determinations, respectively.

X-ray Crystallographic Analysis. 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 F^2 (SHELXTL-97).[20] All non-hydrogen atoms were refined anisotropically except some 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 solvent molecules cannot be generated and were included in the molecular formula directly. In addition, the high R_1 and wR_2 factor of compounds **1**−**3** might be due to the weak high-angle diffractions and the disorder. All of the crystal data and structure refinement details

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Table 1. Crystallographic Data for Compounds **1**−**3**

	1	**2**	**3**
formula	$C_{43}H_{58}Co_4N_{18}O_7S_4$	$C_{96}H_{134}Co_8N_{18}O_{26}S_8$	$C_{164}H_{192}Co_{10}N_{12}O_{20}S_{16}$
formula wt	1303.03	2684.13	3753.56
cryst. syst.	monoclinic	orthorhombic	triclinic
space group	*C*2/*c*	*Fmm*2	$P\bar{1}$
a (Å)	33.735(1)	21.0575(8)	13.9395(4)
b (Å)	19.1376(7)	43.512(2)	18.7983(6)
c (Å)	18.1344(6)	12.9662(5)	19.7210(6)
α (°)	90	90	65.54
β (°)	109.388(1)	90	73.631(1)
γ (°)	90	90	70.897(1)
V (Å ^{3})	11043.8(7)	11880.4(8)	4379.9(2)
Z	8	4	1
D_c/g cm^{-3}	1.567	1.501	1.423
μ/mm^{-1}	1.397	1.304	1.176
F(000)	5360	5552	1946
total data	39183	21110	42060
unique data	9738	5478	15388
R_{int}	0.0343	0.0301	0.0236
GOF	1.09	1.06	1.04
$R1^a$ [$I > 2\sigma(I)$]	0.0681	0.0488	0.0456
$wR2^b$(all data)	0.2354	0.1432	0.1439

$^a R1 = \sum||F_0| - |F_c||/\Sigma|F_0|$. $^b wR2 = \{\sum[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$.

for these three compounds are given in Table 1. CCDC reference numbers are 764071−764073 for **1**−**3**, respectively.

Results and Discussion

Syntheses. The title compounds were obtained solvothermally in one pot at 130 °C over 3 days from the mixture of $Co(CH_3COO)_2 \cdot 4H_2O$, H_4TC4A, and NaN_3 in a ratio of 4:1.25:10 in CH_3OH solutions with several drops of water. With the decreasing amount of NaN_3, only **1** and **3** can be obtained within a same batch when the molar ratio of NaN_3 to Co is more than 4:4. If the amount of NaN_3 decreases further, only compound **3** was isolated. **1** and **3** also can be obtained by replacing $Co(CH_3COO)_2 \cdot 4H_2O$ with $CoCl_2 \cdot 6H_2O$. In addition, if the acetate salts were replaced with the sulfate or nitrate, only **3** can be obtained. However, we cannot obtain onefold **1** or **2** from a similar experiment. To be pointed out, the formation of **2** is indeterminate, and we cannot make sure it will form or not in an experiment. Though the further increase of the amount of NaN_3 might be helpful to the formation of **2**, we did not make this attempt for safety considerations.

Crystal Structures. All three extended structures are stacked by some sandwich-like bicalixarene units, and azide is involved in all of these compounds. Analysis of the bond lengths (Table S1 in the Supporting Information), charge balance, and bond valence sum calculations (BVS) suggests that all of the cobalt ions in the title compounds are divalent. Compounds **1** and **2** are unprecedented due to both the longer distance between two calixarenes in a bicalixarene unit,[21] which is different from those in most reported sandwich-like units,[9] and the in situ formed N_6H_2 ligands. To be noted, compound **1** presents the first example with the one-dimensional azide-linking bicalixarene chains. In situ formation of the N_6H_2 ligands in compounds **1** and **2** was confirmed by X-ray diffraction and IR spectra (with the characteristic N−H vibrations of the $-NH_2$ group; see Figure S1). It can be thought as the (2 + 3) cycloaddition of two azide molecules, which might be similar to the (2 + 3) cycloaddition of azide with organic nitriles,[15,16] but has not been reported before. As shown in Figure 1, the coordination mode of the N_6H_2 ligand can be termed as Harris notation 4.111100.[22] The azide ligand adopts three coordination modes in **1** (Harris notation: 1.100, 2.101/EE, and 2.200/EO), one in **2** (Harris notation: 2.200/EE), and two in **3** (Harris notation: 2.200/EE and 1.100). It is not common that three coordination modes of azide occurred in one structure.[14]

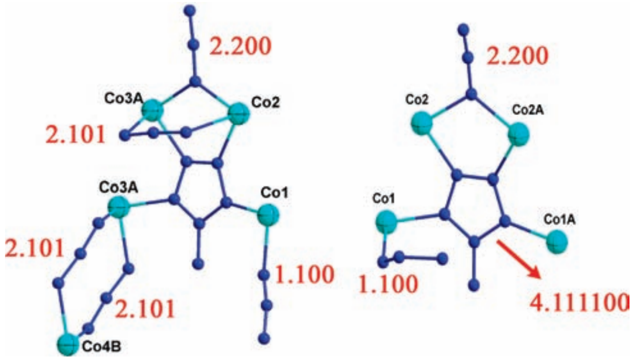

Figure 1. Coordination of azide ligands in compounds **1** (left) and **2** (right). Symmetry codes: (A) −*x*, *y*, 0.5 − *z*; (B) *x*, −*y*, −0.5 + *z* for **1**; (A) *x*, 1 − *y*, *z* for **2**.

Compound **1** crystallizes in a monoclinic system with space group *C*2/*c*. Figure 2a shows a cobalt octanuclear dumbbell unit of compound **1**. Because there is a crystallographic two-fold axis for this octanuclear unit, the

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(22) Harris notation describes the binding mode as [X.Y1Y2Y3...Yn], where X is the overall number of metals bound by the whole ligand, and each value of Y refers to the number of metal atoms attached to the different donor atoms. The ordering of Y is listed by the Cahn−Ingold−Prelog priority rules. For details, see: Coxall, R. A.; Harris, S. G.; Henderson, D. K.; Parsons, S.; Tasker, P. A.; Winpenny, R. E. P. *J. Chem. Soc., Dalton Trans.* **2000**, 2349.

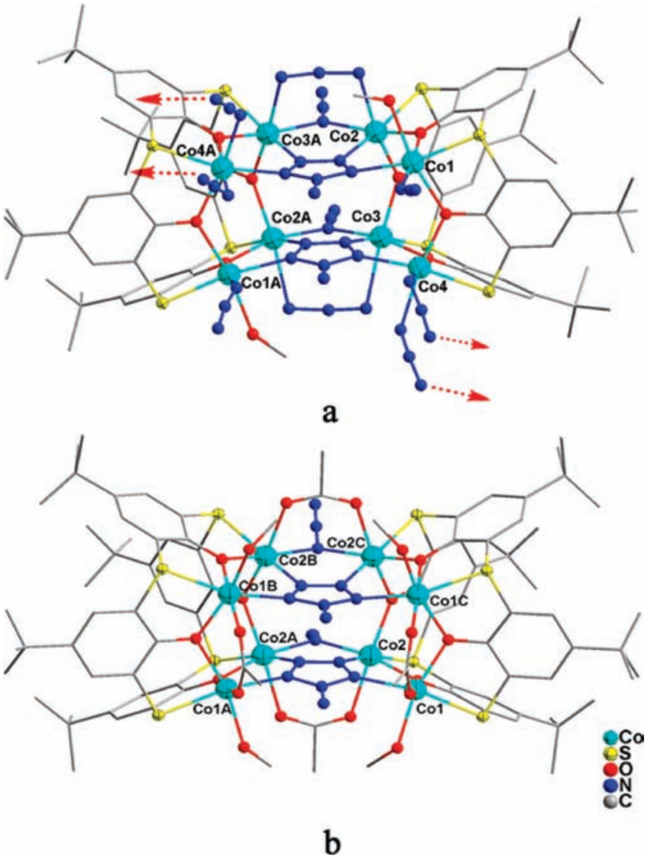

Figure 2. Molecular structures of **1** (a) and **2** (b). Symmetry codes: (A) $-x, y, 0.5 - z$ for **1**; (A) $x, 1 - y, z$; (B) $1 - x, 1 - y, z$; (C) $1 - x, y, z$ for **2**. The hydrogen atoms and isolated solvent molecules are omitted for clarity.

asymmetry unit should be half of the octanuclear unit; that is, there are four different crystallographic Co^{II} sites (namely, Co1−Co4). Except one sulfur atom and two phenoxyl oxygen atoms, the six-coordinated Co^{II} sites are also coordinated by three nitrogen atoms for Co3 and Co4 while two nitrogen atoms and one methanol oxygen atom for Co1 and Co2. The TC4A ligand adopts a cone conformation and captures four Co^{II} atoms by four phenoxyl oxygen atoms and four bridging sulfur atoms at the low rim as in other TC4A compounds. Eight cobalt atoms are bridged by some azide ligands and N_6H_2 entries into an octanuclear unit. Then, two pairs of azide ligands with 2.101/EE mode (shown with the arrows in Figure 2a) connected the octanuclear units into some 1D infinite chains along the *c* axis (Figure 3). Each chain is surrounded by six chains, and the chains are stacked by supramolecular interactions into a 3D extended structure (Figure S4).

Compound **2** crystallizes in an orthorhombic system with space group *Fmm*2. The crystal structure of compound **2** is stacked by some isolated octanuclear units whose coordination environment is similar to those in **1** except that four azides with 2.101/EE mode are replaced by four acetate molecules. Complex **2** has a crystallographic four-fold axis, so that there are two independent crystallographic Co^{II} sites in each asymmetry unit. Both Co1 and Co2 are six-coordinated by three nitrogen atoms and three oxygen atoms forming distorted octahedron geometry. Each octanuclear unit is surrounded by six others with the nearest Co···Co distance between two adjacent units of ca. 7.71 Å and interconnected by the C−H···O/N hydrogen bonds (ca. 2.71/2.65 Å) to form a two-dimensional layer (Figure S5). These supramolecular layers are stacked along the *b* axis to form an extended structure (Figure S6).

The crystal structure of compound **3** is made up of neutral, centrosymmetrical decanuclear Co^{II} moieties which are constructed by two pentanuclear sandwich-like $[Co^{II}_5(TC4A)_2(N_3)_2]$ units bridged by a pairs of azide ligands with 2.200/EE mode (Figure 4). The coordination of TC4A is drastically different from that found in the structures of **1** and **2** but is quite similar to that in $[Fe_{10}(TC4A)_4Cl_4]$ compound reported by Luneau et al.,[11f] except that the chloride ions are replaced by azides. In compounds **1** and **2**, each TC4A ligand bonds four Co^{II} ions by its four μ_2-oxygen phenoxy atoms and four bridging sulfur atoms to form a shuttlecock subunit, and then two shuttlecock subunits are interconnected by the azide ligands and a N_6H_2 entity to form an octanuclear unit. In this case, two TC4A molecules in one sandwich unit stagger from each other and bond five same metal centers. Then, two pentanuclear sandwich-like units are bridged by two azides to form a decanuclear unit. There are five crystallographic independent Co^{II} sites. Among them, the six-coordinated sites Co1, Co3, and Co4 are bonded by three μ_2-oxygens, one μ_3-oxygen, and two sulfur atoms while the Co2 site by two μ_2-oxygens, one μ_3-oxygen, one sulfur, and two nitrogen atoms. The five-coordinated Co5 adopts a distorted pyramidal geometry bonded by two μ_2-oxygens, one μ_3-oxygen, one sulfur atom, and one azide with 1.100 mode. Although both TC4A ligands in one pentanuclear sandwich-like unit adopt cone conformation, they are different from each other; that is, one adopts an approximately symmetrical cone conformation (with two oppositely oriented $C_{butyl}\cdots C_{butyl}$ distances of 9.40 and 9.74 Å and the dihedral angles between the opposite aromatic rings being 52.20 and 57.04°), while the other adopts a pinched cone conformation (with $C_{butyl}\cdots C_{butyl}$ distances of 5.69 and 12.01 Å; the dihedral angles being 8.07 and 89.32°). Two different conformations of TC4A ligands were also observed for one sandwich unit in a tetranuclear $\{Mn^{II}_2Gd^{III}_2\}$ compound.[13b]

DFT Calculations. Polynitrogen molecules would be the possible candidates for high-energy density materials (HEDM).[17,23] Although there have been numbers of theoretical and experimental studies on N_x molecules, N_6 isomer has not been found with a five-membered circular ring and a $-NH_2$ group so far.[23] Herein, all theoretical calculations were performed with Gaussian 03 employing Becke's three-parameter using Lee−Yang−Parr functionals (B3LYP) with the 6-311++g(d,p) basis set. DFT calculations on the optimized N_6H_2 models derived from the crystallographic data of **1** revealed that the electronic energy (Hartrees), polarizability, heat of formation ($2N_3^- + 2H^+ \rightarrow N_6H_2$, kcal/mol), and decomposition energy

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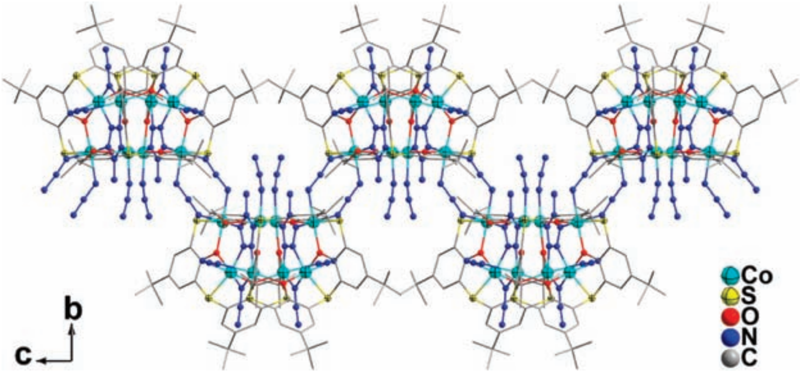

Figure 3. View of a one-dimensional (1D) chain in **1**.

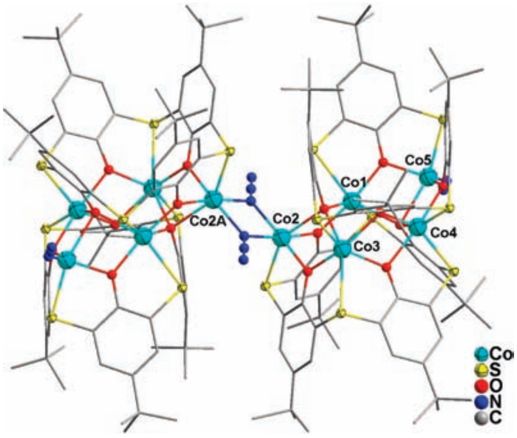

Figure 4. Molecular structure of compound **3.** Symmetry code: (A) $-x$, $1 - y$, $1 - z$.

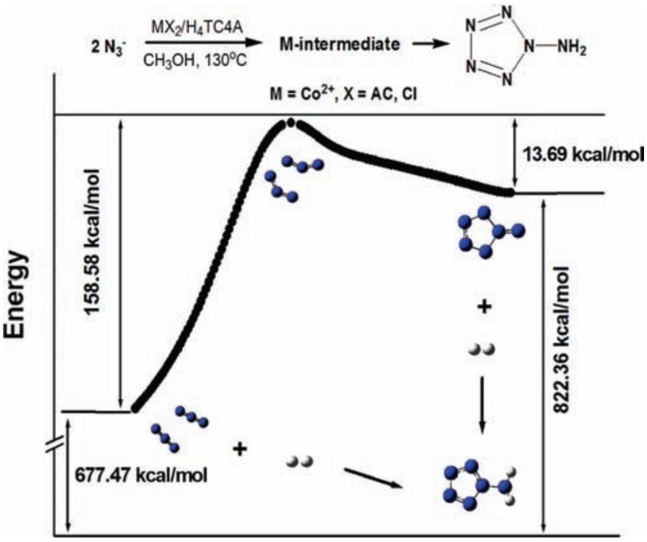

Figure 5. Schematic representation of the possible reaction mechanism of N_6H_2 formation showing energy differences (enthalpy) between $2N^{3-}$, intergradation, N_6^{2-}, and N_6H_2 entities; zero-point correction and thermal correction are applied to the obtained data.

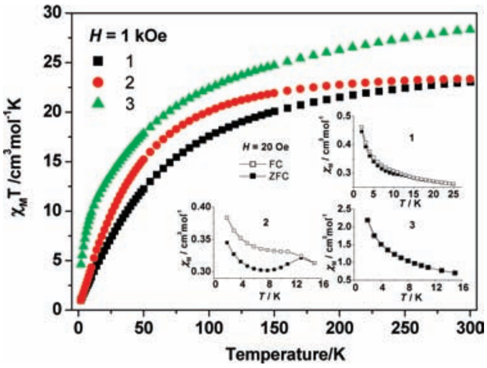

Figure 6. Plots of $\chi_M T$ vs T for compounds **1**−**3**. Inset: ZFC−FC plots of **1**−**3** at 20 Oe.

($N_6H_2 \rightarrow 3N_2 + H_2$, kcal/mol) are −329.68, 44.07, 677.47, and 124.85, respectively. These values are compatible with those for other N_6 isomers termed as HEDMs, which indicates that the N_6H_2 molecule might be another potential HEDM. Furthermore, a peak at ca. 1633 cm^{-1} found in the experimental IR spectra (both of **1** and **2**) is correlated to the calculated frequency (1668 cm^{-1}) of the typical N−H vibration. Moreover, all nitrogen atoms in the N_6H_2 entity form N−N bonds in the range of 1.31−1.34 Å in **1** and 1.32−1.38 Å in **2** (structure determination) that are consistent with the calculated ones (1.31−1.39 Å). These observations further demonstrated the correct assignment of the N_6H_2 molecule as illustrated by X-ray analysis. A possible formation mechanism of the N_6H_2 molecule can be depicted, as shown in Figure 5, according to Sharpless's results[15] and the DFT calculations. The reaction mechanism can be described as follows: two azide ions react with each other to form an intergradation (N_6^{2-} ion) by the (2 + 3) cycloaddition; N_6^{2-} ion reacts with two H^+ (from the deprotonation of H_4TC4A) to achieve the N_6H_2 molecule. Co^{II} ions may play an important role in stabilizing the intergradation and favor the N_6H_2 formation. Although the N_6H_2 molecules have not been isolated for further investigations, such studies might shed light on the design and synthesis of novel polynitrogen high-energy density materials with azide.

Magnetic Properties. Magnetic susceptibility measurements were carried out on polycrystalline samples of compounds **1**−**3** over 2−300 K and with a 1000 Oe applied field (Figure 6). The $\chi_M T$ values at 300 K are 23.04, 23.34, and 28.34 $cm^3\ mol^{-1}$ K for compounds **1**−**3**, respectively, which are much larger than the spin-only value of 8 (15.0 $cm^3\ mol^{-1}$ K) or 10 (18.7 $cm^3\ mol^{-1}$ K) isolated high-spin d^7 ions, indicating significant orbital contributions of the distorted octahedral Co^{II} ions. The experimental $\chi_M T$ values (per Co^{II} center) at room temperature are 2.88, 2.92, and 2.83 $cm^3\ mol^{-1}$ K for **1**−**3**, respectively, which

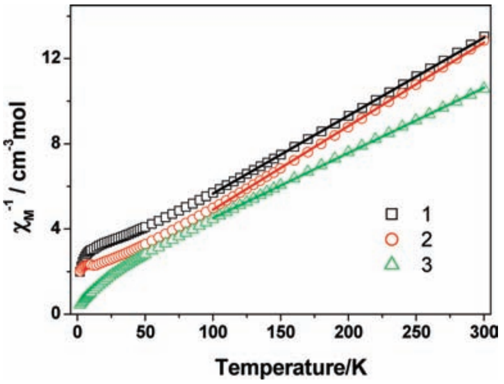

Figure 7. Plots of $1/\chi_M$ vs T for compound **1**−**3**. Solid lines represent the Curie−Weiss fitting.

are consistent with the typical value of Co^{II} ion (for Co^{II}, $\chi_M T$ value normally ranges from 2.7 to 3.4 cm^3 mol^{-1} K). As described above, all of the Co^{II} sites in compounds **1**−**3**, except Co5 in **3** (which exhibits a distorted pyramidal coordination), are in an octahedral environment. Generally, a six-coordinated Co^{II} ion in an octahedral geometry presents a high-spin state.[24] That is, the high-spin state of the Co^{II} ions, except Co5 in **3**, can be roughly ascertained. The $\chi_M T$ value at room temperature for **3** (for per Co^{II} ions) is lower than those for **1** and **2**. If the Co5 site is assigned to the uncoupled low-spin cobalt atom ($S = 1/2$), the experimental $\chi_M T$ value per high-spin Co^{II} ion would be $(28.34-1.87 \times 2)/8 = 3.07$ cm^3 mol^{-1} K, which is also consistent with the typical Co^{II} ion in an octahedral field ($^4T_{1g}$ ground state). So the spin state of the Co5 center in **3** cannot be properly determined with the obtained magnetic data. Any reported models for the Co cluster would be abrupt for further calcucaltions. The $\chi_M T$ values decrease continuously and fall rapidly in the lower temperature region for all three compounds. Fitting the experimental data ranging from 100 to 300 K to Curie−Weiss law gives Curie constants (C) of 27.19, 25.27, and 32.82 cm^3 mol^{-1} K and Weiss constants (θ) of −54.45, −24.80, and −47.52 K for **1**−**3**, respectively (Figure 7). The divergence between the ZFC and FC magnetizations of **1** and **2** can be caused by spin glasses, superparamagnetism, magnetic anisotropy, or other effects. Unfortunately, it is more complicated, and we cannot determine the reason with the present magnetic data.

We also investigated the variation of the magnetization M with the applied magnetic field H for **1**−**3** in the range of 0−50 kOe at 2 K (Figure 8). The magnetization increases linearly to 3.11 and 3.69 Nβ per Co^{II}_8 unit at 50 kOe for **1** and **2**, respectively, far from the saturation sum values of eight Co^{II} ions. The $M-H$ plot of **3** shows a gradual increase with H, and the magnetization is 9.61 Nβ at 50 kOe, still lower than the saturation value of 10 Co^{II} ions. No obvious hysteresis loops are observed for all three compounds. Such magnetic properties of these three compounds might be mainly attributed to the orbital contributions of the distorted octahedral Co^{II} ions.[24]

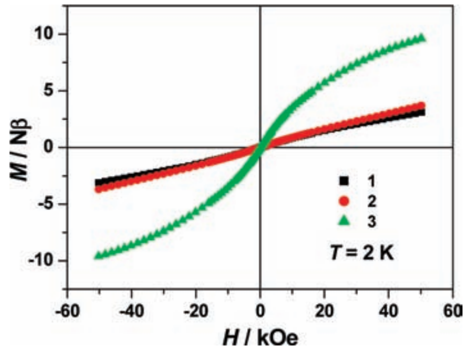

Figure 8. Field dependency of magnetization of **1**−**3** at 2 K.

Conclusions

Three *p*-*tert*-butyltetrathiacalix[4]arene-based cobalt compounds have been solvothermally obtained in the presence of a co-chelant azide and structurally determined, which added new cobalt cluster compounds to the high-nuclearity compounds of *p*-*tert*-butylthiacalix[4]arene. To be pointed out, the first one-dimensional (1D) metal cluster was observed for the thiacalix[4]arene compounds, and a novel N_6H_2 ligand was formed in situ. This work also demonstrated that small ancillary ligands play a crucial role in constructing the high-nuclearity compounds by separating shuttlecock-like building units to a proper distance. In addition, the in situ formed N_6H_2 ligand may shed light on the design and synthesis of some polynitrogen high-energy density materials. The efforts to prepare polynuclear compounds with other metals or other co-chelate ligands are ongoing.

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Supporting Information Available: Crystallographic data in CIF, IR spectra, powder XRD patterns, TGA/DTA curves, additional figures, and other materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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[24] Orchard, A. F. *Magnetochemistry*; Oxford University Press: Oxford, 2003.