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$\mathrm{Co_3[Co(CN)_5]_2}$: A Microporous Magnet with an Ordering Temperature of 38 K

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The synthesis of a microporous solid that behaves as a magnet at room temperature remains an open challenge. Such a material is of interest for its potential utility in performing magnetic separations, the idea being that the greater magnetic flux within the pores of the solid will attract paramagnetic molecules while repelling diamagnetic molecules. Ensuing applications might include the extraction of dioxygen from air through an efficient noncryogenic process. To date, only a few compounds have been shown to display both long-range magnetic ordering and a porous framework structure.[1] Among these, the highest ordering temperature established reliably is 37 K, occurring in $\mathrm{[H_3N(CH_2)_4NH_3][Fe_3(PO_4)_3F_2]}$.[1b] However, like many of the other examples,[1adf] this compound is an antiferromagnet,[1b] possessing no net magnetic moment in the ordered state. Indeed, to our knowledge, magnetic hysteresis has never been demonstrated for a truly microporous solid.

Prussian blue analogues offer intriguing possibilities for the design of porous magnets. Dehydration of Prussian blue, $\mathrm{Fe_4[Fe(CN)_6]_3 \cdot 14H_2O}$, leaves its iron−cyanide framework intact,[2] resulting in a microporous solid capable of absorbing small molecules such as dinitrogen and methanol.[3] Here, the porosity is a consequence of both the square $\mathrm{Fe_4(\mu\text{-}CN)_4}$ openings in the cubic framework and the vacancies at one-quarter of the $\mathrm{[Fe(CN)_6]^{4-}}$ sites. With the use of appropriate paramagnetic precursors, analogous solids can be prepared that order magnetically at temperatures as high as 376 K.[4] Although apparently not yet tested, the porosity of many of these compounds is likely to be limited, owing to poor crystallinity, a lack of framework vacancies, or the presence of alkali metal cations in the framework cavities. Herein, we report the synthesis of $\mathrm{Co_3[Co(CN)_5]_2 \cdot 8H_2O}$ (**1**), a highly crystalline Prussian blue analogue that can be dehydrated to generate a microporous ferrimagnet with $T_N = 38$ K.

Pentacyano complexes such as $\mathrm{[Fe(CN)_5(NO)]^{2-}}$ and $\mathrm{[Fe(CN)_5L]^{3-}}$ ($\mathrm{L = CO, H_2O, NH_3}$) have long been known to serve as replacement units for hexacyanometalates in Prussian blue-type frameworks.[5] Surprisingly, however, we could find no prior reports in which the paramagnetic square-pyramidal[6] complex $\mathrm{[Co(CN)_5]^{3-}}$ was employed for this purpose. Test reactions performed in deoxygenated water[7] were particularly successful with the use of cobalt(II) as a countercation. Under a dinitrogen atmosphere, a 10-mL aqueous solution of $\mathrm{CoCl_2}$ (0.28 g, 2.1 mmol) was added to a 10-mL aqueous solution of $\mathrm{(Et_4N)_3[Co(CN)_5]}$[6a] (0.61 g, 1.1 mmol). After 1 h, the resulting dark blue precipitate was collected by centrifugation, washed with deoxygenated water (2 × 20 mL), and dried under a flow of dinitrogen to afford 0.31 g (84%) of **1**.[8] On the basis of comparisons of colors and infrared spectra, it is likely that this compound is identical to the "$\mathrm{Co(CN)_2 \cdot \mathit{x}H_2O}$" solids prepared by a variety of alternate routes.[9]

The X-ray powder diffraction pattern of **1** indexes to a face-centered cubic lattice with a unit cell parameter of $a = 10.1415(7)$ Å. The relative peak intensities closely match those of a pattern simulated using a defect variant of the usual cubic Prussian blue framework (see Figure S1 in the Supporting Information). In this model, charge neutrality was maintained by assuming vacancies at one-third of the cyanometalate sites, similar to the situation in the many related solids of formula $\mathrm{M^{II}_3[M^{III}(CN)_6]_2 \cdot \mathit{x}H_2O}$.[3c,10] In addition, the occupancy factors for all C and N atoms were reduced by a factor of 5/6 to account for the missing cyanide ligand. The resulting framework is highly porous, having an average cyanide coordination number of only 3.33 for the nitrogen-bound $\mathrm{Co^{II}}$ centers.

The spectral properties of **1** are consistent with the foregoing structural model. In the infrared spectrum, both ν_{CN} bands are shifted to higher energy relative to $\mathrm{(Et_4N)_3[Co(CN)_5]}$, as expected for exclusively bridging cyanide ligands. The diffuse reflectance spectrum displays peaks at 280 and 308 nm, reminiscent of $\mathrm{[Co(CN)_5]^{3-}}$ in aqueous solution.[6a] Additional peaks at 560 and 590 nm give rise to the blue color of the solid and suggest the presence of four-coordinate $\mathrm{Co^{II}}$ with a distorted tetrahedral $\mathrm{(NC)_3(H_2O)}$ ligand set.[11,12] The less intense shoulder at 500 nm signals the presence of some octahedrally coordinated $\mathrm{Co^{II}}$ sites, perhaps with an $\mathrm{(NC)_4(H_2O)_2}$ ligand set.

Compound **1** retains much of its crystallinity upon dehydration. A thermogravimetric analysis revealed a steady loss of water up to 100 °C, followed by a plateau extending to 220 °C, whereafter the cobalt−cyanide framework begins to decompose. Accordingly, dehydrated samples of **1** were prepared by heating the solid at 100 °C for 15 min under dynamic vacuum.[13] Subsequent analysis by X-ray powder diffraction gave a pattern with somewhat broadened peaks and a contracted unit cell parameter of $a = 9.95(3)$ Å.

The porosity of dehydrated **1** was probed via dinitrogen sorption measurements. As shown in Figure 1, the solid immediately adsorbs dinitrogen until the molecules fill the internal pores and cover the external surfaces, resulting in an initial sharp rise in sorption followed by a plateau. The additional uptake at partial pressures nearing unity is likely due to the small particle sizes rendered upon dehydration. In all, the behavior corresponds to a Type I sorption isotherm characteristic of a microporous solid.[14] The observed sorption capacity of 179 $\mathrm{cm^3/g}$ at 700 Torr and 77 K is in the range typical of zeolites[15] and, as expected from the greater concentration of framework vacancies, lies significantly above that measured for Prussian blue (38 $\mathrm{cm^3/g}$).[3c]

The magnetic properties of **1** in its fully hydrated form are indicative of a ferrimagnet with an ordering temperature of $T_N = 48$ K. At room temperature, the compound displays an effective moment of 8.64 μ_B, in reasonable agreement with the presence of three high-spin and two low-spin $\mathrm{Co^{II}}$ centers per formula unit. In an applied field of 1000 G, the moment gradually drops with

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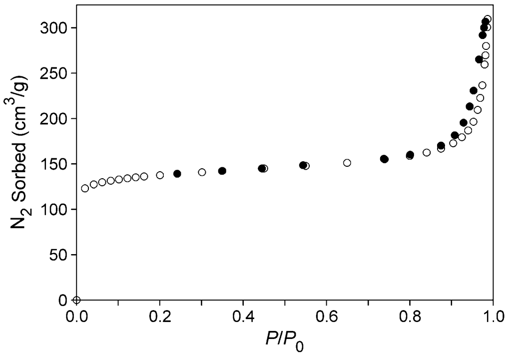

Figure 1. Dinitrogen sorption isotherm for dehydrated **1** at 77 K. Adsorption and desorption are indicated by open and filled circles, respectively. The ratio of gas pressure to saturation pressure, P/P_0, was obtained with $P_0 = 763$ Torr. Using the BET model, the surface area of the sample was determined to be 480 m^2/g.

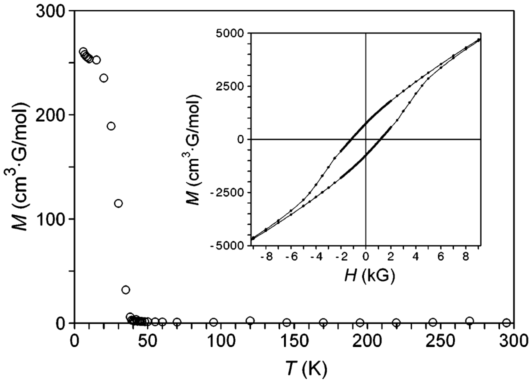

Figure 2. Field-cooled magnetization data for dehydrated **1**, as measured in an applied field of 10 G. Inset shows the magnetic hysteresis loop observed for the same sample at 5 K.

decreasing temperature, reaching a shallow minimum at ca. 75 K, before rising steeply to a maximum of 17.8 μ_B at 30 K. This and the negative Weiss constant of $\theta = -31(2)$ K obtained using Néel's hyperbolic equation[16] indicate antiferromagnetic exchange coupling between neighboring cobalt centers, as expected for symmetry-compatible spin−orbitals engaged in superexchange through cyanide.[17] Magnetization data collected in an applied field of 10 G show an abrupt rise at 48 K, signifying the onset of long-range magnetic ordering. Consistent with ferrimagnetism, magnetic hysteresis is apparent at 5 K, with a loop characterized by a coercive field of 1160 G and a remnant magnetization of 1540 cm^{3}G/mol. The sizable coercive field, which is the highest yet reported for a cubic Prussian blue analogue,[4,17] can be attributed to the anisotropy associated with the Co^{II} centers.

Remarkably, these magnetic properties are largely retained by the porous cobalt−cyanide framework of dehydrated **1**. As shown in Figure 2, magnetization data indicate the onset of magnetic ordering at the slightly lower temperature of 38 K. Hysteresis is again observed at 5 K (see the inset in Figure 2), with the coercive field remaining unchanged at 1160 G while the remnant magnetization is reduced to 745 cm^{3}G/mol. At 22 K, the hysteresis is somewhat attenuated, exhibiting a coercive field of 240 G and a remnant magnetization of 455 cm^{3}G/mol. Thus, dehydrated **1** constitutes the first compound in which long-range magnetic ordering and microporosity have been rigorously demonstrated to coexist. Experiments probing the magnetic induction within its cavities are under consideration.

Future work will include the investigation of porosity in magnetic Prussian blue solids with higher ordering temperatures more suitable for sieving applications. In addition, the ability of the square pyramidal $[Co(CN)_5]^{3-}$ units in the open framework of dehydrated **1** to bind dioxygen selectively and reversibly will be tested.[18] Preliminary measurements indicate a room-temperature sorption capacity of 11.6 cm^3/g at 700 Torr of dioxygen.

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Supporting Information Available: X-ray powder diffraction data and additional magnetic data for **1** before and after dehydration (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Cavellec, M.; Riou, D.; Ninlaus, C.; Grenèche, J.-M.; Férey, G. *Zeolites* **1996**, *17*, 250. (b) Cavellec, M.; Riou, D.; Grenèche, J.-M.; Férey, G. *J. Magn. Magn. Mater.* **1996**, *163*, 173. (c) Zhang, X. X.; Chui, S. S.-Y.; Williams, I. D. *J. Appl. Phys.* **2000**, *87*, 6007. (d) Guillou, N.; Gao, Q.; Forster, P. M.; Chang, J.-S.; Noguès, M.; Park, S.-E.; Férey, G.; Cheetham, A. K. *Angew. Chem., Int. Ed.* **2001**, *40*, 2831. (e) Rujiwatra, A.; Kepert, C. J.; Claridge, J. B.; Rosseinsky, M. J.; Kumagai, H.; Kurmoo, M. *J. Am. Chem. Soc.* **2001**, *123*, 10584. (f) Barthelet, K.; Marrot, J.; Riou, D.; Férey, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 281.

(2) Herren, F.; Fischer, P.; Ludi, A.; Hälg, W. *Inorg. Chem.* **1980**, *19*, 956.

(3) (a) Seifer, G. B. *Russ. J. Inorg. Chem.* **1959**, *4*, 841. (b) Shores, M. P.; Beauvais, L. G.; Long, J. R. *J. Am. Chem. Soc.* **1999**, *121*, 775. (c) Bennett, M. V.; Beauvais, L. G.; Shores, M. P.; Long, J. R. *J. Am. Chem. Soc.* **2001**, *123*, 8022.

(4) (a) Ferlay, S.; Mallah, T.; Ouahès, R.; Veillet, P.; Verdaguer, M. *Nature* **1995**, *378*, 701. (b) Hatlevik, Ø.; Buschmann, W. E.; Zhang, J.; Manson, J. L.; Miller, J. S. *Adv. Mater.* **1999**, *11*, 914. (c) Holmes, S. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1999**, *121*, 5593.

(5) (a) Salvadeo, P. G. *Gazz. Chim.* **1959**, *89*, 2184. (b) Ayers, J. B.; Waggoner, W. H. *J. Inorg. Nucl. Chem.* **1969**, *31*, 22045. (c) Fluck, E.; Inoue, H.; Nagao, M.; Yanagisawa, S. *J. Inorg. Nucl. Chem.* **1979**, *41*, 287. (d) Holmes, S. M.; Girolami, G. S. *Mol. Cryst. Liq. Cryst.* **1997**, *305*, 279 and references therein.

(6) (a) Alexander, J. J.; Gray, H. B. *J. Am. Chem. Soc.* **1967**, *89*, 3356. (b) Brown, L. D.; Raymond, K. N. *Inorg. Chem.* **1975**, *14*, 2590.

(7) The use of deoxygenated water and an inert atmosphere is necessary, because $[Co(CN)_5]^{3-}$ reacts with O_2 to give $[Co(CN)_5(O_2)]^{3-}$: (a) White, D. A.; Solodar, A. J.; Baizer, M. M. *Inorg. Chem.* **1972**, *11*, 2160. (b) Brown, L. D.; Raymond, K. N. *Inorg. Chem.* **1975**, *14*, 2595.

(8) Characterization of **1**: Diffuse reflectance spectrum: λ_{max} 280, 308, 380 (sh), 500 (sh), 560 (sh), 590, 1215 (br) nm. IR: ν_{CN} 2178 (s), 2140 (m) cm^{-1}. $\mu_{eff} = 8.64\ \mu_B$ at 295 K. Anal. Calcd for $C_{10}H_{16}Co_5N_{10}O_8$: C, 17.18; H, 2.31; N, 20.04. Found: C, 17.73; H, 2.53; N, 19.38. The water content of the solid was confirmed by thermogravimetric analysis.

(9) (a) Weiss, A.; Rothenstein, W. *Angew. Chem.* **1963**, *75*, 575. (b) Güdel, H. U.; Ludi, A. *Helv. Chim. Acta* **1969**, *52*, 2255. (c) Poskozim, P. S.; Shute, R.; Taylor, R.; Wysocki, J. *J. Inorg. Nucl. Chem.* **1973**, *35*, 687. (d) Mosha, D. M. S.; Nicholls, D. *Inorg. Chim. Acta* **1980**, *38*, 127. (e) Mosha, D. M. S. *J. Chem. Soc. Pak.* **1985**, *7*, 173.

(10) (a) Ludi, A.; Güdel, H. U. *Helv. Chim. Acta* **1968**, *51*, 2006. (b) Shriver, D. F.; Brown, D. B. *Inorg. Chem.* **1969**, *8*, 42. (c) Ludi, A.; Güdel, H. U.; Rüegg, M. *Inorg. Chem.* **1970**, *9*, 2224.

(11) Pratt, J. M.; Williams, R. J. P. *J. Chem. Soc. A* **1967**, 1291.

(12) Note that the presence of four-coordinate cobalt centers is consistent with the lower water content of blue **1** versus pink $Co_3[Co(CN)_6]_2 \cdot 12H_2O$, wherein all cobalt centers exhibit octahedral coordination.[10ab]

(13) Characterization of dehydrated **1**: Diffuse reflectance spectrum: λ_{max} 261, 307, 554 (sh), 590, 1209 (br) nm. IR: ν_{CN} 2178 (s), 2139 (m) cm^{-1}. $\mu_{eff} = 8.17\ \mu_B$ at 295 K.

(14) Rouquerol, F.; Rouquerol, J.; Sing, K. *Adsorption by Powders and Solids: Principles, Methodology, and Applications*; Academic Press: London, 1999.

(15) For comparison, at 77 K and 700 torr of dinitrogen, erionite and faujasite exhibit sorption capacities of 155 and 192 cm^3/g, respectively: Breck, D. W. *Zeolite Molecular Sieves*; John Wiley & Sons: New York, 1974; pp 607−627.

(16) Smart, J. S. *Am. J. Phys.* **1955**, *23*, 356.

(17) (a) Entley, W. R.; Treadway, C. R.; Girolami, G. S. *Mol. Cryst. Liq. Cryst.* **1995**, *273*, 153 and references therein. (b) Weihe, H.; Güdel, H. U. *Comments Inorg. Chem.* **2000**, *22*, 75.

(18) Such behavior has been demonstrated for zeolites and molecular salts containing $[Co(CN)_5]^{3-}$: (a) Taylor, R. J.; Drago, R. S.; Hage, J. P. *Inorg. Chem.* **1992**, *31*, 253. (b) Ramprasad, D.; Pez, G. P.; Toby, B. H.; Markley, T. J.; Pearlstein, R. M. *J. Am. Chem. Soc.* **1995**, *117*, 10694.

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