

# A Series of Octanuclear-Nickel(II) Complexes Supported by Thiacalix[4]arenes

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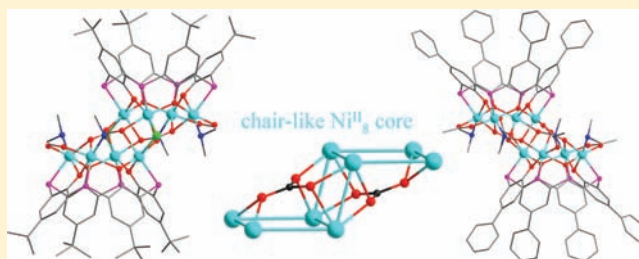
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## S Supporting Information

**ABSTRACT:** A series of discrete complexes,  $[\text{Ni}_8(\text{BTC4A})_2(\mu_6\text{-CO}_3)_2(\mu\text{-CH}_3\text{COO})_4(\text{dma})_4]\cdot\text{H}_2\text{O}$  (1),  $[\text{Ni}_8(\text{BTC4A})_2(\mu_6\text{-CO}_3)_2(\mu\text{-Cl})_2(\mu\text{-HCOO})_2(\text{dma})_4]\cdot 2\text{DMF}\cdot 2\text{CH}_3\text{CN}$  (2),  $[\text{Ni}_8(\text{PTC4A})_2(\mu_6\text{-CO}_3)_2(\mu\text{-CH}_3\text{COO})_4(\text{dma})_4]\cdot\text{DMF}$  (3), and  $[\text{Ni}_8(\text{PTC4A})_2(\mu_6\text{-CO}_3)_2(\mu\text{-OH})(\mu\text{-HCOO})_3(\text{dma})_4]$  (4) (*p*-*tert*-butylthiacalix[4]arene =  $\text{H}_4\text{BTC4A}$ , *p*-phenylthiacalix[4]arene =  $\text{H}_4\text{PTC4A}$ , dma = dimethylamine, and DMF = *N,N'*-dimethylformamide), have been prepared under solvothermal conditions and structurally characterized by single-crystal X-ray diffraction analyses, powder XRD, and IR spectroscopy. These four complexes are stacked by dumbbell-like building blocks with one chairlike octanuclear-nickel(II) core, which is capped by two thiacalix[4]arene molecules and connected by two in situ generated carbonato anions and different auxiliary anions. This work implied that not only the solvent molecules but also the upper-rim groups of thiacalix[4]arenes have significant effects on the self-assembly of the dumbbell-like building blocks. The magnetic properties of complexes 1–4 were examined, indicating strong antiferromagnetic interactions between the nickel(II) ions in the temperature range of 50–300 K.



## INTRODUCTION

Polynuclear clusters of paramagnetic metal ions have attracted extensive attention in recent years not only due to their structural beauty but also because they are nanosized metal aggregates that can be potentially functionalized as magnetic materials.<sup>1</sup> A variety of polynuclear clusters with distinct geometries have been synthesized with the use of multidentate ligands and hydro(solvo)thermal techniques, which may promote some interesting inorganic and organic reactions accompanied by new ligand generation or some sophisticated architectures induced by in situ generated anions.<sup>2</sup> Recently, calixarenes are attracting considerable attention as versatile ligands possessing several phenolic groups, which present these ligands as excellent candidates to construct polynuclear clusters of paramagnetic metal ions.<sup>3,4</sup> Dalgarno and co-workers have done a great deal of creative and standard work in this field.<sup>4</sup> A large number of polynuclear clusters have been synthesized based on transition and/or lanthanide metal ions (3d and/or 4f) and calix[4]arenes (including *p*-*tert*-butyl-calix[4]arene and its derivatives). The calix[4]arenes act as the support of one transition or lanthanide metal ion forming the monometal calix[4]arene-supported secondary building units (SBUs), and these SBUs could be used in the construction of 3d and/or 4f

polynuclear clusters with significant magnetic properties, such as single-molecule magnets (SMMs)<sup>4a,f</sup> and magnetic refrigerants.<sup>4b,c</sup> Thiacalixarenes are a new family of cyclic oligomers, possessing homologous shapes and structures with calixarenes. However, many studies have revealed that thiacalixarenes could be regarded as a unique ligand for the second-generation calixarene chemistry, rather than as a simple substitute for conventional calixarenes, because the replacement of the methylene linkages of calixarenes by sulfide groups of thiacalixarenes provides various intrinsic characteristics (more coordination sites, lower electron density, and more flexibility).<sup>5</sup> Furthermore, oxidized derivatives, including sulfinylcalixarenes and sulfonylcalixarenes, can be easily obtained, which could lead to the formation of a variety of new polynuclear clusters depending on the reaction conditions.<sup>6</sup> Therefore, thiacalixarenes can be treated as potential supramolecular building blocks in addition to calixarenes to construct significant supramolecular assemblies under proper conditions. Among them, thiacalix[4]arenes, including *p*-*tert*-butylthiacalix[4]arene and *p*-phenylthiacalix[4]arene (abbreviated as

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Table 1. Crystal Data and Data Collection and Refinement Parameters for 1–4

complexes	1	2	3	4
formula	C <sub>98</sub> H <sub>50</sub> N <sub>4</sub> Ni <sub>8</sub> O <sub>23</sub> S <sub>8</sub>	C <sub>102</sub> H <sub>138</sub> N <sub>8</sub> Ni <sub>8</sub> O <sub>20</sub> S <sub>8</sub>	C <sub>117</sub> H <sub>103</sub> N <sub>5</sub> Ni <sub>8</sub> O <sub>23</sub> S <sub>8</sub>	C <sub>109</sub> H <sub>86</sub> N <sub>4</sub> Ni <sub>8</sub> O <sub>21</sub> S <sub>8</sub>
formula wt	2377.60	2593.26	2673.20	2513.98
temperature (K)	293(2)	293(2)	293(2)	293(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	triclinic	triclinic
space group	C2/m	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$
a (Å)	25.516 (4)	12.492(3)	14.295(7)	14.219(9)
b (Å)	15.5261 (12)	15.554(4)	16.270(8)	15.205(9)
c (Å)	18.427 (3)	17.590(5)	16.402(8)	16.206(11)
$\alpha$ (deg)	90	77.173(7)	66.51(2)	69.11(3)
$\beta$ (deg)	123.834 (6)	80.819(7)	67.47(2)	65.77(3)
$\gamma$ (deg)	90	66.372(7)	72.84(2)	71.51(3)
volume (Å <sup>3</sup> )	6064.0 (14)	3043.4(13)	3186(3)	2924(3)
Z	2	1	1	1
D <sub>c</sub> (g/cm <sup>3</sup> )	1.302	1.415	1.393	1.428
$\mu$ (mm <sup>-1</sup> )	1.412	1.454	1.352	1.466
data collected	20473	19988	21055	22375
unique data (R <sub>int</sub> )	6066	11115	11801	13134
parameters	359	741	752	701
GOF on F <sup>2</sup>	1.072	1.044	1.062	1.061
R <sub>1</sub> <sup>a</sup> [I > 2 $\sigma$ (I)]	0.0632	0.0540	0.0956	0.0830
wR <sub>2</sub> <sup>b</sup>	0.1803	0.1437	0.2811	0.2198

$$^a R_1 = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|, \quad ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

H<sub>4</sub>BTC4A and H<sub>4</sub>PTC4A, respectively), are the smallest ones, which usually prefer the cone conformations. With the aid of sulfur atoms, one thiacalix[4]arene molecule can simultaneously bond and stabilize four 3d and/or 4f metal ions, leading to tetranuclear thiacalix[4]arene-supported SBUs. Despite the fact that thiacalix[4]arenes are facile to construct polynuclear clusters with higher nuclearity and have received extensive attention in the context of constructing 3d and/or 4f polynuclear clusters, thiacalix[4]arene-supported polynuclear nickel(II) clusters were rarely described to date.<sup>5e,6b</sup> In this context, we employed H<sub>4</sub>BTC4A and H<sub>4</sub>PTC4A to react with nickel(II) salts under solvothermal conditions. Herein, we present the preparations, structures, and magnetic properties of four new nickel(II) complexes, namely, [Ni<sub>8</sub>(BTC4A)<sub>2</sub>( $\mu_6$ -CO<sub>3</sub>)<sub>2</sub>( $\mu$ -CH<sub>3</sub>COO)<sub>4</sub>(dma)<sub>4</sub>] $\cdot$ H<sub>2</sub>O (**1**), [Ni<sub>8</sub>(BTC4A)<sub>2</sub>( $\mu_6$ -CO<sub>3</sub>)<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>( $\mu$ -HCOO)<sub>2</sub>(dma)<sub>4</sub>] $\cdot$ 2DMF $\cdot$ 2CH<sub>3</sub>CN (**2**), [Ni<sub>8</sub>(PTC4A)<sub>2</sub>( $\mu_6$ -CO<sub>3</sub>)<sub>2</sub>( $\mu$ -CH<sub>3</sub>COO)<sub>4</sub>(dma)<sub>4</sub>] $\cdot$ DMF (**3**), and [Ni<sub>8</sub>(PTC4A)<sub>2</sub>( $\mu_6$ -CO<sub>3</sub>)<sub>2</sub>( $\mu$ -OH)( $\mu$ -HCOO)<sub>3</sub>(dma)<sub>4</sub>] (**4**) (dma = dimethylamine; DMF = *N,N*-dimethylformamide), which feature chairlike octanuclear-nickel(II) cores supported by two thiacalix[4]arenes and anions generated in situ.

## EXPERIMENTAL SECTION

**Materials and Measurements.** *p*-*tert*-Butylthiacalix[4]arene and *p*-phenylthiacalix[4]arene were prepared according to literature methods,<sup>7</sup> while other chemicals were of reagent-grade quality obtained from commercial sources and used without further purification. Elemental analyses were performed with a German Elementary Varil EL III instrument. IR spectra were recorded in the range of 4000–400 cm<sup>-1</sup> with a Magna 750 FT-IR spectrometer using KBr pellets. Metal elemental analysis was carried out on an Ultima-2 ICP emission spectrometer. The powder X-ray diffraction (PXRD) were recorded by a RIGAKU-DMAX2500 X-ray diffractometer using Cu K $\alpha$  radiation ( $\lambda$  = 0.154 nm) at a scanning rate of 3°/min for 2 $\theta$  ranging from 5° to 50°. Magnetic susceptibilities were measured on polycrystalline samples with the Quantum Design PPMS-9T and MPMS-XL systems.

**Caution!** Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.

**Syntheses of Complexes 1–4.** **Complex 1.** A mixture of H<sub>4</sub>BTC4A $\cdot$ CHCl<sub>3</sub> (0.1 mmol, 82 mg) and Ni-(CH<sub>3</sub>COO)<sub>2</sub> $\cdot$ 4H<sub>2</sub>O (0.6 mmol, 150 mg) in DMF/CH<sub>3</sub>CN/Et<sub>3</sub>N (4/4/0.5 mL) was sealed in a 25 mL Teflon-lined bomb at 120 °C for 4 days, then cooled slowly at 4 °C h<sup>-1</sup> to room temperature. Green prismatic crystals of **1** were isolated by filtration, washed with DMF/CH<sub>3</sub>CN (1:1), and air-dried (85 mg, 72% based upon H<sub>4</sub>BTC4A). Anal. Calcd for complex **1**: calcd C, 49.50; H, 2.12; N, 2.36; found C, 49.32; H, 2.22; N, 2.45. IR (KBr disk,  $\nu$  cm<sup>-1</sup>): 3431 (w), 3278 (m), 2961 (s), 2873 (m), 1668 (m), 1585 (s), 1444 (s), 1362 (m), 1314 (w), 1295 (m), 1259 (s), 1202 (w), 1088 (w), 1024 (m), 909 (m), 882 (w), 855 (w), 833 (m), 746 (w), 733 (w), 671 (m), 541 (w).

**Complex 2.** Equivalent synthesis procedures were carried out employing Ni(ClO<sub>4</sub>)<sub>2</sub> $\cdot$ 6H<sub>2</sub>O (0.6 mmol, 200 mg) to obtain the corresponding products. Green prismatic crystals of **2** (86 mg) were obtained in 66% yield based on H<sub>4</sub>BTC4A. Anal. Calcd for complex **2**: calcd C, 47.24; H, 5.36; N, 4.32; Ni, 18.10; found C, 47.04; H, 5.30; N, 4.22; Ni, 18.7. IR (KBr disk,  $\nu$  cm<sup>-1</sup>): 3445 (w), 3275 (m), 2961 (s), 2871 (m), 1683 (s), 1599 (s), 1446 (s), 1361 (m), 1315 (m), 1258 (s), 1203 (w), 1089 (m), 1025 (m), 911 (w), 884 (w), 856 (w), 833 (m), 748 (m), 733 (m), 663 (w), 542 (w).

**Complex 3.** A mixture of H<sub>4</sub>PTC4A (0.1 mmol, 80 mg) and Ni(ClO<sub>4</sub>)<sub>2</sub> $\cdot$ 6H<sub>2</sub>O (0.6 mmol, 200 mg) in DMF/CH<sub>3</sub>OH/Et<sub>3</sub>N (4/4/0.5 mL) was sealed in a 25 mL Teflon-lined bomb at 120 °C for 4 days, then cooled slowly at 4 °C h<sup>-1</sup> to room temperature. Green prismatic crystals of **3** were isolated by filtration, washed with DMF/CH<sub>3</sub>OH (1:1), and air-dried (82 mg, 61% based upon H<sub>4</sub>BTC4A). Anal. Calcd for complex **3**: calcd C, 52.56; H, 3.88; N, 2.62; found C, 52.38; H, 3.92; N, 2.74. IR (KBr disk,  $\nu$  cm<sup>-1</sup>): 3432 (w), 3284 (m), 2901 (m), 2836 (m), 1674 (m), 1574 (s), 1434 (s), 1306 (s), 1249 (s), 1128 (w), 1088 (m), 1059 (w), 1023 (m), 909 (m), 880 (m), 857 (w), 760 (s), 697 (s), 670 (m), 614 (m), 522 (w).

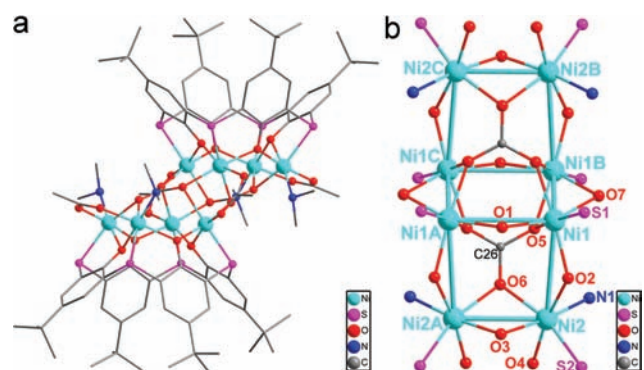
**Complex 4.** Equivalent synthesis procedures were carried out employing Ni(CH<sub>3</sub>COO)<sub>2</sub> $\cdot$ 4H<sub>2</sub>O (0.6 mmol, 150 mg) to obtain the corresponding products. Green prismatic crystals of **4** (80 mg) were

obtained in 64% yield based on  $H_4$ PTC4A. Anal. Calcd for complex 4: calcd C, 52.08; H, 3.44; N, 2.23; found C, 51.78; H, 3.57; N, 2.42. IR (KBr disk,  $\nu$   $cm^{-1}$ ): 3432 (w), 3274 (m), 2902 (w), 2836 (w), 1675 (s), 1591 (s), 1444 (s), 1360 (s), 1325 (m), 1306 (s), 1250 (s), 1125 (w), 1088 (m), 1059 (w), 1023 (m), 908 (m), 880 (m), 857 (w), 759 (s), 697 (s), 660 (w), 614 (m), 522 (m).

**X-ray Data Collection and Structure Determination.** Data collection for complexes 1–4 was performed on Rigaku-CCD diffractometers equipped with graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) by using the  $\omega$ -scan mode at 293 K. All absorption corrections were applied using the CrystalClear program.<sup>8</sup> The structures were solved by direct methods, the metal atoms were located from the  $E$ -maps, and other non-hydrogen atoms were derived from the successive difference Fourier peaks. The structures were refined on  $F^2$  by full-matrix least-squares using the SHELXTL-97 program package.<sup>9</sup> All non-hydrogen atoms were refined anisotropically except some solvent molecules and some badly disordered atoms. Hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. Some 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 complexes 1–4 might be due to the weak high-angle diffractions and the disorder. Details of the structure solution and final refinements for the compounds are given in Table 1. CCDC-855457 (1), 851308 (2), 851309 (3), and 855458 (4) 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](http://www.ccdc.cam.ac.uk/-data_request/cif).

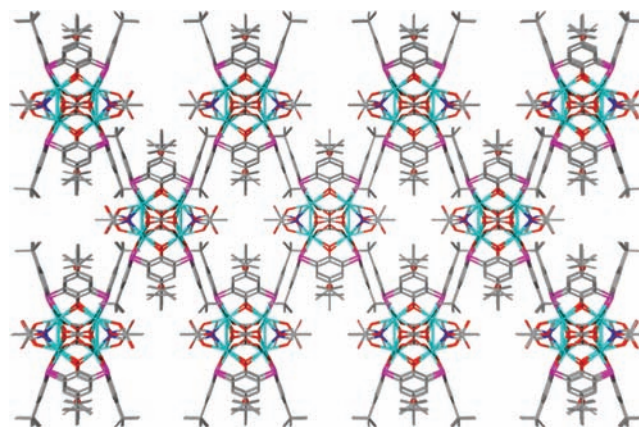
## RESULTS AND DISCUSSION

**Crystal Structures.** Single-crystal X-ray diffraction experiments revealed that complex 1 crystallized in the monoclinic system with space group  $C2/m$ , whereas complexes 2–4 crystallized in the triclinic system with space group  $P\bar{1}$ . These four thiacalix[4]arene-supported nickel(II) complexes are structurally analogous, which have the same chairlike octanuclear-nickel(II) core capped by two thiacalix[4]arene molecules. However, complexes 2 and 4 possess formate anions (and  $OH^-$  anions) and chloride anions generated in situ instead of acetate anions within complexes 1 and 3 as the linkers of two  $Ni^{II}_4$ -thiacalix[4]arene building blocks due to the absence of acetate anions in the reactants. Within the chairlike octanuclear-nickel(II) core of complex 1, there are two crystallographic unique nickel(II) centers, and they are both six-coordinated in a distorted octahedron geometry, as can be seen from Figure 1. The Ni1 atom is coordinated by two



**Figure 1.** (a) Molecular structure of complex 1. Hydrogen atoms are omitted for clarity. (b) The chairlike octanuclear-nickel(II) core within complex 1. Symmetry code: (A)  $x, 1 - y, z$ ; (B)  $-x, y, -z$ ; (C)  $-x, 1 - y, -z$ .

oxygen atoms of the fully deprotonated BTC4A, two oxygen atoms from two different carbonate anions, one oxygen atom of the disordered acetic anion, and one bridging sulfur atom. Ni2 is bonded by two oxygen atoms of the  $BTC4A^{4-}$  anion, one oxygen atom from carbonate anions, one sulfur atom, one oxygen atom from the acetic anion, and one nitrogen atom of dma. Four nickel(II) ions are bonded to the lower rim of the  $BTC4A^{4-}$  anion through phenoxy oxygens and bridge sulfur atoms to form a shuttlecock-like tetranuclear nickel-calixarene block in the presence of other anions. Thereinto, the carbonate anion acts as the cork base instead of the reported  $OH^-$  anion.<sup>4c</sup> Interestingly, two shuttlecock-like blocks are connected in a head-by-head fashion by two carbonate anions and two acetic anions, forming a dumbbell-like entity with a chairlike octanuclear-nickel(II) core. Usually, octanuclear-nickel(II) cores adopt a cubelike structure with other structural forms, such as linear, wheel-like, and ringlike structures, being also reported.<sup>10</sup> However, this chairlike architecture is not seen heretofore. In the dumbbell-like entity, two planes formed by four nickel(II) ions from the upper and bottom of the “chair” are parallel to each other. The Ni···Ni distances at the bottom of the shuttlecock-like block range from 3.120(1) to 3.558(1) Å, while the Ni···Ni distance between the adjacent shuttlecock-like blocks is 2.930(1) Å. The examination of the extended structure of complex 1 shows that the dumbbell-like entities assemble into a bilayer array (Figure 2). In complex 2, MeCN

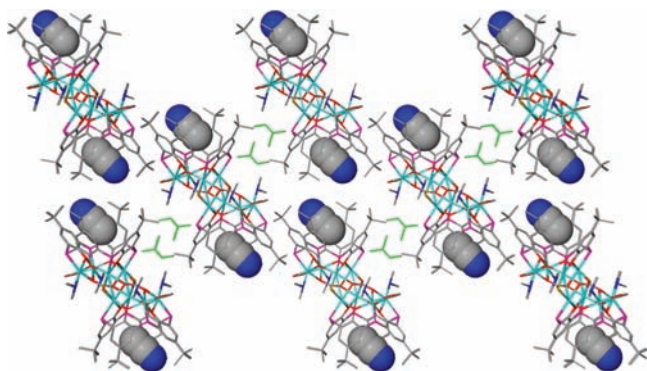


**Figure 2.** Extended structure of complex 1 showing self-assembly into a bilayer array and positioning of cocrystallized water molecules (red ball) view along  $c$  axis. Hydrogen atoms are omitted for clarity.

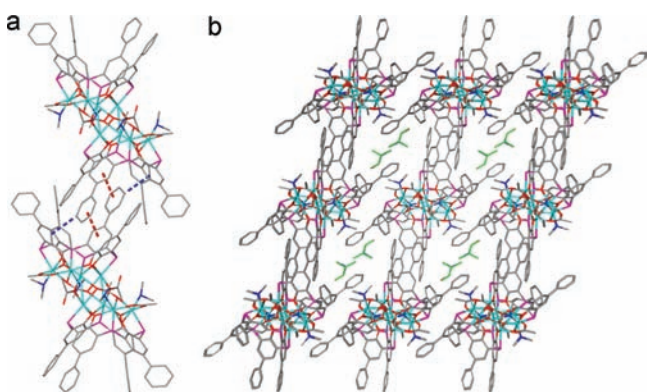
molecules penetrate slantwise into the thiacalixarene cavities stabilized by two  $C-H\cdots\pi$  interactions. Upon crystal packing, complex 2 exhibits a skewed bilayer structure, which is different from the bilayer structure of complex 1 due to the presence of DMF molecules at the “hydrophobic” layers (Figure 3).

By replacing  $H_4$ BTC4A with  $H_4$ PTC4A in the similar reaction, structurally analogous complexes 3 and 4 were obtained. Both of them are composed of the similar dumbbell-like octanuclear-nickel(II) entities where the capping ligands are two PTC4A ligands (Figure S2, Supporting Information). In complexes 3 and 4, one phenyl group of PTC4A penetrates into the cavity of an opposite PTC4A stabilized by  $\pi\cdots\pi$  and  $C-H\cdots\pi$  interactions, and two  $Ni^{II}_8$ -( $PTC4A$ )<sub>2</sub> units form a “hand-shake” motif (Figures 4a and S3a (Supporting Information)). Further symmetry expansion shows the extended structure to be a bilayer array (Figures 4b and S3b (Supporting Information)), which is different to that found in





**Figure 3.** Extended structure of complex 2 showing self-assembly into a skewed bilayer array and positioning of cocrystallized DMF (green) and MeCN (spacefill) molecules view along *a* axis. Hydrogen atoms are omitted for clarity.

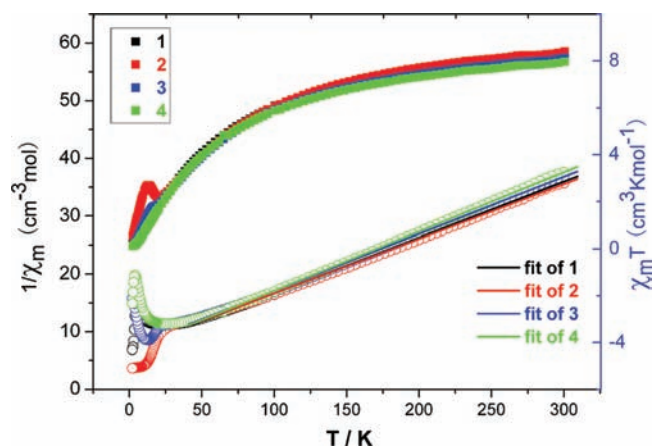


**Figure 4.** (a) The “hand-shake” motif stabilized by  $\pi\cdots\pi$  and C–H $\cdots\pi$  interactions. (b) Extended structure of complex 3 showing self-assembly into a skewed bilayer array (viewing along *b* axis) and positioning of cocrystallized DMF (green) molecules. Hydrogen atoms are omitted for clarity.

complexes 1 and 2 owing to the substituent of the upper-rim groups on the reactant of thiacalixarene resulting in the penetration of the adjacent PTC4A molecules.

It should be noted that DMF played an important role in the syntheses of these complexes. Besides behaving as the solvent for the crystals to separate out, DMF also serves as the source of formate anions, carbonate anions, and dma molecules. According to the literature, these formate anions and dma molecules were generated through the decarbonylation of DMF under the solvothermal conditions.<sup>11</sup> Furthermore, with the aid of water molecules, partial formate anion would be slowly oxidized to carbonate anion at the high temperatures under basic conditions.<sup>12</sup> On the other hand, the chloride anions in the structure could come from the decomposition of chloroform (Figure S1, Supporting Information).<sup>5f</sup> The assignments of the aforementioned anions and dma molecule generated in situ were based on X-ray structures, elemental analyses, charge balance considerations, and the long bond distances. All the Ni–N, Ni–O, and Ni–Cl bond distances are located in the normal bond length range (2.078(1)–2.094(4) Å for the Ni–N bond, 2.001(2)–2.194(5) Å for the Ni–O bond, and 2.445(2)–2.448(2) Å for the Ni–Cl bond).<sup>13</sup>

**Magnetic Studies.** The magnetic susceptibilities were measured on the polycrystalline samples of complexes 1–4 under an applied field of 1000 Oe, as shown in Figure 5 as  $\chi_m T(T)$  and  $1/\chi_m(T)$ . The  $\chi_m T$  values at 300 K are 8.35, 8.40,



**Figure 5.** Temperature dependence of magnetic susceptibilities of complexes 1–4 in a 1000 Oe field. The solid lines are the best fitting to the Curie–Weiss Law.

8.14, and 7.97  $\text{cm}^3 \text{K mol}^{-1}$  for 1–4, which agree with the expected spin-only value of 8.00  $\text{cm}^3 \text{K mol}^{-1}$  for eight uncoupled Ni(II).<sup>11a</sup> Upon cooling to ca. 20.0 K, the  $\chi_m T$  values decrease smoothly to 1.77, 1.89, and 1.74  $\text{cm}^3 \text{K mol}^{-1}$  for complexes 1, 3, and 4, respectively. The  $\chi_m T$  value of complex 2 decreases to 2.19  $\text{cm}^3 \text{K mol}^{-1}$  at 20.0 K and abruptly increases to a maximum value of 2.69  $\text{cm}^3 \text{K mol}^{-1}$  at 13.0 K, and then decreases until the lowest temperature, 2 K. The reciprocal molar magnetic susceptibility data in the high-temperature region of 50–300 K obey the Curie–Weiss Law of  $1/\chi_m = (T - \theta)/C$ , with Curie constants  $C = 10.37, 10.60, 10.15,$  and  $9.79 \text{ cm}^3 \text{K mol}^{-1}$  and Weiss constants  $\theta = -72.9, -76.4, -71.0,$  and  $-67.9 \text{ K}$  for complexes 1–4, respectively. Because of the complicated structures of these chairlike octanuclear-nickel(II) clusters, the actual magnitude of the magnetic interactions between these nickel(II) ions could not be obtained. Nevertheless, the negative values of the Weiss constants and the curves of  $\chi_m T(T)$  clearly indicate the presence of strong antiferromagnetic coupling between nickel(II) ions.

For complex 2, the peak in the low-temperature region of the  $\chi_m T$  curve suggests the onset of some kind of long-range magnetic ordering. To further investigate that, more experiments, including the zero-field-cooled and field-cooled magnetization (ZFC/FC), field-dependent magnetization  $M(H)$ , and ac susceptibilities, were measured at low temperatures. Indeed, the ZFC curve shows a broad peak and diverges from the FC curve at around 9 K (Figure S4a, Supporting Information), suggesting the magnetic history dependence of the sample, which could be from the onset of long-range ordering or the spin glass behavior. Also, the  $M(H)$  curve opens up a small hysteresis loop at 2 K, but the magnetization value at 80 kOe is only 0.025  $\mu_B$ , far from the saturation value  $M_S = 1 \mu_B$  for a spin-only Ni<sup>II</sup> ion (Figure S4b, Supporting Information). Furthermore, broad peaks with frequency dependence were observed in the ac susceptibility data at different frequencies (Figure S5, Supporting Information). All these data point to the possibility of the superparamagnetism of complex 2.<sup>14</sup> From the structural point of view, complex 2 should not undergo a long-range magnetic ordering phase transition because the octanuclear-nickel(II) clusters were shielded from each other by the bulky organic ligands. Furthermore, the intracuster antiferromagnetic interaction results in the very small magnetic

ground state of these octanuclear-nickel(II) clusters, which again makes the dipole–dipole interactions among these octanuclear-nickel(II) clusters negligible. As a matter of fact, complexes **1**, **3**, and **4** with the similar structures show regular paramagnetic behaviors. Considering the solvothermal synthetic conditions for **2**, we suggest that the origin of the superparamagnetism of **2** should come from the trace amount of NiO nanoparticles, although it is not detectable from the other conventional analytical methods. Actually, the presence of the NiO nanoparticle in the products of the hydrothermal reactions has been reported in the literature.<sup>15</sup> Our results on complex **2** gives another good example that the purity of the sample is crucial to the analysis of its magnetic properties, and extreme care should be taken especially for those hydro/solvothermal products.

## CONCLUSION

In conclusion, a series of discrete complexes **1–4** have been synthesized by the self-assembly of nickel(II) ions and thiacalix[4]arene ligands under solvothermal conditions. Within all the four complexes, one thiacalix[4]arene ligand ligates four nickel(II) ions, leading to a shuttlecock-like block, in which the carbonate anion generated in situ acts as the cork base. Two shuttlecock-like blocks are interconnected in a head-by-head model by two carbonate anions, forming a dumbbell-like entity with a chairlike octanuclear-nickel(II) core. As far as we know, these are the first examples of octanuclear-nickel(II) complexes that possess chairlike octanuclear-nickel(II) cores. Furthermore, DMF played a vital role in the syntheses of these complexes not only behaving as the solvent for the crystals to be separated out but also serving as the source of formate anions, carbonate anions, and dma molecules and affecting the self-assembly of dumbbell-like building blocks. In addition, the upper-rim groups on the reactant of thiacalixarenes also have significant effects on the self-assembly of dumbbell-like building blocks. The magnetic properties of complexes **1–4** were examined, indicating strong antiferromagnetic interactions between the nickel(II) ions in the temperature range of 50–300 K. The successful preparation of these complexes provides a valuable approach to the construction of other polynuclear clusters of paramagnetic transition-metal ions with multifunctional properties. Further work is in progress to explore new hybrids with novel architectures and interesting magnetic properties based on thiacalix[4]arene ligands.

## ASSOCIATED CONTENT

### Supporting Information

Crystallographic data in CIF format, PXRD patterns, and additional figures for **1–4**. 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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