Inorganic Chemistry

Article

pubs.acs.org/IC

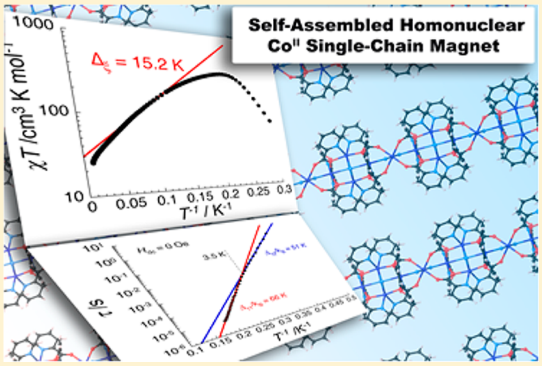
A Single-Chain Magnet Based on $\{Co^{II}_4\}$ Complexes and Azido/Picolinate Ligands

Jiang Liu,[†] Mei Qu,[†] Mathieu Rouzières,[‡] Xian-Ming Zhang,*[,†] and Rodolphe Clérac*[,‡,§]

[†]School of Chemistry & Material Science, Shanxi Normal University, Linfen, 041004, People's Republic of China
[‡]CNRS, CRPP, UPR 8641, F-33600 Pessac, France
[§]Univ. Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France

S *Supporting Information*

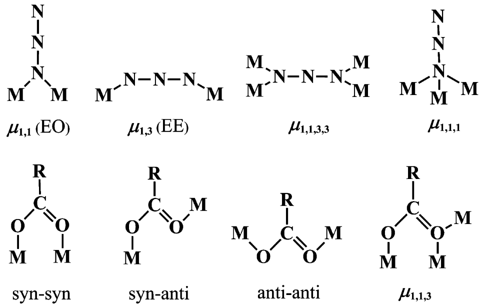
ABSTRACT: A new homonuclear single-chain magnet self-assembles as a one-dimensional coordination network of defective dicubane $\{Co^{II}_4\}$ complexes linked by single Co^{II} ions with the assistance of azido and picolinate ligands. Dominating intrachain ferromagnetic interactions, intrinsic Ising-like Co^{II} anisotropy, and negligible interchain magnetic interactions lead to a thermally activated relaxation time of the magnetization below 8 K. Two thermally activated regimes above and below 3.5 K are observed with the following energy barriers: $\Delta_{\tau1}/k_B$ = 66 K (τ_0 = 3.7 × 10^{-11} s) and $\Delta_{\tau2}/k_B$ = 51 K (τ_0 = 2.3 × 10^{-9} s), respectively. The difference between the two energy barriers of the relaxation time, 15 K, agrees well with the experimental energy, Δ_ξ, to create a domain wall along the chain.



INTRODUCTION

About 10 years after the first report on single-molecule magnets (SMMs) in the beginning of the 1990s,[1,2] the discovery of the single-chain magnets (SCMs)[3−12] opened a new trend of research in the field of molecular magnetism with potential application in one-dimensional (1D) information storage and molecular electronics. Different synthetic strategies have been explored to obtain these molecule-based magnets relying on the well-known coordination abilities of metal ions, ligands, sometimes coligands, and mainly on the expertise of the chemists who built up an impressive library of materials. In the quest for these new magnets, serendipity played a major role in the synthesis of key systems, leading in some cases to important breakthroughs.[13−15] For instance, the first and most cited SMMs, $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ (R = Me or Ph), were prepared by accident, but the scientific impact of these magnetic molecules has still no equivalent in the field for both chemists and physicists.[1,2,16] In parallel to this serendipity approach, chemists have also developed "more rational" synthetic strategies to design molecule-based magnets using building-block or modular precursors to get a better control and a possible fine-tune of their physical properties.[17−19] It is interesting to note that the design of materials in coordination chemistry relies often on principles originating from serendipitous findings. Remarkably, these synthetic strategies have proved their efficiency to obtain fascinating magnetic materials.[17,20,21] In this work, the serendipitous hydrothermal assembly of Co^{II} metal ions with picolinate (pic) and azido ligands leads to an interesting one-dimensional coordination network $[Co_5(pic)_6(N_3)_4]$ (**1**) that displays single-chain magnet properties (vide infra). Targeting the synthesis of SMM or SCMs, a certain degree of "design" is indeed present in our choice of the reagents: (i) Co^{II} metal ions were chosen for their strong Ising-like magnetic anisotropy requested to create an energy barrier for the magnetization reversal in SMM and SCMs.[22−28] (ii) The azido anion is a versatile ligand that is known to display various coordination geometries (Scheme 1).[23,25,29−32] In addition, when adopting end-on (EO, $\mu_{1,1}$) or $\mu_{1,1,1}$ bridging modes, the azido ligand mediates often ferromagnetic interactions observed in previous Co-based SCMs.[23,25] Finally, (iii) the picolinate ligand (pic) was used as a coligand to limit the extension of coordination network. Indeed, this ligand is known to adopt chelating (by pyridine and carboxylate groups) and bridging modes (carboxylate

Scheme 1. Selected Azido and Carboxylate Bridging Modes



Received: February 21, 2014
Published: July 24, 2014

group),[33−36] which favor the formation of molecular complexes or 1D systems.[34−36]

EXPERIMENTAL SECTION

General Procedures. All of the starting materials were purchased commercially reagent grade and used without further purification. ***Caution!*** *Although not encountered in our experiments, azido compounds of metal ions are potentially explosive. Only a small amount of the materials should be prepared, and it should be handled with care.*

Synthetic Procedure. For the syntheses of $[Co_5(pic)_6(N_3)_4]$ (**1**), a suspension of $Co(NO_3)_2{\cdot}3H_2O$ (0.14 g, 0.59 mmol), picolinic acid (0.049 g, 0.4 mmol), NaN_3 (0.052 g, 0.8 mmol), and ethanol (5 mL) was sealed in a 12-mL Teflon-lined stainless steel container that was heated to 140 °C and held at this temperature for 96 h. After being cooled to room temperature, red columnar single crystals of **1** (83%) were obtained. Anal. Calcd for $C_{36}H_{24}Co_5N_{18}O_{12}$: C, 36.17; H, 2.02; N, 21.09. Found: C, 36.22; H, 1.76; N, 21.15. IR (KBr): 3433s, 2061s, 1639s, 1386s, 763m, 2926w, 700m, 1586w, 1565w, 1301w, 1006w, 847w.

Crystal Structure Determination. The diffraction data of **1** were collected at 298 K on a Bruker Apex diffractometer (Mo Kα, λ = 0.71073 Å). Lorentz-polarization and absorption corrections were applied. The structures were solved with direct methods and refined with the full matrix least-squares technique (SHELX-97). Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of organic ligands were geometrically placed and refined with isotropic temperature factors (Table 1).

Physical Measurements. Elemental analyses were performed on a PerkinElmer 240 elemental analyzer. The FT-IR spectra were recorded on KBr pellets in the 400−4000 cm^{-1} range on a Nicolet 5DX spectrometer. The magnetic susceptibility measurements were obtained with the use of MPMS-XL Quantum Design SQUID magnetometer and PPMS-9 susceptometer. The magnetometer and susceptometer work between 1.8 and 400 K for dc applied fields ranging from −7 to 7 T (MPMS-XL). Measurements were performed on a polycrystalline sample of 11.08 mg introduced in a polyethylene bag (3 × 0.5 × 0.02 cm). The ac susceptibility measurements were measured with an oscillating ac field of 1 Oe with frequency between 10 and 10 000 Hz (PPMS-9) and with an oscillating ac field of 3 Oe with frequency between 1 and 1500 Hz (MPMS-XL). *M* versus *H* measurements have been performed at 100 K to check for the presence of ferromagnetic impurities that have been found absent. The magnetic data were corrected for the sample holder and the diamagnetic contributions.

Table 1. Crystallographic Parameters for 1

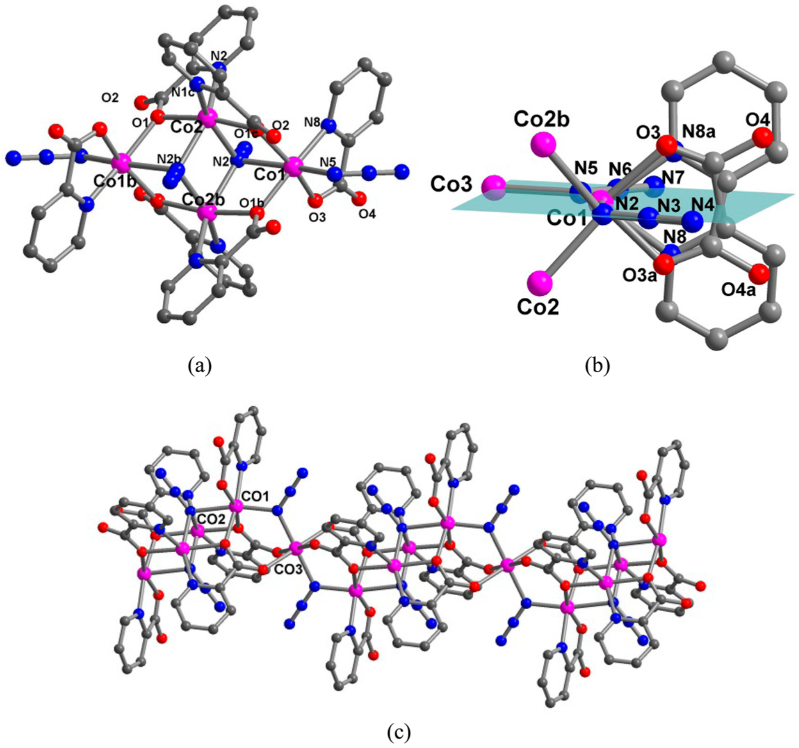
compound	**1**
empirical formula	$C_{36}H_{24}Co_5N_{18}O_{12}$
formula weight	1195.38
crystal system	monoclinic
space group	*C*2/*m*
a (Å)	18.981(4)
b (Å)	13.878(3)
c (Å)	10.4284(19)
α (deg)	90
β (deg)	114.289(3)
γ (deg)	90
V (Å^3)	2503.9(8)
Z	2
ρ_{calc} (g cm^{-3})	1.585
μ (mm^{-1})	1.695
F(000)	1194
crystal size (mm)	0.31 × 0.18 × 0.15
reflections	6476/2832
R_{int}	0.0167
T_{max}/T_{min}	0.7851/0.6216
data/parameters	2832/48/202
S	1.035
R_1,[a] wR_2[b] $[I > 2\sigma(I)]$	0.0634/0.1073
R_1, wR_2 (all data)	0.1695/0.1941
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.785/−0.714

[a] $R_1 = \sum||F_0| - |F_c||/\sum|F_0|$. [b] $wR_2 = [\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]]^{1/2}$.

RESULTS AND DISCUSSION

Synthesis and Crystal Structure. Compound **1** was obtained in high yield (~83%) combining the selected ingredients by hydrothermal technique in a 12-mL Teflon-lined stainless steel container using a Co^{II}/Hpic/NaN$_3$/ethanol stoichiometric molar ratio of 5.9:4:8:109. Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the *C*2/*m* monoclinic space group with an asymmetric unit containing three Co^{II} ions, two pic$^-$, and two azido ligands (Figure 1a and Supporting Information Figure S1). The Co1 site and the azido N atoms (N2−N7) are located on a crystallographic mirror plane, resulting in a site occupancy of 0.5 (Figure 1b). The Co1 site possesses a distorted octahedral coordination sphere occupied by two azido groups in *trans* positions, three O, and one N atoms from three pic$^-$ ligands. Two of these picolinates μ-bridge the Co1 and Co2 sites, while the third one, disordered on two positions, is N,O-chelating the Co1 metal ion perpendicularly to the mirror plane [Co1−N/O = 2.029(3)−2.287(4) Å, N2−Co1−N5 = 167.7°(2), N5−Co1−O3 = 102.5°(5)] (Figure 1b). The Co2 metal ion resides on a 2-fold axis with a site occupancy of 0.5. Its strongly distorted octahedral coordination sphere is occupied by two N,O-chelating picolinate and two azido ligands [Co2−N/O = 2.074(4)−2.165(3) Å]. Both anionic ligands are bridging efficiently the Co1 and Co2 sites forming a defective dicubane $\{Co_4(\mu_3\text{-}N)_2(\mu\text{-}O)_4\}$ unit with two $\mu_{1,1,1}$-azido and four $\mu_{1,1}$-carboxylate atoms (Supporting Information Figure S1a). The bond angles of Co1−N2−Co2 and Co2−N2−Co2a are 96.969(6)° and 96.226(4)°, respectively. The resulting tetranuclear unit, $[Co_4(pic)_6(N_3)_4]^{2-}$, is shown in Figure 1a. Adjacent [Co$_4$] moieties are linked by the Co3 ions assisted by two EO azido and four $\mu_{1,1,3}$-carboxylate (Scheme 1) groups to form the one-dimensional coordination polymer shown in Figure 1c. While the $\mu_{1,1}$-azido groups bridge only Co3 and Co2 sites, each $\mu_{1,1,3}$-picolinate ligand coordinated to Co3 links concomitantly Co1 and Co2 in *syn*−*syn* and *anti*−*syn* modes, respectively. The Co3 center is exactly situated on both a mirror plane and a 2-fold axis leading to a 0.25 site occupancy. This Co ion adopts a symmetrical axially compressed octahedral $(N5)_2(O2)_4$ coordination sphere with *trans*-positioned atoms forming 180° angles with Co3 by symmetry, and Co(3)−O(2) and Co(3)−N(5) bond distances of 2.136(3) and 2.066(4) Å. It is worth mentioning that the shortest Co···Co separations between chains are overall greater than 8.73 Å, and there are no significant interchain hydrogen bonding or π−π stacking interactions (Supporting Information Figure S1).

Magnetic Properties. Magnetic susceptibility measurements for **1** were performed between 1.8 and 300 K (Figure 2). At room temperature, the χT product is 18.2 cm^3 K mol^{-1}, which is in good agreement with the presence of five Co^{II} metal ions with a strong orbital contribution expected for an octahedral high-spin configuration ($g \approx 2.8$).[22−28,37−42] As



(a)

(b)

(c)

Figure 1. Ball and stick views of the crystal structure of **1**: (a) The $[Co_4(pic)_6(N_3)_4]^{2-}$ defective dicubane tetranuclear unit; (b) view of the crystal structure illustrating the disorder of picolinate ligand induced by crystallographic mirror plane; and (c) one-dimensional coordination polymer formed by the $[Co_4]$ complexes linked by a single Co(3) metal ion; Co, N, O, and C atoms are represented in pink, blue, red, and gray, respectively. Hydrogen atoms have been omitted for clarity.

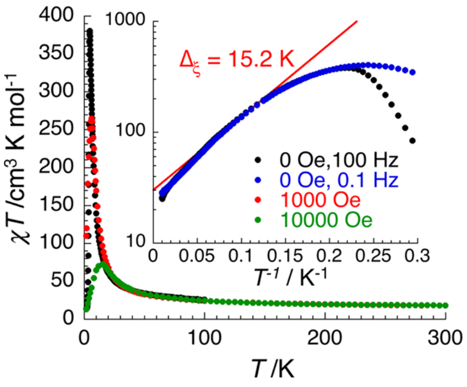


Figure 2. Temperature dependence of χT product at 0 (0.1 and 100 Hz, 3-Oe ac field), 1000, and 10 000 Oe (where χ is the molar magnetic susceptibility equal to M/H for 1000 and 10 000 Oe and χ' at 0 Oe and 0.1 or 100 Hz) between 1.8 and 300 K for a polycrystalline sample of **1**. Inset: $\chi' T$ versus T^{-1} semilogarithm plot (χ' being the in-phase ac magnetic susceptibility in zero dc field). The solid line is the best fit obtained using a 1D Ising model.

the temperature decreases, the χT product in zero-dc field increases to 380 cm^3 K mol^{-1} at 4.5 K (Figure 2) as an indication of the dominant intrachain ferromagnetic interactions already observed in related azido-bridged Co^{II} systems.[23,25,39] At lower temperatures, the χT products at 0.1 and 100 Hz decrease due mainly to the blocking of the magnetization at 3.8 and 2.6 K (vide infra, inset of Figure 2 and Supporting Information Figure S2) and also to the possible additional effect of weak interchain antiferromagnetic interactions. In the presence of the combined complexity of the chain topology and the Co^{II} magnetism, no physically meaningful simulation of these susceptibility data has been obtained. Nevertheless, the temperature dependence of the correlation length, ξ, was estimated from these χT versus T data to probe the one-dimensional nature of the observed magnetic properties. In any 1D classical systems, ξ is directly proportional to χT in zero-dc field. For Ising-like or anisotropic Heisenberg spin chains, the χT product increases exponentially with cooling temperature with $\chi T \approx C_{eff} \times \exp(\Delta_\xi / k_B T)$ (C_{eff} is the effective Curie constant and Δ_ξ is the energy to create a domain wall along the chain).[10−12,43−45] As shown in the inset of Figure 2, the ln(χT) versus T^{-1} plot is linear between 21 and 7.5 K with Δ_ξ / k_B evaluated at 15.2 K (and C_{eff} = 30.1 cm^3 K mol^{-1}), thus demonstrating the 1D nature of the magnetic properties of **1**. Below this linear regime, ln(χT) saturates first around 380−400 cm^3 K mol^{-1} as expected when the correlation length is physically limited by structural defects (the average chain length is estimated around 13 units, i.e., 13.9 nm).[12] Below 4 K, the χT product decreases mainly due to the blocking of the magnetization (see ac susceptibility data below).

The field dependence of the magnetization was measured below 15 K (Figure 3, Supporting Information Figure S3). The magnetization at 1.85 K does not even saturate under 7 T (reaching 14.2 μ_B) due to the strong magnetic anisotropy of the Co^{II} metal ions. It is worth mentioning that no inflection point is observed on the M versus H data above 1.8 K, highlighting the absence of significant antiferromagnetic (AF) interactions between chains and thus the lack of 3D magnetic ordering. Moreover, M versus H data do not exhibit any hysteresis effect at the field sweep-rates (50−400 Oe/min) used in commercial magnetometers. Nevertheless, the dynamics of the magnetization in **1** was studied using ac susceptibility measurements. Below 8 K, both the real (χ') and the imaginary (χ'')

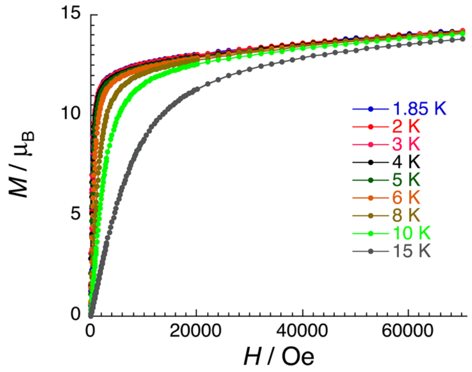


Figure 3. Field dependence of the magnetization for **1** between 1.8 and 15 K with sweep-rates of 100−200 Oe/min between 0 and 7 T.

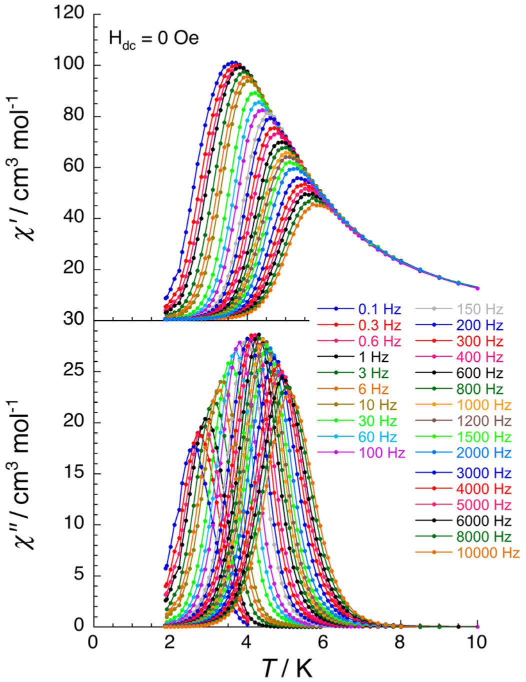


Figure 4. Temperature dependence below 10 K of the real (χ', left) and imaginary (χ'', right) parts of the ac susceptibility for **1** in zero dc-field at different ac frequencies between 0.1 and 10 000 Hz and with 3-Oe (0.1−1000 Hz) and 1-Oe (1000−10 000 Hz) ac fields. Solid lines are guides.

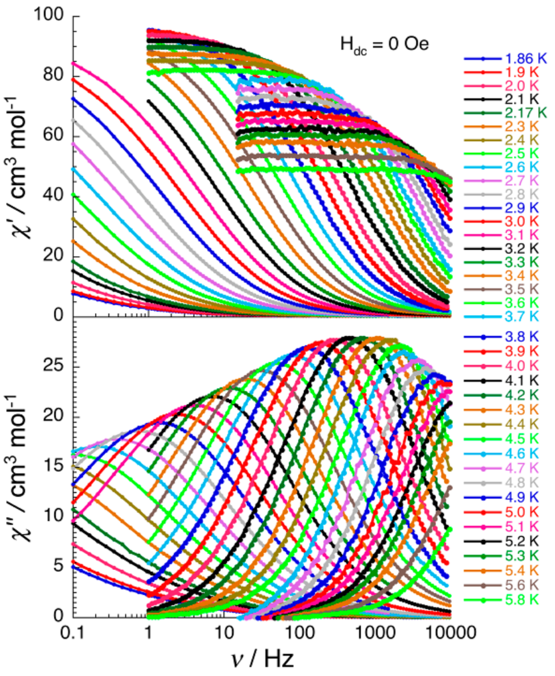


Figure 5. Frequency dependence of the real (χ', top) and imaginary (χ'', bottom) parts of the ac susceptibility for **1** in zero dc-field at different temperatures (1.86−5.8 K) with 3-Oe (0.1−1000 Hz) and 1-Oe (1000−10 000 Hz) ac fields. Solid lines are guides for the eyes.

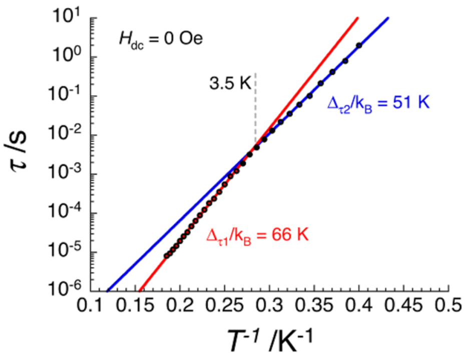


Figure 6. Magnetization relaxation time (τ) versus T^{-1} plot for **1** under zero dc-field. The solid lines are the Arrhenius laws discussed in the text below (blue) and above (red) the crossover temperature (3.5 K).

components of the ac susceptibility (Figures 4 and 5, and Supporting Information Figure S4) are strongly frequency dependent as typically observed in SCMs.[3−12,23−28,43−45] Using ac frequencies between 0.1 and 10 000 Hz, the temperature dependence of the magnetization relaxation time, τ, was deduced from the maximum of the χ'' versus ν data ($\tau = 1/(2\pi\nu_{max})$) between 2.5 and 5.4 K. Two thermally activated regimes above and below 3.5 K are observed with the following energy barriers: $\Delta_{\tau1}/k_B = 66$ K ($\tau_0 = 3.7 \times 10^{-11}$ s) and $\Delta_{\tau2}/k_B = 51$ K ($\tau_0 = 2.3 \times 10^{-9}$ s), respectively (Figure 6). As it is well established for SCMs, these two regimes correspond to the infinite and finite-size chain dynamics and highlight the importance of chain defects as already observed on the correlation length (inset of Figure 2).[12] Subsequently, the ac susceptibility was studied under small dc fields (Supporting Information Figures S5 and S6). As expected in the absence of significantly interchain AF interactions or three-dimensional magnetic order, τ becomes faster with increasing dc field, confirming the 1D properties of **1** and thus its SCM behavior.[46] On the basis of the known theory for SCM systems,[12] the difference between the two energy barriers of the relaxation time, 15 K, agrees well with the experimental Δ_ξ (15.2 K, inset of Figure 2). The anisotropy contribution, Δ_A, of the energy barriers can also be evaluated at 36 K from $\Delta_{\tau2}-\Delta_\xi$.[12]

■ CONCLUSION

A new homospin single-chain magnet was synthesized by self-assembly of tetranuclear Co^{II} complexes linked by single Co(II) metal ions. The intrachain ferromagnetic interactions combined to the intrinsic Ising-like Co(II) anisotropy and negligible interchain magnetic interactions induced the observed SCM behavior that has been demonstrated by complementary static and dynamic magnetic measurements. Even if this compound was obtained by a serendipitous hydrothermal assembly, the one-dimensional coordination polymer observed in this system could be well extended to synthesize other magnetically interesting materials by combining the strong N,O-chelated ability of the picolinate ligand with the coordination flexibility of the azide anion. In particular, the substitution of the Co(II) ion by other anisotropic magnetic centers like lanthanides, 4d, or 5d transition metal ions might lead to novel magnetic systems. Exploration of these new systems is currently underway in our laboratories.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables of selected bond lengths and angles, asymmetric unit of the crystal structure, and more details about magnetic measurements in dc and ac modes for **1**; and crystallographic data in CIF, CCDC 937179. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: zhangxm@dns.sxnu.edu.cn.
*E-mail: clerac@crpp-bordeaux.cnrs.fr.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Basic Research Program of China (973 Program 2012CB821701), IRT1156, the National Science Fund for Distinguished Young Scholars (20925101), the University of Bordeaux, the Région Aquitaine, the ANR, and the CNRS.

■ REFERENCES

(1) Sessoli, R.; Tsai, H. L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804−1816.

(2) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141−143.

(3) (a) Caneschi, A.; Gatteschi, D.; Lalioti, N.; Sangregorio, C.; Sessoli, R.; Venturi, G.; Vindigni, A.; Rettori, A.; Pini, M. G.; Novak, M. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 1760−1763. (b) Clérac, R.; Miyasaka, H.; Yamashita, M.; Coulon, C. *J. Am. Chem. Soc.* **2002**, *124*, 12837−12844.

(4) Lescouëzec, R.; Vaissermann, J.; Ruiz-Pérez, C.; Lloret, F.; Carrasco, R.; Julve, M.; Verdaguer, M.; Dromzée, Y.; Gatteschi, D.; Wernsdorfer, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 1483−1486.

(5) Kajiwara, T.; Nakano, M.; Kaneko, Y.; Takaishi, S.; Ito, T.; Yamashita, M.; Igashira-Kamiyama, A.; Nojiri, H.; Ono, Y.; Kojima, N. *J. Am. Chem. Soc.* **2005**, *127*, 10150−10151.

(6) Bernot, K.; Bogani, L.; Caneschi, A.; Gatteschi, D.; Sessoli, R. *J. Am. Chem. Soc.* **2006**, *128*, 7947−7956.

(7) Palii, A. V.; S. Ostrovsky, M.; Klokishner, S. I.; Reu, O. S.; Sun, Z.-M.; Prosvirin, A. V.; Zhao, H.-H.; Mao, J.-G.; Dunbar, K. R. *J. Phys. Chem. A* **2006**, *110*, 14003−14012.

(8) Zheng, Y.-Z.; Tong, M.-L.; Zhang, W.-X.; Chen, X.-M. *Angew. Chem., Int. Ed.* **2006**, *45*, 6310−6314.

(9) Liu, C.-M.; Zhang, D.-Q.; Zhu, D.-B. *Inorg. Chem.* **2009**, *48*, 4980−4987.

(10) Harris, T. D.; Bennett, M. V.; Clérac, R.; Long, J. R. *J. Am. Chem. Soc.* **2010**, *132*, 3980.

(11) Miyasaka, H.; Madanbashi, T.; Saitoh, A.; Motokawa, N.; Ishikawa, R.; Yamashita, M.; Bahr, S.; Wernsdorfer, W.; Clérac, R. *Chem.—Eur. J.* **2012**, *18*, 3942.

(12) (a) Coulon, C.; Miyasaka, H.; Clérac, R. *Struct. Bonding (Berlin)* **2006**, *122*, 163−206. (b) Miyasaka, H.; Julve, M.; Yamashita, M.; Clérac, R. *Inorg. Chem.* **2009**, *48*, 3420−3437.

(13) Winpenny, R. E. P. *Dalton Trans.* **2002**, 1−10.

(14) Tangoulis, V.; Lalia-Kantouri, M.; Gdaniec, M.; Papadopoulos, Ch.; Miletic, V.; Czapik, A. *Inorg. Chem.* **2013**, *52*, 6559−6569.

(15) Zhao, J.-P.; Yang, Q.; Liu, Z.-Y.; Zhao, R.; Hu, B.-W.; Du, M.; Chang, Z.; Bu, X.-H. *Chem. Commun.* **2012**, *48*, 6568−6570.

(16) Bagai, R.; Christou, G. *Chem. Soc. Rev.* **2009**, *38*, 1011−1026.

(17) (a) Pedersen, K. S.; Bendix, J.; Clérac, R. *Chem. Commun.* **2014**, *50*, 4396−4415. (b) Jeon, I.-R.; Clérac, R. *Dalton Trans.* **2012**, *41*, 9569−9586.

(18) Lescouëzec, R. L.; Toma, M.; Vaissermann, J.; Verdaguer, M.; Delgado, F. S.; Ruiz-Pérez, C.; Lloret, F.; Julve, M. *Coord. Chem. Rev.* **2005**, *249*, 2691−2729.

(19) Sun, H.-L.; Wang, Z.-M.; Gao, S. *Coord. Chem. Rev.* **2010**, *254*, 1081−1100.

(20) Leong, W. L.; Vittal, J. J. *Chem. Rev.* **2011**, *111*, 688−764.

(21) Yang, C.-I.; Tsai, Y.-J.; Hung, S.-P.; Tsai, H.-L.; Nakano, M. *Chem. Commun.* **2010**, *46*, 5716−5718.

(22) (a) Murrie, M.; Teat, S. J.; Stoeckli-Evans, H.; Güdel, H. U. *Angew. Chem., Int. Ed.* **2003**, *42*, 4653−4656. (b) Murrie, M. *Chem. Soc. Rev.* **2010**, *39*, 1986−1995.

(23) Liu, T.-F.; Fu, D.; Gao, S.; Zhang, Y.-Z.; Sun, H.-L.; Su, G.; Liu, Y.-J. *J. Am. Chem. Soc.* **2003**, *125*, 13976−13977.

(24) Palii, A. V.; Reu, O. S.; Ostrovsky, S. M.; Klokishner, S. I.; Tsukerblat, B. S.; Sun, Z.-M.; Mao, J.-G.; Prosvirin, A. V.; Zhao, H.-H.; Dunbar, K. R. *J. Am. Chem. Soc.* **2008**, *130*, 14729−14738.

(25) Wang, Y.-Q.; Sun, W.-W.; Wang, Z.-D.; Jia, Q.-X; Gao, E.-Q.; Song, Y. *Chem. Commun.* **2011**, *47*, 6386−6388.

(26) Cheng, X. N.; Zhang, W.-X.; Zheng, Y.-Z.; Chen, X.-M. *Chem. Commun.* **2006**, 3603−3605.

(27) Xiao, D.-R.; Zhang, G.-J.; Liu, J.-L.; Fan, L.-L.; Yuan, R.; Tong, M.-L. *Dalton Trans.* **2011**, *40*, 5680−5683.

(28) Liu, B.; Liu, B.; Pang, L.; Yang, G.; Cui, L.; Wang, Y.-Y.; Shi, Q. *CrystEngComm* **2013**, *15*, 5205−5208.

(29) Zeng, Y.-F.; Hu, X.; Liu, F.-C.; Bu, X.-H. *Chem. Soc. Rev.* **2009**, *38*, 469−480.

(30) Adhikary, C.; Koner, S. *Coord. Chem. Rev.* **2010**, *254*, 2933−2958.

(31) Yoon, J. H.; Ryu, D. W.; Kim, H. C.; Yoon, S. W.; Suh, B. J.; Hong, C. S. *Chem.—Eur. J.* **2009**, *15*, 3661−3665.

(32) (a) Stamatatos, T. C.; Abboud, K. A.; Wernsdorfer, W.; Christou, G. *Inorg. Chem.* **2009**, *48*, 807−809. (b) Stamatatos, T. C.; Christou, G. *Inorg. Chem.* **2009**, *48*, 3308−3322.

(33) Jeon, I.-R.; Ababei, R.; Lecren, L.; Li, Y.-G.; Wernsdorfer, W.; Roubeau, O.; Mathonière, C.; Clérac, R. *Dalton Trans.* **2010**, *39*, 4744−4746.

(34) Liu, J.; Qin, Y.-L.; Qu, M.; Clérac, R.; Zhang, X.-M. *Dalton Trans.* **2013**, *42*, 11571−11575.

(35) Biswas, C.; Mukherjee, P.; Drew, M. G. B.; Gomez-Garcia, C. J.; Clemente-Juan, J. M.; Ghosh, A. *Inorg. Chem.* **2007**, *46*, 10771−10780.

(36) Mautner, F. A.; Abu-Youssef, M. A. M.; Goher, M. A. S. *Polyhedron* **1997**, *16*, 235−242.

(37) Yang, C.-I.; Chuang, P.-H.; Lu, K.-L. *Chem. Commun.* **2011**, *47*, 4445−4447.

(38) Vallejo, J.; Castro, I.; Ruiz-García, R.; Cano, J.; Julve, M.; Lloret, F.; De Munno, G.; Wernsdorfer, W.; Pardo, E. *J. Am. Chem. Soc.* **2012**, *134*, 15704−15707.

(39) Wang, Y.-Q.; Zhang, X.-M.; Li, X.-B.; Wang, B.-W.; Gao, E.-Q. *Inorg. Chem.* **2011**, *50*, 6314−6322.

(40) Pardo, E.; Train, C.; Lescouëzec, R.; Journaux, Y.; Pasán, J.; Ruiz-Pérez, C.; Delgado, F. S.; Ruiz-Garcia, R.; Lloret, F.; Paulsen, C. *Chem. Commun.* **2010**, *46*, 2322−2324.

(41) Chorazy, S.; Nakabayashi, K.; Imoto, K.; Mlynarski, J.; Sieklucka, B.; i. Ohkoshi, S. *J. Am. Chem. Soc.* **2012**, *134*, 16151−16154.

(42) Sengupta, O.; Mukherjee, P. S. *Inorg. Chem.* **2010**, *49*, 8583−8590.

(43) Coulon, C.; Clérac, R.; Lecren, L.; Wernsdorfer, W.; Miyasaka, H. *Phys. Rev. B* **2004**, *69*, 132408.

(44) Mougel, V.; Chatelain, L.; Hermle, J.; Caciuffo, R.; Colineau, E.; Tuna, F.; Magnani, N.; de Geyer, A.; Pécaut, J.; Mazzanti, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 1−6.

(45) Ferbinteanu, M.; Miyasaka, H.; Wernsdorfer, W.; Nakata, K.; Sugiura, K.-i.; Yamashita, M.; Coulon, C.; Clérac, R. *J. Am. Chem. Soc.* **2005**, *127*, 3090−3099.

(46) (a) Coulon, C.; Clérac, R.; Wernsdorfer, W.; Colin, T.; Miyasaka, H. *Phys. Rev. Lett.* **2009**, *102*, 167204−167207. (b) Miyasaka, H.; Takayama, K.; Saitoh, A.; Furukawa, S.; Yamashita, M.; Clérac, R. *Chem.—Eur. J.* **2010**, *16*, 3656−3662. (c) Bhowmick, I.; Hillard, E. A.; Dechambenoit, P.; Coulon, C.; Harris, T. D.; Clérac, R. *Chem. Commun.* **2012**, *48*, 9717−9719.