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$MH_2P_2O_7$ (M = Co, Ni): Metamagnetic Interaction between the Zigzag Octahedral Chains

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$CoH_2P_2O_7$ and $NiH_2P_2O_7$, which contain edge-sharing zigzag octahedral chains, were hydrothermally synthesized and structurally characterized. Both compounds exhibit field-induced metamagnetic behavior because of the strong intrachain ferromagnetic and relatively weak interchain antiferromagnetic interactions.

An extraordinarily large number of phosphates have been characterized during the past 2 decades, initiated by the discovery of the vast structural variety in aluminum phosphates[1] (1982) and zinc phosphates[2] (1991). Phosphates containing transition metals are particularly interesting because of their potential applications as cathodes for lithium batteries,[3] proton conductors,[4] and heterogeneous catalysts.[5] On the other hand, the complex structures of the transition-metal phosphates have also been used to trace the magnetic interaction of transition-metal ions. In many cases, iron,[6] manganese,[7] cobalt,[8] nickel,[8b,9] and chromium ions[10] are octahedrally coordinated in phosphates and could form an oligomer, a chain, or a layer via corner- or edge-sharing. The interaction between the transition-metal ions may lead to metamagnetic behavior under certain conditions, such as a field-induced antiferromagnetic (AF) to ferromagnetic (FM) transition in MIL-38[6e] and field-induced spin flip in $SrFe_2(PO_4)_2$.[6f] Here we report two new transition-metal phosphates, $CoH_2P_2O_7$ (**1**) and $NiH_2P_2O_7$ (**2**). The intra- and interchain magnetic interactions lead to interesting field-induced effects in these compounds.

1 and **2** ($MH_2P_2O_7$; M = Co, Ni)[11] are isostructural, crystallizing in $P2_1/c$, as shown in Table 1. An asymmetric unit contains 2 M, 4 P, and 14 O, all located in the general positions. The transition-metal ions are octahedrally coordinated by O atoms, which share two edges, forming a zigzag chain. The P atoms are tetrahedrally coordinated in a polyphosphate P_2O_7 group, which further shares corners with the octahedra via two kinds of 3-rings, i.e., the 3-ring of two octahedra and one tetrahedron and of one octahedron and two tetrahedra (Figure 1a). The bond distances and angles in **1** and **2** are all regular, as in other known phosphates. For example, bond distances and angles in **1** range from 1.973(3) to 2.166(3) Å and from 77.80(11) to 99.49(11)° for the CoO_6 octahedron and from 1.485(3) to

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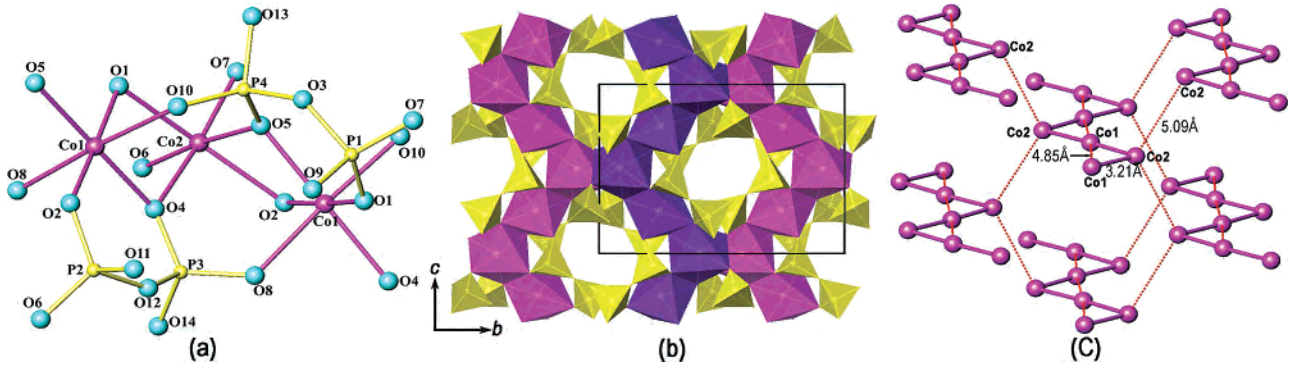

Figure 1. (a) Structure fragment of $CoH_2P_2O_7$. (b) Projection view along the *a* axis. All of the H atoms are omitted for clarity. (c) Transition-metal ion backbone of **1**. A stick line represents the distance between Co1−Co2 in 3.14 Å. Dotted lines represent the distance between Co1−Co1 in 4.85 Å and Co2−Co2 in 5.09 Å.

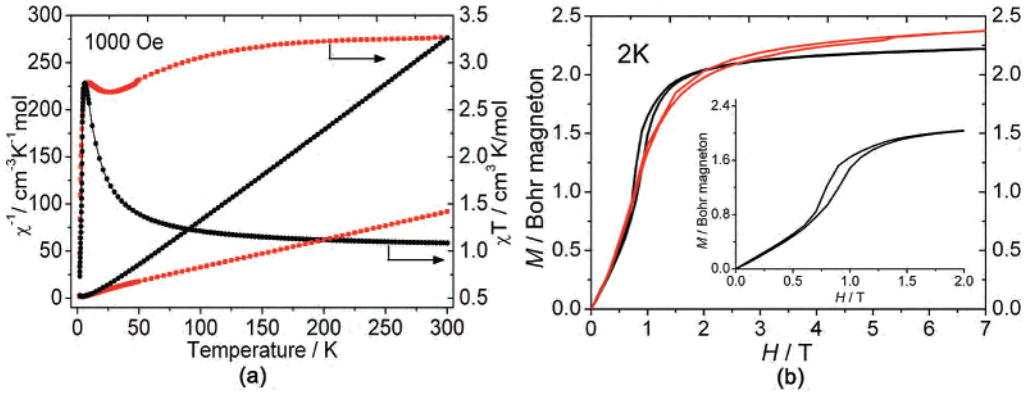

Figure 2. (a) χ_M^{-1} and $\chi_M T$ vs temperature curves of $CoH_2P_2O_7$ (**1**, red) and $NiH_2P_2O_7$ (**2**, black) at 1000 Oe. (b) Magnetization curves of $MH_2P_2O_7$ (M = Co, Ni) at 2 K. The inset is the amplification of a FM hysteresis loop of $NiH_2P_2O_7$.

Table 1. Crystallographic Parameters for Title Compounds

formula	$CoH_2P_2O_7$	$NiH_2P_2O_7$
fw	234.88	234.67
space group	$P2_1/c$	$P2_1/c$
a (Å)	9.1658(18)	9.0960(18)
b (Å)	12.681(3)	12.593(3)
c (Å)	9.6882(19)	9.5999(19)
β (deg)	106.74(3)	106.47(3)
V (Å^3)	1078.3(4)	1054.5(4)
ρ_{calcd} (g/cm^3)	2.894	2.956
μ(Mo Kα) (mm^{-1})	3.753	4.263
R1	0.0454	0.0320
wR2	0.1665	0.1128

1.605(3) Å and from 98.40(17)° to 115.51(18)° in the P_2O_7 group. The calculated bond valence sums (BVSs) of the metal atoms are all close to 2 [BVS = 2.034 (Co1), 2.022 (Co2), 1.997 (Ni1), and 1.981 (Ni2)]. However, the BVS values of some O positions are significantly lower [O9 (1.1), O11 (1.2), O13 (1.1), and O14 (1.1)], indicative of a possible binding with protons. In IR spectra, two broad bands at about 2915 and 3392 cm^{-1} were observed, originating from the vibration of the OH groups. Dehydration of the hydroxyl groups occurs at about 400 °C, accompanied by a weight loss of about 7.0 wt % (calcd 7.7 wt %).

The MO_6 octahedral zigzag chains are running along the *c* axis in the structure, as shown in different colors in Figure 1b for clarity, and are further interconnected through P_2O_7 groups, forming a three-dimensional structure. Although the structure is three-dimensional and, in addition, contains small intersectional 10- and 8-ring channels along the *a* and *c* axes, respectively, the magnetic interaction of the transition-metal ions should be one-dimensional as far as the M−M distances are concerned. The shortest M−M distance is 3.21 Å for Co (**1**) and 3.14 Å for Ni (**2**) within the octahedral chain and 5.09 Å for Co and 5.06 Å for Ni between the chains. In Figure 2c, we show the arrangement of the transition-metal atoms in the structure. Interestingly, this zigzag octahedral chain is quite stable, which may persist in the dehydration products of **1** and **2**. The dehydration products of **1** and **2**

(11) Synthesis: 2 mmol of $M(CH_3COO)_2{\cdot}H_2O$ (M = Co, Ni) and 3 mL of concentrated H_3PO_4 (14.6 mol/L) were charged into a 50-mL Teflon reactor and heated at 220 °C for 4 days. After cooling to room temperature, the solid products were isolated by washing with alcohol or cold water. $CoH_2P_2O_7$ is not stable in hot water. The single crystals are purple for Co and green for Ni. The yield of the product is about 80% according to the transition metal. Other transition-metal resources such as divalent metal chlorides or nitrates are also effectual. Analyses: crystals of $CoH_2P_2O_7$ of about 0.2 × 0.2 × 0.3 mm^3 were used for single-crystal data collection at 293 K on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) by the $\omega-2\theta$ scan method. The structure was solved by using direct methods and refined on F^2 with full-matrix least-squares methods using *SHELXS-97* and *SHELXL-97* programs.[15] A total of 2005 reflections were measured in 2.32° < θ < 25.50°. Magnetic measurements were carried out on a superconducting quantum interference device magnetometer (SQUID, Quantum Design Co.) in the temperature range from 2 to 300 K under an applied field *H* of 1000 Oe. The magnetization curves were measured at 2 K up to *H* = 7 T. Chemical analysis was carried out using an inductively coupled plasma method on an ESCALAB2000 analyzer (Co:P = 1.0:2.1; Ni:P = 1.0:2.0). The thermal stability was analyzed with thermogravimetric analysis (TGA) on a Dupont 951 thermogravimetric analyzer in air with a heating rate of 10 °C/min from 30 to 800 °C. IR spectra (Nicolet Magna-IR-750 series II) confirm the presence of hydroxyl groups.

are the known transition-metal cyclotetraphosphates[12] $Ni_2P_4O_{12}$ and $Co_2P_4O_{12}$. Their structures consist of the zigzag octahedral chains, but they are interconnected by $[P_4O_{12}]^{4-}$ groups instead of $[H_2P_2O_7]^{2-}$ as in **1** and **2**.

The magnetic susceptibility follows Curie−Weiss law at high temperature with $C = 3.3$ cm^3·K/mol and $\theta = -9.4$ K for **1** and $C = 1.1$ cm^3·K/mol and $\theta = 10.9$ K for **2**, corresponding to $\mu_{eff} = 5.1\ \mu_B$ and $3.0\ \mu_B$, respectively (Figure 2a). The observed effective magnetic moment of **2** agrees with the spin-only Ni^{2+} (d^8; $\mu_{cal} = 2.82\ \mu_B$ for $S = 1$) system. For the Co system, however, the observed effective moment is higher than the spin-only value (d^7; $\mu_{cal} = 3.87\ \mu_B$ for $S = {}^3/_2$) owing to the strong spin−orbit coupling in the Co system.[13]

The positive Weiss constant of **2** and an increase of $\chi_M T$ from 40 to 6 K imply a predominant FM interaction within the chains in this temperature range. The sharp decreases in the χT curves below 6 K indicate a long-range AF ordering, and T_N is about 4 K estimated from the $d(\chi_M T)/dT$ curve. According to the structure of the metal sublattice (Figure 1c), it is presumed that the FM coupling originates from intrachain Ni^{2+}−O−Ni^{2+} interaction, while the low-temperature AF ordering may originate from the antiparallel alignment of these FM chains through Ni2−O−P−O−Ni2 interchain superexchange. Additionally, the magnetization plot of **2** exhibits a sigmoidal shape and a large hysteresis loop at a high external field (0.7−1.5 T; Figure 2b). These phenomena are characteristic of metamagnetism, which can also be understood by the above assumption. Under a high external field (>0.90 T) at low temperature, the FM chains switch from mainly an antiparallel setting to mainly a parallel setting, which leads to a FM ordering at a high external field as indicated by the hysteresis loop. The saturation magnetization at 7 T is about $2.2\ \mu_B$, slightly larger than the theoretical value of $2\ \mu_B$. This compound might be an interesting example in which the metamagnetism originated from the coexistence of strong intrachain FM and relatively weak AF interchain couplings. Comparatively, a similar field-induced magnetic transition was also observed for $[Co_3(pyz)(HPO_4)_2F_2]$,[8c] where the magnetic interaction is FM within the layer and AF between the layers.

The magnetic susceptibility ($\chi_M T$) of **1** behaves differently, as shown in Figure 2a. In the high-temperature range (>40 K), the $\chi_M T$ value decreases gradually as the temperature goes down. In addition, the Weiss constant θ has a negative value (−9.4 K). However, this does not definitely mean the magnetic interaction is AF within the octahedral zigzag chain but is rather due to the single-ion behavior of Co^{2+} ions as observed in some other Co-containing compounds, such as $Co[(N(CN)_2]_2$(pzdo) and $Co[(N(CN)_2]_2$(mpdo).[14] At low temperature (<28 K), $\chi_M T$ increases and exhibits a maximum at about 7.8 K and then decreases rapidly, indicating an AF ordering below this temperature. The magnetization curve at 2 K shows a behavior similar to that of **2** (Figure 2b). It increases linearly at low field and then shows a narrow magnetic hysteresis at a high external field. According to the present experimental evidence, we would rather assume that the magnetic interaction in **1** is similar to that in **2**. At low temperature, the AF coupling of the FM chains leads to an AF ground state. With an increase in the external magnetic field ($H_c = 0.85$ T), the FM chains tend to parallelly align, resulting in FM ordering. However, because of the strong spin−orbit coupling of Co^{2+} ions, the magnetic interaction might be more complicated. This needs to be further studied by other techniques, such as neutron diffraction, etc.

In conclusion, we illustrated that two hydrated transition-metal phosphates, $CoH_2P_2O_7$ (**1**) and $NiH_2P_2O_7$ (**2**), exhibit interesting magnetic properties. The structure of these two phosphates contains edge-sharing zigzag octahedral (MO_6) chains, which are interconnected by P_2O_7 groups and thus can be considered as quasi-one-dimensional, in particular, where magnetic interactions are concerned. These two compounds exhibit a field-induced metamagnetic behavior from an AF state to a FM state. The observed metamagnetic property can be understood by assuming strong intrachain FM and weak interchain AF interactions. A high magnetic field may therefore switch the orientation of the magnetic moment of the FM chains, which leads to a primarily FM ordering at a high magnetic field.

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Supporting Information Available: Crystal details in CIF format and IR, TGA, and $d(\chi T)/d(T)$ and $d(M)/d(H)$ curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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