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A two-step field-induced magnetic transition in a novel layered cobalt diphosphonate†

Ping Yin,[a] Song Gao,[b] Li-Min Zheng,*[a] Zheming Wang[b] and Xin-Quan Xin[a]

[a] *State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, Nanjing 210093, P. R. China*

[b] *State Key Laboratory of Rare Earth Materials and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China*

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Compound $Na_6Co_7(hedp)_2(hedpH)_4(H_2O)_4\cdot 8H_2O$ (hedp = 1-hydroxyethylidenediphosphonate) with a novel layer structure is reported in this paper. The layer maybe viewed as made up from two types of chains each of composition $Co_3(hedp)_2$ and $Co_2(hedpH)_2$. Magnetic measurements at 1.8 K reveal a metamagnetic transition at *ca.* 6.5 kOe, followed by a second transition to a ferromagnetic state at *ca.* 30 kOe.

Metal phosphonate materials are of great interest owing to their potential applications in ion exchange, sorption and catalysis.[1] Recently, increasing attention has also been paid to the magnetic properties of these materials in searching for new molecule based magnets.[2–6] Our interest in both the structures and magnetic properties of transition metal diphosphonates, based on 1-hydroxyethylidenediphosphonate [hedp, $CH_3C(OH)(PO_3)_2$], has resulted in several Cu-hedp compounds with metamagnetism.[7] In this paper, we report the synthesis and structure of $Na_6Co_7(hedp)_2(hedpH)_4(H_2O)_4\cdot 8H_2O$ (**1**) which bears not only a novel layered structure with ion exchange capabilities but also a unique field induced magnetic behavior.

Compound **1** was made by hydrothermal reaction of a mixture of $CoCl_2$, $hedpH_4$, pyrazine, NaOH and H_2O in a molar ratio of 1 : 2.6 : 2 : 10 : 444 (pH = 5.58) at 140 °C for 2d.[8] The purple red crystals were collected as a single phase, judged by powder X-ray diffraction measurement. Yield: 39.9% based on Co. The presence of pyrazine, which may serve as a template, is essential to the crystallization of the title compound. Single crystal X-ray diffraction analysis‡ revealed a layer structure of cobalt phosphonate, with the sodium ions and water molecules locating between the layers. Within the layer, four types of cobalt atoms are crystallographically distinguished (Figure 1). The Co(1) atom occupies an inversion center while the other three occupy general positions. Each Co atom has a distorted octahedral coordination environment. The $Co(1)O_6$ and $Co(2)O_6$ octahedra are each corner-shared with CPO_3 tetrahedra and are bridged by equivalent $hedp^{4-}$ groups in an alternative way, forming an infinite chain of $\{Co_3(hedp)_2\}_n$ (chain I). The $Co(3)O_6$ and $Co(4)O_6$ octahedra are edge-shared, each of which is chelated and bridged by $hedpH^{3-}$ groups, thus resulting in a double chain of $\{Co_2(hedpH)_2\}_n$ (chain II) (Figure 1). Chain II may be compared to those in several M-hedp compounds with composition $[NH_3(CH_2)_nNH_3]M_2(hedpH)_2\cdot 2H_2O$ (M = Fe, Mn, Zn).[9] The two types of chains are fused together, alternately, by corner-sharing of $Co(2)O_6$ octahedra from chain I with the CPO_3 tetrahedra from chain II, leading to a two-dimensional layer of $\{Co_7(hedp)_2(hedpH)_4(H_2O)_4\}_n^{6n-}$ in approximately [011] direction (Figure 1). The shortest Co···Co distances are 4.655 Å [Co(2)···Co(2B)] within chain I, 3.243 Å [Co(3)···Co(4)] within chain II, and 5.280 Å [Co(2)···Co(3)] between chains I and II, respectively. Three crystallographically different hedp groups are found in the layer. One ($hedp^{4-}$) bridges the Co(1) and Co(2) atoms into chain I, using five of its six phosphonate oxygens and one hydroxy oxygen. The sixth phosphonate oxygen [O(6)] is terminal. The other two ($hedpH^{3-}$) bridge the Co(3) and Co(4) atoms into chain II. All the phosphonate oxygens in $hedpH^{3-}$, except O(10), O(12) and O(16), are coordinated to Co atoms within chain II or between chains I and II [O(18)]. The O(12) and O(16) are protonated [P(4)–O(12): 1.560(4), P(5)–O(16): 1.576(4) Å]. These two as well as the terminal phosphonate oxygens [O(6), O(10)] are involved in the extensive hydrogen bonds in the lattice, thus resulting in a three-dimensional network structure. The shortest O···O contact between the layers is 2.536(6) Å for O(12)···O(6).

The anionic layer is charge-balanced by sodium cations locating between the cobalt phosphonate layers. There are three crystallographically distinguished sodium atoms, each is co-ordinated by up to seven oxygens either from the phosphonate groups or from lattice water at less than 2.80 Å. Neighboring

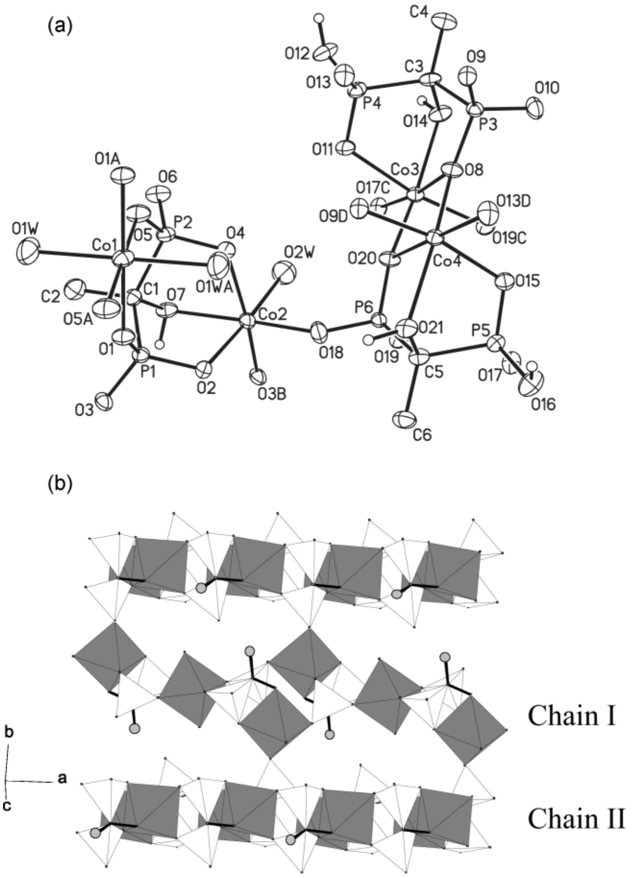

Fig. 1 (a) Coordination geometries of cobalt in compound **1** with the atomic labeling scheme. Thermal ellipsoids are at the 50% probability level. Symmetry codes: A, −x, −y+1, −z+1; B, −x+1, −y+1, −z+1; C, −x+1, −y, −z+2; D, −x, −y, −z+2. (b) Polyhedral representations of one layer of the structure of **1**.

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† Electronic supplementary information (ESI) available: experimental details and Figures S1–S10. See http://www.rsc.org/suppdata/cc/b2/b212674e/

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Na^+ ions are found at 3.83 Å distance within the inter-layer space. Preliminary results show that the Na^+ can be exchanged by K^+, NH_4^+ and Ca^{2+} ions with preservation of the original crystal morphology.

The structure of compound **1** is unique compared with those of $Na_2Co(O_3PCH_2PO_3)\cdot H_2O$[10] and $Co_2(O_3PCH_2PO_3)(H_2O)$[11] in which methylenediphosphonate is involved. The former shows a layer structure where equivalent chains of $\{Co(O_3PCH_2PO_3)\}_n$ are linked together by corner-sharing of CoO_5 square pyramids and CPO_3 tetrahedra. In the latter, a purely inorganic framework is found with the organic moieties filling in the channel walls.

Figure 2 shows the temperature dependent molar magnetic susceptibilities of **1** at different magnetic fields.

The χ_M *vs* T curve measured at 1 kOe shows a sharp peak around 4.2 K, corresponding to an antiferromagnetic (AF) ordering at low field. The Neel temperature, determined by the peak of $d(\chi_M T)/dT$, is 3.6 K. The transition to an AF state is also suggested by the in phase of zero-field *ac* magnetic susceptibility $\chi_M'(T)$, which has a peak at *ca.* 4.0 K under $H_{ac} = 5$ Oe and frequencies of 111, 199, 355, 633 and 1111 Hz. No detected out-of-phase signal and frequency dependence was observed. The low-field AF ground state in compound **1** can be derived from antiparallel alignment of ferrimagnetic layers. The ferrimagnetism within the layer arises from the non-zero net magnetic moment due to the odd number of the antiferromagnetically interacted Co^{II} ions within the layer. The same phenomenon has been found in a few other homometallic systems with an odd number of interacting metal ions.[7,12] When the external field is increased, the peak in the χ_M *vs* T curve becomes broader and disappears above 30 kOe.

The magnetization of **1** at 1.8 K reveals a two-step magnetic phase transition in the field range 0–70 kOe (Figure 3). The first step occurs at *ca.* 6 kOe. The isothermal magnetization below 15 kOe has an S-shaped curve, typical for a metamagnetic transition from an antiferromagnetic state to a ferrimagnetic state. For Co^{II} ion in an octahedral environment, an $S = 1/2$ ground state is usually observed at low temperature because of the overall effect of crystal-field and spin-orbit coupling.[13] The ferrimagnetic layer of $\{Co_7(hedp)_2(hedpH)_4(H_2O)_4\}_n^{6n-}$ would result in one uncompensated $S = 1/2$ spin due to the antiparallel arrangement of spins, and a magnetization value of 2.1–2.5 $N\beta$ would be expected with $g = 4.1$–5.0.[12,14] This value is close to the observed value of 2.8 $N\beta$ at 12.5 kOe. Metamagnetism was also found in a cobalt phosphate compound with formula $Co_7(HPO_4)_4(PO_4)_2$.[15] The second step of the transition occurs at *ca.* 30 kOe. The magnetization is not saturated at 70 kOe. The value of 16.2 $N\beta$ per Co_7 unit is consistent with that (16.1 $N\beta$) calculated for seven Co^{II} ions with $S_{eff} = 1/2$ and $g = 4.6$, but much lower than that (17.5 $N\beta$) with $S_{eff} = 1/2$ and $g = 5.0$. The result indicates the transition from a ferrimagnetic state to a ferromagnetic state. With increasing field the alignments of spins along the opposite directions of the external field on one sublattice are flipped which could response to this transition. The *ac* measurements confirm the two critical fields of *ca.* 6.5 kOe and 30 kOe, respectively. The hysteresis loop at 1.8 K is typical for a soft ferrimagnet.

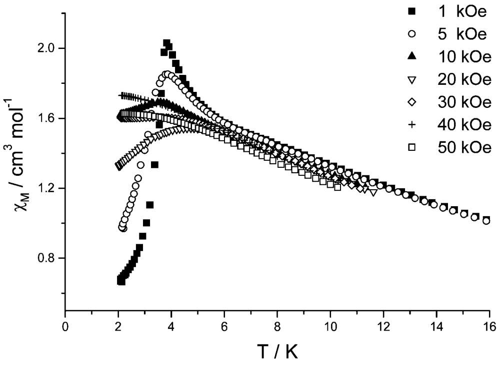

Fig. 2 Temperature dependent molar magnetic susceptibilities of **1** at different external fields.

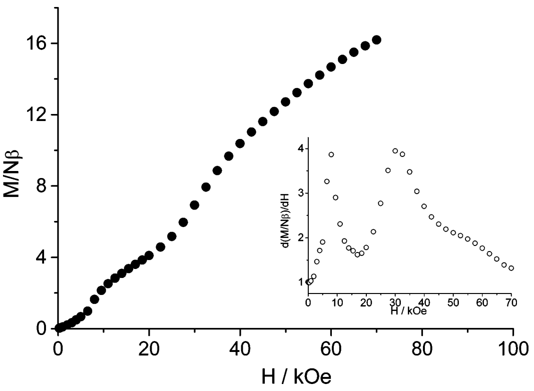

Fig. 3 Magnetization of **1** at 1.8 K. Inset: d(M/Nβ)/dH *vs* H curve.

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Notes and references

‡ *Crystal data*: $C_{12}H_{52}Co_7Na_6O_{54}P_{12}$, $M_r = 1982.63$, triclinic, $P\bar{1}$, $a = 10.712(2)$, $b = 11.203(2)$, $c = 12.311(3)$ Å, $\alpha = 73.62(3)$, $\beta = 86.29(3)$, $\gamma = 86.74(3)°$, $V = 1413.4(5)$ Å^3, $Z = 1$, $D_c = 2.329$ g cm^{-3}, μ(Mo-Kα) = 25.20 cm^{-1}, $F(000) = 991$, $\lambda = 0.71073$ Å, graphite monochromator. A crystal of dimensions 0.32 × 0.08 × 0.025 mm was selected for indexing and intensity data collection at 293 K. Unique reflections: 6346 ($R_{int} = 0.0714$). Least-squares refinements were based on F^2 and converged at $R_1 = 0.0488$, $wR_2 = 0.1187$. In the final Fourier-difference map the deepest hole was −0.811 eÅ^{-3}, the highest peak 1.996 eÅ^{-3} located at a special position (0.5, 0.5, 0.5) near O2 (1.684 Å).

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8 Elemental analysis: found (calcd.) for $C_{12}H_{52}Co_7Na_6O_{54}P_{12}$: C, 7.24 (7.26); H, 3.32 (2.62)%. IR (KBr, cm^{-1}): 3407br, 1639m, 1451w, 1375w, 1106s, 988s, 931m, 818w, 669w, 589m, 474w.

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