A Novel Two-Dimensional Layer Structure Built from a Tetracobalt(II)-*p*-sulfonatothiacalix[4]arene Cluster Unit

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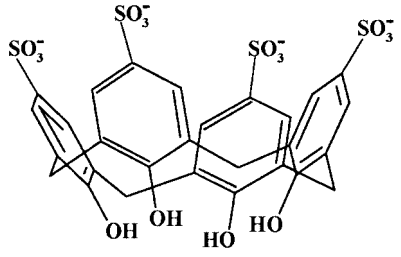
Keywords: *p*-Sulfonatothiacalix[4]arene / Cobalt / Magnetic properties / Coordination polymer

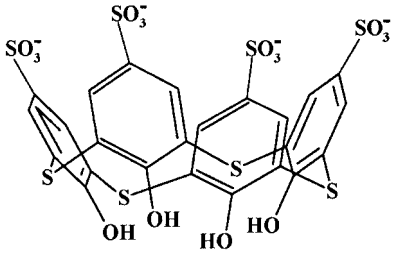
The novel coordination polymer $[Co_4(TCAS)(\mu_4\text{-}SO_4)(4,4'\text{-}Hbipy)_2]_n$ (TCAS = the octaanion of *p*-sulfonatothiacalix[4]arene) (**1**) has been synthesized hydrothermally and characterized. X-ray diffraction analyses reveal a two-dimensional (2D) layer structure built from the $[Co_4(TCAS)(\mu_4\text{-}SO_4)]^{2-}$ unit. The tetranuclear cobalt(II) clusters bridged by the μ_4-SO_4^{2-} and phenoxy groups of the same TCAS provide a unique trapeziform magnetic mode; magnetic studies in the temperature range 2–300 K show weak antiferromagnetic interactions between the four cobalt(II) centers.

Introduction

Water-soluble *p*-sulfonatocalix[4]arene (H_4CAS^{4-}, Scheme 1) is a versatile host for molecules of relevance in areas of materials science such as separation technology, biomimetics, and structural biology.[1] As a multifunctional supramolecular synthon, H_4CAS^{4-} can form capsules, nano-scale spheres, tubes and bi-layer structures with cavities.[2] A new water-soluble *p*-sulfonatothiacalix[4]arene (H_4TCAS^{4-}, Scheme 1) was then obtained by replacing the methylene junctions with thioether sulfur.[3] The sulfur donor atoms in H_4TCAS^{4-} add four new potential coordination sites and has provided a new type of complex.[4] Although many metal-TCAS complexes have been synthesized and studied by X-ray crystallography,[5] complexes possessing a polynuclear structure seem to have been almost neglected.[6] Currently, there is much interest in transition-metal coordination polymers as magnetic, electronic or photooptical molecular materials.[7] One strategy used to obtain such interesting new materials is to increase the structural dimensionality by combining recognizable polynuclear repeating units to form chains, layers or three-dimensional (3D) networks.[8,9] We recently introduced $TCAS^{8-}$ as a polydentate ligand to synthesize polynuclear clusters, and expected the clusters to link into novel structural coordination polymers with special properties. Fortunately, we have successfully synthesized a novel 2D layer coordination polymer with a tetranuclear cobalt(II) cluster unit $[Co_4(TCAS)(\mu_4\text{-}SO_4)(4,4'\text{-}Hbipy)_2]$ (**1**) (4,4′-Hbipy = monocation of 4,4′-H-bipyridine). Herein, we report its synthesis, structural analysis and magnetic properties.



H_4CAS^{4-}



H_4TCAS^{4-}

Scheme 1. Molecular structures of H_4CAS^{4-} and H_4TCAS^{4-}.

Results and Discussion

Synthesis

The hydrothermal reaction of cobalt(II) salt with Na_4H_4TCAS and 4,4′-bipyridine (molar ratio 4:1:2) at

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160 °C for 3 days afforded red crystalline compound **1**, which is insoluble in water and common organic solvents. The preparation is summarised in Equation (1).

$$4n\ CoSO_4{\cdot}6\ H_2O + n\ Na_4H_4TCAS + 2n\ 4,4'\text{-bipy} \xrightarrow[T = 160\ ^\circ C]{pH = 3} [Co_4(TCAS)(SO_4)(4,4'\text{-Hbipy})_2]_n + 2n\ Na_2SO_4 + n\ H_2SO_4 + 24n\ H_2O \quad (1)$$

Structural Description

An X-ray structure analysis showed that **1** exhibits a 2D layer structure built from the $[Co_4(TCAS)(\mu_4\text{-}SO_4)]^{2-}$ anion complex unit and 4,4′-Hbipy cation (Figure 1). Table 1 lists selected bond lengths and bond angles. The structure of the anion complex unit, like a bowl, consists of a trapezoid of four cobalt(II) centers between one TCAS unit and one sulfate ligand. In the complex unit, there is only one $TCAS^{8-}$ ligand arranged about the metal cluster, which differs greatly from the metal-thiacalix[4]arene clusters.[4] Furthermore, a mirror plane is imposed on the complex unit and passes through S(3), S(5), S(6), O(1), O(2), O(8), O(9), O(11), O(12), C(1), C(4), C(12), and C(15). A disordered water molecule is included within the cavity of the $TCAS^{8-}$ unit. The fully deprotonated $TCAS^{8-}$ unit, maintaining a conventional cone conformation, utilizes its phenoxy groups as μ_2-phenoxy bridges to bind four cobalt(II) ions to form the tetracobalt cluster with an average $Co–O_{(phenoxy)}$ distance of 2.073(4) Å. The array of four cobalt(II) ions is close to an isosceles trapezoid, and the Co(1)···Co(2), Co(1A)···Co(2A), Co(1)···Co(1A), and Co(2)···Co(2A) distances are 3.645(1), 3.645(1), 3.604(2), and 3.285(2) Å, respectively. Interestingly, at the lower rim of $TCAS^{8-}$, the $\mu_4\text{-}SO_4^{2-}$ anion binds with the four Co^{II} ions in a rare tridentate coordination mode to form the base of the bowl. There are two types of coordination environments for the four cobalt(II) ions: Co(1) and Co(1A) are in a O_5S octahedral geometry, while Co(2) and Co(2A) are in a NO_4S donor-atom environment. Co(1)–S(1) and Co(2)–S(2) have bond lengths of 2.445(2) and 2.499(2) Å, respectively. The oxygen atoms from sulfonate and sulfate oxygen and/or nitrogen atoms from 4,4′-Hbipy complete the six-coordinate cobalt(II) spheres with average $Co–O_{(sulfonate)}$ $Co–O_{(sulfate)}$, and Co–N distances of, respectively, 2.132(5), 2.124(5) and 2.107(6) Å. The 4,4′-Hbipy acts as terminal ligand rather than common bridging ligand, in which uncoordiated nitrogen is protonated, for charge balance, and shows hydrogen bonding with sulfonate and sulfate oxygen [$N···O_{(sulfonate)}$ 3.161(11) Å; $N···O_{(sulfate)}$ 2.851(12) Å]. Notably, further aggregation of the tetracobalt clusters is directed by the coordination of sulfonate groups of $TCAS^{8-}$ in **1**, where the sulfonate groups adopt two types of coordination modes, one half in monodentate and the other half in O,O′-η^1:η^1:μ_2 bridging bidentate mode (Scheme 2).

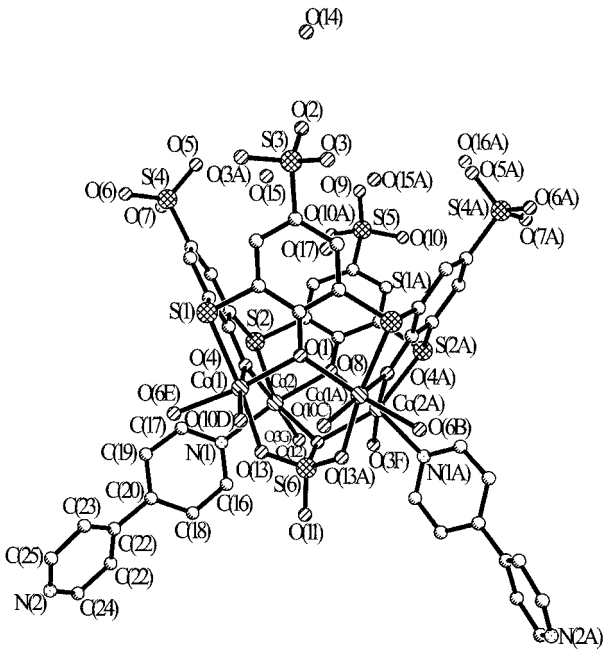


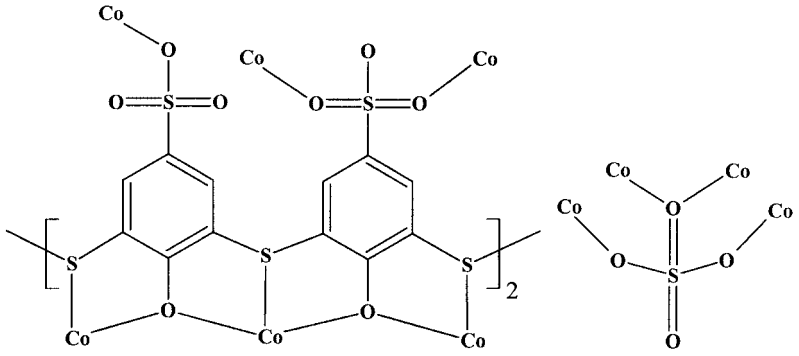
Figure 1. X-ray crystallographic structure of **1**; hydrogen atoms omitted for clarity. Symmetry transformations used to generate equivalent atoms A: *x*, *y*, ½ – *z*; B: 1 – *x*, 1 – *y*, ½ + *z*; C: 1 – *x*, ½ + *y*, *z*; D: 1 – *x*, ½ + *y*, ½ – *z*; E: 1 – *x*, 1 – *y*, – *z*; F: 1 – *x*, *y* – ½, *z*; G: 1 – *x*, *y* – ½, ½ – *z*.

Table 1. Selected bond lengths [Å] and angles [°] in **1**.

Co(1)–O(13)	2.078(4)	O(13)–Co(1)–O(4)	92.10(17)
Co(1)–O(4)	2.085(4)	O(13)–Co(1)–O(1)	103.4(2)
Co(1)–O(1)	2.089(3)	O(4)–Co(1)–O(1)	93.3(2)
Co(1)–O(6E)	2.091(4)	O(13)–Co(1)–O(6E)	86.04(18)
Co(1)–O(10D)	2.147(5)	O(4)–Co(1)–O(6E)	96.44(17)
Co(1)–S(1)	2.4460(19)	O(1)–Co(1)–O(6E)	166.2(2)
Co(2)–O(8)	2.018(4)	O(13)–Co(1)–O(10D)	81.01(18)
Co(2)–O(4)	2.100(4)	O(4)–Co(1)–O(10D)	172.65(17)
Co(2)–N(1)	2.101(6)	O(1)–Co(1)–O(10D)	85.9(2)
Co(2)–O(3G)	2.157(5)	O(6E)–Co(1)–O(10D)	85.70(17)
Co(2)–O(12)	2.174(4)	O(13)–Co(1)–S(1)	172.76(14)
Co(2)–S(2)	2.5004(19)	O(4)–Co(1)–S(1)	83.75(12)
S(1)–C(2)	1.773(6)	O(1)–Co(1)–S(1)	82.82(15)
S(1)–C(6)	1.788(6)	O(6E)–Co(1)–S(1)	88.53(13)
S(2)–C(10)	1.783(7)	O(10D)–Co(1)–S(1)	103.36(13)
S(2)–C(13)	1.796(6)	O(8)–Co(2)–O(4)	95.8(2)
S(3)–O(2)	1.430(7)	O(8)–Co(2)–N(1)	172.5(2)
S(3)–O(3)	1.474(5)	O(4)–Co(2)–N(1)	90.8(2)
S(3)–C(4)	1.769(10)	O(8)–Co(2)–O(3G)	88.2(2)
S(4)–O(5)	1.442(5)	O(4)–Co(2)–O(3G)	175.39(18)
S(4)–O(7)	1.448(6)	N(1)–Co(2)–O(3G)	85.3(2)
S(4)–O(6)	1.480(5)	O(8)–Co(2)–O(12)	75.35(19)
S(4)–C(8)	1.775(7)	O(4)–Co(2)–O(12)	98.5(2)
S(5)–O(9)	1.437(7)	N(1)–Co(2)–O(12)	100.2(2)
S(5)–O(10)	1.470(5)	O(3G)–Co(2)–O(12)	84.7(2)
S(5)–C(15)	1.777(9)	O(8)–Co(2)–S(2)	81.02(15)
S(6)–O(11)	1.433(7)	O(4)–Co(2)–S(2)	82.39(12)
S(6)–O(12)	1.490(7)	N(1)–Co(2)–S(2)	103.39(17)
S(6)–O(13)	1.490(5)	O(3G)–Co(2)–S(2)	96.05(14)
		O(12)–Co(2)–S(2)	156.34(14)

Symmetry transformations used to generate equivalent atoms: D: 1 – *x*, ½ + *y*, ½ – *z*; E: 1 – *x*, 1 – *y*, – *z*; G: 1 – *x*, *y* – ½, ½ – *z*

Each $[Co_4(TCAS)(\mu_4\text{-}SO_4)]^{2-}$ bowl links four other bowl units through $Co–O_{(sulfonate)}$ bonds to generate a layer structure in an alternating up-down bowl alignment (Figure 2). Moreover, each $TCAS^{8-}$ unit forms π–π interactions



Scheme 2. Schematic of the coordination modes of $TCAS^{8-}$ and SO_4^{2-}.

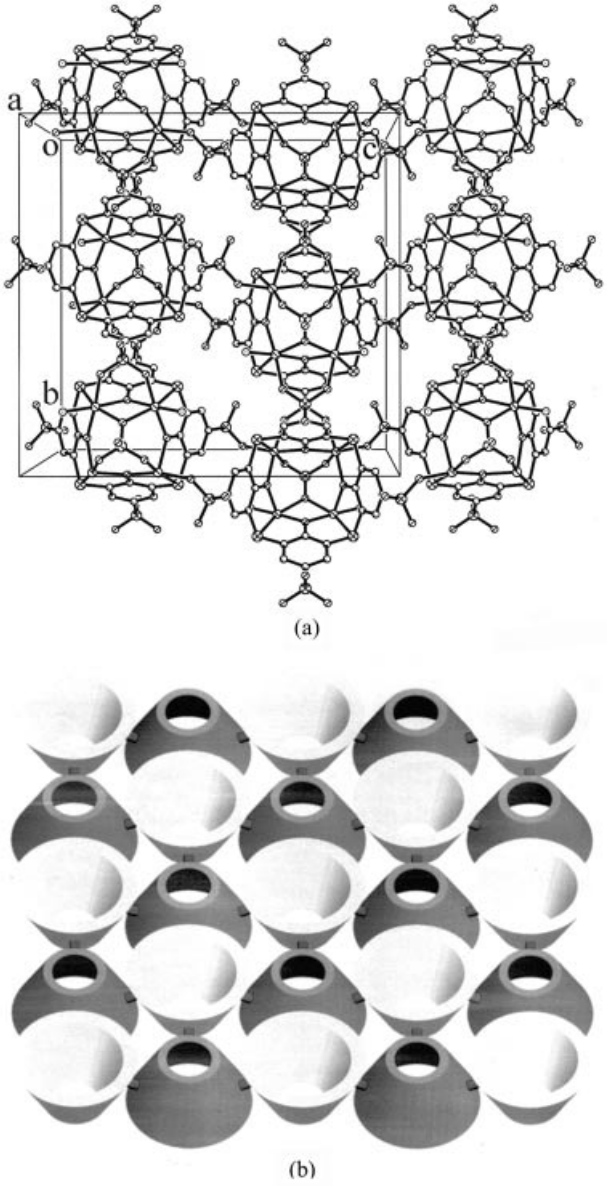


Figure 2. View of the 2D layer structure of **1** (a) and a schematic showing the regular structure with bowl alignment (b).

with four other $TCAS^{8-}$ units within the crystal lattice at ring centroid separations of 3.34, 4.48, 3.34, and 4.48 Å.[10] To date, although many reports have described TCAS complexes, this is the first example showing a 2D layer structure with tetranuclear Co^{II} clusters from $TCAS^{8-}$.

It is pertinent to mention that a disordered water molecule that resides in the cavity of the $TCAS^{8-}$ is located by the OH–aromatic π-hydrogen bonds between the water and aromatic rings, and the O···π centroid distances are 3.45, 3.83, 3.68 and 3.79 Å. Aromatic π-hydrogen bonding to water has been reported for the complex $Na_4H_4CAS{\cdot}13.5\,H_2O$ in which the O···π centroid distances are 3.48, 3.83, 4.78, 4.00 Å.[11] The water molecule penetrates 2.582 Å into the cavity, as measured by how far the water molecule is from the plane of the thiacalix[4]arene bridging sulfur atoms.

Thermal Stability

Thermogravimetric analysis (TGA) was performed on polycrystalline samples of **1**, under nitrogen, to study their stability. The data show two weight loss steps (Figure 3). The first occurs from 30 to 130 °C, with a weight loss of 6.83%, which corresponds to the loss of water molecules. The weight then remains almost unchanged in the plateau from 130 to 510 °C. The second step occurs in the range 510 to 595 °C (weight loss of 29.25%), corresponding to the loss of the 4,4′-bipyridine ligands and the SO_4^{2-}. The compound begins to decompose at 595 °C. The thermogravimetric results demonstrate that the compound is rather stable under nitrogen.

Magnetic Properties

The temperature-dependent magnetic susceptibility of complex **1** was investigated in the range 2–300 K at a 10 kOe applied field. The χ_m and $\chi_m T$ per four Co^{II} ions versus T curves are shown in Figure 4. At 300 K, $\chi_m T$ is 9.80 $cm^3\,mol^{-1}\,K$, which is larger than the expected 7.50 $cm^3\,mol^{-1}\,K$ for four magnetically isolated high-spin Co^{II} ions (S_{Co} = 3/2, g = 2.0). This larger value is the result of contributions to the susceptibility from orbital angular

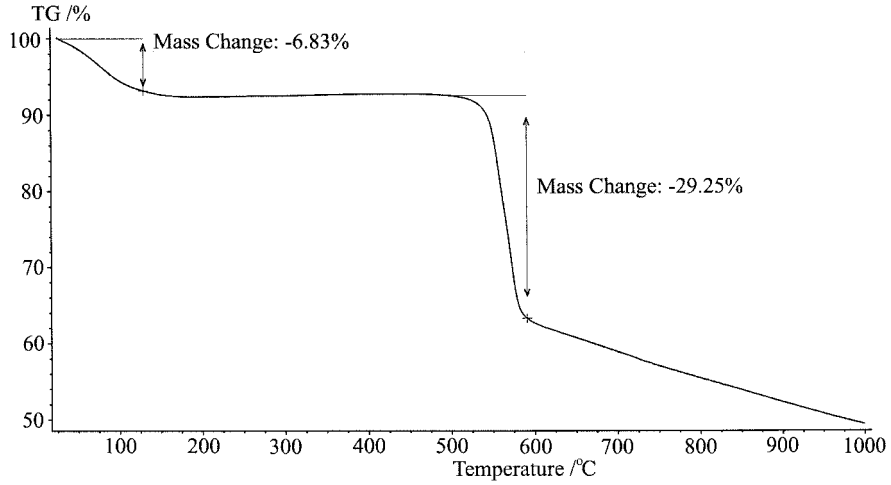


Figure 3. TGA plot for **1** between 30 and 1000 °C.

momentum at high temperature. As the temperature is lowered χ_m increases, reaching a maximum at ca. 14 K. Between 50 and 300 K, χ_m follows the Curie–Weiss law, $\chi_m = C_m/(T - \theta)$, with $C_m = 2.71 \pm 0.01$ cm^{3}kmol (per Co) and $\theta = -28.9 \pm 0.4$ K. These results indicate the antiferromagnetic interactions between cobalt(II) centers.

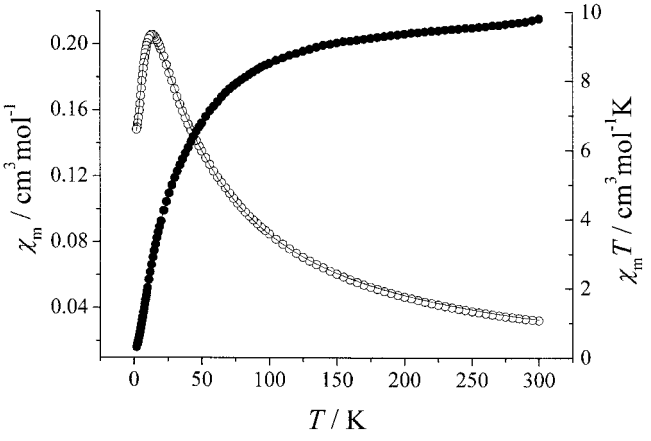


Figure 4. Experimental temperature dependences of χ_m (○) and $\chi_m T$ (●) for **1**; solid lines correspond to the best fit obtained for **1**.

Considering cluster topology and connectivity (Figure 5), an exchange pathway of four cobalt(II) centers of **1** was taken into account. However, we failed to fit the behavior of an array of four orbital degeneration Co^{II} centers by means of an effective spin-Hamiltonian, proposing a four-*J* model, due to the large magnetic anisotropy and spin–orbit coupling of these ions.[12] Therefore, the simplest treatment was carried, considering only isotropic exchange interactions and assuming $J_1 = J_2 = J_3$. The magnetic data were analyzed with the spin Hamiltonian shown in Equation (2).

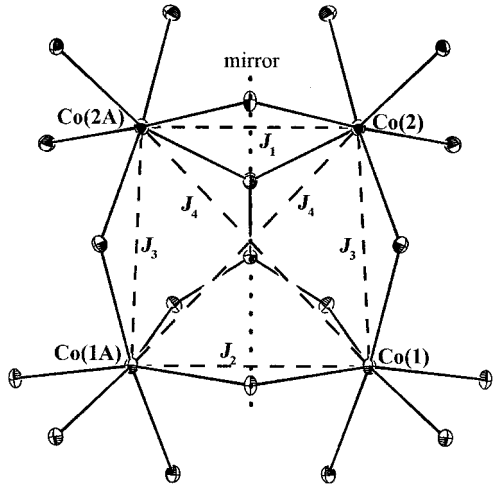


Figure 5. Spin topology for **1** assuming four different *J* values.

The total spin states (S_T) and their energies [$E(S_T)$] can be obtained using the vector-coupling method of Kambe,[13] and substituted into the Van Vleck equation in Equation (3). A Weiss-like temperature correction (θ') to account for intermolecular exchange effects has been applied. The magnetic data were fitted to Equation (3), and gave best-fit parameters of $g = 2.40 \pm 0.01$, $J_1 = -3.07 \pm 0.02$ cm^{-1}, $J_4 = -1.36 \pm 0.06$ cm^{-1}, $\theta' = 1.66 \pm 0.01$ K and an agreement factor $R = 6.12 \times 10^{-6}$. These results show the presence of two kinds of weak antiferromagnetic interactions (J_1 and J_4) associated with the interactions of μ_2-PhO$^-$ and μ_4-SO_4^{2-}. The antiferromagnetic interactions between Co(1) and Co(2) or Co(1) and Co(1A) or Co(2) and Co(2A) through the μ_2-PhO$^-$ originate, presumably, from the high Co–O–Co angles of 121.2° or 119.3° or 108.8°, which differ considerably from 90°.[14]

$$\hat{H}_{ex} = -2J_1(\hat{S}_{Co(2A)}\hat{S}_{Co(2)} + \hat{S}_{Co(1A)}\hat{S}_{Co(1)} + \hat{S}_{Co(2A)}\hat{S}_{Co(1A)} + \hat{S}_{Co(2)}\hat{S}_{Co(1)}) - 2J_4(\hat{S}_{Co(2A)}\hat{S}_{Co(1)} + \hat{S}_{Co(2)}\hat{S}_{Co(1A)}) \quad (2)$$

$$\chi_m = \frac{N\beta^2 g^2}{3k(T-\theta')} \frac{\sum S_T(S_T+1)(2S_T+1)e^{-E(S_T)/kT}}{\sum (2S_T+1)e^{-E(S_T)/kT}} \quad (3)$$

Conclusions

We have successfully used $TCAS^{8-}$ to produce a novel 2D coordination polymer consisting of antiferromagnetically coupled tetranuclear Co^{II} building units. This work suggests that the TCAS-based anion is a versatile ligand with various advantages, including high-nuclearity cluster formation, linking of cluster into polymer arrays, mixed-metal chemistry and ferromagnetic exchange interaction.

Experimental Section

General Remarks: Na_4H_4TCAS was prepared according to a literature method.[3] All other starting chemicals and solvent were commercially available with analytical purity and were used as received. IR spectra were recorded on a Magna 750 FT-IR spectrophotometer (using KBr disks). C, H and N elemental analyses were determined on an Elementary Vario ELIII elemental analyzer and the Co content was determined by atomic absorption. Thermogravimetric analyses (TGA) were performed with a NETSCHZ STA-449C thermoanalyzer under N_2 (30–1000 °C) at a heating rate of 10 °C min^{-1}. Temperature-dependent magnetic-susceptibility measurements on powdered solid samples were performed on Quantum Design MPMS-7 SQUID magnetometer in the range 2–300 K. The magnetic field applied was 10 kOe. Observed susceptibility data were corrected for underlying diamagnetism using Pascal's constants.[15]

Synthesis of 1: The pH of an aqueous mixture (15 mL) containing Na_4H_4TCAS (90.48 mg, 0.1 mmol), 4,4′-bipyridine (31.20 mg, 0.2 mmol) and $CoSO_4{\cdot}6H_2O$ (105.2 mg, 0.4 mmol) was preadjusted to about 3 with 0.1 M H_2SO_4 aqueous solution. The mixture was then transferred to a Teflon-lined stainless vessel (20 mL) that was sealed, heated in an autoclave to 160 °C for 72 h, and then cooled to room temperature at 10 °C h^{-1}. Red crystal of $1{\cdot}3.5H_2O$ were obtained (79.24 mg, yield 52.2% based on Co). Anal. calcd. for $1{\cdot}3.5H_2O$, $C_{44}H_{33}N_4O_{23.5}S_9Co_4$ (1518.00): C 34.81, H 2.19, N 3.69, Co 15.54; found: C 34.53, H 2.11, N 3.82, Co 15.27. IR (KBr): $\tilde{\nu}$ = 3464, 3222, 3116, 3066, 3033, 1637, 1614, 1454, 1423, 1247, 1157, 1141, 1029, 881, 804, 754, 613 cm^{-1}.

Table 2. Crystal data for **1**.

Empirical formula	$C_{44}H_{33}N_4O_{23.5}S_9Co_4$
Formula mass	1518.00
Temperature [K]	298(2)
Wavelength [Å]	0.71073
Crystal system	orthorhombic
Space group	*Pbcm* (No. 57)
a [Å]	15.3120(4)
b [Å]	18.9858(2)
c [Å]	19.8374(4)
α [°]	90
β [°]	90
γ [°]	90
V [Å^3]	5766.9(2)
Z	4
$D_{calcd.}$ [Mg m^{-3}]	1.748
M(Mo-K_α) [mm^{-1}]	1.540
F_{000}	3060
θ range [°]	2.52 to 25.03
Measured reflections	13675
Unique reflections	5222
Observed reflections	3680
R_{int}	0.0614
Goodness-of-fit on F^2	1.131
R_1, wR_2 [$I > 2\sigma(I)$]	0.0636, 0.1379
[all data]	0.1041, 0.1580
Res. electron density [e Å^{-3}]	+0.871, –0.609

X-ray Crystallography Determination: A block crystal (ca. 0.28 × 0.22 × 0.18 mm) of **1** was selected for X-ray diffraction analysis. Data collection was performed on a Siemens SMART-CCD diffractometer equipped with a graphite monochromated Mo-K_α radiation (λ = 0.71073 Å), using the ω-scan mode at 293 K. All absorption corrections were applied using the SADABS program.[16] Structures were solved by direct methods, the metal atoms were located from the E-maps, and other non-hydrogen atoms were derived from successive difference Fourier syntheses. Hydrogen atoms were positioned geometrically, and allowed to ride on their parent C or N atoms. The structure was refined on F^2 by full-matrix least-squares using the SHELXTL-97 program package.[17] Crystallographic data of **1** is summarized in Table 2, and selected bond lengths and bond angles are listed in Table 1. CCDC-221212 (for **1**) contains 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.

Acknowledgments

We are grateful for financial support from NSFC (No. 20231020), the Natural Foundation of Fujian Province and the key project of CAS. We also thank Professor Song Gao for collecting the magnetism data.

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Received: July 12, 2004

