Hydrothermal synthesis and characterization of a layered cobalt phenylphosphonate, Co(PhPO₃)(H₂O)

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We report the hydrothermal synthesis and characterization of a layered cobalt phenylphosphonate. Unlike most metal phosphonates reported to date, the structure was solved by single crystal X-ray diffraction (SC-XRD). Co(II) centres are hexa-coordinated by oxygen and the octahedra corner-share into a layer. The layers are capped by phenylphosphonate groups, where the phenyl groups define a hydrophobic bilayer region. The material was also characterized by powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA) and SQUID (superconducting quantum interference device) magnetometry. The material undergoes an antiferromagnetic transition at a relatively low Néel temperature of 4.0 K, while the Curie–Weiss temperature of -76.5 K reflects the low-dimensionality of the magnetic structure. The effective magnetic moment of $5.01 \,\mu_B$ per Co²⁺ verifies a high-spin configuration and an octahedral coordination of the metal centres. This layered material was correctly predicted in the literature from powder data, adds to the structural diversity of the cobalt phosphonates, and may be useful as an intercalation or exfoliation compound.

Introduction

A large and important class of inorganic–organic hybrid compounds is the extended metal phosphonates. They are related to the inorganic metal phosphites and phosphates, where an organic functionality replaces a hydrogen or oxo group on the phosphorus, respectively. Metal phosphonates have been extensively studied due to their catalytic, ion exchange, sensor and nonlinear optical properties.^{1–8} Magnetic properties have also been described for transition metal phosphonates. For example, manganese phenylphosphonate revealed a canted antiferromagnetic interaction between the spin carriers.⁹ Iron phenylphosphonate exhibits long-range 3D antiferromagnetic ordering, coupled with weak ferromagnetic behaviour below its Néel temperature of 21.5 K.⁸

These materials are most frequently prepared by simple ambient crystallization¹⁻⁹ or solvothermal synthesis.^{6,9-11} The ease of preparing metal phosphonates is due to the strong interaction of phosphate with metalate species and therefore the tendency to polymerize.¹² If the organic group of the phosphonate is long, a layered structure is likely to form, with a bilayer or interdigitated hydrophobic interlamellar region. A small methyl group, on the other hand, tends to give rise to a framework structure, where the methyl groups point into unidimensional, hydrophobic channels.¹³ The wide range of possible phosphonate organic groups has not surprisingly led to a large variety of structure types, for many metals of the periodic table. Accordingly, our research has led to a series of layered phosphonate compounds. We reported several tin¹⁴ and lead¹⁵ phenylphosphonates, where the phosphonates bond to the metal centres of the layers and the phenyl rings point towards the interlamellar space. Of this series of compounds, one also contains pyridine solvent molecules of crystallization, which reside between the layers and increase the layer separation.¹⁵ A wide range of layered metal phenylphosphonates have been reported in the literature based on calcium,¹⁶ strontium,¹⁷ aluminium,¹⁸ uranium¹⁹ and transition metals, such as manganese,^{9,20} iron,⁸ cobalt,^{7,21} copper,²² zinc^{7,20-23} and zirconium.^{24,25}

Only synthesis under ambient conditions and computer simulation of the structure have been reported for many of these transition metal phenylphosphonates,²¹ as the crystals were not large enough for structure analysis. Herein we describe the synthesis, single crystal structure and thermal and magnetic characterization of one member of this isostructural series, the layered transition metal phenylphosphonate, Co(PhPO₃)(H₂O).

Experimental

Synthetic procedure

All reagents were used as-received and added sequentially to a 100 mL Nalgene beaker: (i) solvent (deionized water); (ii) Co source (CoCl₂·6H₂O, Sigma); (iii) phenylphosphonic acid (C₆H₃PO₃H₂, Alfa Aesar). The molar ratio of the reactants water, cobalt chloride hydrate and phenylphosphonic acid—was 50: 1: 1 (13.89 g: 2.43 g: 3.66 g), respectively. The resultant pink solution was mechanically stirred for 5 min until the reactants completely dissolved. The clear mixture was then placed in an 18 mL capacity Teflon-lined autoclave (home constructed) and heated statically between 125 and 175 °C for 3 to 5 days. The pink plate-like crystals were suction-filtered, rinsed with water and allowed to air-dry.

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Elemental analysis (Quantitative Technologies Inc., Whitehouse, NJ) of the as-synthesized product (30.89% C, 2.44% H) agrees well with the theoretical values (30.90% C, 3.03% H).

Characterization methods

PXRD was performed on a Scintag XDS 2000 diffractometer with Cu Ka radiation ($\lambda = 1.5418$ Å), solid-state detector, scan range 2° to 45° (2 θ), step size 0.02° and scan rate 4.0 °C min⁻¹. All samples were ground thoroughly in a mortar and pestle before mounting the resultant powder in the PXRD sample holder. TGA was performed on a TA Instruments 2950, with a 10 °C min⁻¹ scan rate and nitrogen purge. Magnetic measurements were obtained using a SQUID magnetometer (Quantum Design MPMS XL-5). The dc magnetic susceptibility was measured in a magnetic field *H* of 1000 Oe over the temperature range 2 to 298 K.

SC-XRD structure determination

The title compound (which we denote SLUG-4, for University of California, Santa Cruz, Structure No. 4) was determined by manually selecting a pink plate of approximate dimensions $0.24 \times$ 0.17×0.005 mm³. The X-ray intensity data were measured at 294(2) K on a three-circle diffractometer system equipped with a Bruker SmartApex CCD area detector, graphite monochromator and a Mo K α fine-focus sealed tube ($\lambda = 0.71073$ Å) operated

Table 1 Crystal data for Co(PhPO₃)(H₂O)^a

Empirical formula Formula weight Temperature Wavelength Crystal size Crystal shape Crystal system	C ₆ H ₇ Co O ₄ P 233.01 294(2) K 0.71073 Å $0.24 \times 0.17 \times 0.005 \text{ mm}^3$ Pink plate Orthorhombic <i>Brun</i> ?
Unit cell dimensions	$a = 5.6238(10) \text{ Å} a = 90^{\circ}$
	a = 5.0236(10) Å, a = 50 $b = 14.391(3) \text{ Å}, \beta = 90^{\circ}$ $c = 4.8615(9) \text{ Å}, v = 90^{\circ}$
Volume	$393 44(12) Å^3$
Z	2
Density a	$\frac{2}{1.967}$ g cm ⁻³
Absorption coefficient μ	$2 350 \text{ mm}^{-1}$
Observed reflection $L > 2\sigma(I)$	783
Variation in check reflections	-0.46%
Refinement technique	Full-matrix least-squares on F^2
Data /restraints /parameters	890/2/89
Goodness-of-fit on F^2	0 977
Final R indices:	0.977
R $L > 2\sigma(I)$	0.0394
wR_{\star} all data	0.0778
Weighting scheme	$w = 1/[\sigma^2(F^2) + (0.021P)^2]$
weighting seneme	$P = [\max(F_o^2, 0) + 2F_o^2]/3$
$R_1 = \sum F_2 - F_2 / \sum F_2 , wR_2 =$	$[\Sigma w(F_o^2 - F_o^2)^2 / \Sigma w(F_o^2)^2]^{1/2}.$

at 50 kV and 40 mA. The detector was placed at a distance of 5.17 cm from the crystal. A total of 1993 frames were collected with a scan width of 0.3° in ω and an exposure time of 10 s frame⁻¹ using SMART.²⁶ The total data collection time was 7.47 h. The frames were integrated with the SAINT software package using a narrow-frame integration algorithm.²⁶ Data were corrected for absorption effects with the semi-empirical from equivalents method using XPREP.²⁷ The structure was solved and refined using the SHELXS-97²⁷ and SHELXL-97²⁸ software.

Results and discussion

Highly crystalline pink plates sufficiently large for SC-XRD analysis were obtained by optimizing the hydrothermal conditions. Detailed crystallographic data are given in Table 1. The optimum reaction conditions in terms of percent yield were 175 °C and 5 days, with a yield of 76.8% (Table 2, Expt. #1). Lower heating temperature and/or time were attempted to see if other phases would form (Table 2, Expt. #2 to #5). Instead, the yield of the material simply decreased, with only a trace amount of solid at 125 °C or 150 °C. The pH of the reaction mixture was ~6 for all experiments. Lower temperatures did not yield a solid product.

The crystal structure of SLUG-4 consists of inorganic layers of CoO_6 octahedra, which corner-share *via* oxygens into a continuous sheet (view of one layer, Fig. 1a). Each of these in-plane oxygens (four for each octahedron) also bond to one phosphorus, and are therefore triply-bridging. Since each CoO_6 octahedron connects to four octahedra and four phosphonates (Fig. 1a), the Co : P ratio is 1 : 1 as reflected in the formula of the compound. The fifth and sixth vertices of the CoO_6 octahedra are occupied by two out-of-plane oxygens. One is a terminal water molecule involved in an intralayer hydrogen bond (Table 3), while the other is a doubly-bridging oxygen that also connects to a phosphorus centre. This layout was correctly predicted in earlier reports where the crystal structure could not be solved due to the ambient synthesis conditions that led to small particle size.²¹

The phosphonates cap the layers alternately above and below the plane of the layer (side view of two layers, Fig. 1b). As for other metal phenylphosphonates,^{8,20} the phenyl rings point into the interlayer space, defining a hydrophobic bilayer region. The Co–O and P–O distances are given in Table 3, and the thermal ellipsoids at 30% probability and atom labeling scheme are shown in Fig. 2. The C(1) and C(4) carbons of the phenyl ring are ordered, while the beta and gamma carbons are disordered (see CIF file). The structure has mirror plane symmetry, as can be seen from Fig. 1 and 2. The phenyl ring is disordered such that in one orientation it lies in the plane, and the other perpendicular to the plane (Fig. 2). The inorganic layer topology is identical to two very recently reported pillared metal 1,4-phenylbisphosphonates of Cao *et al.*, where the metal is Mn or Co.²⁹ The layers are not surprisingly

 Table 2
 Hydrothermal experiments conducted for the synthesis of the layered cobalt phenylphosphonate (PPA = phenylphosphonic acid)

 Ref. No.	Molar ratios	Synthesis time/days	Synthesis temp./°C	Percent yield
1 2 3	50 H ₂ O: 1 PPA: 1 CoCl ₂ ·6H ₂ O 50 H ₂ O:1 PPA:1 CoCl ₂ ·6H ₂ O 50 H ₂ O:1 PPA:1 CoCl ₂ ·6H ₂ O 50 H ₂ O:1 PPA:1 CoCl ₂ ·6H ₂ O	5 3 5	175 175 150	76.8% 42.5% Trace amount
4 5	50 H ₂ O:1 PPA:1 CoCl ₂ ·6H ₂ O 50 H ₂ O:1 PPA:1 CoCl ₂ ·6H ₂ O	3 1.5	150 125	Trace amount Trace amount



Fig. 1 (a) The *b*-projection of one layer of SLUG-4, showing corner sharing CoO_6 octahedra (dark grey) that link to the phosphonate centres (black circles) *via* bridging oxygens; (b) The projection along the *c*-axis shows the capping phenylphosphonates, with an interlamellar bilayer of partially disordered phenyl groups. All hydrogens are omitted for clarity.



Fig. 2 Thermal ellipsoids at 30% probability level and atom labeling scheme.

Table 3 Selected bond lengths (Å), angles (°) and hydrogen bond information for Co(PhPO_3)(H_2O)

Co1–O3	2.056(4)	Co1–	O2ª	2.069(3)
Co1–O2 ^b	2.069(3)	Co1–	Co1–O1	
$Co1-O2^d$	2.237(3)	Co1–	$O2^{f}$	2.237(3)
P1-O3	1.522(5)	P1–O2 ^e		1.546(3)
P1-O2	1.546(3)	P1-C1		1.780(8)
C1–C2B ^e	1.394(12)	C1–C2B		1.394(12)
C4–C3B	1.377(19)	C4–C	C4–C3B ^e	
C2B–C3B	1.381(18)			
O3–Co1–O2 ^{<i>a</i>}	90.74(12)	O3–Co1–O2 ^b		90.74(12)
O2 ^{<i>a</i>} -Co1-O2 ^{<i>b</i>}	100.19(17)	O3–C	O3-Co1-O1	
O2 ^a -Co1-O1	91.92(14)	O2 ^b -Co1-O1		91.92(14)
O3–Co1–O2 ^d	86.36(14)	$O2^{a}$ -Co1-O2 ^d		162.94(13)
$O2^{b}$ -Co1-O2 ^d	96.66(7)	$O1-Co1-O2^d$		90.16(16)
O3–Co1–O2 ^f	86.36(14)	$O2^{a}$ -Co1-O2 ^f		96.66(7)
O2 ^b -Co1-O2 ^f	162.94(13)	O1–Co1–O2 ^f		90.16(17)
$O2^{d}$ -Co1-O2 ^f	66.40(15)			
O3-P1-O2	113.11(17)	O2 ^e -P1-O2		104.8(3)
O3-P1-C1	107.3(3)	O2 ^e -P1-C1		109.23(18)
O2-P1-C1	109.23(18)			
$\overline{D-H\cdots A}$	d(D–H)	$d(\mathbf{H}\cdots\mathbf{A})$	$d(\mathbf{D}\cdots\mathbf{A})$	∠(DHA)
$\overline{\text{O1-H1}\cdots\text{O3}^{b}}$	0.77(2)	2.33(5)	2.844(1)	125(5)
$O1-H1\cdots O2^{c}$	0.77(2)	2.33(4)	2.993(6)	144(5)
D – donor atom	H — hydrogen	A – acceptor	Symmetry tra	Insformation

D = donor atom, H = hydrogen, A = acceptor. Symmetry transformation codes: x - 1/2, -y + 1, z + 1/2; b - x + 1/2, -y + 1, z + 1/2; c - x + 1/2, -y + 1, z + 3/2; d x, y, z + 1; c - x, y, z; f - x, y, z + 1.

pillared, due to the bisphosphonic functionality.³⁰ These pillars increase the stability of the material, but also limit the potential for intercalation and prevents exfoliation of the layers.

As for known metal phosphonates, the cobalt centres readily coordinate to phosphorus through bridging oxygen atoms. The majority of metal phosphate and phosphonate extended structures are built up from MO_4 , MO_5 and MO_6 units. As previously noted, the dimensionality and topology of the structure formed depends considerably on the organic substituent of the phosphonic acid (RPO₃H₂). Larger R groups such as phenyl or long alkyl chains tend to give rise to layered structures, while less bulky groups tend to result in 3D as well as 1D structures.^{12,13,31} One exception is a 1D cobalt phosphonate chain recently demonstrated by Clearfield and co-workers.³² Despite using a long chain 1,8octylenebisphosphonic acid, the octahedral cobalt atoms connect to phosphonate only at the axial positions to create the chain. Four terminal water molecules terminate the cobalt coordination sphere and therefore the dimensionality.

The TGA of the material shows two distinct steps (Fig. 3). At approximately 150 °C, there is a weight loss that corresponds well to the loss of the covalently bound water molecule (one per formula unit, experimental: 7.6%, theoretical: 7.7%). This result agrees with previous reports of dehydration upon heating, reducing the cobalt coordination number from six to five.²¹ The second weight loss event occurs at approximately 500 °C, and is consistent with the breakdown of the organic phenyl groups (experimental: 33.0%, theoretical: 33.2%), also in agreement with reported thermal data.²¹ The black residue after the TGA run was poorly crystalline and the specific phase could not be elucidated by PXRD, but is likely to be a cobalt phosphate.



Fig. 3 The TGA trace shows two sharp events, with weight losses that agree well with expected values.



Fig. 4 Temperature dependence of the magnetic susceptibility at 1000 Oe. Insets: (a) Expansion of the low temperature region; (b) Plot of the reciprocal of susceptibility *versus* temperature.

Fig. 4 shows the temperature dependence of the magnetic susceptibility χ on temperature. As the temperature decreases, the magnetic susceptibility gradually increases and attains a well-defined peak at $T_{\rm p} \sim 6.5$ K (Fig. 4a), indicative of an antiferromagnetic transition. Similar behavior was reported for the two isostructural Mn- and Co-phenylenebisphosphonates of Cao *et al.* mentioned above²⁹ Both of their compounds exhibit a dominant antiferromagnetic interaction between the magnetic centres below 50 K. For our compound, the Néel temperature $T_{\rm N}$, taken as the maximum of $d(\chi T)/dT$, is around 4.0 K, just below the peak temperature $T_{\rm p}$.

The susceptibility obeys the Curie–Weiss law $[\chi = \chi_0 + C/(T - \theta)]$ in the temperature region 50 to 298 K (Fig. 4b). Data fitting (solid line, Fig. 4b) gives the following parameters: temperature-independent contribution $\chi_0 = 7 \times 10^{-5}$ emu g⁻¹; Curie constant C = 0.014 emu K g⁻¹; Curie–Weiss temperature $\theta = -76.5$ K. The negative sign of θ indicates antiferromagnetic interaction between the Co ions. The magnitude of θ is much larger than the Néel temperature $T_N = 4.0$ K. The ratio $T_N/|\theta| = 0.05$ is well below the predicted value of 1 based solely on molecular field theory of antiferromagnetic systems.³³ This discrepancy can be attributed

to the low dimensionality of the magnetic architecture in the title compound. Low-dimensional magnetic compounds usually exhibit a large suppression of their Curie–Weiss temperature due to short-range correlations above the critical Néel temperature T_N ³³, as observed in a closely related Fe(II) phenylphosphonate system.⁸

The effective magnetic moment of 5.01 μ_B per Co(II) deduced from the Curie constant *C* is in the typical range of magnetic moments (4.7 to5.2 μ_B) observed for octahedral Co²⁺ ions.³⁴ It is much higher than the expected spin only value of 3.87 μ_B for a free Co²⁺ ion with a high-spin state S = 3/2, due to the spinorbit coupling in Co(II) containing compounds.²⁹ From Weiss field theory, the estimated exchange coupling constant is $J/k_B =$ $[3\theta/zS(S + 1)] \sim -15.3$ K, assuming a coordination number (z) of four with respect to magnetic nearest-neighbours. This value is reasonable, as interlayer magnetic interaction is negligible due to the large distance of over 14 Å between two cobaltate layers.

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b510942f

Conclusions

A layered cobalt phenylphosphonate was synthesized readily by hydrothermal techniques. The optimum conditions were found to be 175 °C for 5 days and pH ~ 6. Unlike most metal phosphonates, the crystal plates were of sufficient size and quality for structure determination by SCXRD. The material shows a large weight loss around 500 °C due to decomposition of the phenyl groups. The magnetic properties indicate a long-range antiferromagnetic ordering below $T_N = 4.0$ K, with an estimated intralayer magnetic coupling constant of -15.3 K from Curie–Weiss theory. The effective magnetic moment of 5.01 μ_B was deduced from the Curie–Weiss law above 50 K, falling well within the range typically observed for compounds containing octahedral Co²⁺. This material may show interesting intercalation properties due to its large interlayer distance and hydrophobic interlayer space.

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