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Exploration of the Slow Relaxation Behavior in the Manganese Phosphate Network†

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Our endeavors are devoted to explain the nature of the magnetic relaxation phenomena in the currently prepared [MnII₅(HPO₄)₂(PO₄)₂(H₂O)₄]ₙ (1) herein. The inspection indicates the exotic behaviors have proved prominence of the half-occupied magnetic centers and competence of antiferromagnetic interactions and non-zero magnetic moments. The investigation suggests that the design and synthesis of the odd magnetic center materials with innate unquenched magnetic moments should be a new trend to produce the molecular magnets with relaxations.

Introduction

The field of transition metal phosphate,¹ once dominated by the exploration for open-framework materials with potential applications as absorbents, ion exchangers, and catalysts, has diversified as our understanding of the ingredients manipulating magnetic relaxation (MR).² In this day and age, materials with MR behaviors draw a sprouting interest of theoreticians and experimentalists, in that such behaviors promise the goals of molecule-based information storage, quantum computing, and spin-based electronics closer to reality.²,³ However, the essence of MR phenomena has not been figured out so far due to lack of experimental data. Therefore, our endeavors are devoted to the exploration of the nature concerning the interesting MR phenomena.

We, herein, report the manganese phosphate [MnII₅(HPO₄)₂(PO₄)₂(H₂O)₄]ₙ (1). The three dimensional (3D) structure of complex 1 is constructed by the building blocks−0D penta-manganese clusters and the adhesives phosphate ions and water molecules to offer multiple super-exchange paths and complex magnetic interactions. The magnetic investigation reveals that complex 1 shows canted antiferromagnetic (weak ferromagnetic) behaviors. Noteworthily, the competition between antiferromagnetic interactions and ferromagnetic ones gives rise to the magnetic relaxation. Such exotic magnetic behavior is further comprehensively discussed and the principle leading to the interesting behaviors is summarized for the first time to guide the further synthesis of such MR materials.

Experimental

Materials

All chemicals and solvents used for synthesis are at reagent grade without further purification. The starting materials are MnSO₄·H₂O, morpholine, and 85% phosphoric acid water solution.

Synthesis

[MnII₅(HPO₄)₂(PO₄)₂(H₂O)₄]ₙ (1): MnSO₄·H₂O (0.5 mmol), morpholine (0.2 mmol), and 85% phosphoric acid (0.1 mmol) in 20 ml water were mixed together and stirred for 30 min at the ambient temperature. Then the consequent suspension was moved into the Teflon-lined steel autoclave, heated at 453 K for 72 h, and then slowly cooled to the ambient temperature. X-ray quality light pink needlelike crystals were washed using distilled water and collected by filtration. Yield: 49.2 % (based on metal ions). IR (cm⁻¹): 3448(s), 3305(m), 3171(m), 2939(m), 1306(s), 1157(s), 1104(s), 1074(s), 1022(s), 969(s), 894(m), 760(m), 707(m). H₁₀M₇O₂₅P₄ (728.66): calcd. H 1.38; found H 1.40.

Physical measurements
Infrared Spectroscopy. The infrared spectroscopy (IR) on KBr pellets was performed on a Magna-IR 750 spectroscopy in the 4000–400 cm⁻¹ region.

X-ray Crystallography. Single-crystal X-ray data sets were collected on an Oxford Diffraction Gemini R Ultra detector using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) for 1 at 298(2) K. Intense data were collected by ω scan technique. All data were obtained for Lorentz polarization effects. The diffraction patterns for the complex were indexed using CrysAlis software to obtain the unit cell parameters. The structures were solved with the direct methods (SHELXS-97) and refined on F² by full-matrix least-squares (SHELXL-97).

Elemental Analysis. Elemental analysis was performed on a Perkin-Elmer 2400 CHN elemental analyzer.

Magnetic Measurements. The direct current (DC) and alternate current (AC) magnetic susceptibility measurements on polycrystalline sample of 1 were carried out with Quantum Design SQUID MPMS XL-7 instruments.

Results and discussion

General characterization and structure description

The hydrothermal reaction of MnSO₄·H₂PO₄₉ and morpholine in the molar ratio of 5:1:2 afforded light pink needle like crystals of [Mn₁₂(HPO₄)₅(PO₄)₂(H₂O)₄]ₙ (1). Complex 1 crystallizes in the monoclinic C2/c space group. The subunit structure and its numbering scheme are shown in Fig. 1a. This manganese phosphate is constructed by the penta-manganese [Mn₅(η²-HPO₄)₂(PO₄)₂(H₂O)₄]₀ 0D neutral clusters as secondary building units (Fig. 1b). The five-membered Mn₅ clusters terminated by the water molecule O1W are then connected by the O(5) from the P(1) phosphate and the water molecule O2W to be a 2D layer as depicted in Fig. 1c. The layer is further linked by monohydrate phosphates and phosphates respectively in η¹-η²-Mn⁻ and η¹-η²-Mn⁻ modes to construct a 3D structure (Fig. 1d). The asymmetric unit contains three crystallographically distinct Mn sites and two crystallographically distinct P sites (Fig. 1a). Each Mn⁷⁺ ion possesses a distorted MnO₆ octahedron geometry and noteworthy, Mn(3) is on the mirror plane. The Mn–O bond lengths vary in the range of 2.115(2)–2.260(2) Å. Bond valence sum (BVS) calculations show that all of the Mn ions have the same oxidation state of +2. The bond angles of Mn–O–Mn are from 95.93(6)°–111.49(8)° and the intracluster metal–metal separations through µ-O bridges are 3.383(1) and 3.361(1) Å for Mn(1)···Mn(2) and Mn(2)···Mn(3), respectively. The P(1) phosphate links five Mn ions, while the P(2) one connects seven Mn ions. The Mn–O bond lengths range from 1.518(2) to 1.567(2) Å. Additionally, the metal–metal distances between penta-nuclear clusters are 3.535(1) and 3.764(1) Å through O(5) and O2W, respectively. Given the diversity of bond distances and angles, multiple super-exchange paths and complex magnetic interactions are thus expected.

Magnetic investigations

Direct current (DC) magnetic susceptibility measurements on polycrystalline samples of 1 were then carried out in the temperature range 2–300 K and under the applied magnetic field of 1000 G. The experimental susceptibilities were corrected for diamagnetism of the constituent atoms (Pascal’s constants). The χ_mT value for 1 at 300 K of 26.05 cm³ mol⁻¹ K, which is slightly larger than the five spin only high spin manganese(II) (S = 5/2×5 and g = 2.0) value 21.88 cm³ mol⁻¹ K⁻¹, undergoes a steady decay upon cooling to 4.58 cm³ mol⁻¹ K at 7.8 K. The fitting of 1/χ_m versus T (50–300 K) to the Curie–Weiss law affords C = 32.12 cm³ K⁻¹ mol⁻¹ and θ = −40.06 K for 1 (Fig. 2). The decrease of χ_mT and the negative Weiss constant suggest a dominated antiferromagnetic (AFM) interaction. On further cooling, the χ_mT values abruptly increase to reach a very sharp maximum of 8.74 cm³ mol⁻¹ K at 4.9 K (Fig. 2) and then decrease to 4.72 cm³ mol⁻¹ K at 2 K. This indicates the magnetic behavior of 1 at the low temperature (T < 7.8 K) should be canted antiferromagnetic in the homo-spin system. Below 4.0 K, the second fall of the χ_mT value should arise from the magnetic field saturation effect and/or the antiferromagnetic contribution. In fact, the maximum of the χ_mT value for 1 shows a more noticeable change in lower magnetic fields (50 and 100 Oe) than in higher field (1000 Oe), which suggests the spin-canting phenomenon (Fig. 3).

As seen in Fig. 4, the shape of the M-H curve shows a fast increase of the resulting magnetization at very low fields and a linear variation of M-H at H > 2 kOe, which further indicates the canted antiferromagnetism. In addition, the unsaturated value of M_max/Nβ at 60 kOe is ca. 6 Nβ mol⁻¹ for 1 and suggests an S > 6/2.
ground state. The small hysteresis loop with remnant magnetization of 0.006 N\(\beta\) mol\(^{-1}\) and the coercive field of 40 Oe is observed at 2 K in complex 1 (ESI† Fig. S3). Moreover, as depicted in Fig. S4,† the curves of field-cooled (FC) and zero-field-cooled (ZFC) of 1 show a bifurcation below 7.8 K, which reveals a long-range antiferromagnetic ordering.9

The inspection of the manganese phosphate attests to the prominence of the half-occupied magnetic centers and the competence of antiferromagnetic interactions and non-zero magnetic moments for the exotic MR behaviors. Admittedly, not all the materials that are of the innate magnetic moments, such as the chiral system,6 could be of MR behaviors. Hence, whether the versatile phosphate might be assistant to such amazing MR should be revealed by analogous experiments regarding the various transition metal phosphates. Most critically, the fabrication of this novel complex and the determination of its magnetism suggest that the design and synthesis of the odd magnetic center materials with innate unquenched magnetic moments should be a new trend to produce the molecular magnets with relaxations.

**Conclusions**

The inspection of the manganese phosphate attests to the prominence of the half-occupied magnetic centers and the competence of antiferromagnetic interactions and non-zero magnetic moments for the exotic MR behaviors. Admittedly, not all the materials that are of the innate magnetic moments, such as the chiral system,6 could be of MR behaviors. Hence, whether the versatile phosphate might be assistant to such amazing MR should be revealed by analogous experiments regarding the various transition metal phosphates. Most critically, the fabrication of this novel complex and the determination of its magnetism suggest that the design and synthesis of the odd magnetic center materials with innate unquenched magnetic moments should be a new trend to produce the molecular magnets with relaxations.

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**Notes and references**

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†Electronic Supplementary Information (ESI) available: [Crystal structure files in the CIF format, detailed synthesis procedure, element analysis, infrared spectroscopy, molecular structures of I viewed in different axes, and magnetism.]. See DOI:10.1039/b000000x/


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