

Series of octanuclear clusters of Ni(II)/Co(II) with tunable structures and magnetism supported by thiacalix[4]arenes

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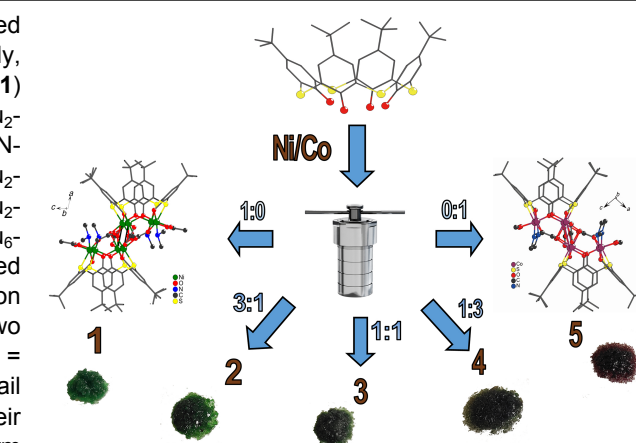
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ABSTRACT: In this study, five thiacalix[4]arene (TC4A)-based octanuclear homometallic or heterometallic clusters, namely, $\{[\text{Ni}_8(\text{TC4A})_2(\mu_6\text{-CO}_3)_2(\mu_2\text{-CH}_3\text{CO}_2)_3(\mu_2\text{-CO}_3)(\text{DMA})_4]\cdot(\text{CH}_3\text{CN})_2\}$ (**1**) (DMA = N,N-dimethylamine), $\{[\text{Ni}_{5.81}\text{Co}_{2.19}(\text{TC4A})_2(\mu_6\text{-CO}_3)_2(\mu_2\text{-HCO}_2)_2(\mu_2\text{-Cl})_2(\text{DMA})_4]\cdot 2\text{DMF}\cdot 2\text{CH}_3\text{CN}\}$ (**2**) (DMF = N,N-dimethylformamide), $\{[\text{Ni}_{4.06}\text{Co}_{3.94}(\text{TC4A})_2(\mu_6\text{-CO}_3)_2(\mu_2\text{-HCO}_2)_2(\mu_2\text{-Cl})_2(\text{DMA})_4]\cdot 2\text{DMF}\cdot 2\text{CH}_3\text{CN}\}$ (**3**), $\{[\text{Ni}_2\text{Co}_6(\text{TC4A})_2(\mu_6\text{-CO}_3)_2(\mu_2\text{-HCO}_2)_2(\mu_2\text{-Cl})_2(\text{DMA})_4]\cdot 2\text{DMF}\cdot 2\text{CH}_3\text{CN}\}$ (**4**), and $\{[\text{Co}_8(\text{TC4A})_2(\mu_6\text{-CO}_3)_2(\mu_2\text{-HCO}_2)_3(\mu_2\text{-CO}_3)_2(\text{DMA})_4]\cdot 4\text{DMF}\}$ (**5**), are synthesized using a solvothermal method. Single-crystal X-ray diffraction analysis reveals that all synthesized compounds comprise two badminton-like secondary building units (SBUs) $[\text{M}_4(\text{TC4A})]$ (M = Co, Ni, Co/Ni) linked by two $\mu_6\text{-CO}_3^{2-}$ anions in a tail-to-tail manner, forming a chair-like octanuclear metal cluster. Their structures were also characterized using Fourier transform infrared spectroscopy, ultraviolet–visible spectroscopy, X-ray photoelectron spectroscopy, powder X-ray diffraction, etc. Magnetism studies indicate an antiferromagnetic interaction between the metal ions of compounds **1–5**, and their magnetic susceptibility $\chi_M T$ increases as the cobalt content increases in the range of 50–300 K. The structures and magnetic properties of the Co(II)/Ni(II) cluster supported by TC4A can be conveniently tuned by varying the Ni(II):Co(II) molar ratio, providing a straightforward approach for fabricating TC4A-based heterometallic clusters.

KEYWORDS: thiacalix[4]arene, magnetism, cobalt, nickel, heterometallic

1 Introduction

Calix[n]arenes (CAs) and thiacalix[n]arenes (TCAs) represent a class of cyclic oligomers with adjustable sizes and structures. Consisting of several para-substituted phenols bridged by methylene or sulfur atoms, these compounds can be used as a new generation of supramolecular hosts [1]. The lower rim of phenolic OH or thiophenolic SH groups can be further modified via substitution or acylation reactions [2, 3] and can also be used as multidentate ligands for coordination assembly [4]. In particular,



thiacalix[4]arene (TC4A) exhibits excellent coordination ability because of its flexible C–S bond length and C–S–C bond angle [5]. Mislin et al. reported a sandwich-like tetracopper(II) square capped by two TC4A ligands. This assembly can be viewed as two tail-to-tail connected, badminton-shaped secondary building units (SBUs) of $\{\text{M}_4(\text{TC4A})\}$ [6]. The SBU of $\{\text{M}_4(\text{TC4A})\}$ not only serves as an excellent LEGO brick for more complicated architectures [7, 8], but also functions as a scaffold that provides various metal clusters, including transition, rare earth, and heterometallic 3d-4f centers with magnetic properties [9].

In the past two decades, several TC4A-supported structures have been reported, including TC4A-protected metal nanoparticles, small metal clusters, metal–organic coordination cages, and TC4A-coordinated metal–organic polyhedral [7]. Kajiwarra et al. reported a series of octalanthanide wheels $[\text{Ln}'_8(\text{L})_4(\text{AcO})_8(\text{EtOH})_4(\text{H}_2\text{O})_4]$ ($\text{Ln}' = \text{Gd}$ (1), Sm (1')) and $[\text{Ln}_8(\text{L})_4(\text{AcO})_8(\text{MeOH})_4(\text{H}_2\text{O})_8]$ ($\text{Ln}' = \text{Nd}$ (2), Pr (2')), which are supported by p-tert-butylsulfonycalix[4]arene and exhibit weak antiferromagnetic

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interactions [10]. Hong et al. reported a series of octanuclear Ni(II) complexes with chair-like metal clusters capped by two thiacalix[4]arene ligands [11]. Bi et al. reported a $\{Co_{32}\}$ nanosphere supported by p-tert-butylthiacalix[4]arene [12]. Liu et al. reported a series of calix-based nanoscale superoctahedral cages comprising six SBUs of $\{M_4(TC4A)\}$ and eight tripodal ternary acids via [6+8] condensation [13]. Xiong et al. reported an anionic truncated octahedral coordination cage comprising six SBUs of $\{M_4(TC4A)\}$ and eight 1,4-benzenedicarboxylic acids via [6 + 12] condensation [14].

Among various nanoparticles [15] or metal clusters based on TC4A, heterometallic clusters have received significant research attention owing to their potential applications in catalysis [16], magnetism [17], and luminescence [18]. 3d-4f or 3d-4d heterometallic clusters supported by TC4A have been reported. For example, Bi et al. reported a series of nanocages ($M_{20}V_8$, $M = Fe, Co, Ni$) comprising the polynuclear SBUs of $\{M_4(TC4A)\}$ and vanadate anion units in [5+8] condensation modes, and the $Fe_{20}V_8$ cage exhibited significant photothermal conversion efficiency (up to 80%) [19]. Liao et al. reported one 3d-4f heterometallic tetranuclear compound of $\{Mn_2Gd_2(TC4A)_2\}$ with a sandwich-like structure and ferromagnetic interaction [20]. Bi et al. reported a class of TC4A-functionalized heterometallic clusters involving the Keggin-type $PM_4Mo_8(M = Co, Ni)$ motif. These clusters not only electrocatalytically reduce IO_3^- but also exhibit photothermal conversion efficiency up to $52.5\% \pm 1.7\%$ [21]. Zhang et al. reported two mixed-valent heterometallic clusters $[Cu^{II}_2Cu^I Ti(O^Pr)_2(TC4A)_2CH_3CN]$ (Ti_1Cu_4) and $[Cu^{II}_3Cu^I Ti_2(\mu_2-O)(\mu_3-O)(O^Pr)_2(CH_3COO)_2(TC4A)_2(CH_3CN)_2]$ (Ti_2Cu_5), which can electrocatalytically reduce CO_2 to form HCO_2H (Ti_1Cu_4) or CH_4 (Ti_2Cu_5) in a wide potential range. Liu et al. reported a series of Ag-doped titanium-oxo clusters $Ti_{12}Ag_{4.5}$ supported by TC4A, which can electroreduce CO_2 into CO with a broad potential window [22]. Su et al. reported a series of thiacalix[4]arene-supported kite-like heterometallic tetranuclear $Zn^II Ln^{III}$ ($Ln = Gd, Tb, Dy, Ho$) complexes with the characteristic luminescence of Ln^{III} and antiferromagnetic interactions between Ln^{III} ions [23]. Although TC4A-based 3d-4f or 3d-4d heterometallic clusters have been reported, TC4A-based 3d-3d heterometallic clusters remain less explored. A major challenge in investigating 3d-3d heterometallic cluster complexes arises from their similar ionic radii and competing coordination tendencies. In addition, crystallographically differentiating cobalt from nickel remains a significant challenge. Gao et al. reported a series of random Co(II)–Ni(II) ferromagnetic chains with coexistent antiferromagnetism, metamagnetism, and single-chain magnetism [24].

In our previous study, we reported a luminescent ionic compound containing a TC4A anion and a $[Ag(PPh_3)_4]^+$ cation [25]. Recently, late transition metal ions, including Ni(II) and Co(II), have been coordinated with tert-butylthiacalix[4]arene to yield TC4A-based heterometallic clusters. In this study, five new compounds, namely, $\{[Ni_8(TC4A)_2(\mu_6-CO_3)_2(\mu_2-CH_3CO_2)_3(\mu_2-CO_3)(DMA)_4]\cdot(CH_3CN)_2\}$ (**1**), $\{[Ni_{5.81}Co_{2.19}(TC4A)_2(\mu_6-CO_3)_2(\mu_2-HCO_2)_2(\mu_2-Cl)_2(DMA)_4]\cdot 2DMF\cdot 2CH_3CN\}$ (**2**), $\{[Ni_{4.06}Co_{3.94}(TC4A)_2(\mu_6-CO_3)_2(\mu_2-HCO_2)_2(\mu_2-Cl)_2(DMA)_4]\cdot 2DMF\cdot 2CH_3CN\}$ (**3**), $\{[Ni_2Co_6(TC4A)_2(\mu_6-CO_3)_2(\mu_2-HCO_2)_2(\mu_2-Cl)_2(DMA)_4]\cdot 2DMF\cdot 2CH_3CN\}$ (**4**), and $\{[Co_8(TC4A)_2(\mu_6-CO_3)_2(\mu_2-HCO_2)_3(\mu_2-CO_3)_2(DMA)_4]\cdot 4DMF\}$ (**5**), were synthesized through a solvothermal reaction by varying the molar ratio of the metal ions. Their structures were characterized using various methods,

including single-crystal X-ray diffraction (SCXRD), Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS). Structural and magnetism analyses demonstrate that varying the Co:Ni molar ratio is a simple approach for tuning the structure and magnetism of TC4A-supported Ni/Co heterometallic compounds.

2 Experimental

2.1 Materials and measurements

p-tert-Butylthiacalix[4]arene (H_4TC4A) was synthesized according to a previously reported procedure [26]. The other reagents were of analytical grade and were used as received without further purification. Further information about the reagents and instrument characterization can be found in the Electronic Supplementary Material (ESM).

2.2 General synthesis procedure of compounds 1–5

A mixture of 0.1-mmol H_4TC4A (0.082 g), 0.6-mmol metal salt, N, N-dimethylformamide (DMF, 5 mL), triethylamine (0.5 mL), and CH_3CN (5 mL) was placed in a 20-mL Teflon-lined autoclave, stirred for 0.5 h, sealed, kept at 130 °C for 4 days, and then slowly cooled to 20 °C at approximately 4 °C/h. A significant amount of crystals was collected through filtration, washed with CH_3CN/DMF (1:1), and dried in air.

2.2.1 $\{[Ni_8(TC4A)_2(\mu_6-CO_3)_2(\mu_2-CH_3CO_2)_3(\mu_2-CO_3)(DMA)_4]\cdot(CH_3CN)_2\}$ (**1**)

Compound **1** was prepared using $Ni(CH_3CO_2)_2\cdot 4H_2O$ (0.15 g, 0.6 mmol), yielding green crystals (0.10 g, ca. 81% based on H_4TC4A). CHN analysis found (%): C, 46.48; H, 4.89; N, 2.64; inductively coupled plasma mass spectrometry (ICP-MS) found (%): Ni, 18.17. Calc. for $C_{98}H_{122}N_5O_{23}Ni_8S_8$: C, 47.77; H, 4.99; N, 2.84; Ni, 19.06%. FTIR (KBr pellet, cm^{-1}): 3452(m), 3277(m), 2961(m), 2902(w), 1668(m), 1585(m), 1469(m, shoulder), 1444(s), 1385(w), 1361(m), 1313(m), 1295(m), 1258(m), 1202(w), 1129(w), 1088(w), 1024(w), 909(w), 883(w), 855(w), 832(m), 755(m), 734(m), 672(w), 541(w), 496(w), and 453(w).

2.2.2 $\{[Ni_{5.81}Co_{2.19}(TC4A)_2(\mu_6-CO_3)_2(\mu_2-HCO_2)_2(\mu_2-Cl)_2(DMA)_4]\cdot 2DMF\cdot 2CH_3CN\}$ (**2**)

Compound **2** was prepared using $NiCl_2\cdot 6H_2O$ (0.1070 g, 0.45 mmol) and $CoCl_2\cdot 6H_2O$ (0.0357 g, 0.15 mmol) at a molar ratio of 3:1, yielding green crystals (0.098 g, ca. 76% based on H_4TC4A). CHN analysis found (%): C, 46.59; H, 5.21; N, 3.37; ICP-MS found (%): Ni, 16.29; Co, 6.14. Calc. for $C_{96}H_{124}N_5O_{18}Ni_{5.81}Co_{2.19}Cl_2S_8$ ($M\cdot 2DMF$): C, 47.11; H, 5.11; N, 3.43; Ni, 14.82; Co, 4.86. FTIR (KBr pellet, cm^{-1}): 3423(m, br), 3275(m), 2961(m), 2870(m), 1676(m), 1598(s), 1466(m), 1445(vs), 1416(s, shoulder), 1385(m), 1362(m), 1316(w), 1298(w), 1258(m), 1122(w), 1090(w), 1025(w), 883(w), 856(w), 769(w), 761(w), 753(w), 734(w), 662(w), 635(w), 542(w), 452(w).

2.2.3 $\{[Ni_{4.06}Co_{3.94}(TC4A)_2(\mu_6-CO_3)_2(\mu_2-HCO_2)_2(\mu_2-Cl)_2(DMA)_4]\cdot 2DMF\cdot 2CH_3CN\}$ (**3**)

Compound **3** was prepared using $NiCl_2\cdot 6H_2O$ (0.0713 g, 0.30 mmol) and $CoCl_2\cdot 6H_2O$ (0.0714 g, 0.30 mmol) at a molar ratio of 1:1, yielding green crystals (0.096 g, ca. 74% based on H_4TC4A). CHN analysis found (%): C, 46.67; H, 5.29; N, 3.63; ICP-MS found

(%): Ni, 11.15; Co, 10.82. Calc. for $C_{96}H_{124}N_6O_{18}Ni_{4.06}Co_{3.94}Cl_2S_8$: C, 47.10; H, 5.11; N, 3.43; Ni, 9.59; Co, 9.63. FTIR (KBr pellet, cm^{-1}): 3423(m), 3272(m), 2960(m), 2865(w), 1674(m), 1599(s), 1469(m), 1441(s), 1417(m), 1385(s), 1362(w), 1315(w), 1258(m), 1122(w), 1090(w), 881(w), 833(w), 753(w), 676(w), 636(w), 608(w), and 542(w).

2.2.4 $\{[Ni_2Co_6(TC4A)_2(\mu_6-CO_3)_2(\mu_2-HCO_2)_2(\mu_2-Cl)_2(DMA)_4]\}-2DMF \cdot 2CH_3CN$ (**4**)

Compound **4** was prepared using $NiCl_2 \cdot 6H_2O$ (0.0356 g, 0.15 mmol) and $CoCl_2 \cdot 6H_2O$ (0.1070 g, 0.45 mmol) at a molar ratio of 1:3, yielding yellow-green crystals (0.092 g, ca. 71% based on H_4TC4A). CHN analysis found (%): C, 46.71; H, 5.25; N, 3.47; ICP-MS found (%): Ni, 4.67; Co, 13.99. Calc. for $C_{96}H_{124}N_6O_{18}Ni_2Co_6Cl_2S_8$ (M-2DMF): C, 47.09; H, 5.10; N, 3.43; Ni, 4.79; Co, 14.44. FTIR (KBr pellet, cm^{-1}): 3473(s), 3414(s), 3276(m), 2961(m), 2867(w), 1676(m), 1638(w), 1599(s), 1469(m), 1441(s), 1385(m), 1363(m), 1286(w), 1257(m), 1203(w), 1122(w), 1090(w), 1026(w), 906(w), 885(w), 833(w), 754(w), 733(w), 634(w), 543(w), and 450(w).

2.2.5 $\{[Co_8(TC4A)_2(\mu_6-CO_3)_2(\mu_2-HCO_2)_2(\mu_2-CO_3)_2(DMA)_4]\}-4DMF$ (**5**)

Compound **5** was prepared using $Co(CH_3CO_2)_2 \cdot 4H_2O$ (0.1494 g, 0.6 mmol), yielding purple crystals (0.072 g, ca. 54% based on H_4TC4A). CHN analysis found (%): C, 45.25; H, 5.29; N, 2.07; ICP-MS found (%): Co, 20.69. Calc. for $C_{96}H_{124}N_4O_{22}Co_8S_8$ (M-4DMF): C, 47.76; H, 5.18; N, 2.32; Co, 20.67%. FTIR (KBr pellet, cm^{-1}): 3421(m, broad), 2963(m), 2870(w), 1661(s), 1570(s), 1465(m), 1442(s), 1422(s), 1361(w), 1314(w), 1257(s), 1115(w), 890(w), 838(m), 752(m), 737(w), 661(m), 544(w), 531(w), 455(w).

2.3 X-ray crystallographic analyses

Crystals suitable for the synthesized compounds were selected for SCXRD, covered with inert oil, mounted on a loop ring, and rapidly transferred to the diffractometer. All XRD data were collected at cryogenic temperatures (100, 150, or 170 K) via graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) using an Agilent SuperNova diffractometer. CrysAlisPro (Version 1.171.37.34k) software was used for data collection, reduction, cell refinement, and empirical absorption corrections in all compounds. The structures of all compounds were solved using direct or heavy atom methods using SHELXT [27] and refined using the full matrix least squares method for F^2 using SHELXL-2018 [28]. The site occupancy sum of cobalt atoms in the metal sites of compounds **2–4** was restrained using the cobalt content according to ICP-MS. All nonhydrogen atoms, except for some disordered atoms, were anisotropically refined. All calculations were performed using the program package of OLEX1.5 [29]. Table S1 in the Electronic Supplementary Material (ESM) summarizes the crystallography data and structural refinement details for the four complexes. Table S2 in the ESM summarizes the selected bond lengths and angles.

3 Results and discussion

Under the reaction condition at $130^\circ C$ for 4 days, the solvothermal reaction of TC4A with $Ni(CH_3CO_2)_2 \cdot 4H_2O$ and $Co(CH_3CO_2)_2 \cdot 4H_2O$ at the molar ratio of 1:4 successfully yielded compounds **1** (green) and **5** (violet), respectively. Under a similar reaction condition, the mixed metal salts of $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$ at the ratios of 3:1, 1:1, and 1:3 afforded compounds **2**, **3**, and **4**, respectively. The crystal colors of compounds **1–5** gradually transitioned from green to violet (Fig. 1), along with a decrease in Ni content and an increase in Co content. This consistent color evolution demonstrates that 3d-3d heterometallic compounds can be successfully prepared through the direct solvothermal reaction of corresponding mixed metal salts with TC4A. Moreover, dimethylamine, carbonate, and formate, which are generated *in situ* by the decomposition of DMF under solvothermal conditions [30, 31], play an important role in the formation of compounds **1–5**. DMF is an important reagent for fabricating metal-organic frameworks [32] and metal cluster compounds based on TC4A [33].

Considering their close ionic radius and similar X-ray scattering ability of cobalt and nickel, crystallographically differentiating cobalt from nickel remains a significant challenge. ICP-MS was performed to determine the atomic ratio of nickel and cobalt atoms in the title compounds. The ICP-MS results indicate that the Ni/Co atomic ratios of compounds **2**, **3**, and **4** are 5.81/2.19 (3:1), 4.06/3.94 (1:1), and 2.00/6.00 (1:3), respectively. The measured Ni/Co atomic ratios were used to constrain the occupancy of cobalt atoms in compounds **2–4**.

SCXRD analysis reveals that compound **1**, $\{[Ni_8(TC4A)_2(\mu_6-CO_3)_2(\mu_2-CH_3CO_2)_3(\mu_2-CO_3)(DMA)_4]\} \cdot (CH_3CN)_2$, crystallizes in the tetragonal system with the $I2/m$ space group. As shown in Fig. 2(a), there are two crystallographically independent nickel sites, one six-coordinated carbonate, one two-coordinated carbonate, half acetate, half TC4A ligand, one DMA, half acetonitrile molecule, one quarter disordered acetate, and one quarter disordered carbonate in the asymmetric unit. Four nickel atoms are first coordinated with one TC4A ligand to form a badminton-like secondary building block of $[Ni_4(TC4A)]$. Two adjacent SBUs of $[Ni_4(TC4A)]$ are then connected by two six-coordinated carbonates and two bridged acetates to form a chair-like octanuclear nickel cluster, which is capped by two TC4A ligands on both sides. Nickel atoms are six-coordinated with one nitrogen atom, one sulfur atom, and four oxygen atoms to form a distorted octahedron. The bond lengths of Ni–N, Ni–S, and Ni–O are in the ranges of 2.086(5), 2.3545(8)–2.4666(8), and 1.9910(19)–2.144(5) $\text{\AA}$, respectively (Table S2 in the ESM). Four vertex-sharing Ni octahedra form a planar square of a tetranuclear nickel cluster with the Ni–Ni distance of 3.31–3.54 $\text{\AA}$, and the Ni–Ni distance between the adjacent layers of the Ni4 plane is 2.9405 $\text{\AA}$.

SCXRD analysis reveals that compounds **2–4** are allomerism, with the respective formula of $\{[Ni_{5.81}Co_{2.19}(TC4A)_2(\mu_6-CO_3)_2(\mu_2-$

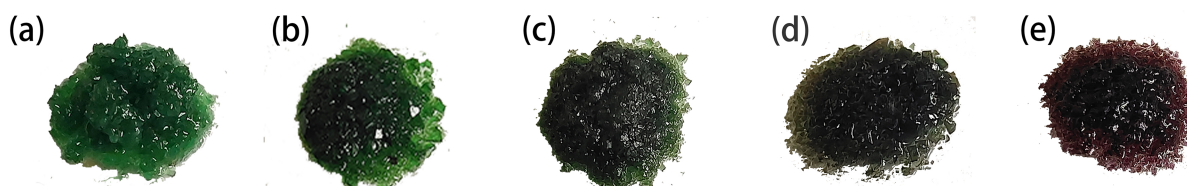


Figure 1 (a)–(e) Crystal photographs of compounds **1–5**.

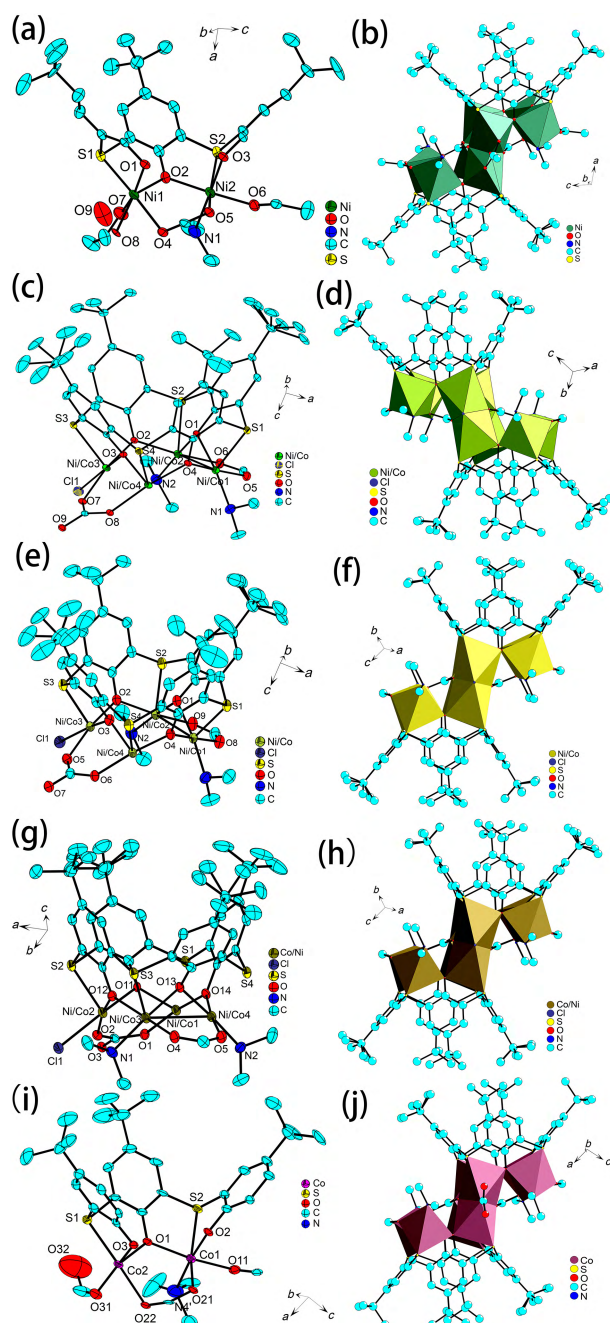


Figure 2 ORTEP drawings with 40% ellipsoid probability of compounds **1** (a), **2** (c), **3** (e), **4** (g), and **5** (i) (solvent molecule and hydrogen atoms are omitted for clarity); polyhedron diagrams of compounds **1** (b), **2** (d), **3** (f), **4** (h), and **5** (j).

$\text{HCO}_2)_2(\mu_2\text{-Cl})_2(\text{DMA})_4\} \cdot 2\text{DMF} \cdot 2\text{CH}_3\text{CN}$ (**2**), $\{[\text{Ni}_{4.06}\text{Co}_{3.94}(\text{TC4A})_2(\mu_6\text{-CO}_3)_2(\mu_2\text{-HCO}_2)_2(\mu_2\text{-Cl})_2(\text{DMA})_4]\} \cdot 2\text{DMF} \cdot 2\text{CH}_3\text{CN}$ (**3**), $\{[\text{Ni}_2\text{Co}_6(\text{TC4A})_2(\mu_6\text{-CO}_3)_2(\mu_2\text{-HCO}_2)_2(\mu_2\text{-Cl})_2(\text{DMA})_4]\} \cdot 2\text{DMF} \cdot 2\text{CH}_3\text{CN}$ (**4**). All compounds crystallize in the triclinic system with the $P\bar{1}$ space group with similar unit cell parameters. As shown in Figs. 2(c), 2(e), and 2(g), there are four crystallographically independent metal sites, one TC4A ligand, one bridged chlorine atom, one formate, two DMA molecules, one acetonitrile molecule, and one DMF solvent molecule in the asymmetric units of **2–4**. Their structures are similar to that of compound **1**, except that the Ni atoms are replaced by disordered Ni and Co atoms, and the bridged acetates are replaced by bridged chloride atoms. In

compound **2**, Co and Ni share the same metal sites, and the refined site occupancy values of Co atoms in the M1–M4 metal sites are 0.26918, 0.30963, 0.25391, and 0.26459, respectively. They are close to the random distribution of 0.25 and their molar ratio (Co:Ni = 1:3). The refined site occupancy values of Ni atoms in the M1–M4 metal sites in compound **3** are 0.54823, 0.51338, 0.4822, and 0.48652, respectively. This is also in good agreement with the theoretical random distribution (Co:Ni = 1:1). For compound **4**, the refined site occupancy values of Co atoms in the M1–M4 metal sites are 0.8818, 0.86106, 0.6922, and 0.62756, respectively. This slightly deviates from the ideal random distribution (Co:Ni = 3:1), indicating that Co atoms are inclined to occupy the central M1 and M2 sites because of their larger ionic radius.

The bond lengths of M–N, M–Cl, M–S, and M–O in compound **2** are in the range of 2.064(2)–2.072(2), 2.4412(6)–2.4466(8), 2.3591(6)–2.4781(6), and 1.9946(16)–2.1145(15) Å, respectively (Table S2 in the ESM). In compound **3**, the bond lengths of M–N, M–Cl, M–S, and M–O are in the range of 2.066(3)–2.068(3), 2.4486(9)–2.4538(10), 2.3737(10)–2.4798(11), and 1.995(2)–2.131(2) Å, respectively. In compound **4**, the bond lengths of M–N, M–Cl, M–S, and M–O are in the range of 2.082(4), 2.4626(12)–2.4626(12), 2.4044(12)–2.4875(13), and 1.993(3)–2.166(3) Å, respectively. In the cluster skeletons of compounds **2–4**, the M···M distance in the tetranuclear square and the M···M distance between the adjacent layers of the M4 plane are 3.14–3.57 and 2.9157(5), 3.14–3.57 and 2.9410(8), and 3.15–3.57 and 2.9842(10) Å for compounds **2**, **3**, and **4**, respectively.

SCXRD analysis reveals that compound **5**, $\{[\text{Co}_8(\text{TC4A})_2(\mu_6\text{-CO}_3)_2(\mu_2\text{-HCO}_2)_3(\mu_2\text{-CO}_3)_2(\text{DMA})_4]\} \cdot 4\text{DMF}$, crystallizes in the monoclinic system with the $C2/m$ space group. As shown in Fig. 2, there are two crystallographically independent cobalt sites, half six-coordinated carbonate, half two-coordinated carbonate, half acetate, half TC4A ligand, one DMA, and 1.5 DMF molecules in the asymmetric unit. The structure of compound **5** is similar to that of compound **1** except for the replacement of Ni(II) by Co(II). The bond lengths of Co–N, Co–S, and Co–O are in the range of 2.116(9), 2.385(2)–2.491(2), and 2.006(5)–2.142(5) Å, respectively. They are slightly longer than those of Ni–N, Ni–S, and Ni–O bonds owing to the larger ionic radius of Co^{II} (74 pm) than that of Ni^{II} (72 pm). The Co···Co distance in the square of the tetranuclear cobalt cluster and the Co···Co distance between the adjacent layers of the Co4 plane are 3.18–3.55 and 2.920(2) Å, respectively.

Continuous shape measure (CShM), a useful method for quantitatively evaluating coordination geometry [34], was used to analyze the metal sites in compounds **1–5** and the chlorine-bridged analog of Ni8 (**6**) using SHAPE 2.0 [35]. The results indicate that all metal sites adopt the octahedron configuration (OC-6) with the smallest CShM value compared with the other configurations. In similar coordination environments, for example, in compounds **1** and **5**, the nickel sites in compound **1** exhibit a smaller CShM value than the cobalt sites in compound **5** (Fig. 3), implying that cobalt atoms more significantly deviate from the ideal octahedron than the nickel atoms. In compounds **2–4**, the CShM value of the metal sites increases gradually with an increase in nickel content and a decrease in cobalt content.

Bond valence sum (BVS), as a powerful and empirical tool for estimating the oxidation state, was used to calculate the BVS of the metal sites in compounds **1–5** [36, 37]. As shown in Table S3 in the ESM, the BVS values of the Ni sites (ranging from 1.97 to 2.25) and Co sites (ranging from 2.10 to 2.40) in compounds **1–5** are close to

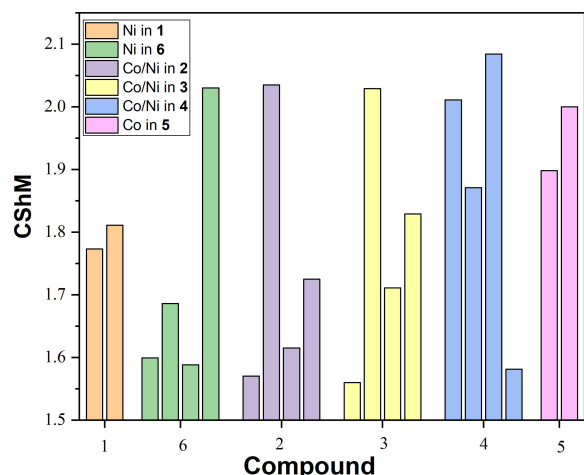


Figure 3 Column distribution of CShM of compounds 1, 6, and 2-5.

2.00, indicating that the valence states of the Ni and Co sites in the compounds are +2, consistent with the valence states of the Ni and Co metal sites in the compounds, as evidenced by the SCXRD analysis.

Figures S1–S5 in the ESM show the crystal packing diagrams of compounds 1–5. No hydrogen bonding or $\pi\cdots\pi$ interaction is observed in the packing modes of the compounds, and van der Waals interactions affect cell packing.

3.1 XPS spectra

XPS analysis of compounds 1–5 was performed to confirm their oxidation states and elemental compositions. According to the XPS spectra, the full survey scans of compounds 1–5 reveal the presence of C, O, N, S, and Ni in compound 1, the presence of C, O, N, S, Cl, Ni, and Co in compounds 2–4, and the presence of C, O, N, S, and Co in compound 5 (Figs. S21–S25 in the ESM). The narrow XPS spectra (Fig. 4) fitting reveals the characteristic Ni(2p) doublets Ni 2p_{1/2} and Ni 2p_{3/2} around ca. 861.54 and 856.51 eV for compound 1, 861.65 and 856.01 eV for compound 2, 860.89 and 855.77 eV for compound 3, and 861.06 and 855.70 eV for compound 4. These results are consistent with previously reported values for Ni(II) in Ref. [38]. The four peaks of Co(2p) (Co 2p_{1/2} sat, Co 2p_{1/2}, Co 2p_{3/2} sat, and Co 2p_{3/2}) are, respectively, found at ca. 798.20, 792.50, 781.59, and 776.54 eV for 2; 801.68, 796.35, 787.06, and 781.73 eV for 3; 801.98, 796.72, 787.37, and 781.19 eV for 4; 801.82, 797.02, 787.21, and 781.53 eV for 5. These values align well with previously

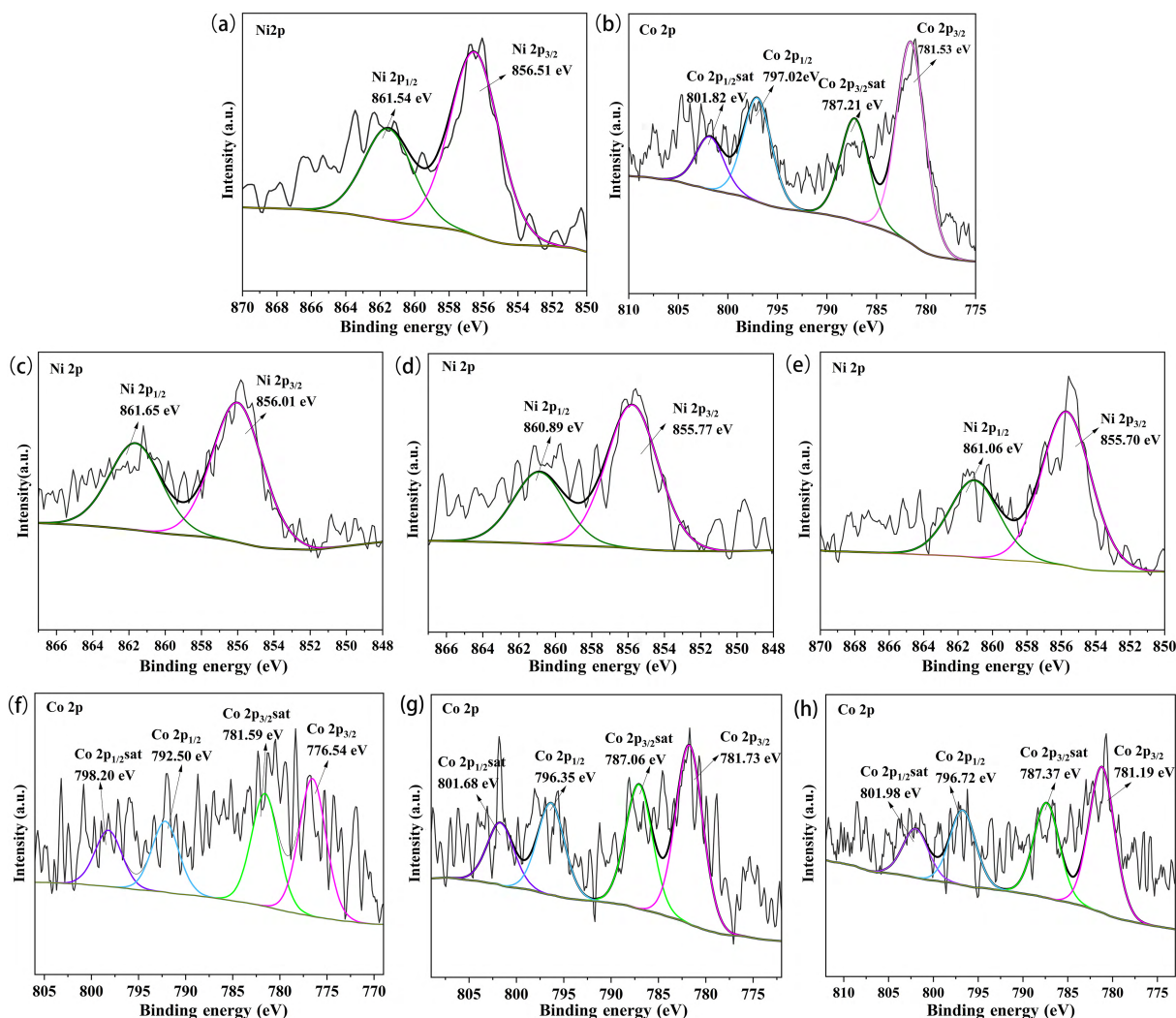


Figure 4 (a) The Ni 2p high-resolution spectrum of 1. (b) The Co 2p high-resolution spectrum of 5. The (c) Ni 2p and (f) Co 2p high-resolution spectra of 2. The (d) Ni 2p and (g) Co 2p high-resolution spectra of 3. The (e) Ni 2p and (h) Co 2p high-resolution spectra of 4.

reported values for Co(II) in Refs. [39, 40]. Thus, the XPS analysis confirms the presence of Ni and Co in these compounds and verifies that their oxidation states are +2, which is fully consistent with the results of the SCXRD analysis.

3.2 FTIR spectroscopy

The FTIR spectra of compounds 1–5 in the range of 400–4000 cm^{-1} were recorded to further explore their structures (Figs. S7–S11 in the ESM). The peaks at 1450–1600 cm^{-1} correspond to the skeleton stretching vibration characteristic peaks of the benzene ring. The strong absorption peaks appear at ca. 2961 and 2902 cm^{-1} in compound 1 (2961 and 2870 cm^{-1} in 2; 2960 and 2865 cm^{-1} in 3; 2961 and 2867 cm^{-1} in 4; 2963 and 2870 cm^{-1} in 5) correspond to the antisymmetric and symmetric stretching vibrations of methyl, respectively, indicating the presence of tert-butyl. The bending vibration of C–H in *t*-Bu appears at approximately 1469 and 1385 cm^{-1} in 1; 1466 and 1385 cm^{-1} in 2; 1469 and 1385 cm^{-1} in 3; 1469 and 1385 cm^{-1} in 4; 1465 and 1385 cm^{-1} in 5. Peaks associated with the phenyl ring skeleton appear at ca. 1585 and 1444 cm^{-1} in 1; 1598 and 1445 cm^{-1} in 2; 1599 and 1441 cm^{-1} in 3; 1599 and 1441 cm^{-1} in 4; 1570 and 1442 cm^{-1} in 5. The fingerprint peaks of the phenyl rings of TC4A appear at ca. 832, 834, 833, 833, and 838 cm^{-1} in 1, 2, 3, 4, and 5, respectively. There is a blue shift of ca. 10 cm^{-1} compared with the free ligand of H₄TC4A owing to the loss of protons on the phenolic hydroxyl group (822 cm^{-1}). The stretching vibrations of C–O and C–S, respectively, appear at ca. 1258 and 883 cm^{-1} in 1, 1258 and 883 cm^{-1} in 2, 1258 and 881 cm^{-1} in 3, 1257 and 885 cm^{-1} in 4, and 1257 and 890 cm^{-1} in 5. The FTIR spectra of compounds 1–5 verify the presence of the TC4A ligand in those compounds.

3.3 SEM and EDS

Scanning electron microscopy (SEM) was used to examine the

surface morphologies of compounds 1–5. The SEM images reveal that compounds 1–4 maintain a regular morphology after being dispersed in ethanol (Figs. 5(a)–5(j)), whereas compound 5 exhibits a plate-like morphology after being dispersed in ethanol. Subsequently, energy-dispersive X-ray spectroscopy (EDS) was performed to investigate the elemental composition of the selected regions. As shown in Figs. 6(a)–6(e), the EDS spectra of compounds 1 and 5 show characteristic peaks corresponding to C, N, O, S, and Ni for (1) or Co (5), whereas compounds 2–4 possess the characteristic peaks of C, N, O, S, Cl, Ni, and Co, further verifying the coexistence of Co and Ni in the synthesized compounds. The elemental distributions of the compounds are uniform without local enrichment. This further confirms that compounds 2 and 3 are heterometallic solid solutions rather than a mixture of different compounds.

3.4 Electron absorption spectroscopy

The ultraviolet–visible (UV–vis) spectra of compounds 1–5 in an acetonitrile solution with a concentration of ca. 1.0×10^{-5} mol/L were recorded at room temperature in the wavelength range of 200–600 nm. As shown in Fig. 7, all compounds exhibit two absorption bands: (1) a strong absorption band with maxima at 209, 202, 203, 204, and 224 nm for 1, 2, 3, 4, and 5, respectively. These results are attributed to π – π^* electronic transitions in the TC4A ligand [1]. (2) A weak absorption band with maxima at 336, 340, 335, 333, and 320 nm for 1, 2, 3, 4, and 5, respectively. These results are attributed to ligand-to-metal charge transfer [41]. The hypsochromic tendency of the weak absorption band from compounds 1–5 agrees with the decrease in nickel content and the increase in cobalt content in the compounds.

3.5 PXRD

To assess the phase purity of the title compounds, PXRD was

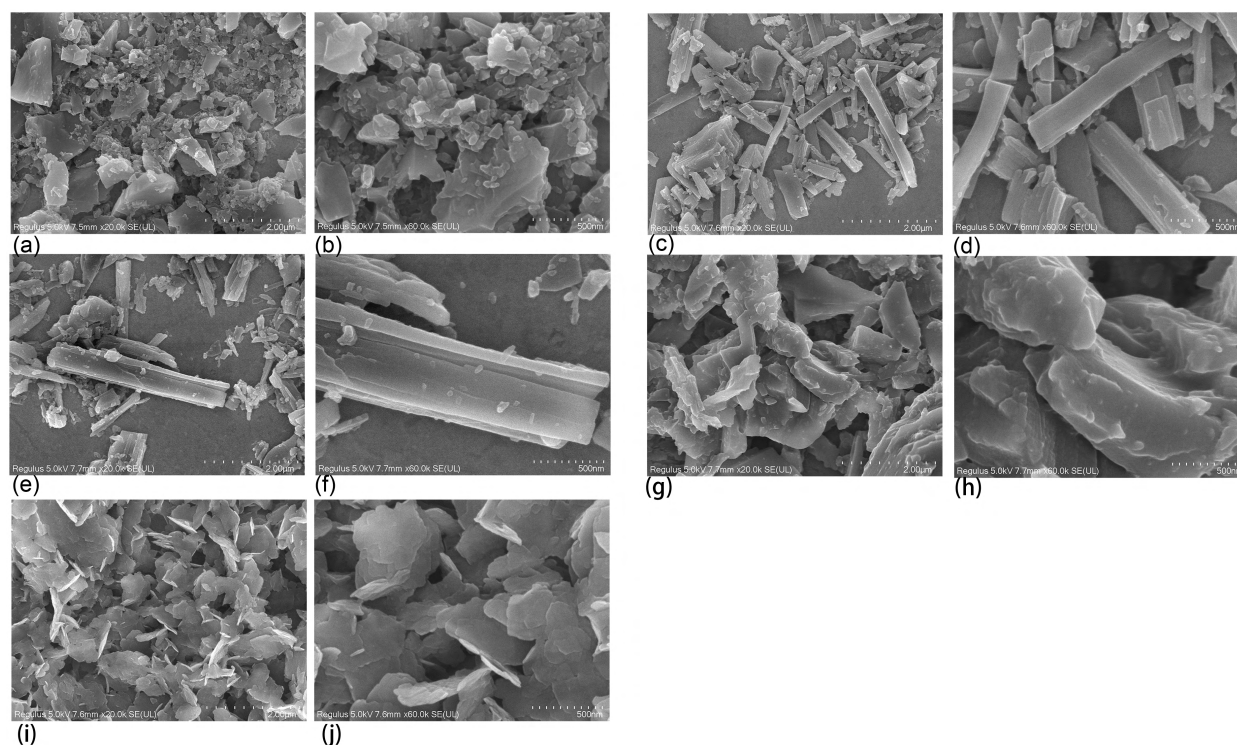


Figure 5 SEM images of compounds 1–5 ((a) and (b) for 1; (c) and (d) for 2; (e) and (f) for 3; (g) and (h) for 4; (i) and (j) for 5).

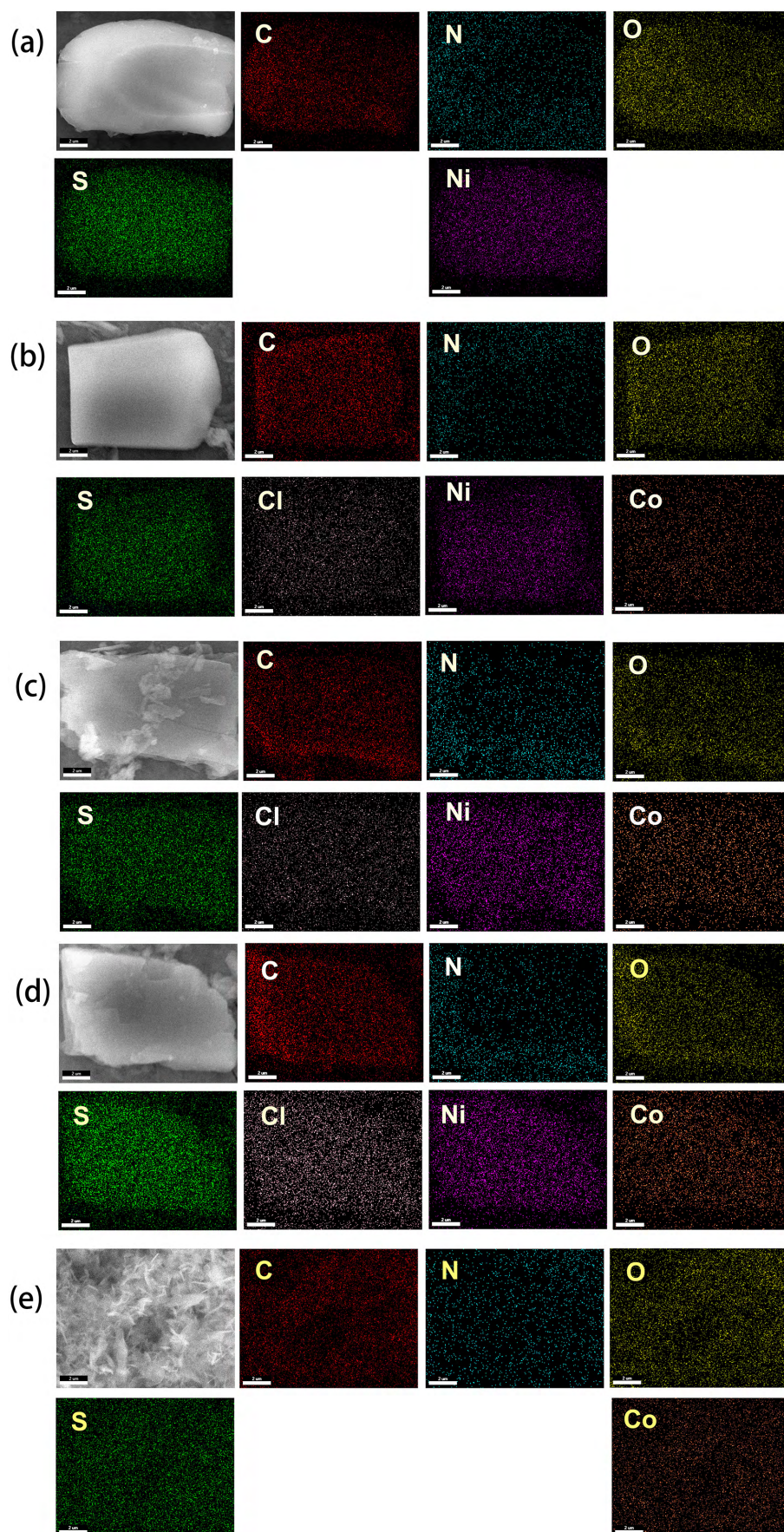


Figure 6 EDS diagrams of compounds 1–5 (a)–(e) (scale bar represents 2 μm).

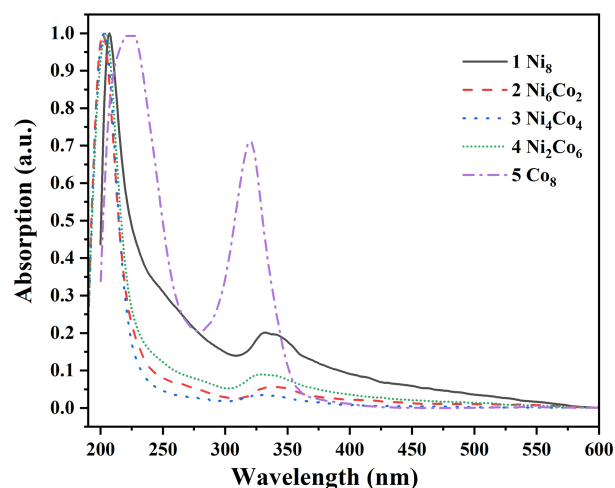


Figure 7 UV-vis spectra of compounds 1–5 in the acetonitrile solution with the concentration of about 1.0×10^{-5} mol/L.

performed in the range of 5° – 60° . The experimental PXRD patterns are in good agreement with the simulated patterns generated from the SC XRD data (Figs. S15–S19 in the ESM), indicating that compounds 1–5 are phase-pure. Differences in peak intensities can be attributed to the preferred orientation in the powder samples.

3.6 TGA

The thermal stability of compounds 1–5 was investigated via TGA under a nitrogen atmosphere at a constant heating rate of 10 K/min from room temperature to 800 $^{\circ}\text{C}$ (Fig. S13 in the ESM). Compound 1 exhibits a gradual weight loss of 8.7% between 30 and 314 $^{\circ}\text{C}$, corresponding to the release of two acetonitrile and two DMF molecules (calcd 8.9%). This was accompanied by a rapid weight loss of 51.1% between 363 and 644 $^{\circ}\text{C}$, corresponding to the loss of four coordinated DMA molecules, decomposition of three acetates and three carbonates, and loss of the TC4A ligand (51.1%). In the TGA diagram of compound 2, there is a weight loss (calcd 7.0%) between 111 and 186 $^{\circ}\text{C}$, corresponding to the loss of crystallized molecules of two acetonitrile and two DMF molecules (calcd 8.9%). This was accompanied by a rapid weight loss (14.2%) between 186 and 362 $^{\circ}\text{C}$, corresponding to the loss of four coordinated DMA molecules and the decomposition of formate and carbonate (13.2%). Another rapid weight loss (26.5%) occurred between 411 and 506 $^{\circ}\text{C}$, corresponding to the decomposition and loss of one TC4A ligand (27.8%). Compounds 3–5 exhibit similar weight losses because of their similar structures, differing only in their compositions. Compound 3 undergoes a weight loss (6.9%) between 83 and 155 $^{\circ}\text{C}$, corresponding to the loss of two crystallized acetonitrile and two DMF molecules (calcd 6.9%). This was accompanied by a second weight loss (14.1%) between 265 and 400 $^{\circ}\text{C}$, corresponding to the decomposition and loss of the coordinated four DMA, two formates, and two carbonates (14.9%). The third rapid weight loss (27.8%) between 400 and 505 $^{\circ}\text{C}$ corresponds to the loss of one TC4A ligand (27.8%). Compound 4 undergoes weight loss (8.2%) between 97 and 182 $^{\circ}\text{C}$, corresponding to the loss of two crystallized acetonitrile and two DMF molecules (calcd 8.8%). A second weight loss (12.4%) occurred between 182 and 331 $^{\circ}\text{C}$, corresponding to the decomposition and loss of the four coordinated DMA molecules, two formates, and two carbonates (14.9%). The third rapid weight loss (27.6%) between 331 and 558 $^{\circ}\text{C}$ corresponds to the loss of one

TC4A ligand (27.8%). Compound 5 undergoes weight loss (5.1%) between 65 and 92 $^{\circ}\text{C}$, corresponding to the loss of two crystallized DMF molecules (calcd 5.1%). The second weight loss (15.6%) occurred between 125 and 230 $^{\circ}\text{C}$, corresponding to the decomposition and loss of the four coordinated DMA molecules and the decomposition of formates and carbonates (14.9%). The third rapid weight loss (28.5%) between 384 and 540 $^{\circ}\text{C}$ corresponds to the loss of one TC4A ligand (27.8%).

3.7 Magnetic measurements

Magnetic susceptibility ($\chi_M T$) measurements were performed on polycrystalline samples of compounds 1–5 and the Ni_8 reference compound 6 in the temperature range of 2–300 K under an applied field of 1000 Oe (Fig. 8 and Fig. S29 in the SM). For compound 1, the room-temperature $\chi_M T$ for the Ni(II) centers is 8.43 $\text{cm}^3\cdot\text{K}/\text{mol}$, which is close to the theoretical value of 8.00 $\text{cm}^3\cdot\text{K}/\text{mol}$ for eight uncoupled Ni(II) centers [11]. The Cl-bridged Ni_8 reference compound 6 exhibits a room-temperature $\chi_M T$ of 8.56 $\text{cm}^3\cdot\text{K}/\text{mol}$, indicating that in a uniform anionic environment, the overall magnetic behavior is primarily determined by the metal centers. Upon cooling, the $\chi_M T$ of compound 1 gradually decreases from 80 to 8 K, then slightly increases between 3 and 10 K, and finally decreases to 2.69 $\text{cm}^3\cdot\text{K}/\text{mol}$ at 2 K. This low-temperature $\chi_M T$ upturn, accompanied by a small hysteresis and low saturation in the magnetization–magnetic field curve, indicates predominantly antiferromagnetic interactions. Similar low-temperature behavior and structures have been reported for octanuclear Ni(II) complexes [42]. In contrast, compound 6 does not exhibit a low-temperature $\chi_M T$ upturn [11]. For compound 5, the room-temperature $\chi_M T$ for Co(II) centers is 20.16 $\text{cm}^3\cdot\text{K}/\text{mol}$ (the $\chi_M T$ for free Co(II) is typically 2.7–3.4 $\text{cm}^3\cdot\text{K}/\text{mol}$), consistent with typical Co(II) coordination complexes [43]. For compounds 2–4, where Ni(II) is partially replaced by Co(II), the room-temperature $\chi_M T$ values are 10.43, 12.90, and 16.35 $\text{cm}^3\cdot\text{K}/\text{mol}$, respectively, and the corresponding 2 K values are 0.26, 0.71, and 1.24 $\text{cm}^3\cdot\text{K}/\text{mol}$, respectively. Curie–Weiss fitting of compounds 1–6 in the range of 50–300 K yields Curie constants (C) of 10.83, 14.05, 16.12, 19.75, 22.19, and 10.58 $\text{cm}^3\cdot\text{K}/\text{mol}$, respectively, and Weiss constants (θ) of –86.56, –103.77, –76.32, –63.59, –32.13, and –79.54 K, respectively (all negative), further confirming antiferromagnetic interactions. The measured magnetic susceptibility $\chi_M T$ of compounds 1–5 increases as the cobalt content increases in the range of 50–300 K. This trend demonstrates that the magnetic behavior of TC4A-supported Co(II)/Ni(II) clusters can be rationally modulated by adjusting the Ni(II)/Co(II) molar ratio.

4 Conclusion

In this study, we synthesized a series of TC4A-based transition metal clusters, namely, $\{[\text{Ni}_8(\text{TC4A})_2(\mu_6\text{-CO}_3)_2(\mu_2\text{-CH}_3\text{CO}_2)_3(\mu_2\text{-CO}_3)(\text{DMA})_4]\cdot(\text{CH}_3\text{CN})_2\}$ (1), $\{[\text{Ni}_{5.81}\text{Co}_{2.19}(\text{TC4A})_2(\mu_6\text{-CO}_3)_2(\mu_2\text{-HCO}_2)_2(\mu_2\text{-Cl})_2(\text{DMA})_4]\cdot 2\text{DMF}\cdot 2\text{CH}_3\text{CN}\}$ (2), $\{[\text{Ni}_{4.06}\text{Co}_{3.94}(\text{TC4A})_2(\mu_6\text{-CO}_3)_2(\mu_2\text{-HCO}_2)_2(\mu_2\text{-Cl})_2(\text{DMA})_4]\cdot 2\text{DMF}\cdot 2\text{CH}_3\text{CN}\}$ (3), $\{[\text{Ni}_2\text{Co}_6(\text{TC4A})_2(\mu_6\text{-CO}_3)_2(\mu_2\text{-HCO}_2)_2(\mu_2\text{-Cl})_2(\text{DMA})_4]\cdot 2\text{DMF}\cdot 2\text{CH}_3\text{CN}\}$ (4), and $\{[\text{Co}_8(\text{TC4A})_2(\mu_6\text{-CO}_3)_2(\mu_2\text{-HCO}_2)_3(\mu_2\text{-CO}_3)_2(\text{DMA})_4]\cdot 6\text{DMF}\}$ (5), through a solvothermal reaction by controlling the molar ratio of Ni/Co (1, 1:0; 2, 3:1; 3, 1:1; 4, 1:3; 5, 0:1). SCXRD analysis reveals that all synthesized compounds possess similar structures featuring an octanuclear chair-like metal

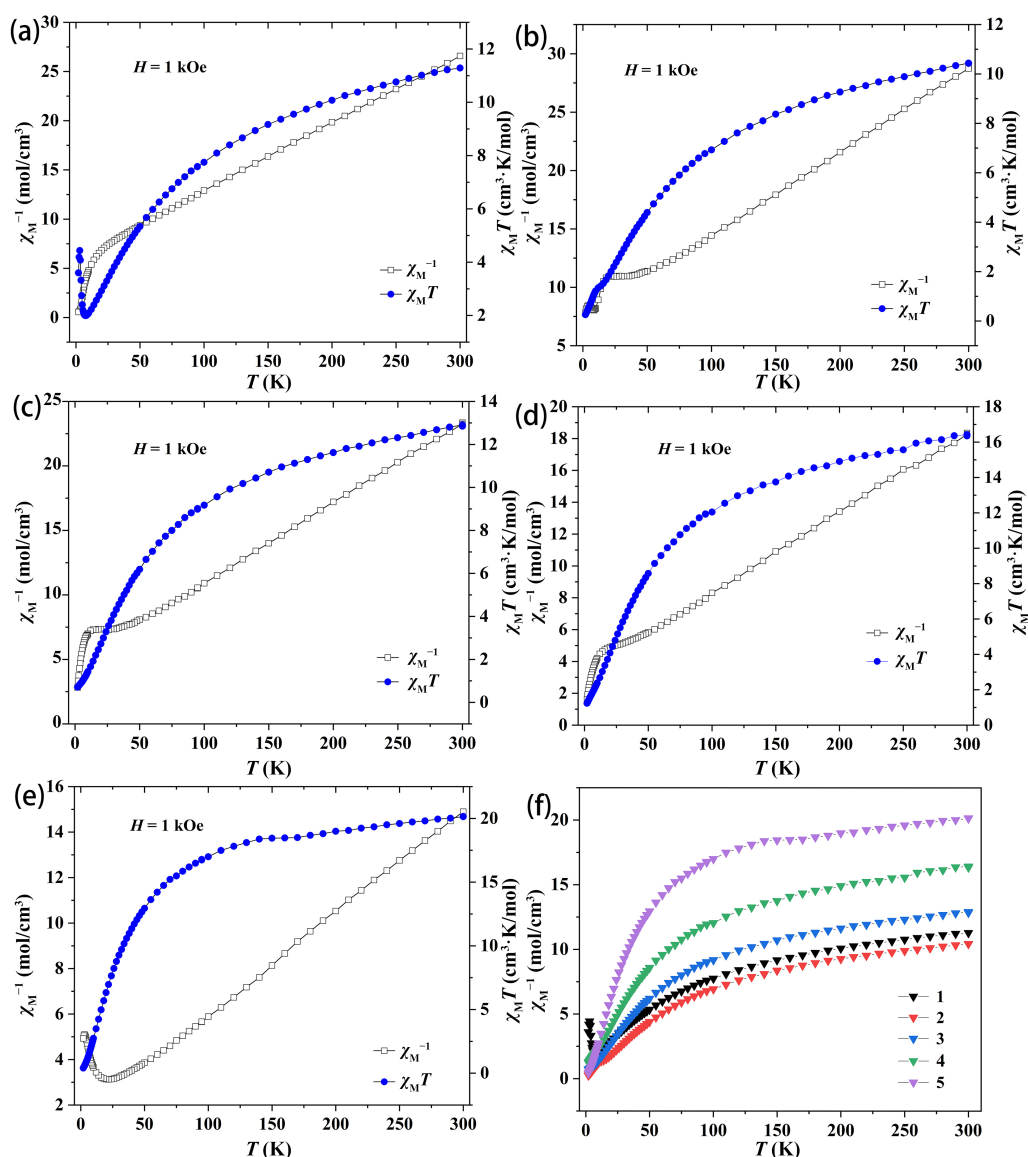


Figure 8 (a)–(e) The temperature dependence of the magnetic susceptibility of compounds 1–5 in a 1000 Oe magnetic field and (f) the total magnetic susceptibility diagram of compounds 1–5.

skeleton supported by two TC4A ligands, which can also be viewed as two badminton-shaped SBUs of $\{M_4TC4A\}$ connected by two six-coordinated carbonates and two bridged acetates (1, 5) or chlorine atoms (2, 3, 4) in a tail-to-tail manner. The refined Ni/Co occupancy ratios in 2, 3, and 4 are close to the theoretical distribution of Ni/Co. Their structures were also evidenced by FTIR, PXRD, TGA, and XPS analyses. The magnetic studies of compounds 1–5 indicate an antiferromagnetic interaction between their metal ions, and the measured magnetic susceptibility $\chi_M T$ of compounds 1–5 increases as the cobalt content increases in the range of 50–300 K. This study provides a convenient approach for tuning the structures and magnetic properties of heterometallic compounds.

Electronic Supplementary Material: Supplementary material (synthesis, FT-IR, PXRD, XPS, TGA, the packing diagram of compounds 1–5, tables of crystallographic data, the selected bond lengths and angles) is available in the online version of this article at <https://doi.org/10.26599/POM.2026.9140141>.

CCDC 2537383 (for 1), 2537384–2537386 (for 3–5), 2537387 (for 2) contains the supplementary crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

Author contribution statement

The manuscript was written through contributions from all authors. T. G. and J.-C. Y.: performed the synthetic experiments and TGA tests, analyzed the magnetism data, and prepared the original draft. M.-L. Y. and Y.-L. L.: conducted some synthetic experiments, finished the FT-IR and UV-Vis spectroscopy test, and analyzed corresponding data. J.-P. M.: collected and analyzed the single crystal X-ray diffraction data and revised the paper. L.-S. W.: refined the crystal data, supervised the research and revised the paper. Y.-M. L.: performed the magnetism test and revised the paper. All authors had read and approved the final manuscript.

Use of AI statement

None.

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