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Synthesis, Structure, and Magnetic Properties of a New Eight-Connected Metal–Organic Framework (MOF) based on Co_4 Clusters

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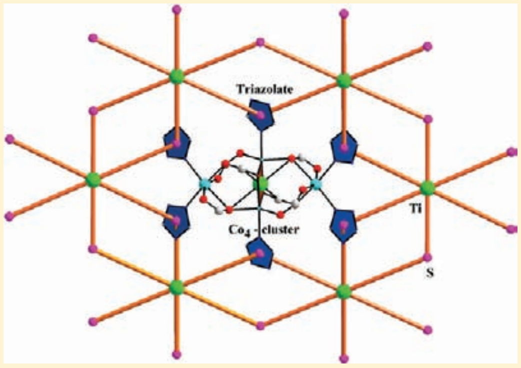
Supporting Information

ABSTRACT: A hydrothermal reaction of cobalt nitrate, 4,4′-oxybis(benzoic acid) (OBA), 1,2,4-triazole, and NaOH gave rise to a deep purple colored compound $[Co_4(\text{triazolate})_2(\text{OBA})_3]$, **I**, possessing Co_4 clusters. The Co_4 clusters are connected together through the tirazolate moieties forming a two-dimensional layer that closely resembles the TiS_2 layer. The layers are pillared by the OBA units forming the three-dimensional structure. To the best of our knowledge, this is the first observation of a pillared TiS_2 layer in a metal–organic framework compound. Magnetic studies in the temperature range 1.8–300 K indicate strong antiferromagetic interactions for Co_4 clusters. The structure as well as the magnetic behavior of the present compound has been compared with the previously reported related compound $[Co_2(\mu_3\text{-OH})(\mu_2\text{-H}_2O)(\text{pyrazine})(\text{OBA})(\text{OBAH})]$ prepared using pyrazine as the linker between the Co_4 clusters.



■ INTRODUCTION

The clever blend of inorganic and organic chemistry created a new family of compounds with unique structures and properties known as inorganic coordination polymers or metal–organic frameworks (MOFs).[1] Many of the properties of MOFs arise due to the porous nature of the structure,[2] though the variability of the coordination around the metal ions can also play an important role.[3] In addition, it is conceivable that different physical and chemical properties can arise out of the oxidation changes of the metal ions as well.[4] Thus, MOFs produce considerable variety in the structure and can be used for many types of applications.

The complex connectivities observed in some of the MOFs have been simplified by invoking node and net descriptions. This, in fact, allows researchers to visualize them as simple topologies based on well-known networks. The topological description of the structures, originally by Wells,[5] has been exploited for the understanding of many metal–organic framework structures.[6] Thus, three-dimensional MOF structures based on diamond, α-Po, $CdSO_4$, NbO, perovskite, etc., have been realized.[7] Many of the structures are based on three-, four-, or six-connected nodes. An eight-connected node is generally rare as it requires eight bulky ligands to bind with the central metal atom, which would create considerable steric hindrance. A metal cluster, on the other hand, can act as a node in place of a single metal center and form the 8-connected node. This was realized recently in our laboratory in the cobalt compound $[Co_2(\mu_3\text{-OH})(\mu_2\text{-H}_2O)(\text{pyrazine})(\text{OBA})(\text{OBAH})]$.[8] Here, the Co_4 clusters are employed as a node and the pyrazine and OBA molecules were utilized as the linkers between the nodes forming a body-centered arrangement.

It has been well established that nitrogen-containing ligands are useful in the design and synthesis of MOFs. Thus, MOFs formed with pyridine, pyrazine, pyrimidine, imidazole, etc., as linkers are known in the literature.[9] Triazole as a linker has also been utilized in the assembly of MOFs.[10] In addition to linking the metal centers, the nitrogen-containing ligands have been found to be useful in facilitating magnetic exchanges between the magnetic metal centers.[11] The continuing research on MOFs clearly suggests the possibility of stabilizing new metal clusters with many different nuclearities. Thus, MOFs containing different types of metal clusters have been encountered. Of these, the dimer,[12] trimer,[13] tetramer,[14] hexamer,[15] and heptamer[16] appear to have unique and interesting structures. In addition, MOFs possessing one- or two-dimensional extended M–O–M connectivity have also been isolated and investigated.[17]

We were interested in the study of transition metal clusters not only to investigate the physical and chemical properties but also to correlate the structure–property relationships. To this end, we now isolated a new MOF $[Co_4(\text{triazolate})_2(\text{OBA})_3]$, **I**, formed by the connectivity between Co_4 clusters, triazole, and

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oxy-bis-benzoic acid (OBA). The Co_4 clusters and triazole ligands are connected to form 2D layers, which are pillared by the oxy-bis-benzoic acid (OBA). The CO_4 cluster–triazolate layer exhibit 3^6 topology and appears to have close structural resemblance with the well-known TiS_2 layer structure. The present structure of **I**, thus, can be considered to be the pillared layered analogue of the TiS_2 structure.

EXPERIMENTAL SECTION

Materials. The reagents needed for synthesis were used as received; $Co(NO_3)_2{\cdot}6H_2O$ [CDH (India), 98%], 4,4′-oxybis(benzoic acid) [Lancaster (U.K.), 99%], 1,2,4-triazole [CDH (India), 98%], and NaOH [CDH (India), 98%]. The water used was double distilled through a Millipore membrane.

Synthesis. A mixture containing $Co(NO_3)_2{\cdot}6H_2O$ (0.291 g, 1 mM), 4,4′-oxybis(benzoic acid) (0.26 g, 1 mM), 1,2,4-triazole (0.069 g, 1 mM), NaOH (0.08 g, 2 mM), and 10 mL of water was heated in a PTFE-lined stainless steel autoclave at 180 °C for 48 h to give deep purple crystals of **I** (yield was ~73% based on Co). The product was washed with deionized water under vacuum and dried at ambient conditions. Anal. Calcd for **I**: C, 48.45; H, 2.47; N, 7.37. Found: C, 48.86; H, 3.27; N, 7.58.

Initial Characterization and Physical Measurements. Powder X-ray diffraction (XRD) patterns were recorded on well-ground samples in the 2θ range 5–50° using Cu Kα radiation (Philips X'pert) (Supporting Information, Figure S1). XRD patterns indicated that the product is a new material; the pattern is entirely consistent with the simulated XRD pattern generated based on the structure determined using single-crystal X-ray studies. The IR spectrum was recorded on a KBr pellet (Perkin-Elmer, SPECTRUM 1000) (Supporting Information, Figure S2). IR (KBr) (cm^{-1}): $\gamma_s(C{-}H)_{aromatic} = 2983$, $\gamma_s(C{=}O) = 1595$, δ (COO) = 1421, $\gamma_s(C{-}C)_{skeletal} = 968$, and $\delta\ (CH_{aromatic})_{out\ of\ plane} = 770$. Thermogravimetric analysis (TGA) (Metler-Toledo) was carried out in an oxygen atmosphere (flow rate = 20 mL/min) in the temperature range 30–800 °C (heating rate = 5 °C/min) (Supporting Information, Figure S3). TGA studies exhibited weight loss in two steps in the temperature range 270–380 °C. The total observed weight loss of 76% corresponds well with loss of the triazolate and carboxylate molecules (calcd 71.9%). The final calcined product was found to be crystalline by powder XRD and corresponds to Co_3O_4 (JCPDS 42-1467).

Single-Crystal Structure Determination. A suitable single crystal was carefully selected under a polarizing microscope and glued carefully to a thin glass fiber. Single-crystal data were collected on a Bruker AXS smart Apex CCD diffractometer at 120(2) K. The X-ray generator was operated at 50 kV and 35 mA using Mo Kα (λ = 0.71073 Å) radiation. Data were collected with ω scan width of 0.3°. A total of 606 frames were collected in three different settings of φ (0°, 90°, 180°) keeping the sample-to-detector distance fixed at 6.03 cm and the detector position (2θ) fixed at −25°. Data were reduced using SAINTPLUS,[18] and an empirical absorption correction was applied using the SADABS program.[19] The structure was solved and refined using SHELXL97[20] present in the WinGx suit of programs (version 1.63.04a).[21] All hydrogen atoms of the carboxylic acids and triazolate molecules were placed in geometrically ideal positions and held in the riding mode. Final refinement included atomic positions for all atoms, anisotropic thermal parameters for all non-hydrogen atoms, and isotropic thermal parameters for all hydrogen atoms. Full-matrix least-squares refinement against $|F^2|$ was carried out using the WinGx package of programs.[21] Details of the structure solution and final refinements are given in Table 1. CCDC: 796763 contains the crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Center (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

Magnetic Measurements. Magnetic measurements were performed on a Quantum Design MPMS-XL SQUID magnetometer. Static susceptibility measurements were performed in the 1.8–300 K temperature range with an applied field of 50 Oe. Field-dependent magnetization measurements at a given temperature confirm the absence of ferromagnetic impurities. Data were corrected for the sample holder, and diamagnetism was estimated from Pascal constants.

Table 1. Crystal Data and Structure Refinement Parameters for Compound $[Co_4(triazolate)_2(OBA)_3]^a$

empirical formula	$[Co_4(triazolate)_2(OBA)_3]$
fw	1140.46
cryst syst	monoclinic
space group	$P21/c$
a/Å	28.5598(19)
b/Å	14.0774(9)
c/Å	10.7417(6)
α/deg	90
β/deg	91.123(3)
γ/deg	90
vol./Å^3	4317.8(5)
Z	4
T/K	120(2)
ρ_{calcd} (g cm^{-3})	1.754
μ (mm^{-1})	1.593
θ range (deg)	1.61–26.00
λ (Mo Kα) (Å)	0.71073
R_{int}	0.0396
no. of reflns collected	30 671
no. of unique reflns	8189
no. of params	622
R indices [$I > 2\sigma(I)$]	R1 = 0.0805, wR2 = 0.1743
R indices (all data)	R1 = 0.0873, wR2 = 0.1767

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)]/\Sigma[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\rho^2(F_o)^2 + (aP)^2 + bP]$. $P = [\max(F_o, O) + 2(F_c)^2]/3$, where a = 0.0194 and b = 78.8761.

RESULTS AND DISCUSSION

Structure of $[Co_4(triazolate)_2(OBA)_3]$. The asymmetric unit of $[Co_4(triazolate)_2(OBA)_3]$ consists of four Co^{2+} ions, three oxybisbenzoate (OBA) anions, and two triazolate anions (Supporting Information, Figure S4). Of the four Co^{2+} ions, the cobalt atoms Co(1) and Co(2) form a CoO_4N distorted trigonal bipyramid, while Co(3) and Co(4) form distorted CoO_4N_2 octahedra with an average Co–O bond distance of 2.112 Å and Co–N distance of 2.064 Å. Selected bond distances are listed in Table 2. Of the three oxybisbenzoic acids, OBA(1) exhibits a monodentate connectivity with four Co^{2+} (Supporting Information, Figure S5). The carboxylate groups of OBA(2) and OBA(3) exhibit similar connectivity, bonding with five cobalt atoms (Supporting Information, Figures S6 and S7). The connectivity between the four Co^{2+} ions gives rise to two distinct tetranuclear Co_4 clusters (Figure 1). The five-coordinated cobalt atoms [Co(1) and Co(2)] are independently connected with Co(1a) and Co(2a) through a μ_2 oxygen [O(5)], forming a dimer. The dimers are connected with Co(3) and Co(3a) and Co(4) and Co(4a) through the oxygen, O(6) and O(3), forming the tetranuclear cluster. Thus, Co(1), Co(1a), Co(4), and Co(4a) form one CoO_4N_2 cluster, while Co(2), Co(2a), Co(3), and Co(3a) form the other CoO_4N_2 cluster. The Co_4 clusters exhibit short Co–Co distances: 3.221 [Co(2) and Co(2a)] and 3.229 Å [Co(1) and Co(1a)]. The striking aspect of structure **I** is the way in which the tetranuclear cluster is connected. While one set of Co_4 clusters is exclusively present [Co(2), Co(2a), Co(3), and Co(3a)] in one layer, the other Co_4 cluster [Co(1), Co(1a), Co(4), and Co(4a)]

Table 2. Selected Observed Bond Distances in the Compound $[Co_4(triazolate)_2(OBA)_3]$[a]

bond	distance (Å)	bond	distance (Å)
Co(1)−O(1)	1.938(5)	Co(3)−O(7)	2.008(5)
Co(1)−O(2)	2.018(5)	Co(3)−N(4)	2.074(6)
Co(1)−O(3)	2.031(5)	Co(3)−N(3)#4	2.081(6)
Co(1)−N(1)	2.042(6)	Co(3)−O(8)#5	2.149(6)
Co(1)−O(2)#1	2.294(5)	Co(3)−O(9)#2	2.152(5)
Co(2)−O(4)	1.968(5)	Co(3)−O(6)#5	2.310(5)
Co(2)−O(5)#2	1.993(5)	Co(4)−O(10)#6	2.004(5)
Co(2)−O(6)#1	2.028(5)	Co(4)−N(6)	2.069(5)
Co(2)−N(2)#3	2.049(6)	Co(4)−N(5)#7	2.071(6)
Co(2)−O(5)	2.256(5)	Co(4)−O(11)#8	2.152(5)
		Co(4)−O(12)#6	2.180(5)
		Co(4)−O(3)#8	2.303(4)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+2, -y+1, -z+1$; #2 $-x+1, -y+1, -z+1$; #3 $-x, -y+3/2, z+1/2$; #4 $-x+1, -y+1, -z$; #5 $x-1, y, z$; #6 $x, -y+1/2, z+1/2$; #7 $-x+2, -y, -z+1$; #8 $-x+2, y-1/2, -z+3/2$.

occupies the adjacent one. This is indeed a unique arrangement.

The three-dimensional structure of **I** can be well understood if we consider the connectivity between the Co_4 clusters and the triazolate as well as the Co_4 cluster and OBA units independently. Thus, the Co_4 clusters are connected by three OBA units to form one-dimensional ladder-like units (Figure 2). The triazolate ligands, expectedly, bond with the Co_4 cluster through Co−N bonds. Thus, each Co_4 cluster is connected with six triazolate ligands, and each triazolate ligand is connected with three Co_4 clusters (Supporting Information, Figure S8). The connectivity between the Co_4 cluster and the triazolate units thus forms an extended two-dimensional cationic layer (Figure 3). Alternatively, if we consider the Co−N−N−Co connectivity along with Co−O−Co we have a one-dimensional Co−O/N−N−Co rod-like arrangement. The one-dimensional rod-like structures are connected through the triazolate units, forming the two-dimensional layer, which are pillared by the oxybisbenzoate, leading to the overall three-dimensional structure. Closer examination of this connectivity reveals that the Co_4−triazolate layer can be simplified using a binodal net (6- and 3-connected nodes) with a Schlafli symbol of $(4^3)_2(4^6.6^6.8^3)$ (Figure 4). The cross-linking between the Co_4−OBA ladders and the Co_4−triazolate layers gives rise to the observed three-dimensional structure in $[Co_4(triazolate)_2(OBA)_3]$, **I** (Figure 5). As mentioned earlier, though there are two types of Co4 clusters in **I**, the connectivity between the participating ligands (triazolate and OBA) is exactly the same. Since the two different Co_4 clusters occupy alternate layers and are identical, one can consider the layer arrangement of Co_4−triazolate as a *ABABAB*...-type arrangement. Examination of the 3^6 net structures in the literature reveals that the classical inorganic structures such as $CdCl_2$, CdI_2, and TiS_2 (Supporting Information, Figures S9−S11) have comparable connectivity between the metal and the participating anions. Of these inorganic structures, it appears that the present structure is closely related to the TiS_2 structure and can be considered to be a pillared TiS_2 structure (Figure 6). Pillared layer structures are well documented in hydroxide derivative organic−inorganic materials.[22] We also observed pillared brucite layers, Kagome layers, and $CdCl_2$ layers during our investigation on MOFs.[23] Presently, we stabilized a pillared TiS_2 layer structure. It is worthwhile noting that earlier we stabilized the anionic TiS_2 layers in [HImd][Mn(BTC)(H_2O)].[24]

Further examination of the structure of **I** reveals that the connectivity can be simplified by considering the Co_4 cluster alone as the node. As can be noted, each Co_4 cluster is bonded with six OBA units (three OBA units connect below and three OBA units connect above the Co_4−triazolate layers) (Figure 7). If we consider all the connectivities, it is clear that the structure has the signature of the eight-connected node (Figures 7 and 8). Formation of eight-connected nodal structure is not common,[25] and observation of such an arrangement in **I** is noteworthy. A topological analysis of the whole structure indicates that it has a 5 nodal net with three-connected (triazolate), four-connected (OBA), and five-connected (Co^{2+} ion) nodes to give an overall Schlafli symbol for the net as $(4.8^2)_2(4^3.6.8^6)_2(4^3.6^2.8)(4^5.6.8^4)_2(4^8.6^2)_2$ (Supporting Information, Figure S12).

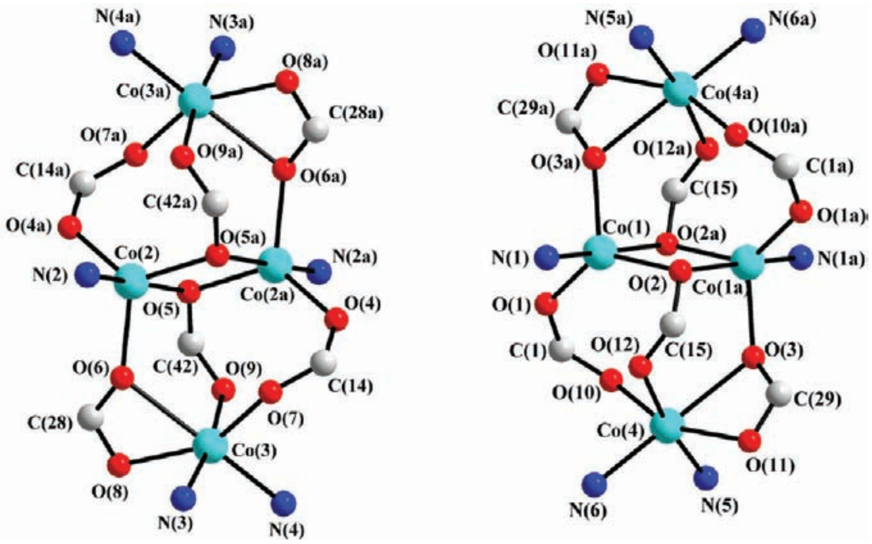


Figure 1. Two tetrameric cobalt clusters observed in $[Co_4(triazolate)_2(OBA)_3]$, **I**. Note the presence of the five-coordinated cobalt species.

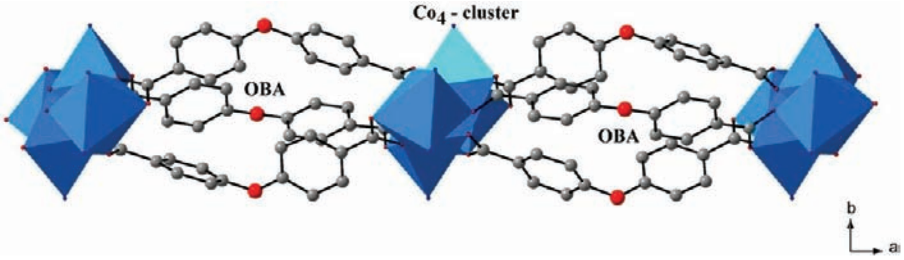


Figure 2. One-dimensional ladder-like units formed by the connectivity between OBA and the Co$_4$ clusters in **I**.

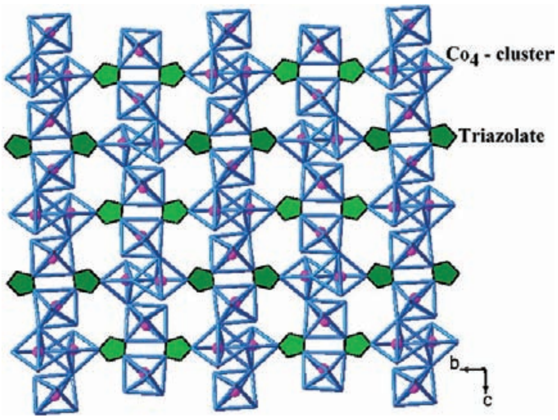


Figure 3. Two-dimensional layers formed by the connectivity between the cobalt tetranuclear clusters and the triazolate ligands.

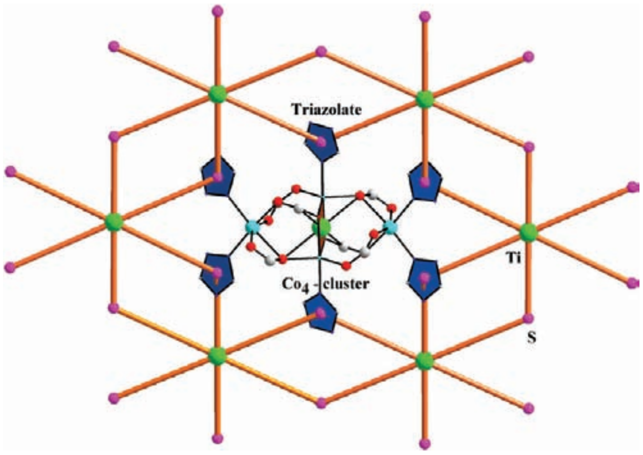


Figure 4. 3^6 layer. Note that the Co$_4$ cluster exhibits a six-connected node, and the triazole has a three-connected node (see text).

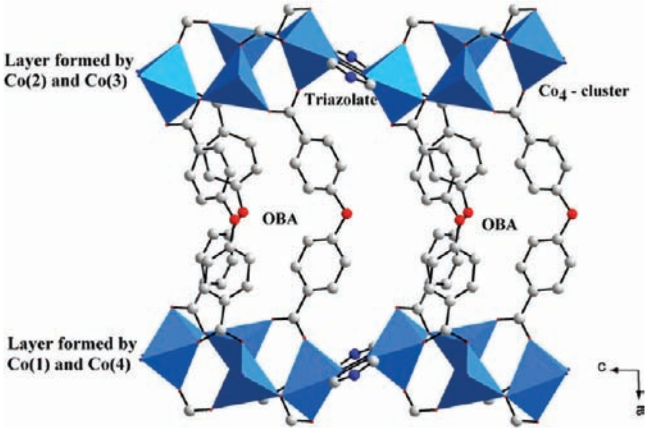


Figure 5. View of the three-dimensional structure of **I**.

Formation of Co$_4$ clusters in MOFs has been encountered in many compounds.[14] Recently, we isolated a Co$_4$ cluster compound [Co$_2$(μ_3-OH)(μ_2-H$_2$O)(pyrazine)(OBA)(OBAH)] in which the Co$_4$ clusters are connected by a pyrazine unit, forming a layer, which is cross-linked by the OBA units.[8] The Co$_4$ clusters present in [Co$_2$(μ_3-OH)(μ_2-H$_2$O)(pyrazine)(OBA)(OBAH)] exhibit differences structurally when compared with **I**. The Co$_4$ clusters in [Co$_2$(μ_3-OH)(μ_2-H$_2$O)(pyrazine)(OBA)(OBAH)] are formed only by octahedral cobalt species, whereas in **I** both the octahedral as well as the distorted trigonal bipyramidal cobalt species have been observed. The connectivity between the Co$_4$ cluster through the pyrazine and the OBA units in [Co$_2$(μ_3-OH)(μ_2-H$_2$O)(pyrazine)(OBA)(OBAH)] gives rise to a body-centered arrangement as the connectivity between the clusters is uniform (the Co$_4$ clusters have an 8-connected node, four of which is from the pyrazine unit and the other four come from the OBA unit). In **I**, however, the Co$_4$ clusters have six nodal connectivity from the triazolate units and the remaining two nodal connectivity arising from the OBA units (Figure 7). This creates subtle differences in the final structure between the pyrazine-connected Co$_4$ cluster compound [Co$_2$(μ_3-OH)(μ_2-H$_2$O)(pyrazine)(OBA)(OBAH)] and the present structure of **I**.

The unique structural features of **I** along with the close similarity with the earlier isolated Co$_4$ cluster[8] prompted us to investigate the magnetic behavior of the present compound, **I**. In addition, it was interesting to compare the magnetic behavior of **I** with that of the earlier reported cobalt compound [Co$_2$(μ_3-OH)(μ_2-H$_2$O)(pyrazine)(OBA)(OBAH)].

Magnetic Studies. The dc magnetic susceptibility of **I** has been measured from 1.8 to 300 K in an applied field of 50 Oe (Figure 9). In the paper, all magnetic data refer to the asymmetric unit cell, i.e., one Co$_4$ cluster. The χT value at room temperature, 10 emu·mol^{-1}·K, is slightly smaller than usually observed for Co^{2+} ions (2.5−3 × 10 emu·mol^{-1}·K per ion) (Figure S13, Supporting Information), which may indicate a lower value for the spin−orbit coupling (in accordance with the fact that two out of four Co^{2+} ions are trigonal bipyramid). The small value may also be due to the clear occurrence of strong antiferromagnetic (AF) interactions, indicated by the pronounced decrease of the χT product when decreasing the temperature from 300 to 2 K. Upon cooling, the χT product actually decreases steadily down to 0.25 × 10 emu·mol^{-1}·K at 2 K due likely to a combination of the spin−orbit coupling of the Co^{2+} ions and the AF interactions. Different from what was observed for the previously reported Co$_4$-based compound,[8] no weak ferromagnetic ordering could be observed at low temperature in the present compound. The small increase in

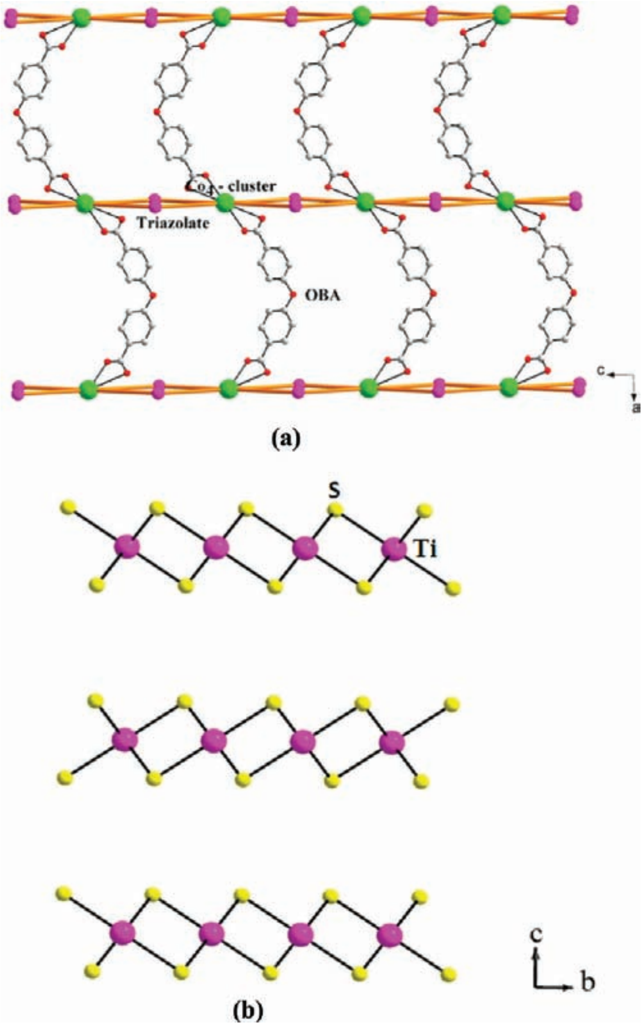


Figure 6. (a) 3^6 layers pillared by the OBA units (for clarity only one OBA unit is shown). (b) Layer arrangement in TiS_2. Note the close similarity between the two layers.

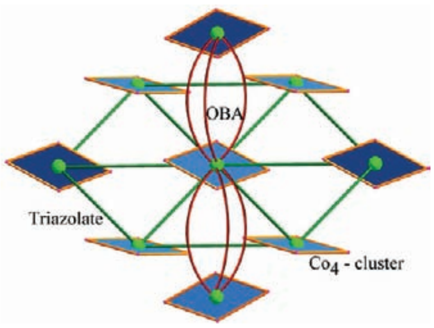


Figure 7. View of the eight-connected node. Note that three OBA units connect each of the Co_4 clusters.

the χ value at low temperature could probably be due to small a paramagnetic impurity. The ac susceptibility measurements show the onset of a peak in χ' below 5 K, but no corresponding peak in the out-of-phase signal χ'' was evidenced (Figure S14, Supporting Information). This indicates that neither ferromagnetic ordering nor glassy behavior between the resulting moments of the Co_4 clusters occurs, down to 2 K, due to the weak magnetic interactions between the clusters mediated through the triazole ligand.

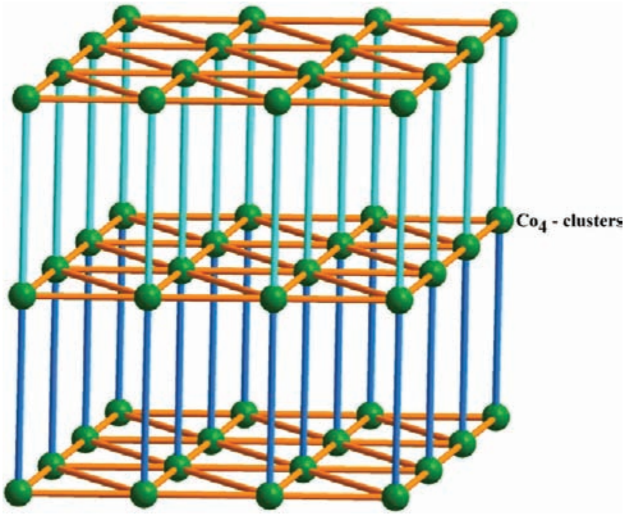


Figure 8. Node-based view of the structure of **I**, showing the hex $3^6.4^{18}.5^3.6$ net for the cluster connectivity in structure **I**.

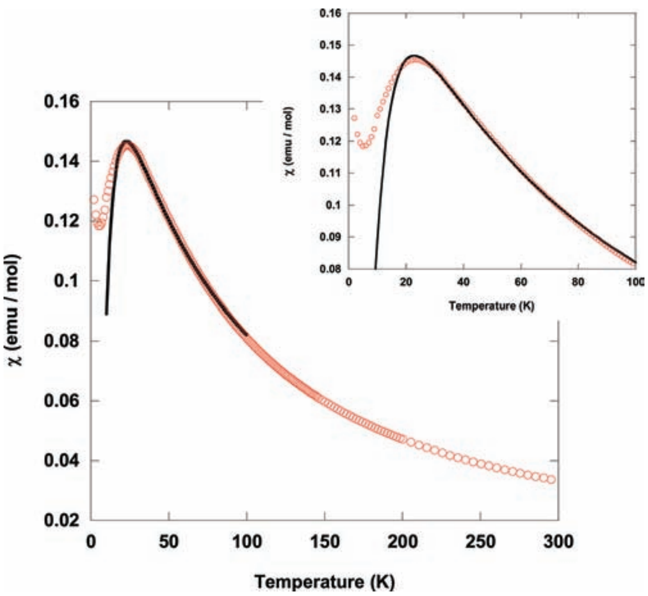
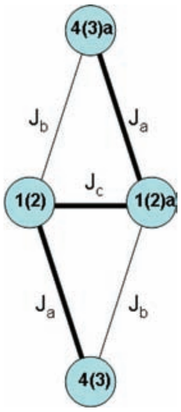


Figure 9. Temperature dependence of the magnetic susceptibility (χ) of **I** in an applied field of 50 Oe (open squares, experimental points; full line, best fit in the 18−35 K region; and calculation in the 10−100 K region, see text). (Inset) Zoom of the 2−100 K region).

In order to compare the intracluster magnetic interactions in **I** and the related Co_4−pyrazine compound,[8] we performed a fit of the $\chi = f(T)$ data in the 18−35 K range using the spin topology (Scheme 1) with an Ising interaction scheme (considering Co^{2+} with a pseudo spin $S' = 1/2$). It is worth noticing that even though the two Co_4 clusters in **I** do not present exactly the same distances or angles, their topologies appears to be identical as well as the ligands connecting the Co^{2+} ions. At higher temperatures, even though the calculation performed using the parameters obtained from the fit looks in accordance with the experimental results, the hypothesis of a completely quenched orbital moment for Co^{2+} ions is actually no longer valid, whereas at lower temperatures the anisotropy of the Co^{2+} ions should be taken into account more accurately. In addition, the possible presence of the paramagnetic impurity prevents any reasonable fit at very low temperature.

Scheme 1. Spin Topology of the Co_4 Clusters of **I**



The best fit leads to $J_a = -21$ K (±2 K), $J_b = -8$ K (±2 K), and $J_c = -17$ K (±3 K) with $g = 5.6$ (±0.2) (in all the paper and for the sake of comparison with the related Co_4–pyrazine compound J values are given in JS^2/k_B units with J defined according to the Hamiltonian $H = -J\sum S_iS_j$). With these parameters being strongly correlated, the set of parameters reported here is the most physically reasonable but might not be unique. Moreover, considering the fact that the two Co_4 clusters are not strictly identical, the J values can only be viewed as mean values. It is worth noticing that this set of parameters still fulfils the conditions for which a classical spin model predicts the stability of a canted structure ($J_c/(J_a + J_b) > 1/2$, $J_a/(J_c/2 + J_b) > 1/4$, and $J_b/(J_c/2 + J_a) > 1/4$). Actually using a classical spin model with the same topology and the same set of parameters one should observe a net magnetic moment resulting from a canting between Co^{2+} moments within the cluster, which is clearly not the case experimentally (Figure S15, Supporting Information). Yet considering that the J values obtained from the fit of the $\chi = f(T)$ curve are actually just mean values, this apparent discrepancy between the classical spin model and the experiments is indeed not a surprise. Moreover, calculations using the classical spin approach show that changing J_b from −8 to −7 K, i.e., within the error bar, keeping J_a and J_c unchanged, leads to stabilization of a nonmagnetic state.

Nevertheless, the J values obtained from the quantum spin simulation compare quite well with the ones obtained for the parent Co_4–pyrazine compound ($J_a = -33.5$ K, $J_b = -16.3$ K, and $J_c = -29$ K. The main difference actually lies in the very small value of J_b in **I** compared to the one obtained for the Co_4–pyrazine cluster. This much smaller J_b value is the main reason why **I** possesses a nonmagnetic ground state whereas the Co_4–pyrazine cluster possesses a canted ground state. The difference in J_b values is easy to rationalize by observing the structures of the two parent clusters, for **I** Co(4(3)a) and Co(1(2)a) are linked by one $(\kappa^1-\kappa^1)$-μ_2 and one $(\kappa^1-\kappa^1)$-μ_3 carboxylate, whereas for the Co_4–pyrazine cluster, Co(2) and Co(1a) are linked by one $(\kappa^1-\kappa^1)$-μ_2 carboxylate and μ_3 hydroxide, which provides a much stronger magnetic interaction.

■ CONCLUSIONS

The synthesis, structure, and magnetic studies on a three-dimensional MOF $[Co_4(triazolate)_2(OBA)_3]$, **I**, have been accomplished. The 8-connected node structure is closely related to the pillared TiS_2 structure and has been observed for the first time. The structure and magnetic behavior has been correlated with the previously discovered 8-connected node structure $[Co_2(\mu_3\text{-}OH)(\mu_2\text{-}H_2O)(pyrazine)(OBA)(OBAH)]$.[8] Magnetic studies clearly indicate the presence of antiferromagnetic interactions both within as well as in between the Co_4 clusters. The present work clearly demonstrates that it is possible to form related structures by carefully controlling the experimental parameters. Though the structures of **I** and the earlier reported Co_4-containing MOF[8] appear to be correlated, the differences in the observed magnetic behavior suggest the subtle role played by the organic linkers (pyrazine vs triazole). Further work is necessary to understand such effects.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Simulated and experimental powder XRD patterns, TGA curves, IR spectra, structural figures, topological analysis, magnetic studies, and bond angles for compound **I**. 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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