Solvent-Tuned Azido-Bridged Co²⁺ Layers: Square, Honeycomb, and *Kagomé*

Xin-Yi Wang, Lu Wang, Zhe-Ming Wang, and Song Gao*

College of Chemistry and Molecular Engineering, State Key Laboratory of Rare Earth Materials Chemistry and Applications, Peking University, Beijing 100871, P. R. China

Received August 21, 2005; E-mail: gaosong@pku.edu.cn

Two-dimensional (2D) spin-half antiferromagnets have generated a great deal of recent interest because of their fascinating magnetic properties and their pertinence to high-temperature superconductivity and spin chirality.[1] Among various possible 2D lattice structures,[1d] the geometrically frustrated *Kagomé* lattice, characterized by interlaced triangles whose lattice points each have four neighboring points, occupies a special position. Substances with an ideal *Kagomé* structure cannot gain magnetic ordering even at zero temperature as a result of strong quantum fluctuations originated from geometrical frustration. As such, they represent ideal candidates for the study of magnetic frustration phenomenon.[1] However, most magnetic studies of *Kagomé* structured materials have been with jarosite $KFe_3(SO_4)_2(OH)_6$ and its analogues.[1e,2−3]

Manipulation of metal−ligand coordination and other intermolecular interactions in the context of supramolecular construction offers great prospects of generating structurally unique architectures,[4] including *Kagomé* lattices. Zaworotko and co-workers reported the first crystal engineered *Kagomé* lattice whose lattice vertexes are occupied by paramagnetic dicopper(II) tetracarboxylate spin pairs.[5a] However, the Cu²⁺ ions within the metal dimer are coupled antiferromagnetically, and the bridges between these dimers are too long to allow effective magnetic coupling. A scant few other *Kagomé*-type coordination or organic radical networks have since appeared in the literature,[5b−e,6] but preparation of such uniquely structured materials, especially those featuring strong antiferromagnetically coupled spins, remains a challenge.

In this report, we present a new example of a *Kagomé*-type coordination network constructed from Co²⁺ ions and azido ligands. The *Kagomé* layer is further linked by bridging *meso*-α,β-bi(4-pyridyl) glycol (bpg) ligands to generate a 3D framework, wherein crystallization solvent molecules, presumably assisting in the formation of the observed structure, are found interacting with the bridging ligand. Interestingly, simply by changing the solvent used, two other networks, one of azido-bridged Co²⁺ squares and the other of honeycombs, were also obtained. This series of complexes thus provide a good system for comparative structural and magnetic studies.

The three complexes are of the general formula $Co(N_3)_2(bpg)$·S_n (**1**, S = nothing; **2**, S = DMSO, n = 1; **3**, S = DMF, n = 4/3) and were synthesized by reacting NaN_3 with $CoCl_2$ and bpg in a 2:1:1 molar ratio in $MeOH/H_2O$ (**1**), $DMSO/H_2O$ (**2**), and DMF/H_2O (**3**), respectively. All are 3D coordination frameworks featuring different 2D cobalt-azido layers bridged by bpg ligands.[7] Specifically, Co²⁺ in the square-structured layer in complex **1** is octahedrally coordinated with six N atoms, four from the equivalent end-to-end (*EE*) azides ($Co-N_{azide}$ = 2.113 and 2.142 Å) and two from *trans*-bpg ($Co-N_{bpg}$ = 2.185 Å) (Figure 1a). The 2D square layer lies in the *bc* plane with an intralayer Co−Co distance of 5.932 Å (Figure 1b). The longer axes of the slightly distorted octahedra noticeably tilt toward each other. Lack of an inversion center between the *EE* azido-bridged Co²⁺ ions due to this distortion
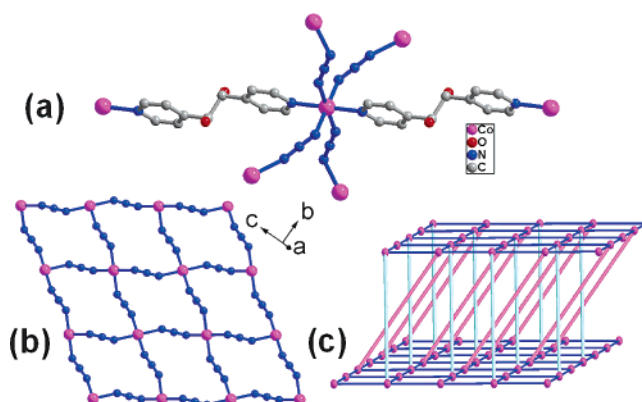

Figure 1. Structure of **1**: (a) the local coordination environment of Co²⁺; (b) the square layer bridged by *EE* azide; (c) the 3D network bridged by bpg.
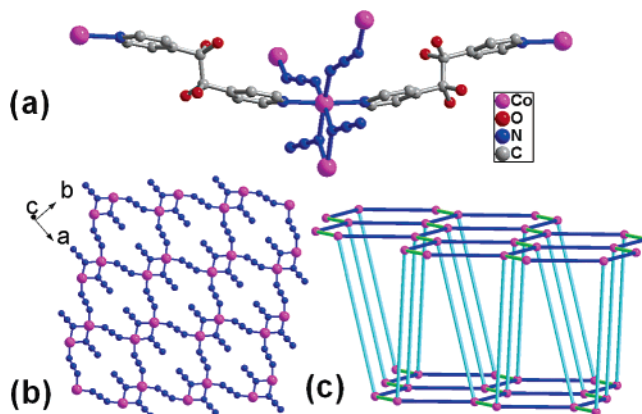

Figure 2. Structure of **2**: (a) the local environment of Co²⁺; (b) the honeycomb layer bridged by *EE* and *EO* azide; (c) the 3D structure bridged by bpg.

suggests the possibility of **1** being a spin-canted weak ferromagnet.[8] The bpg ligands crisscross to bridge at two different angles relative to the sheets (Figure 1c), leading to an overall network topology previously reported for $Cd(CN)_2(pyrazine)$.[9] The shortest Co−Co distance between adjacent layers is 13.6 Å.

In complex **2**, the Co²⁺-bridging azido ligands adopt two kinds of bridging modes, *EE*, as in the case of **1**, and *EO* (end-on), leading to a 2D honeycomb layer along the *ab* plane (Figure 2). Each of the Co²⁺ ions is coordinated by six N atoms, four from the azido ligands ($Co-N_{azide}$ = 2.134 and 2.158 Å) and two from bpg ligands ($Co-N_{bpg}$ = 2.173 Å) (Figure 2a). Intralayer Co−Co distances are 3.341 and 6.313 Å, respectively, for *EO*- and *EE*-bridged pairs. The angle of $Co-N_{EO}-Co$ is 101.33°, propitious to ferromagnetic exchange between the involved Co²⁺ centers.[10] If the two ferromagnetically coupled Co²⁺ ions are treated as one node, this honeycomb layer turns into a square one. Similar to **1**, spin-canting
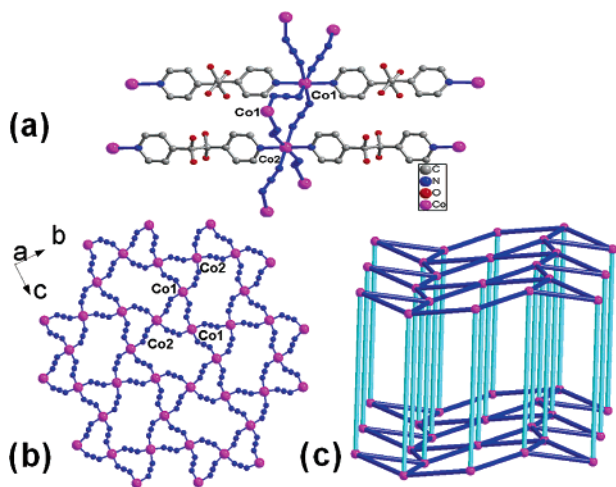
Figure 3. Structure of **3**: (a) the local environment of Co1 and Co2; (b) the *Kagom*é layer bridged by *EE* azide; (c) the 3D structure bridged by bpg.

may occur as a result of the absence of an inversion center between the dimeric nodes. The layers are connected by bpg ligands to generate a 3D structure, wherein disordered DMSO molecules are hydrogen bonded to the bpg ligands (Figure S1). The shortest interlayer Co–Co distance is 13.4 Å, similar to the corresponding value found in **1** (Figure 2c). Both the square and honeycomb structures are new for the $Co^{2+}–N_3^-$ system, though they have been observed for other metals.[11]

Complex **3** is the most interesting one of the three. There are two unique Co^{2+} centers (Co1 and Co2), as indicated in Figure 3a. Each is coordinated with six N atoms, two from *trans*-bpg ligands and four from azido ligands. The metric values of Co–N bonds are comparable to those observed for **1** and **2**. The azido ligands link the Co^{2+} ions in the *EE* fashion, affording along the *bc* plane a novel *Kagom*é layer featuring vertex-sharing triangles (Figure 3b). The wavy *Kagom*é layers are bridged by bpg ligands to generate a 3D framework whose hexagonal channels are filled by DMF molecules (Figure S2). Like DMSO in **2**, DMF molecules are hydrogen bonded to the hydroxyl groups of the bpg ligands. The Co–Co separations within a particular triangle are close to one another at 5.776, 6.084, and 5.981 Å. This slight distortion from an ideal triangle is expected to influence the magnetic property of the complex as it lowers the symmetry of the metal centers, leading potentially to long-range ordering.

Tilting of adjacent coordination octahedra of Co^{2+} in **3** may also affect its magnetic property. As in **1**, this tilting allows the Dzyaloshinsky–Moriya interaction between Co^{2+} ions to occur; such interactions are believed to be largely responsible for the spin-canted long-range ordering of jarosite.[1e,2d] However, complex **3** may be a better 2D magnetic system because even the shortest interlayer Co–Co distance is 13.5 Å, significantly longer than the corresponding value of 6.7 Å found in jarosite.

Preliminary magnetic measurements were carried out for **1–3** ($\chi T(T)$ and $\chi^{-1}(T)$ for **1–3** and $\chi_{ac}(T)$ for **3**, Figure S6–9). Fitting of the $\chi^{-1}–T$ using the Curie–Weiss law gives the Curie constant $C = 3.25, 3.76$, and 4.05 cm^3 mol^{-1} K and the Weiss constant $\theta = -54.1, -26.6$, and -165.8 K for **1**, **2**, and **3**, respectively. All three complexes show apparent antiferromagnetic coupling. Complexes

1 and **2** are weak ferromagnets as a result of spin canting with T_N at about 10 K. For **3**, the sharp peaks in χT and χ_{ac} at about 16 K suggest a weak-ferromagnet state below $T_N = 16$ K. The observed slightly frequency-dependent hump at about 9.5 K in χ_{ac} for **3** suggests a re-entered magnetically disordered spin-glass state. The large $|\theta|/T_N$ value (10) for **3** indicates strong frustration, as is expected in a *Kagom*é lattice.[1b] Thus, complex **3** provides a good molecule-based system to investigate the spin frustration phenomenon in a more isolated *Kagom*é lattice. Detailed magnetic studies of **1–3** are in progress, and the results will be reported soon.

Supporting Information Available: Crystal data (CIFs); syntheses, more structure figures, XRD patterns of all compounds; preliminary magnetic results of **1–3**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) For examples: (a) Sachdev, S.; Park, K. *Cond-mat/0108214 v2*; 2001. (b) Greedan, J. E. *J. Mater. Chem.* **2001**, *11*, 37. (c) Misguich, G.; Lhuillier, C. *Cond-mat/0310405 v1*; 2003. (d) Richter, J.; Schulenburg, J.; Honecker, A. *Quantum Magnetism*; Springer-Verlag: Berlin, Heidelberg, 2004; Chapter 2. (e) Grohol, D.; Matan, K.; Cho, J. H.; Lee, S.-H.; Lynn, J. W.; Nocera, D. G.; Lee, Y. S. *Nat. Mater.* **2005**, *4*, 323. (f) Shores, M. P.; Nytko, E. A.; Bartlett, B. M.; Nocera, D. G. *J. Am. Chem. Soc.* **2005**, *127*, 13462.
(2) (a) Harris, A. B.; Kallin, C.; Berlinsky, A. J. *Phys. Rev. B* **1992**, *45*, 2899. (b) Inami, T.; Nishiyama, M.; Maegawa, S. *Phys. Rev. B* **2000**, *61*, 12181. (c) Will, A. S.; Harrison, A.; Ritter, C.; Smith, R. I. *Phys. Rev. B* **2000**, *61*, 6156. (d) Elhajal, M.; Canals, B.; Lacroix, C. *Phys. Rev. B* **2002**, *66*, 014422. (e) Nocera, D. G.; Bartlett, B. M.; Grohol, D.; Papoutsakis, D.; Shores, M. P. *Chem.—Eur. J.* **2004**, *10*, 3850.
(3) (a) Behera, J. N.; Paul, G.; Choudhury, A.; Rao, C. N. R. *Chem. Commun.* **2004**, 456. (b) Rao, C. N. R.; Sampathkumaran, E. V.; Nagarajan, R.; Paul, G.; Behera, J. N.; Choudhury, A. *Chem. Mater.* **2004**, *16*, 1441.
(4) For examples: (a) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (b) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 369.
(5) (a) Moulton, B.; Lu, J.; Hajndl, R.; Hariharan, S.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2821. (b) Rusanov, E. B.; Ponomarova, V. V.; Komarchuk, V. V.; Stoeckli-Evans, H.; Fernandez-Ibañez, E.; Stoeckli, F.; Sieler, J.; Domasevitch, K. V. *Angew. Chem., Int. Ed.* **2003**, *42*, 2499. (c) Perry, J. J.; McManus, G. J.; Zaworotko, M. J. *Chem. Commun.* **2004**, 2534. (d) Liu, Y. L.; Kravtsov, V. Ch.; Beauchamp, A.; Eubank, J. F.; Eddaoudi, M. *J. Am. Chem. Soc.* **2005**, *127*, 7266. (e) Baudron, S. A.; Batail, P.; Coulon, C.; Clérac, R.; Canadell, E.; Laukhin, V.; Melzi, R.; Wzietek, P.; Jérome, D.; Auban-Senzier, P.; Ravy, S. *J. Am. Chem. Soc.* **2005**, *127*, 11785.
(6) Awaga, K.; Okuno, T.; Yamaguchi, A.; Hasegawa, M.; Inabe, T.; Maruyama, Y.; Wada, N. *Phys. Rev. B* **1994**, *49*, 3975.
(7) Crystal data. **1**: $C_{12}H_{12}N_8O_2Co$, $M = 359.23$, monoclinic, $P2_1/c$, $a = 11.1733(4)$ Å $b = 6.7391(3)$ Å, $c = 9.7645(3)$ Å, $\beta = 111.347(2)°$, $V = 684.80(4)$ Å^3, $R1 = 0.0358$, $wR2 = 0.0924$ ($I > 2\sigma(I)$). **2**: $C_{14}H_{18}N_8O_3\cdot SCo$, $M = 437.35$, monoclinic, $C2/m$, $a = 10.6544(2)$ Å, $b = 13.4568(4)$ Å, $c = 13.4163(3)$ Å, $\beta = 106.0560(10)°$, $V = 1848.52(8)$ Å^3, $R1 = 0.0362$, $wR2 = 0.1050$ ($I > 2\sigma(I)$). **3**: $C_{48}H_{64}N_{28}O_{10}Co_3$, $M = 1370.06$, monoclinic, $P2_1/c$, $a = 13.5054(2)$ Å, $b = 19.8150(3)$ Å, $c = 11.6353(2)$ Å, $\beta = 96.5779(7)°$, $V = 3093.22(9)$ Å^3, $R1 = 0.0424$, $wR2 = 0.0985$ ($I > 2\sigma(I)$).
(8) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, Heidelberg, 1986.
(9) Abrahams, B. F.; Hardie, M. J.; Hoskins, B. F.; Robson, R.; Sutherland, E. E. *Chem. Commun.* **1994**, 1049.
(10) 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.
(11) (a) Ribas, J.; Escuer, A.; Monfort, M.; Vicente, R.; Cortés, R.; Lezama, L.; Rojo, T. *Coord. Chem. Rev.* **1999**, *193–195*, 1027.

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