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# Hybrid Cobalt Hydroxyoxalate Material Containing 3D Co−O−Co Connectivity and Showing Ferrimagnetic Ordering

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A hybrid material constructed of 3/19 site-modified Brucite-like cobalt hydroxide and cobalt-oxalate, two types of new layered structural motifs, has been synthesized that shows rare 3D Co−O−Co connectivity and ferrimagnetic ordering.

Materials containing a Brucite-like transition-metal hydroxide/oxide structural motif have attracted much attention over recent years because of the presence of short metal−metal distances and favorable angles for strong magnetic exchange interactions.[1−3] The discovery of superconductivity in the Brucite-like cobalt oxide layer has highlighted the interest.[4] Generally, structures of Brucite-like materials can be classified as two types: pillaring of site-modified or full Brucite-like layers by rod-shaped links into 3D frameworks and intercalated site-modified or full Brucite-like layers.[2,3] In the Communication, we present a Brucite-related material with rare 3D Co−O−Co connectivity,[6] $K[Co_{14}O(OH)_{21}(ox)_3]$ (**1**), which is constructed of 3/19 site-modified Brucite-like cobalt hydroxide and polymeric cobalt-oxalate, two types of new layered structural motifs.[3,5] The structure of **1** represents the third type of Brucite-like hybrid materials. Preliminary magnetic measurements for **1** reveal long-range ordering of the moments not only within the Brucite-like cobalt hydroxide but also within the cobalt oxalate layered motifs.

Solvothermal reaction of a mixture of $Co_2O_3$, KOH, and uric acid in a stainless autoclave at 160 °C for 5 days resulted in blue rhombic platelike single crystals of **1**. The oxalate ions were in situ generated by oxidized decomposition of uric acid by $Co_2O_3$, which is consistent with critical hydro(solvo)thermal reaction.[7]

Single-crystal X-ray diffraction[8] revealed that **1** has a 3D framework constructed of 3/19 site-modified Brucite-like cobalt hydroxide and trigonal cobalt oxalate $[Co(OH)(ox)]_n^{n-}$, two types of new layered structural motifs (Figure 1). **1** crystallizes in trigonal acentric space group *P*321, and the asymmetric unit consists of 2 crystallographically independent $K^+$ ions, 12 $Co^{II}$ ions, 2 oxalates, 14 hydroxides, and 2 oxo ions. The Flack parameter of 0.33(4) is due to a twinned crystal. Co(1), K(1), K(2), O(9), and O(10) localize at the crystallographic 3-fold axis, while Co(9), Co(10), Co(11), and Co(12) localize at the crystallographic 2-fold axis. The 12 $Co^{II}$ ions can be classified in three classes: octahedral $Co_{br}$ ions coordinated by hydroxides; tetrahedral $Co_t$ ions solely coordinated by hydroxides; octahedral $Co_{ox}$ ions

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(1) Jacobson, A. J. Intercalation Reactions of Layered Compounds. In *Solid State Chemistry: Compounds*; Day, P., Cheetham, A., Eds.; Oxford University Press: Oxford, U.K., 1992.

(2) (a) Salah, M. B.; Vilminot, S.; Richard-Plouet, M.; Andre, G.; Mhirid, T.; Kurmoo, M. *Chem. Commun.* **2004**, 2548. (b) Salah, M. B.; Vilminot, S.; Andre, G.; Richard-Plouet, M.; Mhiri, T.; Takagi, S.; Kurmoo, M. *J. Am. Chem. Soc.* **2006**, *128*, 7972.

(3) (a) Rujiwatra, A.; Kepert, C. J.; Rosseinsky, M. *Chem. Commun.* **1999**, 2307. (b) Rujiwatra, A.; Kepert, C. J.; Claridge, J. B.; Rosseinsky, M. J.; Kumagai, H.; Kurmoo, M. *J. Am. Chem. Soc.* **2001**, *123*, 10584. (c) Kurmoo, M.; Kumagai, H.; Hughes, S. M.; Kepert, C. J. *Inorg. Chem.* **2003**, *42*, 6709. (d) Forster, P. M.; Tafoya, M. M.; Cheetham, A. K. *J. Phys. Chem. Solids* **2004**, *65*, 11–16.

(4) (a) Takada, K.; Sakurai, H.; Takayama-Muromachi, E.; Izumi, F.; Dilanian, R.; Sasaki, T. *Nature* **2003**, *422*, 53. (b) Badding, J. V. *Nat. Mater.* **2003**, *2*, 208. (c) Schaak, R. E.; Klimczuk, T.; Foo, F. L.; Cava, R. J. *Nature* **2003**, *424*, 527.

(5) (a) Pilkington, M.; Decurtins, S. Oxalate-based 2D and 3D Magnets. In *Magnetism: Molecules to Materials. II: Molecule-Based Materials*; Miller, J. S., Drillon, M., Eds.; Wiley-VCH: New York, 2003. (b) Gruselle, M.; Train, C.; Boubekeur, K.; Gredin, P.; Ovanesyan, N. *Coord. Chem. Rev.* **2006**, *250*, 2491.

(6) (a) Livage, C.; Forster, P. M.; Guillou, N.; Tafoya, M. M.; Cheetham, A. K.; Ferey, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 5877. (b) Guillou, N.; Livage, C.; Drillon, M.; Ferey, G. *Angew. Chem., Int. Ed.* **2003**, *42*, 5314. (c) Forster, P. M.; Cheetham, A. K. *Angew. Chem., Int. Ed.* **2002**, *41*, 457. (d) Dybtsev, D. N.; Chun, H.; Yoon, S. H.; Kim, D.; Kim, K. *J. Am. Chem. Soc.* **2004**, *126*, 32. (e) Anokhina, E. V.; Go, Y. B.; Lee, Y.; Vogt, T.; Jacobson, A. J. *J. Am. Chem. Soc.* **2006**, *128*, 9957.

(7) (a) Chen, X.-M.; Tong, M.-L. *Acc. Chem. Res.* **2007**, *40*, 162. (b) Zhang, X.-M. *Coord. Chem. Rev.* **2005**, *249*, 1201.

(8) Crystal data for **1** at 100 K: trigonal, *P*321, $M_r = 1501.35$, $a = b = 13.7651(2)$ Å, $c = 19.7522(3)$ Å, $V = 3241.19(7)$ Å$^3$, $Z = 4$, $D_c = 3.077$ g cm$^{-3}$, $\mu = 7.204$ mm$^{-1}$, $T_{min} = 0.8693$, $T_{max} = 0.5964$, $F(000) = 2904$, R1 = 0.0486, wR2 = 0.1536, GOF = 1.039.

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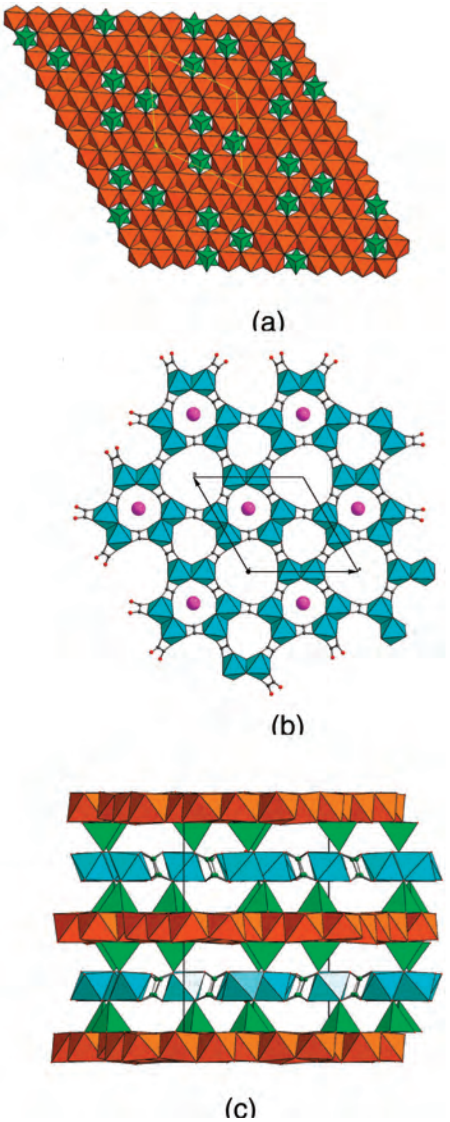

**Figure 1.** View of the 3/19 site-modified Brucite-like cobalt hydroxide motif (a), the polymeric $[Co(OH)(ox)]_n^{n-}$ layered motif showing encapsulation of $K^+$ ions (b), and the structure of **1** showing 3D Co−O−Co connectivity. Brown octahedra, green tetrahedra, and blue octahedra respresent $Co_{br}$, $Co_t$, and $Co_{ox}$ sites, respectively. Purple, red, and gray balls represent K, O, and C atoms in part b.

ligated by four O atoms from oxalates and two hydroxides. The average $Co_{br}$−O, $Co_t$−O, and $Co_{ox}$−O bond lengths are 2.128, 1.987, and 2.086 Å, respectively. The edge-sharing of $Co_{br}(OH)_6$ octahedra resulted in a Brucite-like cobalt hydroxide layer, which is decorated by tetrahedral $Co_t$ sites located above and below the layer at 3/19 vacant sites. Only 1/4, 1/6, and 1/7 site-modified Brucite-like cobalt hydroxide motifs are documented to date,[3] and thus the 3/19 site-modified Brucite-like cobalt hydroxide structural motif in **1** is unprecedented. The average $Co_{br}\cdots Co_{br}$ distance within a Brucite-like cobalt hydroxide layer is 3.17 Å. The $Co_{br}$−O−$Co_{br}$ angles are in the range of 92.5(3)−100.7(5)°. The average $Co_t\cdots Co_{br}$ distance in $Co_t$−O−$Co_{br}$ motifs is 3.59 Å, while the $Co_t$−O−$Co_{br}$ angles are in the range of 119.3(3)−123.8(3)°. The edge-sharing of $Co_{ox}(OH)_2O_4$ octahedra results in dimeric units, each of which is connected to its four neighbors to give rise to an unprecedented trigonal-layered coordination-polymeric $[Co(OH)(ox)]_n^{n-}$ motif. Within a dimeric unit, the $Co_{ox}\cdots Co_{ox}$ distances are 2.965(2) and 2.976(2) Å and the $Co_{ox}$−O−$Co_{ox}$ angles are 91.4(2) and 92.1(2)°. There are two types of cavities within the trigonal coordination-polymeric layer: the larger is formed by six Co ions and six oxalates, while the smaller consists of three $Co_2$ units and three oxalates. Interestingly, $K^+$ ions are encapsulated inside the smaller cavities with a K−O distance of 3.146(5)−3.222(6) Å. The Brucite-like cobalt hydroxide and polymeric cobalt oxalate layers are linked via sharing oxygen of $Co_t$−O−$Co_{ox}$ to generate a 3D hybrid framework with 3D Co−O−Co connectivity. At $Co_t$−O−$Co_{ox}$ joints, the average $Co_t\cdots Co_{ox}$ distance is 3.62 Å and the $Co_t$−O−$Co_{ox}$ angles are in the range of 121.8(3)−125.7(3)°. A marked feature of **1** is that each cell includes two modified Brucite-like cobalt hydroxide layers and two polymeric cobalt oxalate layers along the *c* axis.

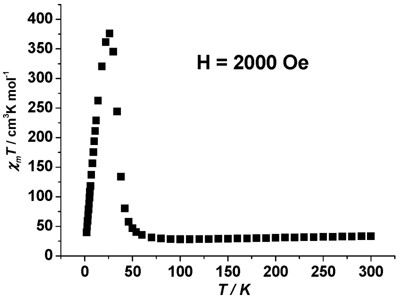

**Figure 2.** $\chi_m T$ vs $T$ curve per $Co_{14}$ unit. To note, there are eight $Co_{br}$, three $Co_t$, and three $Co_{ox}$ ions in a $Co_{14}$ unit.

The temperature dependence of the magnetic susceptibility for **1** is shown in Figure 2. The $\chi_m T$ value at 300 K is 33.27 $cm^3$ K $mol^{-1}$ per $Co_{14}$ unit and slowly decreases with lowering temperature down to a minimum value of 28.17 $cm^3$ K $mol^{-1}$ at 110 K. Upon further cooling, the $\chi_m T$ value increases to a maximum of 376.02 $cm^3$ K $mol^{-1}$ at 26 K and then decreases to 39.56 $cm^3$ K $mol^{-1}$ at 2 K. The observation of a shallow minimum is as expected for a ferrimagnet. In the paramagnetic region above 110 K, the susceptibility obeys the Curie−Weiss law with Curie constant $C = 30.51$ $cm^3$ K $mol^{-1}$ and Weiss constant $\theta = -7.3$ K, giving an effective moment of 4.18 $\mu_B$ per Co ion. At 2 K, the magnetization at the highest field of 70 000 Oe is 14.1 N$\beta$ per $Co_{14}$ unit. For a $Co^{II}$ ion, the effect of spin−orbit coupling usually yields a Kramers $S = {}^1/_2$ state at low temperature with an average $g$ value of ${}^{13}/_3$ and a moment of 2.17 N$\beta$.[9] Assuming this, the moment of 14.1 N$\beta$ at 70 000 Oe field is therefore close to the resultant moment of eight $Co^{II}$ ions, indicating that **1** is a ferrimagnet where all $Co_{br}$ and $Co_{ox}$ spins are parallel but antiparallel to $Co_t$ spins. This is in agreement with magnetostructural analysis of **1**: $Co_{br}$−$Co_{br}$ and $Co_{ox}$−$Co_{ox}$ ferromagnetic coupling due to small $Co_{br}$−O−$Co_{br}$ and $Co_{ox}$−O−$Co_{ox}$ angles; $Co_t$−$Co_{br}$ and $Co_t$−$Co_{ox}$ antiferromagnetic coupling due to large $Co_t$−O−$Co_{br}$ and $Co_t$−O−$Co_{ox}$ angles.[2,3] The hysteresis loop of **1** is observed, with a coercive field of 1350 Oe and remanent magnetization of 6.69 N$\beta$ at 2 K and a coercive

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(9) de Jongh, L. J., Ed. *Magnetic Properties of Layered Transition Metal Compounds*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1990.

field of 740 Oe and remanent magnetization of 6.51 N$\beta$ at 3 K. The bifurcation of zero-field-cooled−field-cooled magnetizations in a field of 50 Oe at 33 K and the nonzero imaginary ac susceptibility confirm the long-range ferrimagnetic ordering. To date, the compound most related to **1** is the $SO_4$−Co−$SO_4$-pillared compound $Co_5(OH)_6(SO_4)_2(H_2O)_4$, in which the moments within $SO_4$−Co−$SO_4$ pillars are random.[2] In summary, in situ solvothermal reaction generated a hybrid cobalt hydroxyoxalate material constructed of 3/19 site-modified Brucite-like cobalt hydroxide and trigonal polymeric cobalt oxalate, two new types of layered structural motifs. The structure of **1** represents a third type of Brucite-like hybrid material and contains rare 3D Co−O−Co connectivity. Compound **1** shows long-range ordering of the moments not only within a Brucite-like cobalt hydroxide but also within cobalt-oxalate layered subunits, whereas in related compound $Co_5(OH)_6(SO_4)_2(H_2O)_4$, only the moments within Brucite-like layers are ordered. I

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**Supporting Information Available:** X-ray crystallographic data in CIF format, synthesis, elemental analysis, IR spectrum, TGA, crystal data, related Brucite-like layers, and other magnetic plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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