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Coordinated Molecule-Modulated Magnetic Phase with Metamagnetism in Metal–Organic Frameworks

Kwanghyo Son,[†] Jin Yeong Kim,[‡] Gisela Schütz,[†] Sung Gu Kang,^{*,§}[®] Hoi Ri Moon,^{*,‡}[®] and Hyunchul Oh*,¹

[†]Max Planck Institute for Intelligent Systems, Heisenbergstrasse 3, Stuttgart 70569, Germany

[‡]Department of Chemistry, Ulsan National Institute of Science and Technology, Ulsan 44919, Republic of Korea

[§]School of Chemical Engineering, University of Ulsan, Ulsan 44610, Republic of Korea

¹Department of Energy Engineering, Gyeongnam National University of Science and Technology, Jinju 52725, Republic of Korea

S Supporting Information

ABSTRACT: Most well-known metal-organic frameworks (MOFs) possessing the magnetic $Ni_2O_2(CO_2)_2$ chains, called Ni-MOF-74, have been investigated with regard to magnetic properties at open-metal sites. We present the modulation of their magnetic phase and metamagnetism via imidazole molecule coordination.

olecule-based magnetic materials have recently attracted Mincreasing interest for use in novel applications (e.g., magnetic switchers, magnetic sensors, and multifunction magnetic devices in molecular spintronics) because of their ability to display ferromagnetism and other more complex magnetic phenomena.¹⁻⁵ In particular, these materials are advantageous because their magnetic properties can be controlled by changing their spin center, the length of their interactive organic ligands, or both. These advantages permit the study of important magnetic features such as magnetic dynamics and magnetic hysteresis with high spontaneous magnetization. Various magnetic systems with designed novel structures in single-molecule magnets (SMMs) and singlechain magnets (SCMs) have been reported.⁶⁻

Among the various types of molecular-based magnets, metal-organic frameworks (MOFs) could represent a potential model system because of their numerous metal clusters within a microporous crystalline structure, their varied functionality (via ligand and metal cluster exchange), and/or their controllable cluster-cluster interactions through tunable pore size and structure.^{10,11} Moreover, open-metal sites (OMSs; unpaired electrons in the metal cluster) in MOFs are very useful for understanding the influence of unpaired electrons on magnetic metal ions, by the design of interior structures in the frameworks.^{12,13} For example, the antiferroand ferromagnetic (AFM and FM, respectively) coupling effects on metal spin centers in OMSs can therefore be elucidated via the gradual occupation of unpaired electrons at OMSs.^{14–18} Moreover, the spin canting and metamagnetism are particular types of AFM coupling effects in some lowdimensional [layers, two-dimensional (2D); chains, onedimensional (1D)] systems. Because the metamagnetism disrupts the AFM ordering and turns into the FM state when a certain external field is applied, FM and canted AFM couplings should be coexist in interchain interactions with intrachain interactions.^{19,20}

In this study, the feasibility of modulating magnetic phases between AFM and FM orderings is therefore explored, as suggested by the literature, by adjusting the coordination of the metal ions, solvents, or organic ligands.²⁰⁻²³ Furthermore, the critical temperatures—Néel temperature (T_N) for AFM ordering and Curie temperature (T_C) for FM ordering—and the critical field (H_{cr}) for the metamagnetism transition can be designed as the FM/AFM ratio in the system.

A hexagonal 1D-channel MOF possessing numerous OMSs (Ni²⁺), called Ni-MOF-74, was chosen as the low-dimensional magnet for this study. The structure of Ni-MOF-74 exhibits helical building units of FM Ni^{II}O₅ 5-fold coordination polyhedral chains with 2,5-dioxide-1,4-benzenedicarboxylate organic linkers (denoted as Ni-MOF-74-ac). Then, three different amounts of imidazole molecules (IMs) were introduced into the OMSs in the channel of Ni-MOF-74, herein referred to as Ni-MOF-74-IM, in order to observe the gradual occupation of the unpaired electron at its OMS (Figure 1). The Fourier transform infrared (FT-IR) spectra of Ni-MOF-74-ac and three Ni-MOF-74-IMs indicate the successful incorporation of IMs in the Ni-MOF-74 systems, and powder X-ray diffraction (PXRD) patterns clearly indicate that the framework structures of the samples were maintained after the introduction of IMs (Figures S1 and S2). On the basis of the elemental analysis results, 10%, 38%, and 70% of all Ni²⁺ (the OMS) in MOF-74-ac are gradually occupied by IM, respectively, denoted as Ni-MOF-74-IM-10, Ni-MOF-74-IM-38, and Ni-MOF-74-IM-70.

As IMs are introduced into the 1D channel, the squarepyramidal 5-fold-coordinated Ni^{II} ion with two unpaired electrons is converted into the octahedral 6-fold-coordinated Ni^{II} species with an IM. The UV-vis-near-IR (NIR) spectra clearly show that the ratio of 6-fold-coordinated Ni^{II} is increased when the amount of IM introduced is increased (Figure S3).²⁰ This conversion ratio (from 5-fold to 6-fold at the Ni^{II} site) results in a dramatic change in the magnetic characteristics. Through this phenomenon, the magnetic properties of MOFs can be investigated as a function of their

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Figure 1. Crystal structures of Ni-MOF-74-ac, Ni-MOF-74-IM-10, Ni-MOF-74-IM-38, and Ni-MOF-74-IM-70. (top) Primary assembling unit.

temperatures and applied fields. In addition, magnetic phase transition diagrams can also be obtained via M-T and M-H curves.

The direct-current (dc) magnetic susceptibilities (χ_m) of the samples were collected under an applied field of 1 kOe in the range of 2–300 K. The $\chi_m T$ versus *T* and χ_m versus *T* (inset) curves of the samples are shown in Figure 2. The values of $\chi_m T$ at 300 K are 4.50, 3.71, 3.57, and 3.92 cm³ K mol⁻¹ per Ni^{II}₃ unit in a 1D metal cluster chain (Figure 1, circle inset) for Ni-MOF-74-ac, Ni-MOF-74-IM-10, Ni-MOF-74-IM-38, and Ni-MOF-74-IM-70, respectively. These values are higher than the



Figure 2. Temperature dependence of $\chi_m T$ measured in an applied field of 1 kOe on powder samples of Ni-MOF-74-ac, Ni-MOF-74-IM-10, Ni-MOF-74-IM-38, and Ni-MOF-74-IM-70. Inset: Temperature dependence of the magnetic susceptibility, χ_m (ZFCFC), of all samples between 2 and 40 K under 1 kOe.

expected spin-only value of 3.00 cm³ K mol⁻¹ for three Ni^{II} ions (S = 1; g = 2) because of the orbital contribution from the octahedral Ni^{II} ions. The value of $\chi_m T(T)$ is increased slowly until 25 K and then rapidly decreased to below 20 K, reaching ~0.3 cm³ K mol⁻¹ for Ni-MOF-74-ac, Ni-MOF-74-IM-10, and Ni-MOF-74-IM-38, and 1.06 cm³ K mol⁻¹ for MOF-74-IM-70. The linear fitting of the inverse magnetic susceptibility, $1/\chi_{m}$ versus T from 150 to 300 K (linear part) to the Curie–Weiss law $[\chi_m(T) = C/(T + \theta)]$, where *C* is the Curie constant and θ is the Weiss constant, indicates the existence of AFM configurations with C = 4.36, 3.89, and 3.48 cm³ mol⁻¹ K (Figure S5). Weiss temperatures of θ = 4.96, 4.11, and 3.28 K can be obtained for Ni-MOF-74-ac, Ni-MOF-74-IM-10, and Ni-MOF-74-IM-38, respectively. Ni-MOF-74-IM-70, however, exhibits FM ordering at $C = 3.69 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, $\theta = -8.92$, and a Curie temperature, $T_{\rm C}$, of 8.83 K. The $\chi_{
m m}(T)$ data show cusps at Néel temperatures (T_N) of ~18.5 K for MOF-74-ac, 17 K for MOF-74-IM-10, and 15 K for MOF-74-IM-38; $T_{\rm N}$ is obtained at the x-axis intersection of $d\chi_m/dT$ to improve accuracy (Figure S6). Note that Ni-MOF-74-IM-70 does not have a cross section. The abrupt decreases below T_N occur because of interchain AFM interactions.

The combination of the Meyer model for AFM coupling $(J_1 < 0)$ and the Monford model for FM coupling $(J_2 > 0)$ was used as a fitting model $(H = -J\sum S_i \cdot S_{i+1})^{24,25}$ (Figure S7). The fitting equation (1) is

$$\chi_{\rm m} = N \left\{ \frac{\left(g_{\rm l}\mu_{\rm B}\right)^2}{k_{\rm B}T} \frac{2 + 0.0194x_{\rm l} + 0.777x_{\rm l}^2}{3 + 4.346x_{\rm l} + 3.232x_{\rm l}^2 + 5.834x_{\rm l}^3} + \left[\frac{2}{3} \frac{\left(g_{\rm l}\mu_{\rm B}\right)^2}{k_{\rm B}T} \right] \frac{1 - 0.3127x_{\rm l} + 0.124x_{\rm l}^2 + 0.541x_{\rm l}^3}{1 - 0.887x_{\rm l} + 0.586x_{\rm l}^2} \right\}$$
(1)

where $x_{1,2} = J_{1,2}/k_BT$, $J_{1,2}$ is the coupling strength, $g_{1,2}$ is the Landé g factor, and k_B is the Boltzmann constant. The best-fit analysis is summarized in Table S1.

This confirms that there were changing interactions between the Ni^{II} centers. The AFM interaction appears to be reduced and the FM interaction increased by the addition of more IMs. The values of the Landé g factors support the theory of a change from 5-fold-coordinated to 6-fold-coordinated Ni ions due to increasing amounts of IMs in the MOF. The magnetic configuration change is also verified by these fitting results. The magnetic ground state of Ni-MOF-74-ac was initially AFM for the interchain and FM for the intrachain. Interestingly, the magnetic ground state then changed to the FM state for both interchain and intrachain Ni atoms in the presence of IMs. Density functional theory (DFT)-calculated results also support the idea that the magnetic phase transition was enabled by IMs (Table S2).

The field-dependent magnetizations of Ni-MOF-74-IMs, measured at the various temperatures, confirm the appearance of the AFM ground state and spin-canting behavior. The M-Hcurves at 2 K (Figure 3) display obvious sigmoidal shapes, typical of the metamagnetism phase transition from AFM to spin canting or of the FM-ordered phase as spontaneous magnetization.^{26,27} As shown in Figures 3 (bottom right inset) and S8, significant hysteresis loops are observed in the field range of 30–55 kOe in Ni-MOF-74-ac, Ni-MOF-74-IM-10,



Figure 3. Field dependence of the magnetic moment at 2K of all samples. Left-top inset: dM/dH from the M-H measurement. Right-bottom inset: Metamagnetism in Ni-MOF-74-IM-10 and Ni-MOF-74-IM-38. The Ni-MOF-74-ac sample also shows metamagnetism at lower field.

and Ni-MOF-74-IM-38 (Ni-MOF-74-IM-70 does not show metamagnetism in the M-H curve). The M values of Ni-MOF-74-ac, Ni-MOF-74-IM-10, and Ni-MOF-74-IM-38 increased to a value of ~3.39 $\mu_{\rm B}$ at 70 kOe, while the magnetization of Ni-MOF-74-IM-70 was 4.67 $\mu_{\rm B}$ at 70 kOe; this did not reach the saturation value of 6 $\mu_{\rm B}$ for Ni^{II} with S = 3 ($g_S = 6 \text{ N}\beta$). Although the spin centers interact, showing FM interaction in a high field, they are not fully saturated because of an orbital contribution. As the remnant spontaneous magnetization, extrapolation of the M-H curve in the high magnetic field range down to the zero field is taken to be an estimate of the canting angle α , following the relationship sin α = $M_{\rm R}/M_{\rm S}$. The canting angle of Ni-MOF-74-ac was determined to be $2.2-2.5^{\circ}$, whereas the canting angles of Ni-MOF-74-IM-10 and Ni-MOF-74-IM-38 were negligibly small because of AFM interaction. The canting angle of MOF-74-IM-70 increased to 24° with FM interaction.^{28,29} By increasing the number of coordinated IMs in the channel, the hysteresis loop and critical field are shifted to higher field. As a result, the values of the critical field (H_{Cr}) at 2 K were estimated as the maximum field of dM/dH to be 42 kOe (Ni-MOF-74-ac), 52 kOe (Ni-MOF-74-IM-10), and 54 kOe (Ni-MOF-74-IM-38) (inset top left in Figure 3). These hysteresis loops of the metamagnetism and spin canting vanished above 12 K. Moreover, the temperature dependence of χ_m was measured to be higher than the critical field (H_{Cr}) , namely, 45, 55, 60, and 70 kOe for Ni-MOF-74-ac, Ni-MOF-74-IM-10, Ni-MOF-74-IM-38, and Ni-MOF-74-IM-70, respectively (Figure S9). Such results demonstrate that Ni-MOF-74-ac and Ni-MOF-74-IM-10 seem to exhibit the AFM effect with cusps, but the final fitting results of the Curie-Weiss law indicate weak FM behavior with positive $T_{\rm C}$ values. This FM configuration of the samples in the M-T curve above H_{cr} verifies the existence of metamagnetism with M-H curves. Hence, the AFM coupling was overcome, and the metamagnetism transition finally occurred because of an external field.

Phase diagrams of the metamagnetic transitions were obtained from a series of field-dependent magnetization M(H) curves at various temperatures and temperaturedependent susceptibility $\chi(T)$ at different dc fields (Figures S8-S10). The H-T phase diagram shown in Figure 4 reveals



Figure 4. Magnetic phase diagram of the Ni-MOF-74-IM series. The dashed/open and line/solid points are from the M-H curves at various temperatures. Open scattering is the critical temperature (T_N) from the M-T curves.

that Ni-MOF-74-IMs possess an AFM ordering at the ground state, below the phase boundary. An anomaly standing field read for spin canting occurred at ~30 kOe (dashed/open points in Figure 4). The hysteresis loops in the M(H) curves exist only at low temperatures, up to ~10 K. The observed irreversibility implies that the field-induced FM phase has a tiny area of hysteresis and is metastable under high fields. The hysteresis ranges were also changed by the amount of coordinated IM on the OMS. Above the magnetic saturated field at ~65 kOe (line/solid points in Figure 4) and the Néel temperature, paramagnetic phase states were present.

The spin dynamics of Ni-MOF-74-ac and Ni-MOF-74-IMs were further studied with alternating-current (ac) susceptibility measurement under 1 and 65 kOe below 22 K (Figures S12–S14). Ni-MOF-74-ac, Ni-MOF-74-IM-10, and Ni-MOF-74-IM-38 exhibited AFM ordering, which was verified by the frequency-independent peaks of the in-phase (χ') at ~18 K. The frequency-dependent out-of-phase (χ'') behavior in the ac susceptibility under 1 kOe is shown. The peak temperature (T_p) shift is inferred to be superparamagnetic with the Mydosh parameter $\phi = \Delta T_p / (T_p \Delta \log f)$ (see Figure S14 for details). Even though MOF-74 is a 1D chain structure, it does not actually show the slow relaxation of the SCM. Nevertheless, the ac susceptibility results confirm that its magnetic phase is strongly influenced by the external field and/or coordinated imidazole.

In conclusion, this study details a novel three-dimensional MOF, consisting of FM Ni^{II} 1D chains with coordinated IMs. Detailed magnetic measurements revealed the rare coexistence of AFM and FM ordering, spin canting, field-induced metamagnetism, and spin dynamics. Significantly, Ni-MOF-74 exhibits phase transition and metamagnetism with IMs, accompanied by a shift in H_{Cr} , the Néel temperature, and the Weiss temperature for AFM ordering. Indeed, the coordinated IM influences the Ni^{II} coordination from the square-pyramidal 5-fold structure to an octahedral 6-fold structure. The 5-fold-coordinated Ni^{II} has two unpaired electrons, which forces it to transfer its magnetic phase from the AFM to FM phase with lower energy. Interpretations made using DFT calculations and fitting data indicate that the material studied here could be fine-tuned for interchain magnetic interaction, and its physical

properties can be controlled by varying the amount of IM; this is of great relevance to applications involving magnetic devices.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b00889.

Materials synthesis, FT-IR, PXRD, UV-vis-NIR, Ar sorption isotherms and magnetic properties (measurements), and DFT calculations (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: sgkang@ulsan.ac.kr (S.G.K.). *E-mail: hoirimoon@unist.ac.kr (H.R.M.).

*E-mail: oh@gntech.ac.kr (H.O.).

ORCID 💿

Sung Gu Kang: 0000-0003-1112-7077 Hoi Ri Moon: 0000-0002-6967-894X Hyunchul Oh: 0000-0001-6258-0002

Author Contributions

S.G.K. DFT calculations, J.Y.K., H.R.M. materials synthesis, and K.S, G.S, H.O. characterizations. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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REFERENCES

Wernsdorfer, W. A long-lasting phase. *Nat. Mater.* 2007, *6*, 174.
 Bogani, L.; Wernsdorfer, W. Molecular spintronics using single-molecule magnets. *Nat. Mater.* 2008, *7*, 179.

(3) Jo, M.-H.; Grose, J. E.; Baheti, K.; Deshmukh, M. M.; Sokol, J. J.; Rumberger, E. M.; Hendrickson, D. N.; Long, J. R.; Park, H.; Ralph, D. C. Signatures of Molecular Magnetism in Single-Molecule Transport Spectroscopy. *Nano Lett.* **2006**, *6*, 2014–2020.

(4) Hao, H.; Zheng, X.; Jia, T.; Zeng, Z. Room temperature memory device using single-molecule magnets. *RSC Adv.* **2015**, *5*, 54667–54671.

(5) Sanvito, S. Molecular spintronics. Chem. Soc. Rev. 2011, 40, 3336–3355.

(6) Caneschi, A.; Gatteschi, D.; Sessoli, R.; Barra, A. L.; Brunel, L. C.; Guillot, M. Alternating current susceptibility, high field magnetization, and millimeter band EPR evidence for a ground S = 10 state in $[Mn_{12}O_{12}(Ch_3COO)_{16}(H_2O)_4]$.2CH₃COOH.4H₂O. *J. Am. Chem. Soc.* **1991**, *113*, 5873–5874.

(7) Heersche, H. B.; de Groot, Z.; Folk, J. A.; van der Zant, H. S. J.; Romeike, C.; Wegewijs, M. R.; Zobbi, L.; Barreca, D.; Tondello, E.; Cornia, A. Electron Transport through Single Mn_{12} Molecular Magnets. *Phys. Rev. Lett.* **2006**, *96*, 206801.

(8) Milios, C. J.; Vinslava, A.; Wood, P. A.; Parsons, S.; Wernsdorfer, W.; Christou, G.; Perlepes, S. P.; Brechin, E. K. A Single-Molecule Magnet with a "Twist. J. Am. Chem. Soc. 2007, 129, 8–9.

(9) Bogani, L.; Vindigni, A.; Sessoli, R.; Gatteschi, D. Single chain magnets: where to from here? *J. Mater. Chem.* **2008**, *18*, 4750–4758.

(10) Murray, L. J.; Dinca, M.; Long, J. R. Hydrogen storage in metalorganic frameworks. *Chem. Soc. Rev.* **2009**, 38, 1294–1314.

(11) Liu, K.; Li, H.; Zhang, X.; Shi, W.; Cheng, P. Constraining and Tuning the Coordination Geometry of a Lanthanide Ion in Metal– Organic Frameworks: Approach toward a Single-Molecule Magnet. *Inorg. Chem.* **2015**, *54*, 10224–10231.

(12) Liu, K.; Zhang, X.; Meng, X.; Shi, W.; Cheng, P.; Powell, A. K. Constraining the coordination geometries of lanthanide centers and magnetic building blocks in frameworks: a new strategy for molecular nanomagnets. *Chem. Soc. Rev.* **2016**, *45*, 2423–2439.

(13) Wang, M.; Meng, X.; Song, F.; He, Y.; Shi, W.; Gao, H.; Tang, J.; Peng, C. Reversible structural transformation induced switchable single-molecule magnet behavior in lanthanide metal–organic frameworks. *Chem. Commun.* **2018**, *54*, 10183–10186.

(14) Kurmoo, M. Magnetic metal-organic frameworks. Chem. Soc. Rev. 2009, 38, 1353-1379.

(15) Farrusseng, D.; Aguado, S.; Pinel, C. Metal–Organic Frameworks: Opportunities for Catalysis. *Angew. Chem., Int. Ed.* **2009**, *48*, 7502–7513.

(16) Tiana, D.; Hendon, C. H.; Walsh, A. Ligand design for longrange magnetic order in metal–organic frameworks. *Chem. Commun.* **2014**, *50*, 13990–13993.

(17) Zhao, J.-P.; Han, S.-D.; Jiang, X.; Xu, J.; Chang, Z.; Bu, X.-H. A three dimensional magnetically frustrated metal–organic framework via the vertices augmentation of underlying net. *Chem. Commun.* **2015**, *51*, 4627–4630.

(18) Dey, C.; Das, R.; Krishna Saha, B.; Poddar, P.; Banerjee, R. Design and in situ synthesis of a Cu-based porous framework featuring isolated double chain magnetic character. *Chem. Commun.* **2011**, *47*, 11008–11010.

(19) Carlin, R. L. Magnetochemistry; Springer-Verlag, 1986.

(20) Sun, W.-W.; Tian, C.-Y.; Jing, X.-H.; Wang, Y.-Q.; Gao, E.-Q. Solvent-modulated metamagnetism in a nickel(ii) coordination polymer with mixed azide and carboxylate bridges. *Chem. Commun.* **2009**, *31*, 4741–4743.

(21) Clérac, R.; Miyasaka, H.; Yamashita, M.; Coulon, C. Evidence for Single-Chain Magnet Behavior in a MnIII–NiII Chain Designed with High Spin Magnetic Units: A Route to High Temperature Metastable Magnets. J. Am. Chem. Soc. **2002**, *124*, 12837–12844.

(22) Maspoch, D.; Domingo, N.; Ruiz-Molina, D.; Wurst, K.; Hernández, J.-M.; Vaughan, G.; Rovira, C.; Lloret, F.; Tejada, J.; Veciana, J. Coexistence of ferro- and antiferromagnetic interactions in a metal-organic radical-based (6,3)-helical network with large channels. *Chem. Commun.* **2005**, *40*, 5035–5037.

(23) Zhang, X.; Vieru, V.; Feng, X.; Liu, J.-L.; Zhang, Z.; Na, B.; Shi, W.; Wang, B.-W.; Powell, A. K.; Chibotaru, L. F.; Gao, S.; Cheng, P.; Long, J. R. Influence of Guest Exchange on the Magnetization Dynamics of Dilanthanide Single-Molecule-Magnet Nodes within a Metal–Organic Framework. *Angew. Chem., Int. Ed.* **2015**, *54*, 9861–9865.

(24) Meyer, A.; Gleizes, A.; Girerd, J. J.; Verdaguer, M.; Kahn, O. Crystal structures, magnetic anisotropy properties and orbital interactions in catena-(.mu.-nitrito)-bis(ethylenediamine)nickel(II) perchlorate and triiodide. *Inorg. Chem.* **1982**, *21*, 1729–1739.

(25) Reis, M. S. Models for one-dimensional molecular magnets. *Comput. Phys. Commun.* **2012**, *183*, 99–105.

(26) Zou, J.-Y.; Shi, W.; Gao, H.-L.; Cui, J.-Z.; Cheng, P. Spin canting and metamagnetism in 3D pillared-layer homospin cobalt(ii) molecular magnetic materials constructed via a mixed ligands approach. *Inorg. Chem. Front.* **2014**, *1*, 242–248.

(27) Liu, J.-L.; Huang, G.-Z.; Tong, M.-L. Field-induced dynamic magnetic behaviour of a canted weak ferromagnetic chain material. *Inorg. Chem. Front.* **2015**, *2*, 403–408.

(28) Park, S.-H.; Oh, I.-H.; Park, S.; Park, Y.; Kim, J. H.; Huh, Y.-D. Canted antiferromagnetism and spin reorientation transition in layered inorganic–organic perovskite $(C_6H_5CH_2CH_2NH_3)2MnC_{l4}$. *Dalton Trans* **2012**, *41*, 1237–1242.

(29) Shao, D.; Zhang, S.-L.; Zhao, X.-H.; Wang, X.-Y. Spin canting, metamagnetism, and single-chain magnetic behaviour in a cyano-

bridged homospin iron(ii) compound. Chem. Commun. 2015, 51, 4360-4363.