

Short communication

## A one-dimensional cobalt phosphonate showing field-induced magnetic transition

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A cobalt phosphonate  $[\text{Co}(\text{H}_2\text{L})(\text{H}_2\text{O})_2] \cdot 0.5\text{H}_2\text{O}$  (**1**) ( $\text{H}_4\text{L} = 5$ -phosphonomethylisophthalic acid) has been synthesized under hydrothermal conditions. It contains a novel double chain with the composition of  $\{\text{Co}_2(\text{H}_2\text{L})_2(\text{H}_2\text{O})_4\}_n$ , where edge-shared  $\{\text{CoO}_6\}$  octahedra are each bridged by  $\{\text{CPO}_3\}$  tetrahedra through corner-sharing. Magnetization measurements reveal that dominant antiferromagnetic interactions are mediated between the Co(II) centers and the compound experiences a field-induced magnetic transition at low temperature with  $H_c$  of ca. 23 kOe at 2 K.

The studies on structural-magneto correlations are necessary for the searching of new magnetic materials [1]. Octahedrally coordinated Co(II) with  $^4\text{T}_{1g}$  ground state is magnetically high anisotropic due to the spin-orbit coupling, which is sensitive to the crystal field [2]. So, the cobalt based coordination compounds have been received great attention in the field of magnetic materials [3]. Cobalt phosphonate showing rich structures that have been studied for the searching of single molecule magnet and ferromagnet [4]. Ladder-like cobalt phosphonates have been studied because these materials exhibit field-induced magnetic transitions that are similar to the quantum antiferromagnetic spin ladders [5]. The transition field and inter-chain couplings can be tuned by the introduction of different counterions and substitute groups on the bisphosphonate ligand [6].

With the aim at studying the correlation between the crystal structures and the magnetic properties of the ladder-like chain compounds, herein, we report the structures and magnetic properties of  $[\text{Co}(\text{H}_2\text{L})(\text{H}_2\text{O})_2] \cdot 0.5\text{H}_2\text{O}$  (**1**), where the isophthalic acid was introduced as the extender between the chains. The hydrothermal treatment of a mixture of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.088 g, 0.3 mmol),  $\text{H}_4\text{L}$  (0.050 g, 0.2 mmol), 5 mL  $\text{H}_2\text{O}$  and 5 mL  $\text{CH}_3\text{CN}$ , in a Teflon-lined autoclave at 120 °C for 72 h

resulted in the formation of the pink crystals of compound **1** as a monophasic material [7]. Thermogravimetric analysis shows a one-step weight loss (2.3%) in the temperature range 30–150 °C, corresponding to the removal of 0.5 lattice water molecule (calcd. 2.5%) (Fig. S1).

Compound **1** crystallizes in space group  $P\bar{1}$  [8]. Fig. 1 shows a fragment of the double chain with the atomic labeling scheme, which contains centrosymmetric dimer units of  $\text{Co}_2(\text{H}_2\text{L})_2(\text{H}_2\text{O})_4$ . In the double chain, each Co atom adopts a distorted octahedral coordination geometry with the four O atoms (O7, O5A, O6C, O6D) from four equivalent  $\text{H}_2\text{L}^{2-}$  ligands and two O atoms (O8, O9) from coordinated  $\text{H}_2\text{O}$ . The Co(1)—O bond lengths fall in the range of 2.076(1)–2.194(1) Å. These values are close to those in  $[\text{Co}(4\text{-pyHhedpH}) \cdot \text{H}_2\text{O}]$  [9].  $\text{H}_2\text{L}^{2-}$  acts as the bridging ligand to coordinate with three Co atoms through the O5, O6, and O7 atoms from phosphonate moieties. It is found that the carboxylic acid does not attend the coordination with Co atom, indicating the relative weaker coordination ability of carboxylate than phosphonate. The O6 atom serves as a  $\mu_3$  bridging ligand which links the two cobalt octahedra through edge sharing, forming infinite double chain along the [100] direction. In the chain, the legs are bridged by two phosphonate groups. Obviously, this structure is unique compared with  $[\text{Co}(4\text{-pyHhedpH}) \cdot \text{H}_2\text{O}]$  [9],  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Co}_2(\text{hedpH})_2 \cdot 2\text{H}_2\text{O}]$  [6a] and  $(\text{NH}_3\text{C}_6\text{H}_4\text{NH}_3)[\text{Co}_2(\text{hedpH})_2 \cdot \text{H}_2\text{O}]$  [10] in which the legs are bridged by four phosphonate groups. The Co...Co distance over the  $\mu_3$  bridge is 3.025 Å, those over the O—P—O bridges (along the leg and diagonal) are 4.567 and 5.472 Å for Co1...Co1B and Co1...Co1C, respectively. The Co1—O6C—Co1A bond angle is 92.4°, smaller than that in  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Co}_2(\text{hedpH})_2 \cdot 2\text{H}_2\text{O}]$  (98.79°). Each double chain is connected to its six equivalent neighbors through hydrogen bonds [O3...O2: 2.615(3) Å], thus forming a three-dimensional supramolecular network with small channels generated along the a-axis (Fig. 2).

Fig. 3 shows the temperature-dependent molar magnetic susceptibilities of compound **1** in a magnetic field of 1000 Oe. The effective magnetic moment at 300 K is  $3.20 \text{ cm}^3 \text{ K mol}^{-1}$ , higher than the expected spin-only value for one Co(II) ion ( $1.875 \text{ cm}^3 \text{ K mol}^{-1}$ ,  $S = 3/2$ ,  $g = 2$ ), attributed to the orbital contribution. The appearance of a peak at ca. 7 K in the  $\chi_M$  versus  $T$  plot, indicates the antiferromagnetic ordering (Fig. 4). Below 7 K,  $\chi_M$  drops sharply toward zero, suggesting that the ground state of system is  $S = 0$ . When the external field is increased, the peak in the  $\chi_M$  vs  $T$  curves disappears above 30 kOe (Fig. 3, inset), suggesting the occurrence of a field-induced magnetic transition. Considering that the shortest Co...Co distance between the chains is 8.88

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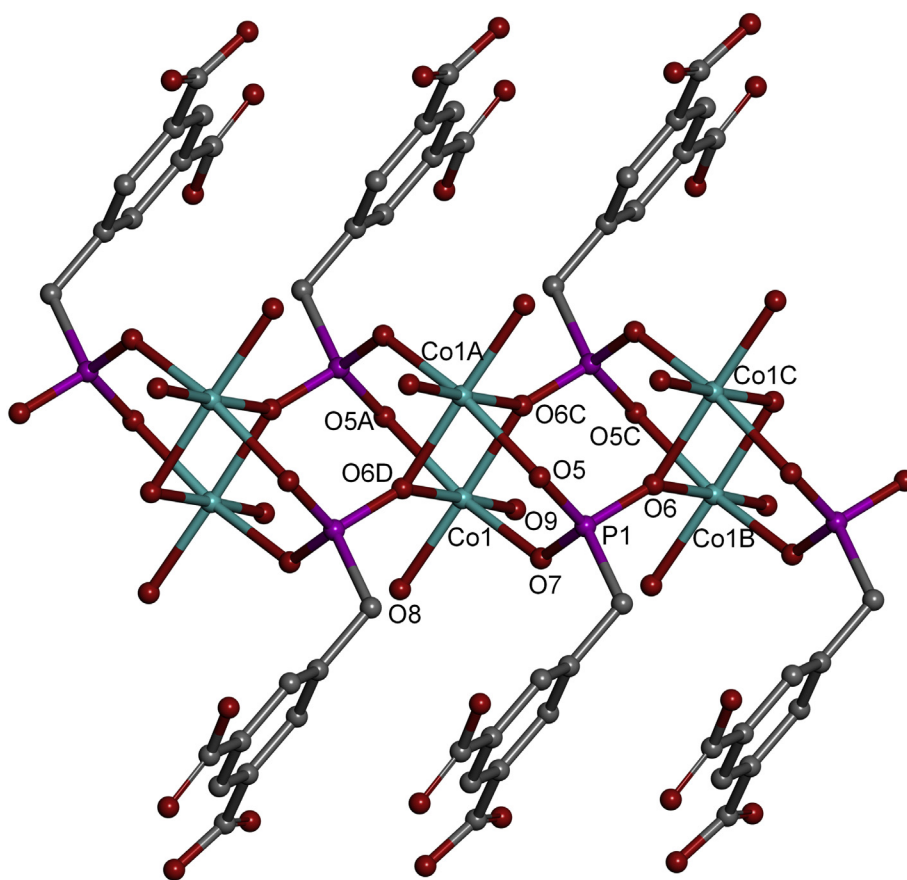


Fig. 1. Fragment of the chain with atomic labeling scheme in compound 1.

Å, the antiferromagnetic exchange coupling should be mainly propagated between the Co(II) centers within the ladder-like chain through  $\mu$ -O and/or O—P—O bridges. As the Co···Co distance over the  $\mu_3$ -O(6)

bridge is much shorter than those over O—P—O bridges, the exchange through  $\mu_3$ -O(6) bridge should be dominant. The susceptibility data were thus analyzed by a dimer model for two  $S = 3/2$  ions based on

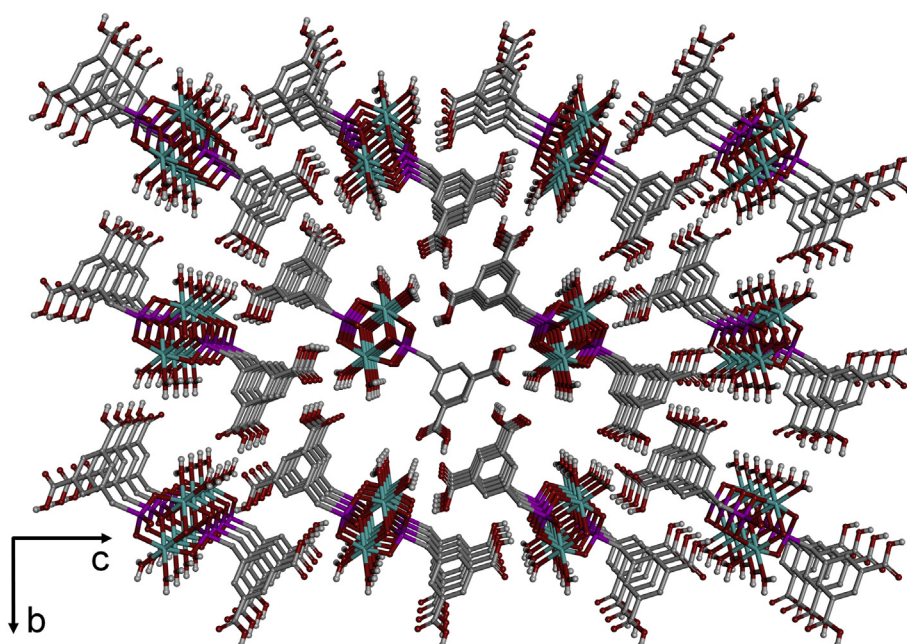


Fig. 2. Packing diagram of compound 1 viewed along the a-axis.

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