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Structure and Magnetic Ordering of $K_xH_{1-x}Ni(OH_2)_4[Ru_2(CO_3)_4]\cdot zH_2O$

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$K_xH_{1-x}Ni(OH_2)_4[Ru_2(CO_3)_4]\cdot zH_2O$ is a ferrimagnet (T_c = 4.3 K) formed from the reaction of $K_3[Ru^{II/III}{}_2(CO_3)_4]$ and Ni^{II} in water. It possesses a new 3-D network structural motif composed of linked chains and μ_3-CO_3 linkages to both Ru and Ni sites. Each Ni(II) bonds to four oxygens and to two $[Ru_2(CO_3)_4]^{3-}$ moieties in a cis manner, and four μ_3-CO_3 groups from each $[Ru_2(CO_3)_4]^{3-}$ have two oxygens bonding to the Ru_2 moiety, forming the typical paddle-wheel core, and trans pairs of the third $CO_3{}^{2-}$ oxygen axially bonded to either another Ru_2 or Ni^{II}.

The use of the mixed-valent $S = 3/2$ $[Ru_2(O_2CMe)_4]^+$ and $[Cr(CN)_6]^{3-}$ ions has enabled the deliberate design of cubic $[Ru_2(O_2CMe)_4]_3[Cr(CN)_6]$, which is a ferrimagnet.[1] In contrast, $[Ru_2(O_2CBu^t)_4]^+$ leads to layered $[Ru_2(O_2CBu^t)_4]_3[Cr(CN)_6]$, which is also a ferrimagnet.[2,3] To control the motif, we targeted $[Ru_2(CO_3)_4]^{3-}$ to make molecule-based magnets due to carbonate's ability to μ_3-bridge to metal ions.

Reaction of $K_3[Ru_2(CO_3)_4]$[4] and $Ni(NO_3)_2$ forms a red-brown polycrystalline material.[5] Although attempts to grow single crystals were unsuccessful, high-resolution X-ray powder patterns[6] were collected and the structure was determined by direct space simulated annealing and Rietveld refinement (Figure S1).[7]

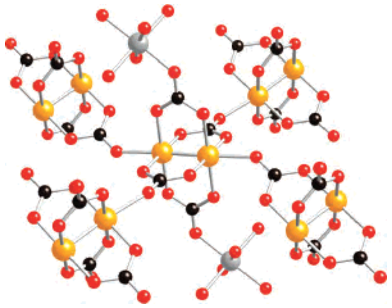

Figure 1. $[Ru_2(CO_3)_4]^{3-}$ bound to four other $[Ru_2(CO_3)_4]^{3-}$ ions (Ru, gold; C, black; O, red) and two Ni^{II} ions (gray). Each Ni^{II} bonds to another $[Ru_2(CO_3)_4]^{3-}$ in a cis manner.

The structure consists of a 3-D network composed of linked chains that differ from that observed for layered $K_3[Ru_2(CO_3)_4]$.[4] Each anion has four μ_3-carbonate ligands, each with two of its oxygens bonding to the diruthenium moiety forming the typical paddle-wheel (D_{4h}) geometry. Trans pairs of the third carbonate oxygen bond to either a site axial to another Ru−Ru moiety, as observed for $K_3[Ru_2(CO_3)_4]$,[4] or to Ni^{II} (Figure 1) with a Ni−O−C angle of 129(1)° and a 2.04(3) Å Ni−OC separation. The pair of axial sites, with respect to the Ru−Ru bond, bonds to the carbonate oxygens (2.23(3) Å) from other anions and have

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(5) **1** was synthesized in ~80% yield via 1.5:1 $Ni(NO_3)_2$ (139.9 mg)/$K_3[Ru_2(CO_3)_4]\cdot 4H_2O$ (200.6 mg) each dissolved in 20 mL of H_2O. The anion was added to the stirring solution of Ni^{II} at the rate of 19.8 mL/h using a syringe pump. The initial black precipitate was removed via centrifugation, and the desired product was precipitated with addition of MeOH, washed with MeOH, and dried in a vacuum desiccator with P_2O_5 overnight. IR (KBr): 1634 ν_{H2O}, 1492(s) ν_{CO}, 1344 ν_{CO}, 1266(s) ν_{CO}, 1065(s), 818, 769, and 715 cm^{-1}. Anal. Calcd for $HNi(OH_2)_{3.35}[Ru_2(CO_3)_4]$: $C_4H_{7.6}NiO_{15.35}Ru_2$: C, 8.54; H, 1.38; N, 0.00; H_2O, 10.70; Found: C, 8.34; H, 1.20; N, <0.2; H_2O (10.7% from the TGA data below 170 °C indicative of 3.35 H_2O/Ni). Anal. Calcd for $K_{0.7}H_{0.3}Ni(OH_2)_4[Ru_2(CO_3)_4]$ or $C_4H_{8.3}NiO_{16}K_{0.7}Ru_2$: C, 8.31; H, 1.51; K, 4.51; Found: C, 8.34; H, 1.44; K, 4.28; N, <0.2.

(6) A Si(111) channel-cut monochromator selected a highly collimated incident beam of 0.69667(1) Å on the X16C beamline at National Synchrotron Light Source, BNL. The diffracted X-rays were analyzed by a Ge(111) single-reflection crystal and detected using NaI scintillation counter. The capillary was rotated during data collection for better averaging of the data. TOPAS-Academic was used to index, assign the space group, and solve the structure by the simulated annealing method and subsequent Rietveld refinement. Rigid-body constraints were imported to describe the D_{4h} Ru dimer, but interatomic distances were refined. Solvent molecules necessary to explain the observed XRPD pattern were observed; we assumed water and oxygen atoms (O13−15); however, occupancy and thermal parameter are refined freely; consequently, atom identifications are not meaningful. (*TOPAS V3: General profile and structure analysis software for powder diffraction data, User's Manual*; Bruker AXS, Karlsruhe: Germany, 2005; TOPAS-Academic is available at http://members.optusnet.com.au/~alancoelho).

(7) Space group = *Pccn* (No. 56); a = 18.195(1) Å, b = 9.3571(3) Å, c = 10.0464(3) Å, V = 1710.4(1) Å^3, Z = 4 g/cm^3, R = 0.049, R_w = 0.062, χ = 1.897; XRPD measurement was done at ~23 °C.

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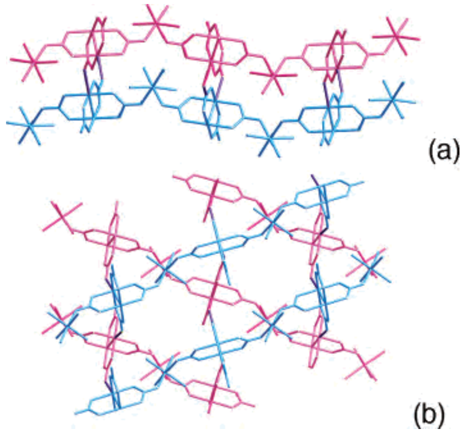

Figure 2. Top (a) and side (b) views of linked parallel extended chains of **1**.

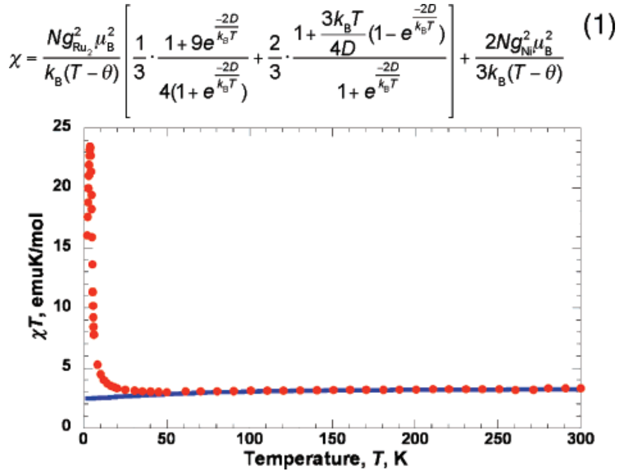

Figure 3. $\chi T(T)$ for **1** (●) and fit (—) with eq 1.

a RuRu−O−C angle of 140(1)°. Each six-coordinate nickel ion bonds cis to two ruthenium carbonate anions (90(1)°), and to four oxygen atoms (average 2.07 Å) from H_2O molecules. The cis linkages form parallel 1-D chains (Figure 2a) with adjacent chains being canted in opposing directions (Figure 2b). These chains are linked together by one CO_3^{2-} axially bonded to a Ru in another chain (Figure 2b).

Besides the linked chain structure, analysis of the diffraction pattern reveals an interstitial site with ∼12 e^- and a thermal parameter close to that of the framework. In view of the observation of sub-stoichiometric K by elemental analysis, this site is regarded as being shared by K^+ and solvent H_2O (and/or MeOH). Two other interstitial sites have the fractional occupancies and large thermal parameters characteristic of water of solvation. Despite attempts to make a material with a 3:2 Ni/Ru_2 ratio, the unit cell has a 1:1 Ni/Ru_2 ratio. This ratio is not charge-compensated assuming that Ni(II) and $[Ru^{II/III}_2(CO_3)_4]^{3-}$ are present. The presence of $[Ru^{III}_2(CO_3)_4]^{2-}$ is unreasonable, as it is reported to be unstable in water.[4a] Likewise, the presence of rare Ni(III) is unlikely, as its expected Jahn−Teller distorted structure[8] is not observed. Thus, neither charge-compensated $Ni^{2+}[Ru^{III/III}_2(CO_3)_4]^{2-}$ nor $Ni^{3+}[Ru^{II/III}_2(CO_3)_4]^{3-}$ formulations are likely and H^+ and/or a K^+ from the reaction media are assumed to be present to balance the charge as $K^{+}_{x}H^{+}_{1-x}[Ni(OH_2)_4]^{2+}[Ru^{II/III}_2(CO_3)_4]^{3-}\cdot zH_2O$ (**1**). This is validated by elemental analysis data observed for $x = 0$ and 0.7 with allowances made for differing amounts of water due to dehydration.[5] Additionally, the presence of Ni(III) and $[Ru^{III/III}_2(CO_3)_4]^{2-}$ can be eliminated from the magnetic data (vide infra). However, observation or refinement of all H positions is not possible.

The presence of a H^+ (and K^+) for related systems has been established, i.e., $[Ru^{II/III}_2(O_2CMe)_4](O_2CMe\cdot HO_2CMe)\cdot 0.7H_2O$ with a H^+ bridge between two axial acetate oxygens[9] and $H[Ru_2(O_2CCH_3)_4(HPhPO_2)_2]$,[10] $H[Ru_2(O_2CC{-}H_3)_4(PhPO_3H)_2]\cdot H_2O$, and $K_2H[Ru_2(SO_4)_4(H_2{-}O)_2]$.[11] The presence of less than one K^+ per Ni^{II} is noted from the elemental analysis.

The 300 K χT value is 3.24 emuK/mol.[12] This exceeds the 2.875-emuK/mol spin-only value, due to the presence of zero-field splitting primarily on the $Ru^{II/III}_2$. The observed $\chi T(T)$ is relatively constant with decreasing temperature until ∼30 K, when it increases with decreasing temperature, reaching 23.0 emuK/mol at 3.6 K (Figure 3), indicative of magnetic ordering. Above 40 K, $\chi T(T)$ can be fit to eq 1 incorporating zero-field splitting (D)[13] and θ accounting for intermolecular interactions. A good fit has been obtained for $g_{Ru} = 2.08$, $g_{Ni} = 2.20$, $D/k_B = 100$ K (70 cm^{-1}), and $\theta = 0$ K. Attempts to fit the $\chi T(T)$ data above 50 K to either $Ni^{3+}(OH_2)_4[Ru^{II/III}_2(CO_3)_4]^{3-}$ [with low-spin Ni(III)],[8] or $Ni^{2+}(OH_2)_4[Ru^{III/III}_2(CO_3)_4]^{2-}$ [with $S = 1$ or 2 Ru_2(III)] formulations required unreasonable g values, and gave poor fits. The D and g values are in good agreement with previous reports for related materials.[4b,13,14]

$$\chi = \frac{Ng^2_{Ru_2}\mu^2_B}{k_B(T-\theta)}\left[\frac{1}{3}\,\frac{1+9\,e^{-2D/k_BT}}{4(1+e^{-2D/k_BT})} + \frac{2}{3}\,\frac{1+\dfrac{3k_BT}{4D}(1-e^{-2D/k_BT})}{1+e^{-2/Dk_BT}}\right] + \frac{2Ng^2_{Ni}\mu^2_B}{3k_B(T-\theta)} \quad (1)$$

Magnetic ordering was established from the absorptions in the ac $\chi'(T)$ and $\chi''(T)$ data (Figure 4). The 10 Hz

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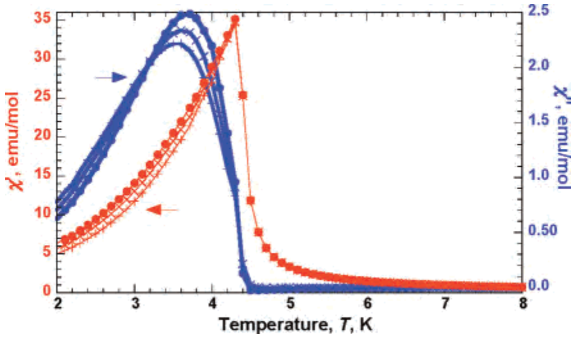

Figure 4. $\chi'(T)$ and $\chi''(T)$ for **1** at 10 (●), 100 (×), and 1000 (+) Hz.

data has a peak at 4.3 K in $\chi'(T)$ and is T_c. The peak in $\chi''(T)$ rules out antiferromagnetic ordering, as occurs for $[Ru_2(O_2CMe)_4]_3[Cr(CN)_6]$ and $[Ru_2(O_2CBu^t)_4]_3[Cr(CN)_6]$, Hysteresis in the $M(H)$ data shows a constricted-like hysteresis loop with a coercive field of 75 Oe and remanent magnetization of 2110 emuOe/mol at 2 K (Figure S2) consistent with ferrimagnetic ordering. The observed saturation magnetization is 11 400 emuOe/mol. The expected values for ferromagnetic and antiferromagnetic coupling between the Ni(II) and $[Ru_2(CO_3)_4]^{3-}$ are 21 800 and 2700 emuOe/mol, respectively. Hence, the observed intermediate value is indicative of a canted ferrimagnet.

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Supporting Information Available: Rietveld fit to the powder diffraction data, hysteresis, and crystallographic CIF file for $K_xH_{1-x}Ni(OH_2)_4[Ru_2(CO_3)_4]\cdot zH_2O$ (CCDC No. 624560). This material is available free of charge via the Internet at http://pubs.acs.org.

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