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ARTICLE TYPE

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 $[\text{Mn}^{\text{II}}_5(\text{HPO}_4)_2(\text{PO}_4)_2(\text{H}_2\text{O})_4]_n$ (**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 $[\text{Mn}^{\text{II}}_5(\text{HPO}_4)_2(\text{PO}_4)_2(\text{H}_2\text{O})_4]_n$ (**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. Noteworthy, 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 $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, morpholine, and 85% phosphoric acid water

45 solution.

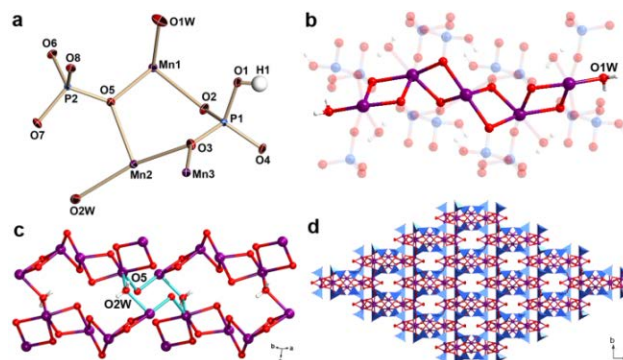


Fig. 1 (a) The thermal ellipsoid plot of the subunit at the 50% probability level and the numbering scheme of **1** (the hydrogen atoms on water molecules are omitted for clarity). (b) The plot concerning the penta-manganese cluster extending along crystallographic *a* axis for **1** (hydrogen (white), oxygen (red), phosphor (blue), and manganese (violet)). (c) The short chains linked by O(5) and O2W for **1**. (d) The dense 3D crystal structures of manganese phosphate **1** (blue tetragons represent phosphate, hydrogen atoms are neglected for clarity).

Synthesis

$[\text{Mn}^{\text{II}}_5(\text{HPO}_4)_2(\text{PO}_4)_2(\text{H}_2\text{O})_4]_n$ (**1**): $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (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). $\text{H}_{10}\text{Mn}_5\text{O}_{20}\text{P}_4$ (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 diffractometer using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) 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 F^2 by full-matrix least-squares (SHELXL-97).⁴

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 MnSO_4 , H_3PO_4 , and morpholine in the molar ratio of 5:1:2 afforded light pink needle like crystals of $[\text{Mn}^{\text{II}}_5(\text{HPO}_4)_2(\text{PO}_4)_2(\text{H}_2\text{O})_4]_n$ (**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 $[\text{Mn}^{\text{II}}_5(\text{HPO}_4)_2(\text{PO}_4)_2(\text{H}_2\text{O})_4]$ 0D neutral clusters as secondary building units (Fig. 1b). The five-membered Mn_5 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 $\eta^1:\eta^2:\eta^2:\mu_5$ and $\eta^2:\eta^2:\eta^2:\eta^1:\mu_7$ 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 Mn^{II} ion possesses a distorted MnO_6 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) \AA . Bond valence sum (BVS) calculations⁵ 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) \AA 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) \AA . Additionally, the metal–metal distances between penta-nuclear clusters are 3.535(1) and 3.764(1) \AA 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

$\chi_m T$ value for **1** at 300 K of 26.05 $\text{cm}^3 \text{ mol}^{-1} \text{ K}$, which is slightly larger than the five spin only high spin manganese(II) ($S = 5/2 \times 5$ and $g = 2.0$) value 21.88 $\text{cm}^3 \text{ K mol}^{-1}$, undergoes a steady decay upon cooling to 4.58 $\text{cm}^3 \text{ mol}^{-1} \text{ K}$ at 7.8 K. The fitting of $1/\chi_m$ versus T (50–300 K) to the Curie–Weiss law affords $C = 32.12 \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -40.06 \text{ K}$ for **1** (Fig. 2). The decrease of $\chi_m T$ and the negative Weiss constant suggest a dominated antiferromagnetic (AFM) interaction. On further cooling, the $\chi_m T$ values abruptly increase to reach a very sharp maximum of 8.74 $\text{cm}^3 \text{ mol}^{-1} \text{ K}$ at 4.9 K (Fig. 2) and then decrease to 4.72 $\text{cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K. This indicates the magnetic behavior of **1** at the low temperature ($T < 7.8 \text{ K}$) should be canted antiferromagnetic in the homo-spin system.⁶ Below 4.0 K, the second fall of the $\chi_m T$ value should arise from the magnetic field saturation effect and/or the antiferromagnetic contribution.⁷ In fact, the maximum of the $\chi_m T$ 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).⁸

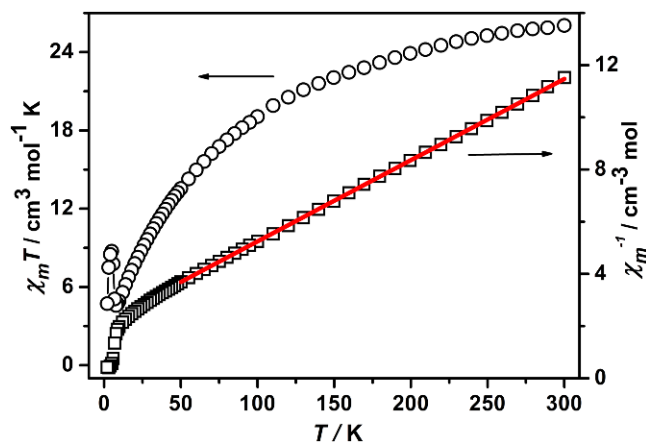


Fig. 2 The plot of $1/\chi_m$ versus T and $\chi_m T$ versus T for the polycrystalline samples of **1** under an applied field of 1 kOe from 2 to 300 K.

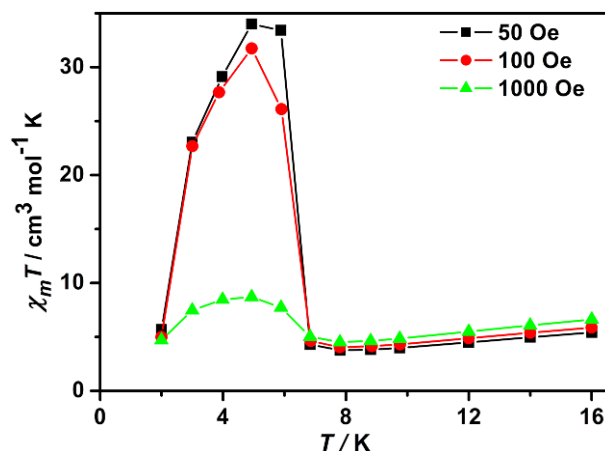


Fig. 3 Plots of $\chi_m T$ versus T for **1** under an applied field of strength 50, 100, and 1000 Oe DC within the temperature range 2–16 K.

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 $H > 2 \text{ kOe}$, which further indicates the canted antiferromagnetism. In addition, the unsaturated value of $M_{\text{mol}}/N\beta$ at 60 kOe is ca. $6 N\beta \text{ mol}^{-1}$ for **1** and suggests an $S > 6/2$

ground state. The small hysteresis loop with remnant magnetization of $0.006 N\beta \text{ mol}^{-1}$ 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

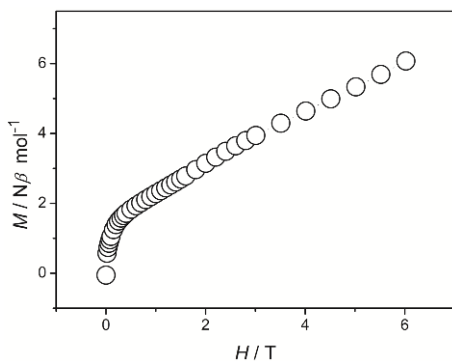


Fig. 4 The M - H curve of **1** in the magnetic field range of 1 to 6 T at 2 K.

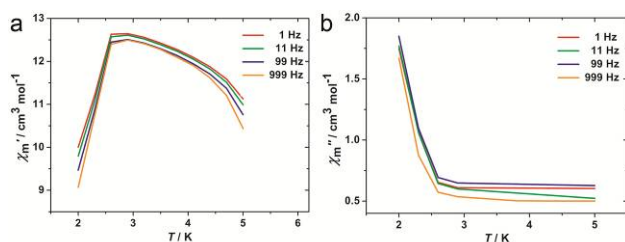


Fig. 5 The plots of χ_m' (a) and χ_m'' (b) versus T of the polycrystalline sample of **1** (solid lines) under a zero-dc field and a 3 Oe oscillating field in the frequency range of 1-999 Hz from 2 to 5 K.

To further the necessary investigation of the dynamics of the magnetization involving the spontaneous magnetic behaviors of **1** below 5 K, alternating current (ac) susceptibility measurements were carried out for **1** under a zero-dc field and a 3 Oe oscillating field in the frequency range of 1–999 Hz. The occurrence of distinct peaks for the in-phase (χ') and out-of-phase (χ'') ac signals is evident (Fig. 5). The absence of frequency-dependent ac magnetic susceptibility further indicates the antiferromagnetic ordering.

The non-zero magnetic moments in the complex **1** should be possibly put down to the following structural feature: the half occupied Mn ions, whose magnetic moments lack of the inversion centers in between are difficult to be totally quenched. Furthermore, the antiferromagnetic featured regime around 2 K could be characteristic of direct relaxation process of the solo manganese ion, as after magnetic moments quenched via antiferromagnetic interactions, only the half-occupied manganese ion remains in a subunit for both complexes (opaque violet ball in Fig. 6). In addition, the unquenched magnetic moments are at least 5.10 \AA away from each other for **1** and thus it might be too far for the magnetic interactions at such a low temperature. Thus, the field saturation effect could give rise to the onset and peaks of the antiferromagnet-like fall.⁷

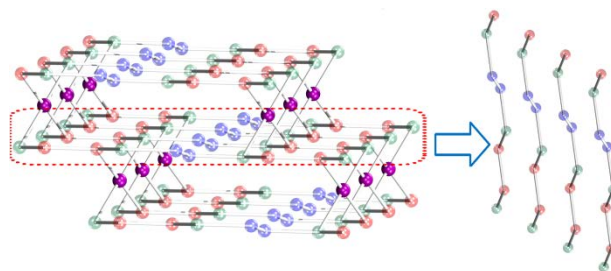


Fig. 6 The simplified polygon network topology of complex **1** consists of different pattern polygons, where only the metal-metal separation distances less than 3.70 \AA are considered for clarity (the opaque violet balls represent the half-occupied Mn(3) ions distinguished from the transparent centre-related ones Mn(1): red; Mn(2): blue; Mn(4): green).

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 **1** viewed in different axes, and magnetism.]. See DOI:10.1039/b000000x/
- ‡ Crystal data of **1**: $M_r = 728.66$, monoclinic, space group $C/2c$, $a = 17.612(4) \text{ \AA}$, $b = 9.135(1) \text{ \AA}$, $c = 9.481(2) \text{ \AA}$, $\beta = 96.491(3)^\circ$, $V = 1515.5(4) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 3.194 \text{ g cm}^{-3}$, 3670 reflections collected, 1279 unique ($R_{\text{int}} = 0.0344$), GOF = 1.009, $R_1 = 0.0233$, $wR_2 = 0.0726$ [$I > 2\sigma(I)$]. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number ICSD-421646.

- 1 (a) A. Corma and H. García, *Chem. Rev.*, 2003, **103**, 4307-4366; (b) H.-
R. Wen, C.-F. Wang, Y.-Z. Li, J.-L. Zuo, Y. Song and X.-Z. You,
Inorg. Chem., 2006, **45**, 7032-7034; (c) H. Xing, W. Yang, T. Su, Y.
Li, J. Xu, T. Nakano, J. Yu and R. Xu, *Angew. Chem. Int. Ed.*, 2010,
5 **49**, 2328 -2331; (d) D. Umeyama, S. Horike, M. Inukai, T. Itakura
and S. Kitagawa, *J. Am. Chem. Soc.*, 2012, **134**, 12780-12785; (e) J.
Yu and R. Xu, *Chem. Soc. Rev.*, 2006, **35**, 593-604.
- 2 (a) J. D. Rinehart, K. R. Meihaus and J. R. Long, *J. Am. Chem. Soc.*,
2010, **132**, 7572-7573; (b) Y.-N. Guo, G.-F. Xu, P. Gamez, L. Zhao,
10 S.-Y. Lin, R. Deng, J. Tang and H.-J. Zhang, *J. Am. Chem. Soc.*,
2010, **132**, 8538-8539; (c) Y.-N. Guo, G.-F. Xu, W. Wernsdorfer, L.
Ungur, Y. Guo, J. Tang, H.-J. Zhang, L. F. Chibotaru and A. K.
Powell, *J. Am. Chem. Soc.*, 2011, **133**, 11948-11951; (d) K. C.
Mondal, A. Sundt, Y. Lan, G. E. Kostakis, O. Waldmann, L. Ungur,
15 L. F. Chibotaru, C. E. Anson and A. K. Powell, *Angew. Chem. Int.
Ed.*, 2012, **51**, 7550-7554.
- 3 (a) W. L. Queen, S.-J. Hwu and L. Wang, *Angew. Chem. Int. Ed.*, 2007,
46, 5344-5347; (b) B. Li, X. Zhang, J. Tian and J. Zhang, *Chem.
Commun.*, 2011, **47**, 1737-1739; (c) L. Bogani, C. Sangregorio, R.
20 Sessoli and D. Gatteschi, *Angew. Chem. Int. Ed.*, 2005, **44**, 5817-
5821; (d) R. Liu, L. Li, X. Wang, P. Yang, C. Wang, D. Liao and J.-
P. Sutter, *Chem. Commun.*, 2010, **46**, 2566-2568; (e) M.
Gonidec, F. Luis, À. Vilchez, J. Esquena, D. B. Amabilino and J.
Veciana, *Angew. Chem. Int. Ed.*, 2010, **49**, 1623-1626.
- 25 4 G. M. Sheldrick, *SHELXS97 and SHELXL97*, University of
Göttingen, Germany, 1997.
- 5 N. E. Brese and M. O'Keeffe, *Acta Crystallogr., Sect. B*, 1991, **47**,
192-197.
- 6 (a) C. Train, M. Gruselle and M. Verdaguer, *Chem. Soc. Rev.*, 2011, **40**,
30 3297-3312; (b) E. Pardo, C. Train, G. Gontard, K. Boubekeur, O.
Fabelo, H. Liu, B. Dkhil, F. Lloret, K. Nakagawa, H. Tokoro, S.-i.
Ohkoshi and M. Verdaguer, *J. Am. Chem. Soc.*, 2011, **133**, 15328-
15331; (c) A. Ueda, H. Wasa, S. Suzuki, K. Okada, K. Sato, T. Takui
and Y. Morita, *Angew. Chem. Int. Ed.*, 2012, **51**, 6691-6695.
- 35 7 M. Yang, J. Yu, L. Shi, P. Chen, G. Li, Y. Chen, R. Xu and S. Gao,
Chem. Mater., 2005, **18**, 476-481.
- 8 (a) J. Tian, W. Li, B. Li, X. Zhang, J. Tang and J. Zhang, *Chem. Eur. J.*,
2013, **19**, 5097-5103; (b) P. Mahata, D. Sen and S. Natarajan, *Chem.
Commun.*, 2008, 1278-1280; (c) A. A. Leitch, J. L. Brusso, K.
40 Cvrkalj, R. W. Reed, C. M. Robertson, P. A. Dube and R. T. Oakley,
Chem. Commun., 2007, **0**, 3368-3370; (d) L. Cheng, W.-X. Zhang,
B.-H. Ye, J.-B. Lin and X.-M. Chen, *Eur. J. Inorg. Chem.*, 2007,
2007, 2668-2676.
- 9 (a) Y.-B. Lu, M.-S. Wang, W.-W. Zhou, G. Xu, G.-C. Guo and J.-S.
45 Huang, *Inorg. Chem.*, 2008, **47**, 8935-8942; (b) M.-H. Zeng, B.
Wang, X.-Y. Wang, W.-X. Zhang, X.-M. Chen and S. Gao, *Inorg.
Chem.*, 2006, **45**, 7069-7076.