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Synthesis and Structure of a New Organic–Inorganic Framework with Tetranuclear Clusters, $[Co_4(OH)_2(H_2O)_2](C_4H_{11}N_2)_2[C_6H_2(COO)_4]_2{\cdot}3H_2O$

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A new hybrid organic–inorganic three-dimensional compound, $[Co_4(OH)_2(H_2O)_2](C_4H_{11}N_2)_2[C_6H_2(CO_2)_4]_2{\cdot}3H_2O$ 1, has been synthesized via hydrothermal reactions and characterized by single-crystal X-ray diffraction, infrared spectroscopy, thermogravimetric analysis, and magnetic techniques. Compound 1 crystallizes in the monoclinic space group $P2_1/n$ (no. 14) with $a = 6.3029(9)$ Å, $b = 16.413(2)$ Å, $c = 17.139(2)$ Å, $\beta = 98.630(2)°$, $V = 1735.0(4)$ Å^3, $Z = 2$. Compound 1 contains tetranuclear $Co_4(\mu_3\text{-}OH)_2(H_2O)_2$ clusters that are inter-linked by pyromellitate bridging ligands into a three-dimensional structure containing one-dimensional tunnels along the *a*-axis with water and pendant monoprotonated piperazine molecules in the center. The variable temperature magnetic susceptibility was measured from 2 to 300 K at 5000 Oe showing a predominantly antiferromagnetic interaction in 1, and the field dependence of magnetization was measured at 2, 5, 15, and 20 K indicating the competition of magnetic interactions in the tetranuclear centers. © Elsevier Science (USA)

Key Words: **structure; cobalt; pyromellitate.**

INTRODUCTION

There is much interest in extended frameworks of coordination polymers based on complexes of transition metals and multifunctional bridging ligands. Ligands containing multi-dentate oxygen, nitrogen, or sulfur donors have been used intensively as links in constructing coordination polymers of various structures (1). Among the many potential applications in such materials, open framework coordination polymers are of special interest. Being contrary to the traditional inorganic framework materials, framework coordination polymers could be synthesized via a more rational way, for example, by adjusting the length of the links to control the size of the pore (2). One successful strategy to build metal-organic open framework is to extend the building blocks of molecular multinuclear metal clusters by bis- or tris-dentate aromatic carboxylate links (3). For the known molecular compounds of high nuclearity, oxo-bridged products in three-dimensional metal carboxylates, their structures are frequently related to the brucite-like hydroxide (4). This is probably due to the fact that the hydrolysis and condensation of the metal salt are stopped at the preliminary stage in the presence of coordinated ligands. With these ideas in mind, coordination polymers containing inorganic clusters, chains, and layers may be expected when parameters such as the choice of bridging ligands, the ligand-to-metal ratio, and the pH are optimized; and the hybrid organic–inorganic materials produced may have dual microporous and magnetic properties (5). We have been interested in synthesizing coordination polymers containing oxo-bridged polynuclear centers by hydrothermal (or solvothermal) syntheses in systems containing both bis-monodentate N-donor and bis-bidentate O-donor bridging ligands (6). In such system the fulfillment of the coordination sphere of metal centers is more flexible because of the combined functional groups of the mixed ligands, and the pH of reactions can be fine tuned by simply adjusting the mixed ligand ratios to the desired condition for producing interesting oxo-bridged transition metal clusters. Here, we report the hydrothermal synthesis and structure of a new hybrid organic–inorganic framework based on mixed piperazine and pyromellitate ligands, $[Co_4(OH)_2(H_2O)_2](C_4H_{11}N_2)_2[C_6H_2(CO_2)_4]_2{\cdot}3H_2O$, which contains new tetranuclear hydroxo-bridged centers.

EXPERIMENTAL

Synthesis

Compound **1** was prepared from the reaction mixture of $CoCl_2{\cdot}6H_2O$ (1 mmol), piperazine (8 mmol), pyromellitic acid (benzene-1,2,4,5-tetracaboxylic acid, 2 mmol), H_3BO_3 (2 mmol), ethanol (3 mL) and distilled water (5 mL) in a Teflon-lined acid digestion bomb with an internal volume of

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23 mL under autogeneous pressure at 160°C for 3 days, followed by slow cooling (4.8°C/h) to room temperature. The resulting solid was filtered off and washed with water. It consisted the title compound as the major product in the form of bundles of purple needle-like crystals (yield of 60% based on Co), together with a small amount of orange crystals and an unidentified pink powder. The orange crystal was identified as $[Co(H_2O)_4(Hppz)_2][C_6H_2(COO)_4]\cdot 2H_2O$ by single-crystal X-ray analysis (7). The presence of H_3BO_3 appeared to be necessary for the successful synthesis of **1**. Reactions without adding the H_3BO_3 led to the formation of $[Co(H_2O)_4(Hppz)_2][C_6H_2(COO)_4]\cdot 2H_2O$ as the major product. Compound **1** can be manually separated under optical microscope for subsequent measurements. Elemental analysis: Calc: C, 32.51; H, 3.70; N, 5.42; Found: C, 32.55; H, 3.70; N, 5.54. Main IR bands (KBr disc, cm^{-1}): 3561 m, 3384 vs 3249 m, 1596 vs 1492 w, 1427 m, 1388 vs 1327 m, 1192 w, 1139 w, 1095 w, 996 w, 910 w, 869 w, 909 w, 869 w, 810 w, 763 w, 691 w, 588 w, 540 w, 451 w.

Single-Crystal X-Ray Structure Analysis

The structures of **1** was determined by single-crystal X-ray methods and the crystallographic data were summarized in Table 1. A suitable crystal ($0.50 \times 0.05 \times 0.05\ mm^3$) was glued on a glass fiber and mounted on a smart CCD diffractometer using Mo$K\alpha$ radiation. Intensity data were collected for indexing in 1271 frames with increasing ω (width of 0.3° per frame). Unit-cell dimensions were determined by a least-squares fit of 821 reflections. The absorption correction was based on symmetry-equivalent reflections using the *SADABS* programs (8). Of the 4223 reflections collected 2658 unique reflections were considered observed $[I_{obs} > 2\sigma(I)]$ after Lp and absorption corrections. On the basis of systematic absences and statistic intensity distribution, the space group was determined to be $P2_1/n$. Direct methods were used to locate the Co atoms first, and the remaining oxygen, carbon, and nitrogen atoms were found from successive difference maps. When the occupancy factors of the O11 and O12 assigned as occluded water were refined, they were close to 0.5 and 1, respectively. The thermal parameter for O(12) was rather large, this may be expected for loosely bound environment. Unlike O(12), O(11) has hydrogen bonds with N(2) (N(2)$\cdots$O(11) = 2.85 Å) and a smaller thermal parameter. All H atoms were located on difference Fourier maps calculated at the final stage of structure refinement. The final cycles of refinement, including the atom coordinates and anisotropic thermal parameters for all nonhydrogen atoms and fixed atomic coordinates and isotropic thermal parameters for the hydrogen atoms, converged at $R_1 = 0.0365$ and w$R_2 = 0.0851$. In the final difference map the deepest hole and the highest peak were -0.67 and 1.00e $Å^{-3}$. Anomalous and secondary extinction corrections were applied. All calculations were performed by using the SHELXTL programs (9).

TABLE 1
Crystallographic Data for 1

Formula	$C_{28}H_{38}Co_4N_4O_{23}$
Crystal system	Monoclinic
Space group	$P2_1/n$
Fw	1034.35
a (Å)	6.3029(9)
b (Å)	16.413(2)
c (Å)	17.139(2)
α (deg)	90.0
β (deg)	98.630(2)
γ (deg)	90.0
V ($Å^3$)	1735.0(4)
Z	2
Temp (°C)	21
λ	0.71073
$T_{max/min}$	0.9688, 0.9120
ρ_{calcd} (g/cm^3)	1.960
μ (cm^1)	19.64
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0365$,[a] w$R_2 = 0.0851$[b]
R indices (all data)	$R_1 = 0.0753$, w$R_2 = 0.0928$

[a] $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + 0.0397P]^2 + 0.0P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Thermogravimetric analysis was carried out in nitrogen at a heating rate of 10°C/min (Perkin-Elmer Instruments, TGA 7). Magnetic susceptibility was measured under 5000 Oe from 2 to 300 K (SQUID, Quantum Design). The diamagnetic contributions of the samples were corrected using Pascal's constants.

RESULTS AND DISCUSSION

Structure of $[Co_4(OH)_2(H_2O)_2(C_4H_{11}N_2)_2$ $C_6H_2(CO_2)_4]_2\cdot 3H_2O$

The atomic coordinates and the thermal parameters of **1** are given in Table 2, and selected bond lengths and bond valence sums are given in Table 3. One of the important structure units in **1** is the tetranuclear cluster, which is built by two types of cobalt atoms, Fig. 1. Co(1) has square pyramid geometry which is coordinated by four oxygen atoms from carboxylate groups of the pyromellitate ligands and one μ_3-oxygen atom. Co(2) has an octahedral geometry which is coordinated by two oxygen atoms from carboxylate groups of the pyromellitate ligands, two μ_3-oxygen atoms, one nitrogen atom from the piperazine molecule, and one oxygen atom from a water molecule. The bond valence calculation [Co(1), 1.80; Co(2), 1.86] suggested both cobalt atoms are in the divalent state (10). The two types of cobalt atoms are bridged by O(2), and are operated by inversion center to form tetranuclear clusters, in which the Co(2) and Co(2′) deviate from the plane composed of Co(1), Co(1′),

TABLE 2
Atomic Coordinates ($\times 10^{-4}$) and Thermal Parameters ($Å^2 \times 10^{-4}$) for 1

	x	y	z	U_{eq}[a]
Co(1)	2406(1)	4773(1)	6773(1)	16(1)
Co(2)	743(1)	4105(1)	4921(1)	16(1)
O(1)	4734(4)	4002(1)	6458(1)	22(1)
O(2)	1649(4)	5128(1)	5619(1)	16(1)
O(3)	732(4)	3720(2)	6951(1)	22(1)
O(4)	337(4)	5425(2)	7340(2)	37(1)
O(5)	4420(4)	5814(2)	6922(2)	39(1)
O(6)	2965(4)	3279(1)	5453(1)	22(1)
O(7)	−1353(4)	3849(1)	5772(1)	21(1)
O(8)	3068(4)	4546(2)	4232(2)	30(1)
O(9)	9650(5)	8(2)	7060(2)	47(1)
O(10)	1072(5)	5046(2)	8595(2)	55(1)
O(11)	195(12)	899(4)	5331(4)	73(3)
O(12)	3119(7)	406(1)	4655(5)	314(6)
N(1)	−562(5)	3106(2)	4108(2)	25(1)
N(2)	−1292(6)	1387(2)	3748(2)	46(1)
C(1)	4410(5)	3379(2)	6041(2)	15(1)
C(2)	−795(5)	3505(2)	6436(2)	16(1)
C(3)	229(6)	5496(2)	8058(2)	26(1)
C(4)	5806(5)	2651(2)	6302(2)	14(1)
C(5)	4833(5)	1898(2)	6375(2)	19(1)
C(6)	5966(5)	1244(2)	6744(2)	17(1)
C(7)	8147(5)	1339(2)	7016(2)	17(1)
C(8)	9150(5)	2080(2)	6926(2)	17(1)
C(9)	7998(5)	2741(2)	6579(2)	14(1)
C(10)	9509(6)	658(2)	7398(2)	25(1)
C(11)	−2098(7)	2611(3)	4474(3)	39(1)
C(12)	−3063(8)	1905(3)	3968(3)	53(1)
C(13)	143(7)	1874(3)	3315(2)	40(1)
C(14)	1050(7)	2582(2)	3820(2)	33(1)
H(1A)	−1271	3376	3688	50
H(2A)	3023	5355	5376	50
H(2B)	−613	1191	4169	50
H(2C)	−1819	1008	3466	50
H(5A)	3365	1887	6182	50
H(8A)	2816	5175	4168	50
H(8B)	3894	4247	3817	50
H(8C)	10778	2122	7178	50
H(11A)	−935	565	5368	50
H(11B)	741	405	5160	50
H(11C)	−3181	3016	4632	50
H(11D)	−1154	2384	4952	50
H(12A)	2934	−232	4604	50
H(12B)	4702	401	4967	50
H(12C)	−3898	2112	3416	50
H(12D)	−3906	1557	4314	50
H(13A)	−848	2110	2816	50
H(13B)	1259	1479	3096	50
H(14A)	2064	2839	3555	50
H(14B)	2093	2371	4344	50

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3
Selected Bond Lengths (Å) and Bond Valence Sums (Σs) for 1

Co(1)–O(1)	2.070(2)	Co(1)–O(2)	2.048(2)
Co(1)–O(3)	2.071(2)	Co(1)–O(4)	2.042(3)
Co(1)–O(5)	2.121(3)		
Σs(Co(1)–O) = 1.80			
Co(2)–O(2)	2.073(2)	Co(2)–O(8)	2.141(3)
Co(2)–O(7)	2.151(2)	Co(2)–O(2)	2.092(2)
Co(2)–N(1)	2.226(3)	Co(2)–O(6)	2.061(2)
Σs(Co(2)–O) = 1.86			

O(2), and O(2′) upward and downward (∠Co(1)–O(2)⋯O(2′) = 137.34). The shortest Co⋯Co separations in the cluster are Co(1)⋯Co(2) = 3.374(2) Å and Co(2)⋯Co(2) = 3.109(1) Å. O(2) atoms are coordinated to three cobalt atoms, and have a bond valence sum of 1.10. This value suggests that O(2) is a hydroxyl group, which is consistent with the strong OH stretching (3561 cm^{-1}) found in IR. The tetranuclear hydroxo-bridged clusters, $Co_4(OH)_2(H_2O)_2$, are further stacked into column along the *a*-axis by multiple inter-cluster hydrogen bonds [O(8)⋯ O(1) = 3.081(1) Å, O(8)⋯O(5) = 2.776(2) Å, O(8)⋯O(7) = 2.847(1) Å], Fig. 2. Each $[Co_4(OH)_2(H_2O)_2]_n$ column is connected to four nearest-neighboring columns by pyromellitate ligands to form large one-dimensional channel with monoprotonated piperazine and water molecules inside, Fig. 3. Each pyromellitate ligand bridges four tetra nuclear clusters via the four carboxylate groups, in which two *ortho*-carboxylate groups are in the bidentate manner, and the other two *ortho*-carboxylate groups are in the monodentate manner, Fig. 3. The piperazine molecules play two roles in **1**; one is as the N-donor ligand, and the other is as the charge-balancing cations in the tunnels. The protonated N(2) atoms of piperazine molecules have hydrogen bonds with the non-coordinated oxygens of the carboxylate groups and the tunnel water [N(2)⋯O(10) = 2.869(1) Å, N(2)⋯O(9) = 2.943(1) Å, N(2)⋯O(11) = 2.850(2) Å].

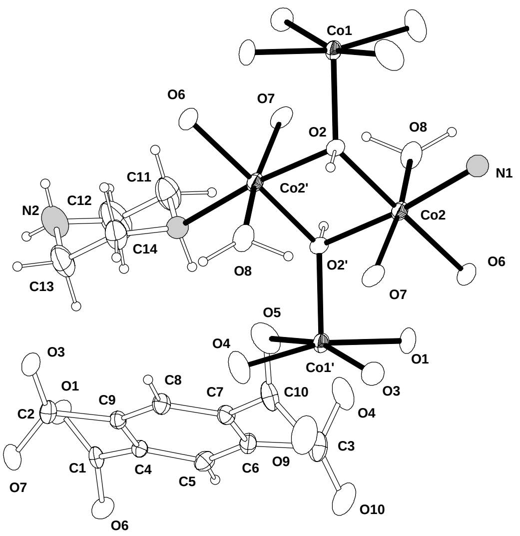

FIG. 1. The structure of the hydroxo-bridged tetranuclear unit of **1** (50% thermal ellipsoids).

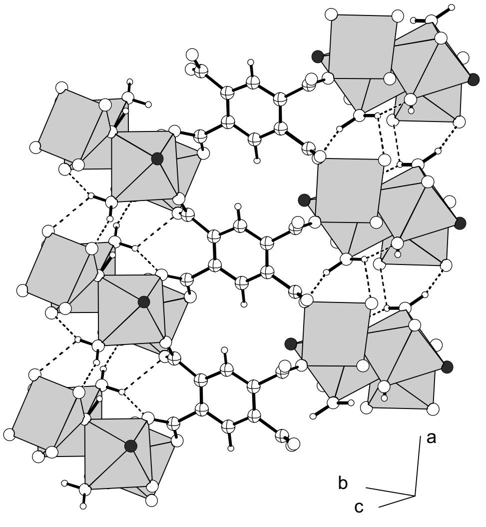

FIG. 2. The structure units of **1** showing the inter-cluster hydrogen bonds and the connection between the pyromellitate ligands and the tetranuclear clusters.

Owing to the flexible coordination modes and the available hydrogen bonding sites, the pyromellitate ligands are known for their abilities to be bridging ligands in building molecular structures (11), 1-D (12), 2-D (13), and 3-D (14) coordination polymers. In conjunction with the N-donor ligands, the structure diversity of compounds from the mixed ligand systems may further be expanded. It is noteworthy that only a small number of compounds containing similar tetranuclear Co clusters with all cobalt atoms in octahedral centers have been reported (15), while many Fe or Mn tetranuclear analogues are known (16). Furthermore, to the best of our knowledge **1** is the first compound containing $Co_4(OH)_2$ tetranuclear cluster bridged by organic ligands to form a 3-D structure. The cluster can be viewed as two $[Co_3(\mu_3\text{-OH})]$ triangular units fused along one edge. The $[Co_3(\mu_3\text{-OH})]$ unit is also found in $Co(OH)_2$ structure. One could envision that the clusters are the preliminary products of hydrolysis and condensation of the metal salt, and the clusters are further self-assembled into an extended structure in the presence of pyromellitate and piperazine ligands.

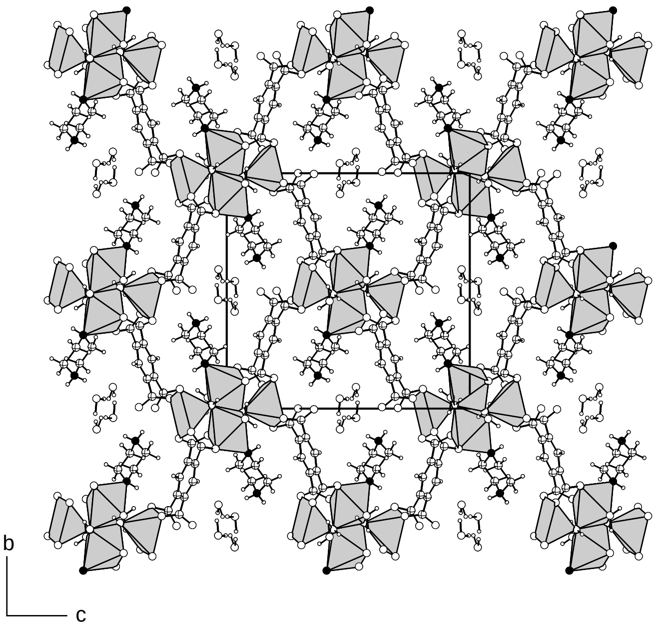

FIG. 3. The structure of **1** showing the 1-D tunnel along the *a*-axis.

Thermal and Magnetic Properties

Thermogravimetric analysis of **1** performed under N_2 showed a first weight loss of 10.8% from room temperature to 300°C, Fig. 4. This corresponds to the loss 6 mol of water per formula from three-tunnel water molecules, two coordinated water molecules, and one water molecule from the condensation of the two OH (theoretical, 10.4%). The second weight loss continued from ∼300 to ∼500°C, and reached to a constant weight of 31.1%. This corresponds to the loss of all the ligands in **1** and forms Co_3O_4 (theoretical, 31.0%).

The variable temperature magnetic susceptibility was measured from 2 to 300 K at 5000 Oe for **1**, Fig. 5. The χT vs T shows a value of 13.4 emu/K/mol at 300 K, and continuously decreases on cooling to a value of 6.2 emu/K/mol at 35 K. From 35 to 10 K the curve drops slower, and then drops abruptly to a value of 2.4 emu/K/mol at 2 K. The behavior of χT curve appears that it has a predominantly antiferromagnetic interaction in **1**. The effective magnetic moment per metal atom at 300 K, 5.18 μ_B, is in the range of experimentally observed values for high-spin Co(II) ions. The field dependence of magnetization was also measured at 2, 5, 15, and 20 K, and no hysteresis was observed, Fig. 6. At

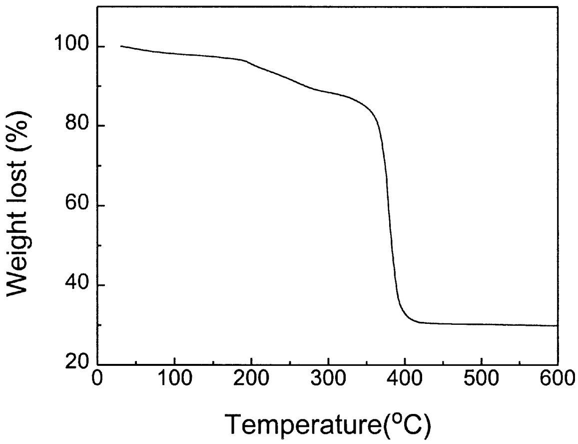

FIG. 4. Thermogravimetric analysis for **1**.

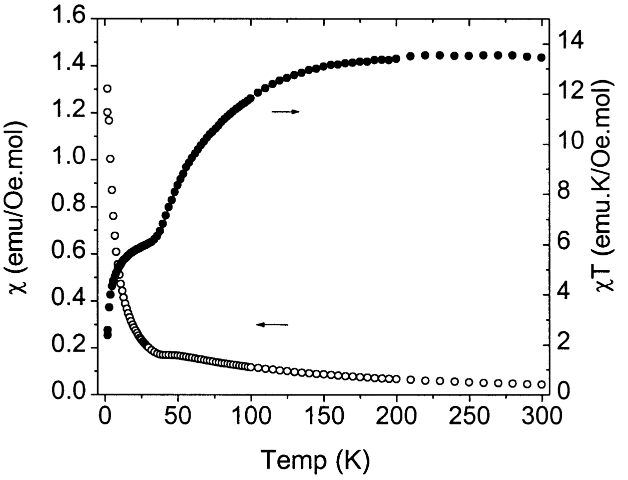

FIG. 5. The thermal dependence of χ and χT for **1**.

15 and 20 K paramagnetic-like behavior was seen, and the thermal energy still dominated. At lower temperature as 2 K the magnetization increased fast to a value of 2 μ_B at 1 T, and continued to increase to a value 5 μ_B at 7 T. The slopes changed from large to small and did not reach a saturation value. This indicates that about a quarter of the unpaired electrons of the four Co atoms in the cluster are much easily driven to the field direction than the rest of the three quarters. Similar behavior was found for 5 K. This M–H behavior is unlike a simple antiferromagnetic case, in which at temperature below T_N the curve generally maintains a low magnetization value at preliminary stage because of the cancellation of spins. More likely, a part of the magnetic moment in the system were loosely interacted and followed similar to the Brillouin function. Due to the special topology of the tetranuclear centers and the antiferromagnetic characteristic shown in **1**, spin frustration effects may occur and the overall magnetic structure depends strongly on the competing of the magnetic interactions in **1**. Hendrickson and Christou *et al.* have reported the spin frustration in several similar Fe or Mn tetranuclear compounds (17).

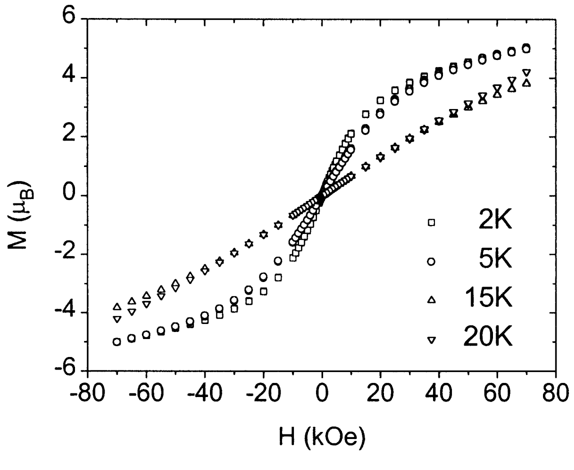

FIG. 6. Field dependence of magnetization at 2, 5, 10, and 15 K for **1**.

In sum, we have successfully used aromatic polycarboxylate ligands, pyromellitate, in conjugated with N-donor ligands, piperazine, as an effective system for the synthesis of a hybrid organic–inorganic framework containing new tetranuclear hydroxo-bridged cobalt clusters.

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