Inorg. Chem. **2007**, *46*, 10452–10454

Inorganic Chemistry

Communication

Honeycomb Layer of Cobalt(II) Azide Hydrazine Showing Weak Ferromagnetism

Xiu-Teng Wang, Zhe-Ming Wang, and Song Gao*

Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China

Received August 26, 2007

Using hydrazine (N_2H_4) as a cobridge with azide, a honeycomb-layered cobalt(II) coordination polymer, $Co(N_2H_4)(N_3)_2$ (**1**), is obtained that exhibits spin-canted weak ferromagnetism with T_N of 13.5 K.

Molecule-based magnets bridged by conjugated ligands have experienced continuous interest because of their fascinating physical properties.[1] Also, up to now, a large number of azide (N_3^-)-bridged magnetic compounds have been synthesized and characterized because of not only the extreme versatility of the bridging modes [end-to-end (EE), end-on (EO), and other more complicated modes] but also the exceptional ability to transmit different types of magnetic coupling.[2] However, not so many cobalt(II) azide complexes have been reported,[3] probably because the oxidation of Co^{II} ions is easy in the presence of N_3^- ions,[4] especially when alkalescent ligands are employed. A possible approach to avoiding the oxidation of Co^{II} is to supply a reduction environment during the synthesis process. Herein, using hydrazine sulfate ($N_2H_4\cdot H_2SO_4$) as the reducing protective agent,[5] we prepared a novel 2D honeycomb-like azide-bridged cobalt(II) compound, $Co(N_2H_4)(N_3)_2$ (**1**), in which N_2H_4, in fact, acts as the second bridging ligand through a bis-monodentate coordination mode.[6] Magnetic studies show that **1** is a weak ferromagnet due to spin-canting, with the critical temperature T_N being 13.5 K. To the best of our knowledge, compound **1** is the first example of an azide-bridged magnetic polymer that contains short bridging hydrazine as the coligand.

The reaction of $CoSO_4\cdot 7H_2O$, $N_2H_4\cdot H_2SO_4$, and NaN_3 in a 1:1:20 molar ratio in water yielded dark-red column crystals of **1**.[7] Single-crystal X-ray analysis[8] revealed that **1** consists

---

* To whom correspondence should be addressed. E-mail: gaosong@pku.edu.cn. Fax: (+86)-10-62751708.

(1) For an example of single-molecule magnet behavior, see: (a) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141. (b) Gatteschi, D.; Caneschi, A.; Pardi, L.; Sessoli, R. *Science* **1994**, *265*, 1054. (c) Wernsdorfer, W.; Aliaga-Alcalde, N.; Hendrickson, D. N.; Christou, G. *Nature* **2002**, *416*, 406. For single-chain magnet behavior, see: (d) 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. (e) Clérac, R.; Miyasaka, H.; Yamashita, M.; Coulon, C.; *J. Am. Chem. Soc.*, **2002**, *124*, 12837. (f) Lescouëzec, R.; Vaissermann, J.; Ruiz-Pérez, C.; Loret, F.; Carrasco, R.; Julve, M.; Verdagurer, M.; Draomzee, Y.; Gatteschi D.; Wernsdorfer, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 1483.

(2) (a) Ribas, J.; Escuer, A.; Monfort, M.; Vicente, R.; Cortés, R.; Lezama, L.; Rojo, T. *Coord. Chem. Rev.* **1999**, *193−195*, 1027. (b) Zhang, Y.-Z.; Wei, H.-Y.; Pan, F.; Wang, Z.-M.; Chen, Z.-D.; Gao, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 5841. (c) Mautner, F. A.; Hanna, S.; Cortés, R.; Lezama, L.; Barandika, M. G.; Rojo, T. *Inorg. Chem.* **1999**, *38*, 4647. (d) Martín, S.; Barandika, M. G.; Lezama, L.; Pizarro, J. L.; Serna, Z. E.; Ruiz de Larramendi, J. I.; Arriortua, M. I.; Rojo, T.; Cortés, R. *Inorg. Chem.* **2001**, *40*, 4109. (e) Monfort, M.; Resino, I.; Ribas, J.; Solans, X.; Font-Bardia, M.; Rabu, P.; Drillon, M. *Inorg. Chem.* **2000**, *39*, 2572.

(3) (a) Papaefstathiou, G. S.; Perlepes, S. P.; Escuer, A.; Vicente, R.; Font-Bardia, M.; Solans, X. *Angew. Chem., Int. Ed.* **2001**, *40*, 884. (b) Zhang, Y.-Z.; Wernsdorfer, W.; Pan, F.; Wang, Z.-M.; Gao, S. *Chem. Commun.* **2006**, 3302. (c) Viau, G.; Lombardi, M. G.; De Munno, G.; Julve, M.; Lloret, F.; Faus, J.; Caneschic, A.; Clemente-Juana, J. M. *Chem. Commun.* **1997**, 1195. (d) Chakraborty, J.; Samanta, B.; Rosair, G.; Gramlich, V.; El Fallah, M. S.; Ribas, J.; Matsushita, T.; Mitra, S. *Polyhedron* **2006**, *25*, 3006. (e) Wang, X.-Y.; Wang, L.; Wang Z.-M.; Gao, S. *J. Am. Chem. Soc.* **2006**, *128*, 674. (f) 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.

(4) (a) Choi, K.-Y.; Lee, H.-K.; Kim, K.-J.; Ryu, H.; Lee, K.-C.; Ko, J.; Kim, M.-J. *Transition Met. Chem.* **2006**, *31*, 1093. (b) Goher, M. A. S.; Youssef, A. A.; Mautner, F. A. *Polyhedron* **2006**, *25*, 1531.

(5) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: Oxford, U.K., 1984; p 493.

(6) (a) Heaton, B. T.; Jacob, C.; Page, P. *Coord. Chem. Rev.* **1996**, *154*, 193. (b) Jahncke, M.; Neels, A.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Organomet. Chem.* **1998**, *565*, 97. (c) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bergamo, M.; Bordignon, E.; Pelizzi, G. *Inorg. Chem.* **1998**, *37*, 479. (d) Hsu, H.-F.; Chu, W.-C.; Hung C.-H.; Liao, J.-H. *Inorg. Chem.* **2003**, *42*, 7369. (e) Redman, J. E.; Feeder, N.; Teat, S. J.; Sanders, J. K. M. *Inorg. Chem.* **2001**, *40*, 3217.

(7) Preparation: All starting chemicals were commercially available reagents and were used without further purification. ***Caution!*** *Azido compounds of metal ions are potentially explosive, and only a small amount of the materials should be prepared and handled with care.* An aqueous solution (10 mL) of hydrazine sulfate (0.13 g, 1.0 mmol) and $CoSO_4\cdot 7H_2O$ (0.28 g, 1.0 mmol) was heated at 93 °C for 10 min and then quickly mixed with a hot aqueous solution (15 mL) of excessive NaN_3(1.3 g, 20 mmol). The mixed purple solution was kept at 93 °C for 10 min without disturbance. After slow cooling down to room temperature at 5 °C/h, X-ray-quality dark-red column crystals were obtained. The crystals was filtered and washed with distilled water and ethanol, respectively, and then dried in vacuo. Yield: 52% based on Co. Anal. Calcd for **1**: H, 2.30; N, 64.02. Found: H, 2.40; N, 63.69. IR bands (cm^{-1}): 2071 (vs) for stretching of the azide, 3319 for ν_{NH_2} of hydrazine, 1577 for δ_{NH_2} of hydrazine.

10.1021/ic7016775 CCC: $37.00

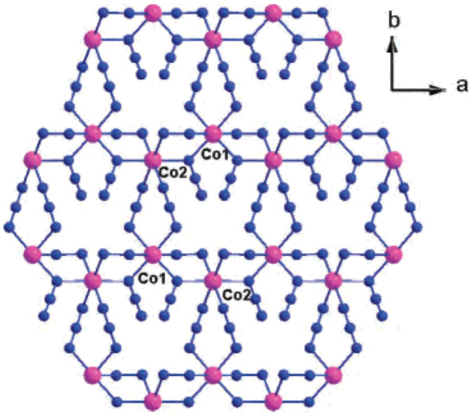

Figure 1. View of the coordination environment of **1** along the *ab* plane and the honeycomb layer bridged by EO/EE azide and hydrazine. Color scheme: Co, purple; N, blue. Hydrogen atoms were omitted for clarity.

of neutral honeycomb 2D networks of stoichiometric Co(N_2H_4)(N_3)$_2$ (Figure 1).

Up to now, several honeycombed cobalt(II) molecule-based magnets have been reported, such as Co(N_3)$_2$(bpg)·DMSO (**2**; bpg = *meso*-α,*β*-bis(4-pyridyl) glycol, DMSO = dimethyl sulfoxide)[3e] and $Co_3Cl_4(H_2O)_2[Co(Hbbiz)_3]_2$ [**3**; H_2bbiz = 2,2′-bis(benzimidazole)];[9] however, they are all different from **1** with regards to the details of connections between cobalt sites. For **2**, the Co^{2+} ions form a honeycomb layer just bridged by N_3^- ligands, which turns into a square structure if the two ferromagnetically coupled Co^{2+} ions are viewed as one node. For **3**, the 2D framework consists of 12-membered rings of alternating tetrahedral and octahedral Co^{2+} ions, creating an extended honeycomb hexagonal lattice. In our compound **1**, the network is along the *ab* plane, made up of Co^{II} ions bridged by N_3^- and N_2H_4. In the network, the two crystallographically independent Co^{2+} ions, Co1 and Co2, possessing distorted CoN_6 octahedral geometries, are linked by one EO azide and one hydrazine in the bis-monodentate mode along the *a* direction, and they are further connected by two EE azido ligands along the *b* direction. In other words, the 2D network can be described as double EE azido-linked Co−N_3/N_2H_4 chains, affording the honeycomb layer. The two coordination hydrazine ligands are in *trans* positions around Co1 but in *cis* sites around Co2. The Co−N distances are Co1−N = 2.120−2.163 Å and Co2−N = 2.118−2.189 Å. In the Co−N_3/N_2H_4 chain, the Co1−$N_{\text{EO azido}}$−Co2 angle is 116.6° and the torsion angle Co1−(N−N)$_{\text{hydrazine}}$−Co2 is 50.0°, with an intrachain Co···Co separation of 3.606 Å. The interchain Co···Co separation spanned by a double EE azido bridge is 5.173 Å. Therefore, the hexagonal window is elongated with two longer opposite sides.

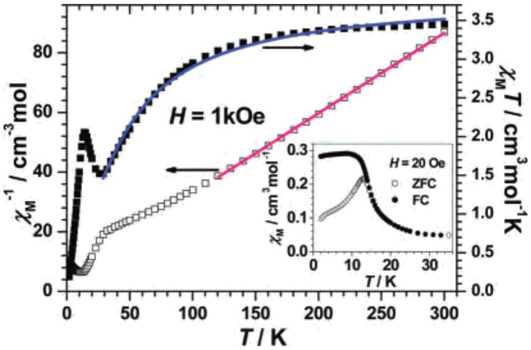

Figure 2. Temperature dependence of $\chi_M T$ and χ_M^{-1} of **1** at $H = 1$ kOe from 2 to 300 K. Inset: ZFC and FC magnetization at $H = 20$ Oe from 2 to 35 K. The pink line represents the best fit to the Curie−Weiss law, and the blue line corresponds to the best fit with Curély's model.

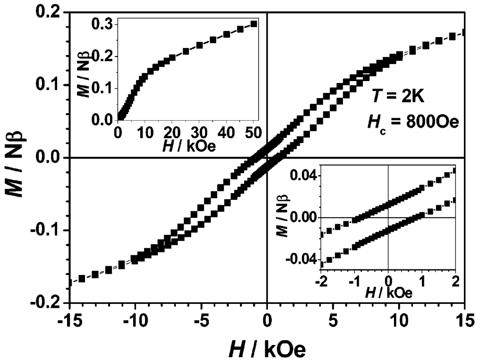

Figure 3. Hysteresis loop at $T = 2$ K for **1**. Inset: hysteresis from −1.5 to +1.5 kOe for clarity and the *M* vs *H* plot.

The 3D structure of **1** is the stacking of these 2D networks or sheets along the *c* direction (Figure S1 of the Supporting Information), and the sheets are glued by the N−$H_{\text{hydrazine}}$···$N_{\text{EO azido}}$ hydrogen bonds between the sheets, with the hydrogen-bonding geometry of N···N distance = 3.040 Å and N−H···N angle = 112.74°. The shortest intersheet Co···Co distance is 6.099 Å. It is noted that **1** belongs to a noncentrosymmetric space group of $C222_1$. There is no inversion center between the neighboring Co^{2+} ions, and the neighboring coordination octahedra are alternately tilted toward each other (Figure S2 of the Supporting Information). These noncentered structural features suggest the possibility of spin-canting by the Dzyaloshinsky−Moriya (D−M) or antisymmetric interaction.[10]

Indeed, magnetic studies reveal that the material is a weak ferromagnet at low temperature (Figures 2 and 3 and Figures S3 and S4 of the Supporting Information). Under a 1 kOe field, the $\chi_M T$ value of 3.45 cm^3 mol^{-1} K at 300 K is typical for high-spin Co^{2+} ions with significant orbital contribution. Upon a lowering of the temperature, the $\chi_M T$ values decrease gradually, reach a minimum of 1.52 cm^3 mol^{-1} K at 28 K, and then increase quickly to a maximum of 2.05 cm^3 mol^{-1}

---

(8) Characterization: The crystallographic data for the single crystal of **1** were collected at 293 K on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation of $\lambda = 0.710\,73$ Å. The structure was solved by direct methods through the *SHELX-97* programs. Crystal data for **1**: $Co_2N_{16}H_8$, $M_w = 350.04$, orthorhombic, red column (0.1 × 0.4 × 0.2 mm), space group $C222_1$, $a = 6.6121(5)$ Å, $b = 13.2285(10)$ Å, $c = 12.0851(11)$ Å, $V = 1057.06(15)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 2.199$ g/cm^3, GOF = 0.923, R1 = 0.0423, wR2 = 0.0694. dc and ac magnetization measurements were performed on a Quantum Design MPMS XL-5 SQUID system. Diamagnetic corrections were estimated using Pascal constants (-87.5×10^{-6} cm^3/mol) and background corrections by experimental measurement on the sample holder.

(9) (a) Galán-Mascarós, J. R.; Dunbar, K. R. *Angew. Chem., Int. Ed.* **2003**, *42*, 2289. (b) Wang, Y.-L.; Yuan, D.-Q.; Bi, W.-H.; Li, X.; Li, X.-J.; Li, F.; Cao, R. *Cryst. Growth Des.* **2005**, *5*, 1849.

(10) (a) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, 1986; Chapter 6. (b) Dzyaloshinsky, I. *J. Phys. Chem. Solids* **1958**, *4*, 241. (c) Moriya, T. *Phys. Rev.* **1960**, *117*, 635; **1960**, *120*, 91.

K at 14 K. Upon further cooling, $\chi_M T$ drops sharply. This behavior indicates the occurrence of weak ferromagnetism (WF) below ca. 14 K. The susceptibility data above 130 K obeys the Curie−Weiss law, with a Curie constant $C = 3.74$ cm^3 mol^{-1} K and a Weiss constant $\theta = -22.7$ K. The negative θ suggests an overall antiferromagnetic (AF) interaction between the Co^{2+} ions and/or the spin−orbit coupling effect of Co^{II}.

The material was further characterized by zero-field-cooled (ZFC) and field-cooled (FC) measurements, alternating current (ac) susceptibility, and isothermal magnetization in a low-temperature region, and the results confirmed the WF. As shown in the inset in Figure 2, in a field of 20 Oe, ZFC/FC measurements revealed spontaneous weak magnetization due to the onset of 3D long-range ordering of WF, and the bifurcation of the ZFC and FC plots below the Néel temperature of 13.5 K indicates irreversibility. In ac data (Figure S3 of the Supporting Information), the almost non-frequency-dependent peaks of χ_M' and χ_M'', being at 13.5 and 13.0 K, respectively, are agreeable to the previous observation in direct current (dc) measurement. Finally, the isothermal magnetization at 2 K (Figure 3) first shows a relatively quick initial increase and not a linear increase with the field up to 10 kOe and then goes almost linearly and more flatly up to 0.30 Nβ per Co^{2+} at 50 kOe, far from the expected saturation value of the Co^{2+} ion, which suggests again the overall AF coupling in the material. The $M(H)$ curve is of somewhat an S shape, which indicates the slight AF interaction between the layers. A hysteresis loop is observed clearly at 2 K with a coercive field $H_c \approx 800$ Oe and a remnant magnetization of $M_r = 0.012$ Nβ. According to the above magnetic study, we can conclude that **1** is a weak ferromagnet.

There are two different magnetic interactions within the network (Figure 1), namely, J_1 and J_2, representing the couplings through the EO-N$_3$/N$_2$H$_4$ bridge and the double EE-N$_3$ bridge, respectively. Because there is no appropriate expression for this complicated system, here, we attempt to evaluate the magnitude of the exchange couplings by a model applied for the honeycomb lattice by Curély et al.[11] (see the Supporting Information). The values of J_1 and J_2 estimated by this model, $+2.16$ and -29.9 cm^{-1}, indicate a ferromagnetic coupling through an EO-N$_3$/N$_2$H$_4$ bridge and an AF coupling through double EE-N$_3$ connections, and the latter is consistent with the values through the same bridges reported in the literature.[12] However, the limitation should be noted that this classical model, viewing J and g as isotropic, is quite approximate because of the great anisotropy for Co^{II}. A more involved theoretical analysis is needed.

As is well-known, the spin-canting is due to the single-ion magnetic anisotropy and/or antisymmetric interactions.[10] In the case of **1**, the lack of an inversion center between Co^{2+} sites, connected by EO-N$_3$/N$_2$H$_4$ bridges or double EE-N$_3$ ones, allows the occurrence of antisymmetric or D−M interaction, and the single-ion anisotropy of Co^{2+} enhances this interaction because the antisymmetric exchange is proportional to the single-ion anisotropy. Therefore, the magnetic behavior observed in **1** is reasonable. The combination of single-ion and structural anisotropies competes with the AF overall ordering and results in canted WF.[13]

In summary, a novel cobalt(II) azide hydrazine complex has been obtained. This is the first example of an azido-bridged molecule-based magnet with N$_2$H$_4$ as the coligand. In the structure, the Co^{2+} ions are connected by EO-N$_3$/N$_2$H$_4$ or double EE-N$_3$ bridges into a 2D honeycomb network. The material exhibits WF behavior with T_N of 13.5 K due to the absence of an inversion center between Co^{2+} sites and the large anisotropy of the Co^{2+} ions. Further studies will explore analogues of other metals and their magnetism, and these are in progress.

Acknowledgment. We acknowledge the financial support from the National Science Fund (Grants 20221101, 20490210, and 20571005) and the National Basic Research Program of China (Grant 2006CB601102).

Supporting Information Available: X-ray crystallographic file in CIF format for **1**, Figures S1−S4, and the model of the honeycomb lattice. This material is available free of charge via the Internet at http://pubs.acs.org.

IC7016775

---

(11) (a) Curély, J.; Lloret, F.; Julve, M. *Phys. Rev. B* **1998**, *58*, 11465. (b) De Munno, G.; Ruiz, R.; Lloret, F.; Faus, J.; Sessoli, R.; Julve, M. *Inorg. Chem.* **1995**, *34*, 408.

(12) Hernández, M. L.; Barandika, M. G.; Urtiaga, M. K.; Cortés, R.; Lezama, L.; Arriortua, M. I. *J. Chem. Soc., Dalton Trans.* **2000**, 79.

(13) (a) Huang, Z. L.; Drillon, M.; Masciocchi, N.; Sironi, A.; Zhao, J.-T.; Rabu, P.; Panissod, P. *Chem. Mater.* **2000**, *12*, 2805. (b) Feyerherm, R.; Loose, A.; Rabu, P.; Drillon, M. *Solid State Sci.* **2003**, *5*, 321.