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Spin-Canting Magnetization in an Unusual Co_4 Cluster-Based Layer Compound from a 2,3-Dihydroxyquinoxaline Ligand

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Supporting Information

ABSTRACT: The self-assembly of $Co(O_2CPh)_2$ with a 2,3-dihydroxyquinoxaline (H_2dhq) linker has revealed a new two-dimensional cluster-based compound, $[Co_4(OMe)_2(O_2CPh)_2(dhq)_2(MeOH)_2]_n$, which shows spin-canted magnetization and a definite magnetic hysteresis loop.

One of the major challenges in the area of molecular magnetism is the construction of magnetic frameworks that show spontaneous magnetization. In studies of the magnetic properties of magnetic frameworks, the main advantage is the availability of numerous types of structures and topologies, in which a large magnetic anisotropy is produced from a single ion and/or there is a situation where structural distortion can result in the production of multifunctional materials with magnetic properties. Several different strategies have been employed, in attempts to achieve such magnetic entities.[1,2] However, the design and synthesis of such molecular materials with predictable magnetic properties continues to remain a challenging task because structural factors governing exchange coupling between paramagnetic centers are complex and elusive.

Despite the reports of some molecule-based magnetic metal−organic frameworks (MOFs) with a spontaneous magnetization, explorations that are relevant to achieving cluster-based magnetic MOFs are relatively rare in the literature.[3] Concerning the design of hybrid magnetic materials, the selection of an appropriate bridging ligand is of primary importance; the ligands may function as superexchange pathways and building units of structural topology. For a ligand such as 2,3-dihydroxyquinoxaline, the two hydroxyl groups and two nitrogen-donor atoms have the capacity to not only connect the metal ions to a multidimensional structure but also shorten the distance between metal ions, which could dominate a magnetic exchange pathway to a significant extent.

We herein report on the production of a new cluster-based two-dimensional (2D) layer, $[Co_4(OMe)_2(O_2CPh)_2(dhq)_2(MeOH)_2]_n$ (**1**), produced from the hydrothermal reaction of 2,3-dihydroxyquinoxaline and $Co(O_2CPh)_2$. This compound not only shows a clustered type of layer structure from the unusual Co_4 building units but also exhibits spontaneous magnetization with a definite coercivity.

The solvothermal treatment of a mixture of H_2dhq and $Co(O_2CPh)_2$ in a molar ratio of 1:1 in MeOH at 160 °C in a Teflon-lined stainless steel autoclave for 3 days resulted in the formation of very fine purple crystals of **1** in a yield of 21%.

An X-ray crystal structural analysis[4] showed that **1** crystallizes in the monoclinic space group $P2_1/c$. Compound **1** adopts a 2D layer structure that is comprised of a tetranuclear Co^{II} cluster repeating unit (see Figure 1, top). In each unit, four cobalt ions are located in the same plane, with a zigzag arrangement in which the angle for Co1−Co2−Co2′ is 105.84(2)°. Co1 and Co2 are coordinated in the CoN_2O_2 tetrahedral and $CoNO_5$ octahedral geometries, respectively. Peripheral ligation around the Co_4 unit is provided by two $PhCO_2^-$, two MeO^-, two dhq^{2-} ligands, and two MeOH molecules. These two dhq^{2-} ligands function as a η^1:η^1:η^2:η^1:μ_4 binding mode, which chelates Co1 and Co2′ terminally with one nitrogen atom and one hydroxyl group, respectively, while Co2 and Co2′ are bridged through the other hydroxyl group, resulting in a planar $[Co_2(OR)_2]$ diamond core with a Co−Co distance of 3.252(1) Å. The MeO^- and benzolate groups show η^2:μ_2 and syn,syn η^1:η^1:μ_2 binding modes, respectively, and bridge Co1 and Co2, resulting in a Co1−Co2 distance of 3.082(1) Å. Moreover, the nitrogen atom in dhq^{2-} is further connected to Co1′ in the next repeating Co_4 unit to form a 2D layer, in which each alternative neighboring unit has an angle of 68° in the Co_4 plane of the structure (see Figure 1, bottom). In the crystal, the layers are well isolated, with the shortest interlayer Co···Co distance being 9.879 Å, and no significant interlayer interactions are observed (Figure S1 in the Supporting Information).

Variable-temperature direct-current (dc) magnetic susceptibility data were collected for complex **1** in the temperature range of 1.8−300 K under an applied field of 1 kOe, and the data (see Figure 2) were plotted as $\chi_M T$ vs T. The room-temperature value of $\chi_M T$ was 12.2 emu K mol^{-1}, and $\chi_M T$ decreases with decreasing temperature to a minimum value of 4.1 emu K mol^{-1} at 20 K, after which it increases, reaching a maximum value of 36.9 emu K mol^{-1} at 10 K, and then decreases again to 8.4 emu K mol^{-1} at 1.8 K. The initial $\chi_M T$ could be a result of the depopulation of higher Kramers doublets from the Co^{II} center with an octahedral coordination environment,[5] and antiferromagnetic coupling within the Co_4 unit. The steep increases in χ_M and $\chi_M T$ below 20 K are clearly indicative of spontaneous magnetization, indicating spin-canted antiferromagnetism, which would lead to weak ferromagnetism

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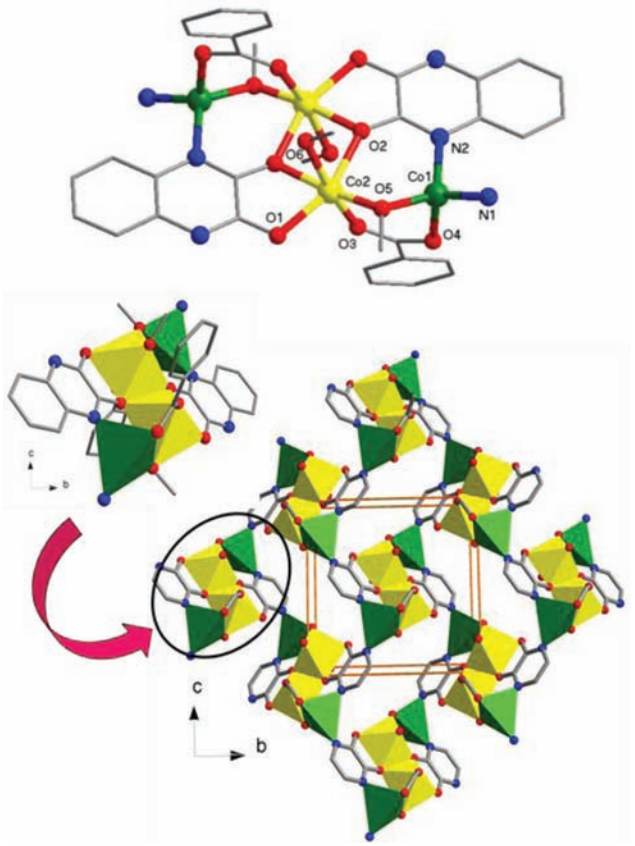

Figure 1. (Top) Crystal structure drawing of the Co_4 unit of **1**. Hydrogen atoms are omitted for clarity. (bottom) Polyhedral representation of the Co_4 cluster-based 2D layer of **1** viewed along the *a* axis.

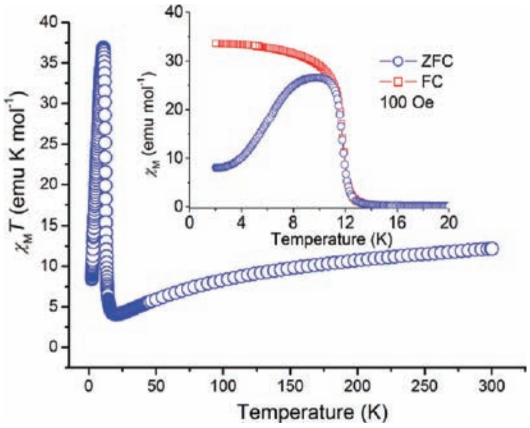

Figure 2. Plots of $\chi_M T$ vs T for **1** in an applied field of 1 kOe from 1.8 to 300 K and FC/ZFC magnetization for **1** at an applied field of 100 Oe (inset).

between the effective spins of adjacent Co^{II} ions. This conclusion was also reinforced by field dependence $\chi_M T$ vs T measurements (see Figure S5 in the Supporting Information). This magnetic behavior suggests that the Co_4 unit is present in a frustrated nonzero spin ground state and that each Co_4 unit is coupled antiferromagnetically, as the result of a noncanceled spin alignment, originating from spin-canted magnetism. The observed spin canting may be attributed to the magnetic anisotropy of Co^{II} ions and to an absence structural symmetry at low temperature, as has been previously reported for some spin-canting MOFs.[6]

To further investigate the possible phase transition suggested by the increase in the $\chi_M T$ curve, zero-field-cooled (ZFC) and field-cooled (FC) magnetization were measured from 2.0 to 50 K under 100 Oe. As can be seen from the inset in Figure 2, the ZFC magnetization shows a broad peak at 10 K and diverges from FC magnetization at about 12 K. This type of divergence reveals a possible transition from a paramagnetic state to either a long-range-ordered, spin-glass, or superparamagnetic state. The hysteresis loops at 2.0, 3.0, 6.0, 8.0, and 10 K and isothermal magnetization $M(H)$ at 2.0 K with a field of up to 70 kOe were measured, and the data are represented in Figures 3 and S6 in the Supporting Information, respectively. A hysteresis loop can be clearly seen, even at 8 K. The coercivity fields and remnant magnetizations are H_C = 4.77, 3.28, 2.43, and 1.79 kOe and M_R = 0.523, 0.519, 0.515, and 0.513 Nβ (β = Bohr magneton) at 2.0, 3.0, 6.0, and 8.0 K, respectively. At 2.0 K, the magnetization shows a step at around 1300 Oe, which then increases slowly to 2.12 Nβ at 70 kOe, which is far from the saturated magnetization value M_S = 13 Nβ but close to a Co^{II} spin of 2.17 Nβ resulting from a Kramers $S = {}^{1}/_{2}$ and average $g = {}^{13}/_{3}$.[7] The existence of a step in the magnetization at low field is indicative of metamagnetism in **1** (Figure S6 in the Supporting Information), and we attribute this behavior to the depression of the antiparallel configuration between spin-canting layers.[3,8]

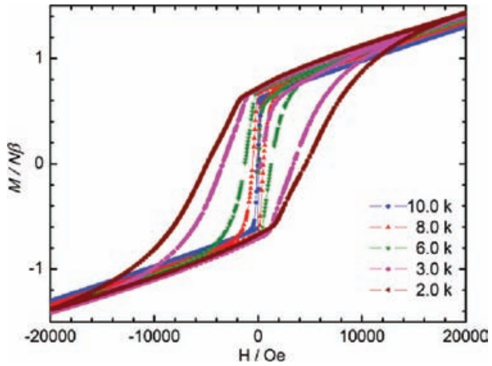

Figure 3. Magnetization vs field hysteresis loop measurements of **1** at the indicated temperatures at a scan rate of 0.03 T s^{-1}.

Furthermore, alternating-current (ac) susceptibilities under dc (H_{dc} = 0 Oe) and ac (H_{ac} = 3.5 Oe) fields were measured from 2 to 20 K with a frequency from 10 to 10 000 Hz. The results show strong peaks in both the in-phase (χ_M') and out-of-phase (χ_M'') parts. Upon decreasing temperature, the in-phase signals χ_M' behave similarly to the ZFC curves; i.e., they increase abruptly at around 12 K, reach a maximum at about 11.5 K, and then decrease slowly toward zero (Figure S7 in the Supporting Information). The out-of-phase signals χ_M'' increase steadily to a maximum of approximately 11.5−9.5 K (see Figure 4). The $d\chi_M'/dT$ curves all show peaks at T_C = 11.6 K, consistent with the dc measurements. While this behavior would not be expected to occur for true three-dimensionally ordered magnets, it is consistent with a spin-glass magnet. The peak temperatures of χ_M' can be measured by the parameter $\phi = (\Delta T_p/T_p)/\Delta(\log f) = 0.003$, indicating spin-glass behavior.[10] Moreover, the specific heat was measured under a zero applied field of 1.8−20 K (see Figure S8 in the Supporting Information). A shoulder peak was observed at around 12 K,

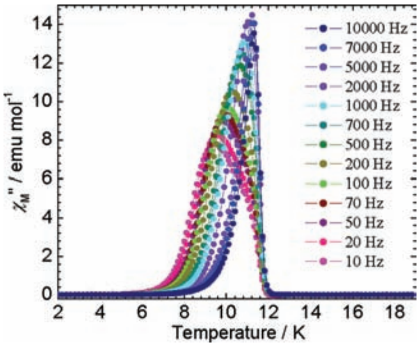

Figure 4. Plots of χ_M'' vs temperature for a powdered sample of complex **1** in a 3.5 G ac field. The data were collected in an ac field oscillating at the indicated frequency.

which is in good agreement with the occurrence of a spontaneous magnetization temperature, T_C, deduced from the ac susceptibility signal. This observation from specific heat measurements may due to spin-glass freezing.[11] Moreover, the ac data were collected using the same sample that had been heated at 350 °C for 2 h (see Figure S9 in the Supporting Information), which shows the absence of out-of phase signals and changing in-phase signals, excluding the contribution of the behavior of cobalt(II) oxide.

In conclusion, we describe the preparation of a new cluster-based 2D layer with an unusual repeating unit of $[Co_4(OMe)_2(O_2CPh)_2(dhq)_2(MeOH)_2]_n$, prepared using a 2,3-dihydroxyquinoxaline ligand (H_2dhq), which exhibits spin-glass behavior resulting from spin-canting magnetic interactions. It thus appears that the H_2dhq ligand utilized here has the potential for generating novel frameworks with promising structural features and properties. Furthermore, these results provide strong justification for further studies of H_2dhq and derivatives thereof with other transition metals and could lead to the development of even more interesting magnetic MOFs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, detailed experimental procedures, additional crystallographic diagrams, and a magnetic diagram. This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) Satisfactory elemental analytical data found (calcd) for $C_{17}H_{16}Co_2N_2O_6$ (**1**): C, 44.14 (44.18); H, 3.60 (3.49); N, 6.28 (6.06). Crystal data for **1**: $C_{17}H_{16}Co_2N_2O_6$, M = 462.18, monoclinic, space group $P2_1/c$, a = 14.2780(7) Å, b = 11.1546(6) Å, c = 11.3505(6) Å, β = 104.082(3)°, V = 1753.42(16) Å^3, Z = 4, T = 150(2) K, R (R_w) = 0.0433 (0.1033).

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