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Honeycomb-like layered cobalt(II) phosphonate with $[O_2CCH(OH)PO_3]^{3-}$ as ligand: Hydrothermal synthesis, crystal structure, and magnetic properties

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Abstract

A new cobalt(II) phosphonate, $[enH_2]_{0.5}[Co(pa)(H_2O)] \cdot H_2O$ (**1**) (H_3pa = hydroxy-phosphono-acetic acid, $HO_2CCH(OH)PO_3H_2$; en = ethylenediamine), has been hydrothermally synthesized and structurally characterized. Compound **1** has a honeycomb-like layer structure which is composed of CoO_6 octahedra and μ_3-pa ligands with the protonated en and lattice water molecules stabilized between the layers. Magnetic studies indicate that **1** shows weak ferromagnetic behavior, spin-glass behavior, and metamagnetic behavior.

Keywords: Cobalt(II) phosphonate; Hydrothermal synthesis; Magnetic properties

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During the past three decades, metal phosphonates as a new class of inorganic–organic hybrid materials have attracted a great deal of research interest due to their structural diversity and many potential and practical applications [1,2]. Recently, increasing attention has also been paid to the magnetic properties of these materials in searching for new molecule based magnets [3–9]. Two strategies have been used for designing new metal phosphonates, including use of organic amine templates and adoption of multifunctional phosphonates (diphosphonates, or carboxyphosphonates, etc.). Now we have chosen a multifunctional phosphonate, pa, as a bischelating ligand to construct alternating chains of metal ions, as shown in Scheme 1. Within the chain, pa ligand should be able to mediate electronic effects between paramagnetic metal ions. Owing to predictable lack of compensation between individual spin moments through asymmetrical exchanging mode of pa, this chain may exhibit weak ferromagnetic character [10]. In addition, the phosphonate group of pa ligand can further interconnect these chains into a 2D structure, leading to stabilization of magnetic ordering. Herein, we report the hydrothermal synthesis [11], crystal structure and magnetic properties of a new metal-pa compound, $[enH_2]_{0.5}[Co(pa)(H_2O)] \cdot H_2O$ (**1**). As far as we are aware, compound **1** is the first example of metal-pa compound with organic amine template in the structure [12,13].

The single crystal X-ray analysis [14] reveals that **1** is composed of anionic layers of $[Co(pa)(H_2O)]_n^{n-}$, with charge-compensating $[enH_2]^{2+}$ cations and the lattice water molecules between the layers (Fig. 1). There are one crystallographically unique Co ion and one pa ligand in the asymmetric unit. Each Co(II) displays a distorted octahedral CoO_6 geometry, in which four oxygens (O1, O2A, O3, O4A) are provided by two pa ligands through two different O,O′-chelating modes (Fig. 2a), and the other two oxygens (O6B and O7) are afforded by the phosphonate group of the third pa and one water molecule, respectively. The Co–O bond distances [2.038(11)–2.169(12) Å] and the O–Co–O bond angles [73.30(4)–170.23(5)°] are similar in value to those observed in other CoO_6 of phosphonate compounds [15–17]. Each pa ligand acts in μ_3-pa mode, utilizing two

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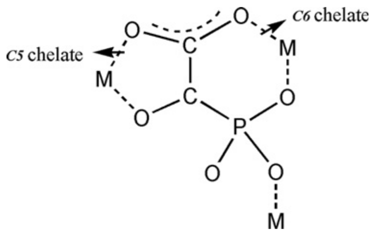

Scheme 1.

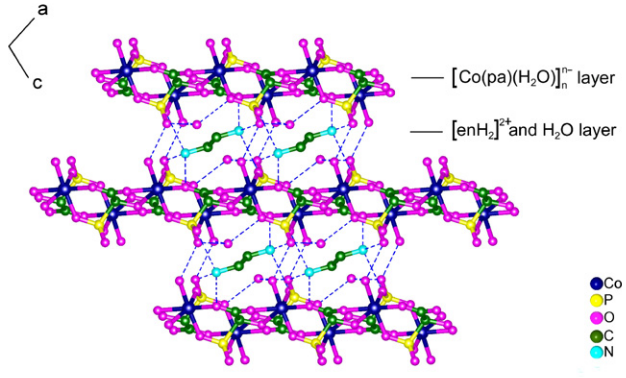

Fig. 1. The hydrogen bonds link the adjacent anionic layers into a 3D supramolecular structure in **1**. Dotted lines represent the various hydrogen bonding interactions. The hydrogen atoms are omitted for clarity.

carboxyl oxygens (O1 and O2), one hydroxyl oxygen (O3), as well as one phosphonate oxygen (O4) to chelate Co(II) ions to form a 1D Co-pa chain, and using the other phosphonate oxygen (O6) to link Co(II) ion from an adjacent chain, producing an infinite 2D $[Co(pa)(H_2O)]_n^{n-}$ layer. The significant structural feature of this 2D layer is that the connectivity between Co ions and μ_3-pa ligands results in a novel honeycomb-like (6, 3) net with two different sub-rings, i.e. 18-membered ring A and 8-membered ring B (Fig. 2b). The A-type ring is formed by four octahedral Co(II) ions, and two O–C–O bridges as well as two O–P–C–O bridges, where the Co···Co distances through O–C–O and O–P–C–O bridges are 5.903(3) and 5.876(4) Å, respectively. Two O–P–O bridges link a pair of cobalt centers to form B-type ring with Co···Co distance of 5.275(3) Å. An alternative way of describing this 2D layer is that it is built up from the interlocking motifs (A + B) through sharing of cobalt atoms.

These anionic layers are arranged in AAA fashion. A calculation using the *PLATON* [18] program shows that the opening size of the voids is 212.8 Å^3, corresponding to 24.9% of the total unit-cell volume. The $[enH_2]^{2+}$ cations and the lattice water molecules are located in the interlayer space via hydrogen bonding interactions (N–H···O 2.773(2), 3.330(19) Å; O–H···O 2.693(2), 3.244(4) Å). Moreover, the terminal coordinated water oxygens (O7) also form strong interlayer hydrogen bonds with phosphonate oxygens (O5G) from the adjacent layer (O–H···O 2.692(18) Å). Thus, the $[Co(pa)(H_2O)]_n^{n-}$ layers are assembled into a 3D supramolecular structure by the extensive hydrogen bonding, where the shortest Co···Co interlayer distance is 7.750 (4) Å.

The temperature-dependent magnetic susceptibility of **1** was measured at a field of 1000 Oe in 2–300 K. Above 25 K, the magnetic behavior of **1** follows the Curie–Weiss law ($C = 3.63\ \mathrm{cm^3\ K\ mol^{-1}}$, $\theta = -26.2$ K), indicating a significant antiferromagnetic coupling between the Co(II) ions. The value of $\chi_m T$ at 300 K is 3.32 cm^3 K mol^{-1} per Co (II), which is much larger than the spin-only value (1.87 cm^3 K mol^{-1}) expected for a high-spin Co (II) ion (with $S = 3/2$) (Fig. 3). Upon cooling $\chi_m T$ first gradually decreases to a minimum value of 1.33 cm^3 K mol^{-1} at 7 K, then abruptly increases to a sharp maximum value of 1.78 cm^3 K mol^{-1} at 4 K, and finally decreases more rapidly on further cooling. The abrupt increase in $\chi_m T$ value below 7 K is characteristic of a weak ferromagnet, in which a predominantly antiferromagnetic phase possesses a small spontaneous magnetization due to the spin canting [19,20]. Further support for this comes from the $\chi_m T$ vs. T curves at different fields that show a pronounced field dependence of the low-temperature phase, i.e. the larger increase of $\chi_m T$ values at a small field (inset in Fig. 3) [19,21].

The temperature dependence of the ac susceptibility measurements show the same features (see Supporting information). The maximum of χ'_m (1 Hz) observed at $T_N = 4.3$ K confirms the occurrence of an antiferromagnetic phase transition. The presence of an out-of-phase signal χ''_m (1 Hz) at 3.3 K indicates that a canted antiferro-

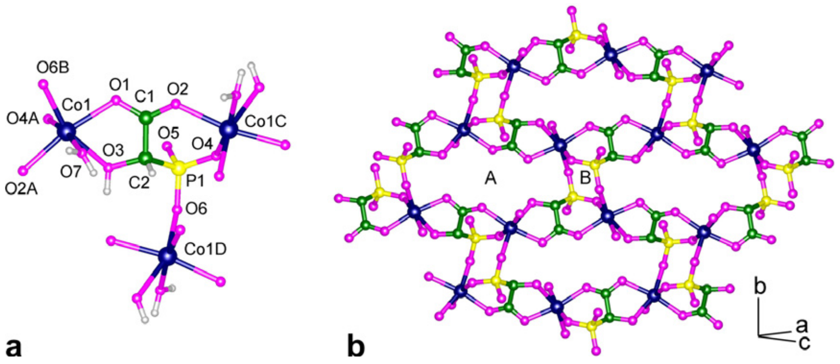

Fig. 2. (a) The coordination geometry of cobalt and μ_3-pa ligand. (b) View of one honeycomb-like layer of **1**, showing A-type ring and B-type ring.

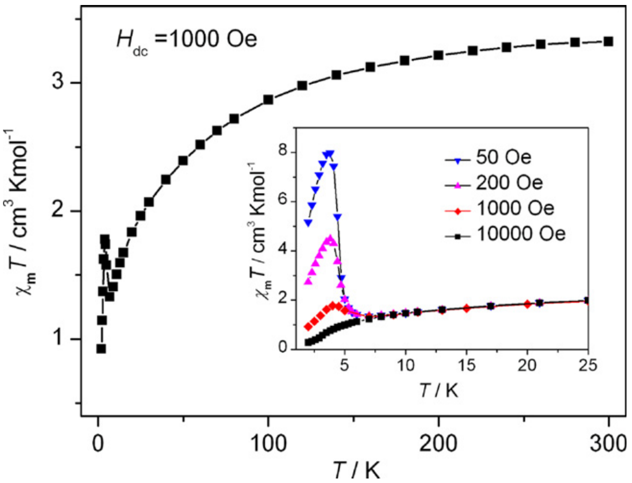

Fig. 3. The temperature dependence of $\chi_m T$ for **1** measured at 1000 Oe. Inset: $\chi_m T$ vs. T plots at different fields.

magnetic structure exists below this temperature [22]. In addition, the out-of-phase χ''_m components are frequency dependent, indicating either spin-glass or superparamagnetic behavior. A quantitative measure of the frequency shift of χ''_m is obtained from $\phi = \Delta T_p/[T_p\Delta(\log f)] = 0.04$, which is comparable to a spin-glass rather than a superparamagnet ($\phi > 0.1$) [23,24]. It should be noted that weak ferromagnetic ordering has been found in several metal phosphonates [4,5,19,25]. However, compound **1** shows the coexistence of spin-glass-like behavior, which is quite rare in metal phosphonate chemistry.

The field dependence of the isothermal magnetization at 2 K shows a sigmoidal curve, suggesting a metamagnetic behavior (see Supporting information). The critical field for such a metamagnetic transition is approximately 1.7 T at 2 K. The isotherm indicates clearly that the saturation is not reached even at 7 T. The occurrence of an obvious hysteresis loop at 2 K exhibits a small remnant magnetization (M_R) of ca. 0.025 μ_B and a coercive field (H_C) around 71 Oe. The spin canting angle α is estimated to be about 0.5° through $\sin(\alpha) = M_R/g\mu_B S$ [25,26].

The magneto-structural correlation indicates that the intralayer antiferromagnetic interactions between Co(II) ions can be mediated through the O–C–O as well as O–P–O bridges. However, a primarily antiferromagnetic phase exhibits a weakly ferromagnetic state below T_N that is due to the canting of spins. The single-ion anisotropy usually causes spin canting, and therefore high-spin octahedral Co(II) with large spin–orbit coupling due to its $^4T_{1g}$ ground term is a good candidate for canting effect of this system. On the other hand, the antisymmetric Dzyaloshinsky–Moriya interaction between different single ion anisotropies is also responsible for the canting in **1** [27–29]. The interlayer dipolar coupling mediated by hydrogen bonding should be considered as the driving force leading to the canted antiferromagnetic state of **1**. In addition, such dipolar coupling, along with strong metal anisotropy from single ions arranged in the chains may play a cooperative role for the observed metamagnetic behavior of **1**. The origin of glassy behavior of **1** may derive from structural disorders or/and the different nearest-neighbor Co···Co interactions competing in the complex network topology. Consequently, bulk magnetic behavior of **1** is complex due to influence of single ion anisotropy, intra- and interlayer exchanges.

In summary, our present studies demonstrate that the pa ligand is a potentially powerful bridge, not only in constructing new metal phosphonate material with the honeycomb-like layer, but also in mediating magnetic couplings between metal ions via a DM mechanism. Owing to its novel structural features, this cobalt-pa compound exhibit interesting magnetic properties at low temperatures, such as weak ferromagnetic behavior, spin-glass behavior, and metamagnetic behavior.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.08.016.

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[11] A mixture of $Co(CH_3CO_2)_2 \cdot 4H_2O$ (1.5 mmol, 0.37 g), 50 wt% aqueous solution of H_3pa (4 mmol, 1.24 g), and H_2O (10 mL), adjusted by en to pH 4.5, was heated at 180 °C for 5 days in a 23 mL Teflon-lined autoclave. The pink crystals of **1** were obtained with 78% yield (based on Co). The powder XRD pattern of the crystals indicated that as-synthesized product was a new material; the pattern was entirely consistent with the simulated one from the single crystal X-ray diffraction (see Supporting information). Anal. Calc. for $C_3H_{11}CoNO_8P$ (%): C 12.91, H 3.97, N 5.02; found: C 12.89, H 3.84, N 4.91. IR (KBr, cm^{-1}): 3411 (vs), 3098 (vs), 2886 (w), 2817 (w),

1647 (s), 1573 (vs), 1539 (vs), 1454 (s), 1391 (m), 1350 (w), 1290 (s), 1191 (vs), 1074 (vs), 976 (s), 833 (m), 651 (s), 455 (m).

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[14] Crystal data for compound **1**: $C_3H_{11}CoNO_8P$, $M_r = 279.03$, monoclinic, space group $P2_1/n$, $a = 8.4216(7)$ Å, $b = 9.7851(8)$ Å, $c = 10.7969(8)$ Å, $\beta = 106.232(10)°$, $V = 854.26(12)$ Å^3, $Z = 4$, $D_{\text{calcd.}} = 2.170$ Mg/m^3, $\mu = 2.220$ mm^{-1}, $R_1 = 0.0233$, $wR_2 = 0.0559$ (for all data). A total of 5593 reflections were collected, of which 2028 ($R_{\text{int}} = 0.0155$) were unique. Intensity data were collected on a Bruker SMART CCD diffractometer equipped with a graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K using the $\omega - 2\theta$ scan technique. The structure was solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELXL-97. All non-hydrogen atoms were located from the initial solution and refined with anisotropic thermal parameters. The hydrogen atoms were positioned geometrically and refined with fixed isotropic thermal parameters. Complete crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC No. 260153) and may be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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