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Two cobalt monophosphonates: Syntheses, structures and magnetic properties

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ABSTRACT

Hydrolysis of diethyl 6-chloro-2-pyridinephosphonate in HCl solution affords 6-hydroxy-2-pyridine-phosphonic acid (H_2hppa 1). In the structure, extensive hydrogen bonding interactions link the phosphonic acid molecules into a two-dimensional network. Reactions of H_2hppa and cobalt acetate under hydrothermal conditions result in a new cobalt phosphonate Co(hppa)(H_2O) (2). Compound 2 shows a layer structure, in which {Co_2O_2} dimers are connected through the corner-sharing of {CoO_5N} octahedra and {PO_3C} tetrahedra, forming an inorganic double-layer. Introduction of a second ligand (1,4-bis(imidazol-1-ylmethyl)benzene, L) in the reaction system, compound [Co(hppa)(L)$_{0.5}$(H_2O)]·H_2O (3) was obtained. In this structure, Co^{2+} ions are bridged by O–P–O bridges into an inorganic layer and the layers are pillared up by 1,4-bis(imidazol-1-ylmethyl)benzene. Magnetic study suggests that the existence of weak ferromagnetic coupling between Co^{2+} ions in the {Co_2O_2} unit for 2. For compound 3, O–P–O bridges mediate very weak antiferromagnetic interactions.

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1. Introduction

Molecule-based magnets have attracted considerable attention for their impressive structural diversity and complicated magneto-structural correlations [1]. In contrast to the three atoms short bridges (formato [2], azido [3], cyano [4] and so on), phosphonate ligands have also become excellent candidates for active magnetic bridges [5]. Molecular magnetic coolants [6], single-molecule magnets [7], single-chain magnets [8], weak ferromagnetic [9], ferrimagnetism [10] etc. have been observed in metal phosphonates. Among the variety of metal phosphonates [11], cobalt phosphonates are rather important because the octahedrally coordinated Co^{II} with $^4T_{1g}$ ground state is magnetically high anistropic due to spin–orbit coupling, which lead to very interesting magnetic behavior [12].

The magnetic properties of cobalt phosphonates may be tuned by such as dehydration-hydration process [13], a controllable second metal coordination sphere [14], or adding a second ligand [15]. Phosphonate attached organic groups can influence the structures of cobalt phosphonates, hence tune the magnetic properties. Cobalt alkyl/aryl monophosphonate with cage-like structures show single-molecule magnet behavior [16]. Cobalt naphthylphosphonate with a chain-like structure shows polarity and weak ferromagnetism [17]. Cobalt thienylphosphonate with layer structure

experiences long-range ferromagnetic ordering. The systematic study on the size-dependent magnetic coercivity of the compound reveals that the coercivity increases with reduced particle size from micrometer to the nanometer scale [18]. Cobalt imidazole diphosphonate with layer structure shows canted antiferromagnetism [19].

There are some cobalt phosphonate compounds reported during the past several years which contain pyridyl groups. Mononuclear [Co($C_6H_4NO_5P$)(H_2O)$_3$]·H_2O is formed when 6-phonopyridine-2-carboxylic acid is allowed to react with cobalt salt [20]. A double chain structure [Co(hpyedpH)(H_2O)] and a layer structure [Co_3(hpyedpH)$_2$(H_2O)$_4$] are built based on hpyedpH$_4$ = 1-hydroxy-2-(3-pyridyl)ethylidene-1,1-diphosphonic acid [10,21]. Layer structures Co(4-$C_5H_4NPO_3$)(H_2O)$_3$[22], Co{(4-C_5H_4N)CH(OH)PO_3}(H_2O) [23] and Co(2-pmp)(H_2O)$_2$[13] have been prepared by using 4-pyridylphosphonate, 4-pyridylmethylphosphonate and 2-pyridylmethylphosphonic acid (2-pmpH_2), respectively. Co(2-pmp)(H_2O)$_2$ shows reversible changes in structures upon dehydration-hydration process. By using 6-phonopyridine-3-carboxylic acid as ligand, a 3D framework structure embedded ferrimagnetic inorganic chains is formed [15]. Clearly, the formation of a particular structure is dependent not only on the substitution position of pridyl groups but also the involvement of additional functional groups.

In this paper, we select 6-hydroxy-2-pyridinephosphonic acid (H_2hppa) (1) to react with cobalt salt under hydrothermal conditions, and investigate the effect of the additional OH group on

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the structures of the final products. Two compounds with formula Co(hppa)(H$_2$O) (**2**) and [Co(hppa)(L)$_{0.5}$(H$_2$O)]·H$_2$O (**3**) (L = 1,4-bis(imidazol-1-ylmethyl)benzene) are isolated and crystallographically and magnetically characterized.

2. Experimental

2.1. Materials and methods

All the starting materials were reagent grade and were used as purchased. 1,4-bis(imidazol-1-ylmethyl)benzene was prepared according to the literature method [24]. Elemental analyses were performed on a PE 240C elemental analyzer. The IR spectra were recorded on a NICOLET 380 spectrometer with pressed KBr pellets. All the magnetic studies were performed on microcrystalline state. The magnetic susceptibilities were measured on a Quantum Design MPMS SQUID-XL7 magnetometer. Diamagnetic corrections were made for both the sample holder and the compound estimated from Pascal's constants [25].

2.2. Synthesis of 6-hydroxy-2-pyridinephosphonic acid (H$_2$hppa) (1)

Dimethyl sulfate (6.3 g, 0.05 mol) was added to 2-chloropyridine N-oxide (6.48 g, 0.05 mol) slowly at room temperature with stirring. After the initial exothermic reaction had occurred, the solution was stirred for 2 h at 60 °C. The syrup product was added with stirring over 0.5 h to a solution of sodium hydride (1.20 g, 0.05 mol) in diethyl phosphite (30 g), keeping the temperature below 20 °C. The mixture was allowed to warm to room temperature and stirred overnight. Water (25 mL) was added and the solution was extracted with chloroform (3 × 50 mL); the organic phase was then extracted with 4 mol L^{-1} HCl (2 × 50 mL) which was neutralized and extracted with chloroform. The chloroform solution was dried and evaporated in vacuum to a brown oil which gave a faintly yellow liquid chromatographed on silica gel (ethyl acetate as eluent). The diethyl ester was acidified with HCl (20%) for ca. 12 h at 100 °C to yield a clear solution. White solid of H$_2$hppa (**1**) was obtained by evaporation of the solution and recrystallized from water. Mp. 258–260 °C. Main IR absorption bands (cm^{-1}): 3451 vs 1627 s, 1547 m, 1397 s, 1355 m, 1214 m, 1153 s, 1096 s, 940 s, 813 m, 729 m, 682 m, 545 s, 510 s. Elemental *Anal.* Calc. for C$_5$H$_6$NO$_4$P: C, 34.30; H, 3.45; N, 8.00. Found: C, 34.05; H, 3.20; N, 8.23%.

2.3. Synthesis of Co(hppa)(H$_2$O) (2)

A mixture of Co(CH$_3$CO$_2$)$_2$·4H$_2$O (0.0249 g, 0.1 mmol) and H$_2$hppa (0.0175 g, 0.1 mmol) was placed in a glass tube containing 2 mL of deionized water. The glass tube was sealed, heated at 160 °C for 2 days, and allowed to cool to room temperature. Pale purple crystals of Co(hppa)(H$_2$O) (**2**) were obtained in 65% yield (based on Co). IR (KBr, cm^{-1}): 2885 bs, 1610 s, 1566 s, 1434 vs 1311 s, 1226 s, 1102 vs 1001 s, 917 m, 852 s, 800 s, 745 m, 696 m, 594 s, 537 m, 483 m. Elemental *Anal.* Calc. for C$_5$H$_6$CoNO$_5$P: C, 24.02; H, 2.42; N, 5.60. Found: C, 23.80; H, 2.15; N, 5.33%.

2.4. Synthesis of [Co(hppa)(L)$_{0.5}$(H$_2$O)]·H$_2$O (3)

A mixture of Co(CH$_3$CO$_2$)$_2$·4H$_2$O (0.0249 g, 0.1 mmol), H$_2$hppa (0.0175 g, 0.1 mmol) and L (L = 1,4-bis(imidazol-1-ylmethyl)benzene) (0.0238 g, 0.1 mmol) was placed in a glass tube containing 2 mL of deionized water, the pH was adjusted to 12. The glass tube was sealed, heated at 160 °C for 2 days, and allowed to cool to room temperature. Pink crystals of [Co(hppa)(L)$_{0.5}$(H$_2$O)]·H$_2$O (**3**) were obtained in 35% yield (based on Co). IR (KBr, cm^{-1}): 3422

bs, 1640 s, 1604 m, 1570 m, 1441 s, 1317 m, 1089 vs 994 s, 800 s, 791 m, 735 m, 594 m, 478 w. Elemental *Anal.* Calc. for C$_{12}$H$_{15}$CoN$_3$O$_6$P: C, 37.23; H, 3.91; N, 10.85. Found: C, 37.60; H, 3.61; N, 10.53%.

2.5. Crystallographic studies

Single crystals with dimensions 0.3 × 0.25 × 0.2 mm^3 for **1**, 0.25 × 0.22 × 0.2 mm^3 for **2** and 0.30 × 0.25 × 0.2 mm^3 for **3** were selected for indexing and intensity data collection on a Rigaku SCX mini CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. A hemisphere of data were collected in the θ range 3.15–27.48° for **1**, 3.02–26.00° for **2** and 3.11–25.00° for **3** using a narrow-frame method with scan widths of 0.03° in ω and an exposure time of 10 s frame^{-1}. Numbers of observed and unique reflections are 6622 and 1515 (R_{int} = 0.0359) for **1**, 6605 and 1471 (R_{int} = 0.0332) for **2** and 6442 and 2615 (R_{int} = 0.021) for **3**. Cell parameters were refined by using the program *CrystalClear* [26] on all observed reflections. The collected data were reduced by using the program *CrystalClear*, and an absorption correction (multi-scan) was applied. The reflection data were also corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined on F^2 by full matrix least squares using SHELXTL [27]. H atoms bound to O and N atoms were located in a difference Fourier map. All the non-hydrogen atoms were located from the Fourier maps, and were refined anisotropically. All H atoms were refined isotropically, with the isotropic vibration parameters related to the non-H atom to which they are bonded. Crystallographic and refinement details of **1–3** are listed in Table 1. Selected bond lengths and angles are given in Tables 2 and 3 for **2** and **3**.

3. Results and discussion

3.1. Syntheses

Hydrohalic acids have been proved to be useful reagent in the hydrolysis of diethyl phosphonate [28]. Refluxing diethyl 6-chloro-2-pyridinephosphonate in the aqueous hydrochloric acid give H$_2$hppa. The in situ formation of hydroxypyridine indicates

Table 1
Crystallographic data for **1**, **2** and **3**.

	1	**2**	**3**
Formula	C$_5$H$_6$NO$_4$P	C$_5$H$_6$CoNO$_5$P	C$_{12}$H$_{15}$CoN$_3$O$_6$P
M	175.08	250.01	387.17
Crystal system	monoclinic	monoclinic	triclinic
Space group	P2$_1$/n	P2$_1$/c	P$\bar{1}$
a (Å)	7.3808(15)	14.142(3)	5.1953(10)
b (Å)	7.0347(14)	5.3219(11)	10.530(2)
c (Å)	12.711(3)	10.330(2)	14.260(3)
α (°)	90	90	74.29(3)
β (°)	91.91(3)	107.30(3)	89.02(3)
γ (°)	90	90	82.30(3)
V	659.6(2)	742.3(3)	744.1(3)
Z	4	4	2
ρ$_{calc}$ (g cm^{-3})	1.763	2.237	1.728
μ (mm^{-1})	3.76	2.513	1.296
F(000)	360	500	396
R$_{int}$	0.0359	0.0332	0.0212
Goodness-of-fit GOF on F^2	1.007	1.018	1.004
R$_1$, wR$_2$ [$I > 2\sigma(I)$][a]	0.0374, 0.0978	0.0286, 0.0620	0.0351, 0.0935
R$_1$, wR$_2$ (all data)	0.048, 0.1036	0.0352, 0.0639	0.0394, 0.0965
(Δρ)$_{max}$, (Δρ)$_{min}$ (e Å^{-3})	0.389, −0.358	0.365, −0.315	0.554, −0.590

[a] ($R_1 = \sum||Fo| - |Fc||/\sum|Fo|$; $wR_2 = \{\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2\}^{1/2}$.