# Solvothermal Synthesis, Crystal Structure, and Magnetic Properties of $[Co_3(SDA)_3(DMF)_2]$; 2-D Layered Metal-organic Framework Derived from 4,4'-Stilbenedicarboxylic Acid ($H_2SDA$)

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Metal-organic frameworks (MOF) have attracted much more attention in the past decade owing to their various intriguing framework topologies and potential applications as functional materials in gas storage,[1] separation,[2] and catalysis.[3] Because high framework stability is fundamental and essential property for many practical applications, multi-dentate linkers such as carboxylates have been extensively investigated for the formation of more rigid frameworks due to their ability to aggregate metal ions into M-O-C clusters called secondary building units (SBUs) rather than N-bound organic linkers such as 4,4-bipyridine (bipy).[4] The versatility of carboxylate anions, which can adopt different bridging modes such as syn–syn, anti–anti, syn–anti, and mono-atomic as units for ligating and connecting metal centers also has led to extensive research on the magnetic properties of carboxylato complexes.[5] Especially low dimensional assemblies of anisotropic metal ion systems in which the magnetic centers interact within chains (1-D) or planes (2-D) by using molecular building blocks for the design of new interconnected networks are of particular interest in the field of molecular based magnets.[6] Single-chain magnets (SCMs), 1-D complexes in low-dimensional assemblies, show slow magnetization relaxation in molecules which function as single-domain magnetic particles.[7] The 2-D assemblies with magnetic anisotropy have been also investigated extensively and show the magnetic behaviors of the assemblies are largely affected by magnetic anisotropy generated from the structure and the magnetic center of the assemblies.[8] Most MOFs derived from the carboxylates have been intensively investigated for the symmetrical carboxylates, such as 1,4-benzenedicarboxylate, 4,4'-biphenyldicarboxylate and 1,3,5-benzenetricarboxylate.[9] However, the coordination properties of *trans*-4,4' stilbene dicarboxylic acid ($H_2SDA$, Figure 1A), a symmetrical bidentate carboxylate, has not been investigated previously to the best of our knowledge. Herein, we report syntheses, the crystal structure, and magnetic properties of two-dimensionally layered coordination polymer, $[Co_3(SDA)_3(DMF)_2]$ (**1**) ($H_2SDA$ = 4,4'-stilbenedicarboxylic acid).

X-ray crystallography analysis of the single crystal of **1**

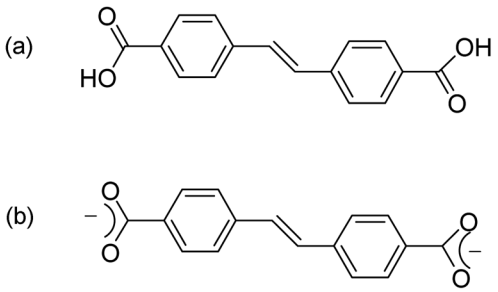


**Figure 1**. (a) $H_2SDA$. (b) SDA (B)

revealed that a trinuclear SBU, known in a molecular cluster, has been polymerized with SDA to a 2-D layered network. In the asymmetric unit, two independent cobalt atoms, one is symmetry-related and the other one is not, are connected by a symmetry-related SDA unit. The symmetry transformations, #1; -x +2/3,- y -2/3, -z +10/3, #2; -y, x-y-1, z, #3; -x+y+1, -x, z, #4; y +2/3, -x+y+1/3, -z +10/3, and #5; x-y -1/3, x -2/3, -z +10/3, generate three $Co_3$ pin-wheel clusters as building blocks and nine SDA ligands as linkers in the unit cell, $Z = 3$. In the building block, each of the $Co_3$ pin-wheel centers, with an inversion center on Co1, are bridged by the bidentate functionalities of six symmetrically equivalent half units of SDA through the syn-syn bridging mode to form a 6-connected $Co_3$ pin-wheel cluster (Figure 2). The coordination environment around the central Co(II) atom, Co1, in the trinuclear center can be described as an octahedral with all six positions occupied by one carboxylate oxygen, O2, from each half unit of six SDA ligands (Figure 2), the SDA units for C1#12 and C1#15 are not shown and coordinated DMF molecules are not shown for clarity except oxygen atoms). The other carboxylate oxygen, O1, in each half unit of six SDA molecules coordinates to one of the two surrounding Co(II) atoms, Co2, generating two individual tetrahedral coordination environments in which a vacant site is occupied by an oxygen atom, O1S in DMF molecule as shown in Figure 2. The building units of the title coordination polymer, $Co_3$ pin-wheel cluster, are

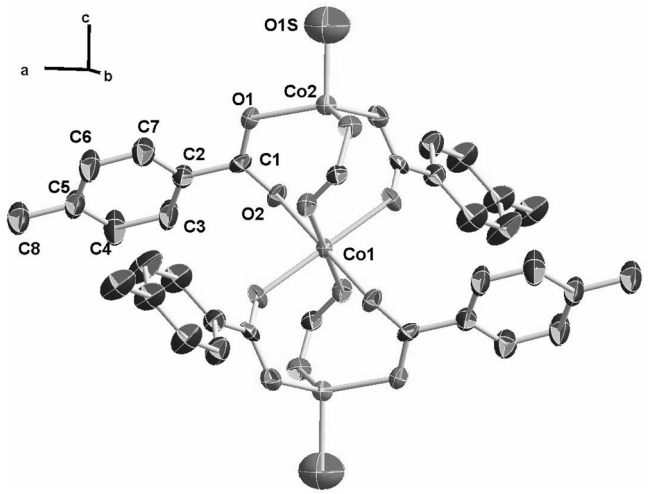


**Figure 2**. The building block unit including the asymmetric unit present in crystalline $[Co(II)_3(SDA)_3(DMF)_2]$ with non-hydrogen atoms represented by thermal ellipsoids drawn to encompass 50% of their electron density. Only carboxylate oxygens of C1#12 and C1#15 are shown, with the remaining parts of the respective SDA units are omitted for clarity. Solvent molecules (DMF) coordinated to Co(II) ions are omitted for clarity except oxygen atom, O1S.

linked through O1 and O2 in the SDA units and their symmetry equivalent units into the *ab* crystallographic plane as shown in Figure 3 in order to generate a 2-D coordination polymer with 5 Å pores (Figure 3(a)). However, the half of pores located in one *ab* crystallographic plane of **1** are filled with another 2-D layer separated about 5.5 Å, a distance from the central Co(II) atom in $Co(II)_3$ cluster of the first layer and to the central Co(II) atom in the $Co(II)_3$ cluster of the second layer. The other half of the pores are also filled the other 2-D layer separated about 11.0 Å, a distance from the central Co(II) atom in the $Co(II)_3$ cluster of the first layer and to the central Co(II) atom in $Co(II)_3$ cluster of the third layer. The distance between Co2-Co2 in one $Co(II)_3$ cluster, 8.4(1) Å, suggest that the title coordination polymer is very tightly packed in a ABCABC packing mode (Figure 3(b)).

The bond lengths of Co1-O2 and Co2-O1 are of 2.073(4) and 1.953(5) Å, respectively. The bond length of the octahedral Co(II) and the carboxylate oxygen, Co1-O2, is slightly longer than that of tetrahedral Co(II) and the carboxylate oxygen, Co2-O1. The bond length of the tetrahedral Co(II) and the oxygen atom in the coordinated DMF molecule, Co2-O1S, is 1.98(2) Å. The bond angle of O2#1-Co1-O2, angle of *trans*-located two O2 through Co in octahedral geometry, is 180.0(2)°. The bond angles of O2#1-Co1-O2#2 and O2-Co1-O2#2, angles of two different *cis*-located two O2 through Co in octahedral geometry, are 89.32(17) and 90.68(17)°, respectively. These bond angles well describe the octahedral environment on the central Co(II) in the $Co_3$ pin-wheel cluster. The bond angle of O1-Co2-O1#2, a angle between carboxylate oxygen-tetrahedral Co2-carboxylate oxygen, is 116.21(9)°. The other bond angle in the coordination sphere of the tetrahedral Co2 is 101.37(14)°, carboxylate oxygen-tetrahedral Co2-oxygen coordinated from DMF molecule.

Magnetic properties of **1** were investigated by using a Squid magnetometer (Quantun Design, MPMS 7). The $\chi T$ product and $\chi^{-1}$ which are plotted as a function of temperature ($3 < T < 300$ *K*) are shown in Figures 4(a) and (b), respectively. Both curves were recorded at applied fields of $H = 100$ and 1000 *Oe* after the sample was cooled to 2 *K* under zero field cooled condition ($H = 0$ *Oe*). As can be seen in the *M-H* curves in Figure 5, the *M-H* curves at $T = 2$ *K* show some saturation behavior with zero coercivity value. Thus, spins of Co (II) may not be completely relaxed to paramagnetic spins at $T = 2$ *K*. A similar saturation behavior had been also observed in two layered cobalt-carboxylate complexes at $T = 2$ *K*.[11a] The *M-H* curves at *T* 10 *K*, however, clearly corresponds to that typical of paramagnetic spins. Thus, the paramagnetic region ($T > 10$ *K*) in the $\chi^{-1}$ curves was fitted to the Curie-Weiss law. From the fitting, we obtained the Curie constant (*C*) of 3.12 $Kcm^3/mol$ for the applied fields of $H = 100$ and 1000 *Oe*. This Curie constant is in good agreement with those of paramagnetic spins of $S = 3/2$, as observed by others.[11] We also obtained the Weiss

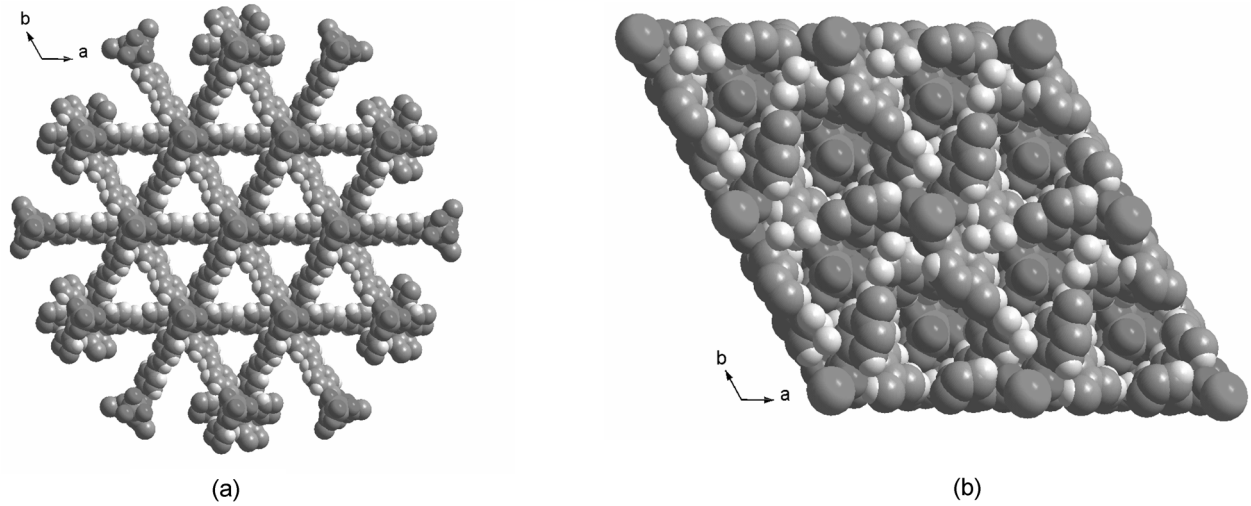


**Figure 3**. (a) A single layer of 2-D coordination polymer of **1**. (b) ABCABC packing mode of **1**.

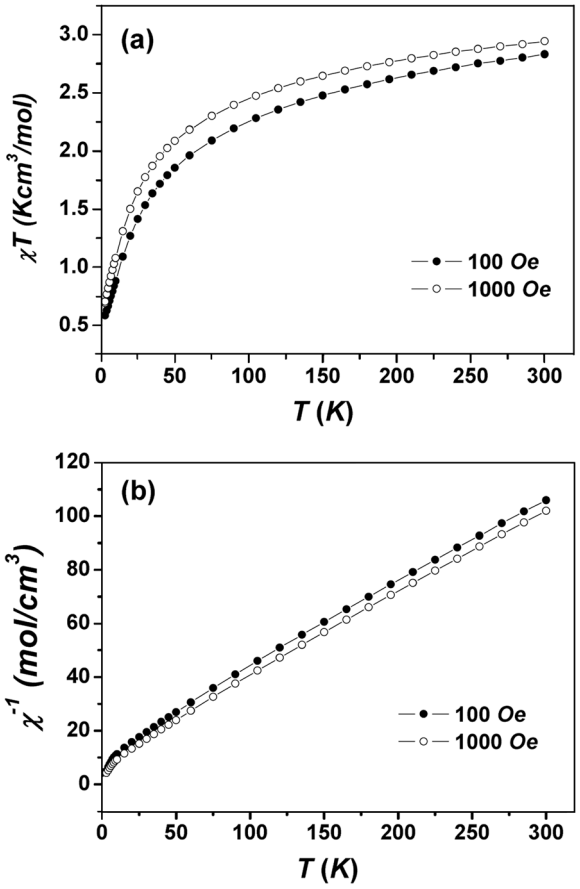


**Figure 4**. (a) The $\chi T$ product curves as a function of temperature at applied fields of $H$ = 100 and 1000 *Oe*. (b) The $\chi^{-1}$ curves as a function of temperature at applied fields of $H$ = 100 and 1000 *Oe*.

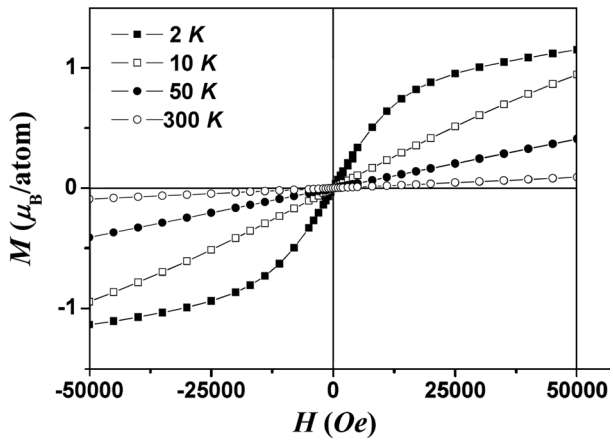


**Figure 5**. The *M-H* curves at $T$ = 2, 10, 50, and 300 *K*.

temperatures ($\Theta$) of −31.32 and −24.69 *K* for the applied fields of $H$ = 100 and 1000 *Oe*, respectively. Note that in a high spin splitting, each Co(II) ion in both tetrahedral and octahedral centers possesses $S$ = 3/2.

In conclusion, a new 2-D coordination polymer has been synthesized and characterized by using a novel 4,4'-stilbene dicarboxylic acid and $Co(ClO_4)_2 \cdot 6H_2O$. The title complex has an unique $Co_3$ pin-wheel cluster in which central Co(II) has octahedral geometry and two surrounding Co(II) have tetrahedral geometry. The $Co_3$ pin-wheel clusters, the building unit, are linked through carboxylate oxygens to generate a 2-D layered coordination polymer in ABCABC packing mode. Variable-temperature magnetic susceptibility data of the title compound confirms the high spin splitting of Co (II) with S=3/2. Syntheses of MOF by using SDA and other transition metal ions, Zn(II), Cd(II), and Mn(II), are on progress in this lab.

## Experimental Section

**Materials and methods.** All the materials were of a research grade or a spectro-quality grade in the highest purity available and were generally used without further purification. Anhydrous grade DMF and $Co(ClO_4)_2 \cdot 6H_2O$ were obtained from Aldrich. $H_2SDA$ was prepared by using a previously reported method.[12]

**Synthesis of $[Co_3(SDA)_3(DMF)_2]$.** The dark purple cubic crystals of **1** suitable for X-ray crystallography were obtained by the solvent-thermal reaction. A mixture of $Co(ClO_4)_2 \cdot 6H_2O$ (0.0822 g, $2.25 \times 10^{-4}$ mol) and $H_2SDA$ (0.0603 g, $2.25 \times 10^{-4}$ mol) was suspended in DMF (1.3 mL), placed in a sealed-pipette, and heated at 110 °C for 3 days. Upon cooling to room temperature, the dark purple crystalline was formed, collected by filtration, washed with DMF, and dried under a reduced pressure at room temperature for 2 h (0.174 g, 69% based on $Co(ClO_4)_2 \cdot 6H_2O$). Anal. Calcd. for $[Co_3(SDA)_3(DMF)_2]$: C, 57.82; H, 3.95; N, 2.50. Found: C, 57.69; H, 4.02; N,2.72

**X-ray crystallography.** The structure of the title compound was determined by single crystal X-ray diffraction analyses. The intensity data were collected on a Siemens SMART CCD diffractometer with graphite-monochromated Mo K$\alpha$ ($\lambda$ = 0.71073 Å) radiation at 203(2) K. Crystal data for the title compound has formula of $C_{54}H_{44}Co_3N_2O_{14}$, rhombohedral, space group R-3 with a = b = 16.171(1) Å, c = 16.606(2) Å, $\alpha = \beta = 90°$, $\gamma = 120°$ , Z = 3, V = 3760.6 (6) Å$^3$, F(000) = 1725, 4633 reflections were collected, 1032 of which were used in the refinement to give the final $R_1$ = 0.1017, $wR_2$ = 0.2451. All crystallographic data were corrected for Lorentz and polarization effects (SAINT), and semiempirical absorption corrections based on equivalent reflections were applied (SADABS). The structures were solved by direct methods and refined by the full-matrix least-squares method on $F^2$ with appropriate software implemented in the SHELXTL program package. Overall structure was refined anisotropically, but DMF molecules coordinated to symmetric two Co(II) units were refined isotropically due to the three-fold disorder problem. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC-285767). These data can be obtained free of charge from www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk).

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