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A tetrahedrally coordinated cobalt(II) aminophosphonate containing one-dimensional channels

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Abstract

A tetrahedrally coordinated cobalt(II) phosphonate, $Co(O_3PCH_2CH_2NH_2)$, has been synthesized using hydrothermal techniques. X-ray diffraction indicates that this material is a three-dimensional open framework with rings aligned along a single axis forming infinite one-dimensional channels. The framework decomposes just above 400 °C. Magnetic susceptibility data are consistent with weak antiferromagnetic ordering at low temperatures.

Keywords: Metal phosphonates; Structure; Magnetic properties; Thermal decomposition; Cobalt(II); 2-(aminoethyl)phosphonic acid

1. Introduction

Because of their potential applications in areas including catalysis, ion exchange, materials chemistry and separations, the chemistry of metal phosphonates has been actively investigated during the past several decades [1–4]. In metal phosphonates, inorganic and organic molecules can be integrated into a single material that could exhibit unique electronic, magnetic or optical properties. While initial work in phosphonate systems focused on simple alkyl- and arylphosphonates, multifunctional ligands have been used to produce materials with a wider range of dimensionalities and structures. Several strategies have been adopted for functionalizing phosphonates, including adding a second, unique functional group such as an amine, hydroxyl or carboxylic acid [5–7]; incorporating a second phosphonate into a single ligand to produce bisphosphonates [8]; or integrating two or more additional functional groups into the phosphonate ligand [9]. The additional functional groups can either serve to coordinate to the metal center [5] or provide a potential reactive site that can be used for a process such as catalysis or adsorption [10]; it is possible for multi-functionalized ligands to do both.

We have been investigating the reactivity of a series of bifunctional *n*-alkylaminophosphonates to better understand how reaction conditions affect connectivity in these materials. The first three members of this series, aminomethyl-, 2-(aminoethyl)- and 3-(aminopropyl)-phosphonic acid adopt structures that include not only the commonly observed layers (two-dimensional), but also materials connected in zero-, one- and three-dimensions. Frameworks of all dimensions have been observed when 2-(aminoethyl)phosphonic acid is used as a ligand [5,11–16]. One of the most interesting materials in this family is $Zn(O_3PCH_2CH_2NH_2)$ because it is a three-dimensional framework that contains one-dimensional channels that run through the entire structure [5]. It is one of a number of open-framework metal phosphonates, and the only one observed in the family of *n*-alkylaminophosphonates [17]. We have been interested in incorporating magnetic ions into this framework. In this paper we report the preparation and characterization of the cobalt(II) analog of this material.

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2. Experimental

2.1. Synthesis of $Co(O_3PCH_2CH_2NH_2)$

$Co(O_3PCH_2CH_2NH_2)$ was synthesized by a hydrothermal reaction. A total of 0.5 mmol cobalt(II) nitrate hexahydrate (Aldrich), 0.5 mmol 2-(aminoethyl)phosphonic acid (Acros) and 1.5 mmol sodium benzoate (Aldrich) were dissolved in 10.0 mL deionized water while stirring. The pH of the resulting solution was 5.1. The mixture was sealed into the Teflon-liner of a stainless steel autoclave with a volume of 23 mL and heated under autogenous pressure at 170 °C for 4 days. The product was collected by filtration, washed with deionized water and ethanol, and dried at room temperature. Blue hexagonal plates and powder were recovered in 90% yield based on cobalt. Crystals were used for single crystal X-ray analysis. Powder X-ray diffraction confirmed that the crystals were representative of the bulk phase. Elemental analysis for $C_2H_6NO_3PCo$: C, 13.05%; H, 3.42%; N, 7.69%. Calculated: C, 13.20%; H, 3.32%; N, 7.70%. Elemental analysis data were obtained from Galbraith Laboratories, Inc., Knoxville, TN, USA.

2.2. Structure determination

A blue plate of dimensions $0.40 \times 0.24 \times 0.05\,\mathrm{mm}^3$ was mounted onto the end of a thin glass fiber with inert oil. X-ray intensity data covering the full sphere of reciprocal space were measured at 150(2) K on a Bruker SMART APEX CCD-based diffractometer (graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å) [18]. The raw data frames were integrated and corrected for Lorentz and polarization effects with SAINT+ [18]. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied with SADABS [18]. All structures were solved by direct methods and refined against F^2 by the full-matrix least-squares technique using SHELX-97 [19] under the WinGX platform [20]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon atoms were calculated and refined as riding atoms; hydrogen atoms bonded to nitrogen atoms were freely refined with isotropic thermal parameters. The final unit cell parameters are based on the least-squares refinement of 5632 reflections from the data set with $I > 5\sigma(I)$. Analysis of all data sets showed negligible crystal decay during data collection.

2.3. Thermal analysis

Thermal decomposition of $Co(O_3PCH_2CH_2NH_2)$ was studied to 800 °C on a TA Instruments Q500 TGA with a heating rate of $10\,^{\circ}\mathrm{C\,min}^{-1}$ under flowing air at $60\,\mathrm{mL\,min}^{-1}$. After heating, the residual product was analyzed by powder X-ray diffraction on a Phillips PW1820 diffractometer.

2.4. Magnetic susceptibility

The magnetic susceptibility of loose crystals of $Co(O_3PCH_2CH_2NH_2)$ was measured using a Quantum Design MPMS XL SQUID magnetometer. The samples were measured under both zero field cooled (ZFC) and field cooled (FC) conditions in an applied field of 10 kG over the temperature range of $2\,\mathrm{K} \leqslant T \leqslant 300\,\mathrm{K}$. The sample was contained in a gel capsule suspended in a plastic straw for immersion into the SQUID. The small diamagnetic contribution of the gelatin capsule containing the sample had a negligible contribution to the overall magnetization.

3. Results and discussion

3.1. Synthesis

While reactant ratios and temperature appear to be important factors for the synthesis of $Co(O_3PCH_2CH_2NH_2)$, time does not seem to play a major role on product formation. Times between 2 days and 1 month were successfully used to synthesize the product. Although it is not incorporated into the product, the presence of sodium benzoate appears to be important for product formation. It likely acts as both as a complexing agent for cobalt and to set the pH during this reaction.

3.2. Crystal structure

A summary of the crystallographic data is presented in Table 1, atomic positions are provided in Table 2 and relevant bond distances and bond angles are listed in Table 3. Fig. 1 shows the asymmetric unit of this structure.

Each cobalt(II) ion is coordinated by oxygen atoms from three separate phosphonate groups and the nitrogen atom of a fourth phosphonate group. The Co(II)–O bond lengths are in the range of 1.934–1.961 Å, which is comparable to other cobalt(II) phosphonates containing cobalt in a tetrahedral environment [21–23]. Bond valence calculations yield a value of 2.07 for the cobalt ion valence [24]. This and the intense blue color of the crystals are consistent with the presence of tetrahedrally coordinated cobalt(II) ions.

The overall structure can be described as a series of two-dimensional inorganic layers in the *bc*-plane that are connected by the aminoethyl group bonded to phosphorus. These layers are highly reminiscent of zeolite structures because of the presence of 4- and 8-member rings, although this particular topology could

Table 1
Crystal data and structural refinement for $Co(O_3PCH_2CH_2NH_2)$

Empirical formula	$C_2H_6CoNO_3P$
Formula weight ($g\,mol^{-1}$)	181.98
Temperature (K)	150(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	6.4172(3)
b (Å)	8.4131(4)
c (Å)	9.8360(4)
β (deg)	90.9970(10)
V (Å^3)	523.00(4)
Z	4
Density (calculated) ($g\,cm^{-3}$)	2.311
Absorption coefficient (mm^{-1})	3.491
$F(000)$	364
Crystal size (mm)	0.40 × 0.24 × 0.05
θ_{max} (deg)	30.26
Reflections collected/unique	6534/1553 ($R_{int} = 0.0320$)
Goodness-of-fit on F^2	0.997
R indices (all data)	$R_1 = 0.0265$, $wR_2 = 0.0684$
Largest diffraction peak and hole (e^- Å^{-3})	0.656 and −0.904

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $Co(O_3PCH_2CH_2NH_2)$

	x	y	z	U_{eq}
Co(1)	0.5091(1)	0.6645(1)	0.3439(1)	12(1)
P(1)	0.2458(1)	0.3573(1)	0.3458(1)	11(1)
C(1)	−0.0351(3)	0.3404(2)	0.2886(2)	14(1)
C(2)	−0.0988(3)	0.3343(2)	0.1319(2)	16(1)
N(1)	−0.3332(2)	0.3439(2)	0.0916(2)	14(1)
O(1)	0.3224(2)	0.4935(2)	0.2638(1)	16(1)
O(2)	0.3529(2)	0.2011(2)	0.3163(1)	15(1)
O(3)	0.2767(2)	0.3920(2)	0.5000(1)	16(1)

Table 3
Selected interatomic distances (Å), bond angles (deg) and tolerance factors for $Co(O_3PCH_2CH_2NH_2)$

Co(1)–O(1)	1.9489(13)	P(1)–O(1)	1.5300(14)
Co(1)–O(2)#2	1.9614(13)	P(1)–O(2)	1.5338(13)
Co(1)–O(3)#1	1.9345(13)	P(1)–O(3)	1.5233(13)
Co(1)–N(1)#3	2.0498(16)	P(1)–C(1)	1.7987(18)
O(3)#1–Co(1)–O(1)	116.25(6)	O(3)–P(1)–O(1)	112.54(8)
O(3)#1–Co(1)–O(2)#2	108.57(6)	O(3)–P(1)–O(2)	111.52(7)
O(1)–Co(1)–O(2)#2	97.06(6)	O(1)–P(1)–O(2)	110.26(8)
O(3)#1–Co(1)–N(1)#3	106.79(6)	O(3)–P(1)–C(1)	106.08(8)
O(1)–Co(1)–N(1)#3	109.62(6)	O(1)–P(1)–C(1)	106.88(8)
O(2)#2–Co(1)-N(1)#3	118.83(6)	O(2)–P(1)–C(1)	109.32(8)

Note: Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y+1$, $-z+1$; #2 $-x+1$, $y+1/2$, $-z+1/2$; #3 $-x$, $y+1/2$, $-z+1/2$.

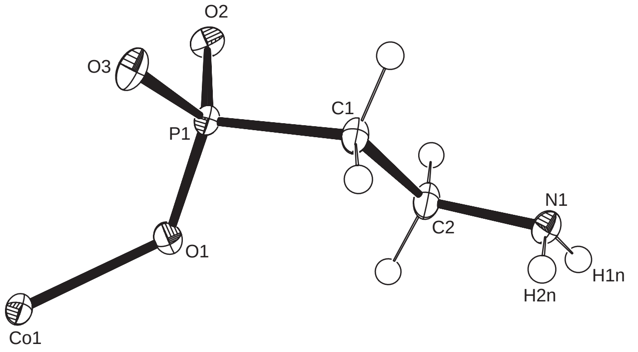

Fig. 1. Asymmetric unit of $Co(O_3PCH_2CH_2NH_2)$ showing the atom labeling. Thermal ellipsoids are shown at the 50% probability level.

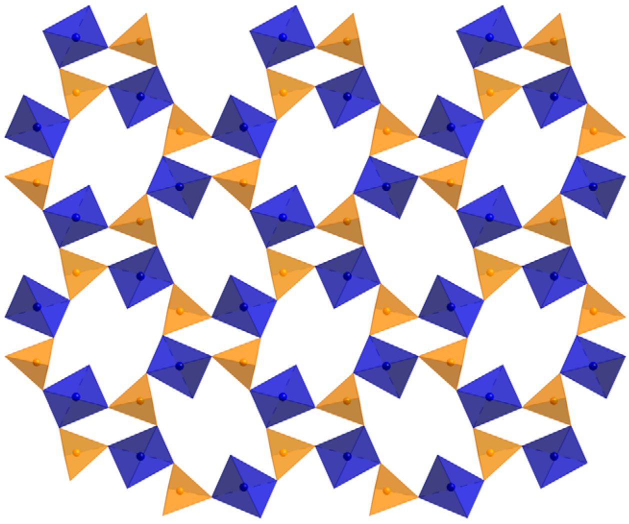

Fig. 2. Orthogonal, corner-sharing $[CoP_2O_4]$ 4-rings that comprise the inorganic layer, viewed down [100] (a-axis). The CoO_3N tetrahedra are shown in dark gray and the PO_3C tetrahedra are light gray. Carbon and hydrogen atoms are omitted for clarity.

not be found in existing zeolite-like structures. The major difference between these materials and their zeolite analogs is that the tetrahedral groups are decorated with the ethylamine moiety of the phosphonate. Each layer contains a set of orthogonal, corner shared $[Co_2P_2O_4]$ chains along the [011] and $[0\bar{1}\bar{1}]$ direction (Fig. 2). Isolated versions of these one-dimensional chains have also been observed in a series of cobalt piperazinium phosphates [25] and in several aluminum phosphates [26]. The ethylamine group serves to bridge between the inorganic layers (Fig. 3). This linkage is also assisted by NH---O hydrogen bonding. Both H1N and H2N of the amino group are involved in hydrogen bonds to two different O2 atoms of neighboring ligands; N(1)–H(1N)---O(2) = 3.105(2) Å, N(1)–H(2N)---O(2) = 3.148(2) Å. The inorganic layers are aligned in such a way that one-dimensional channels of approximate dimensions of 3.66 Å × 6.02 Å run along the a-axis. The title compound is isostructural with its zinc analog, the first example of a functionalized zeolite-like phosphonate [5].

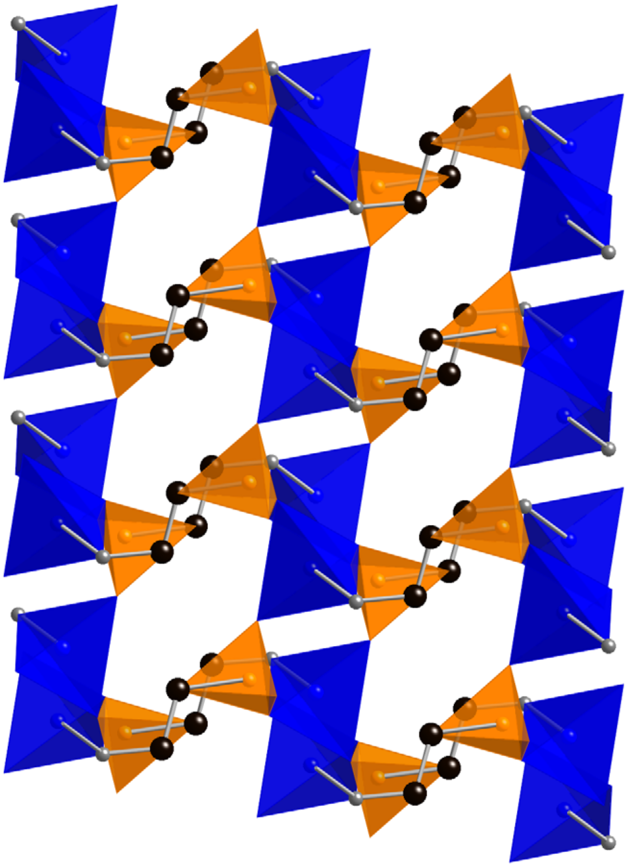

Fig. 3. Inorganic layers, viewed down [010] (*b*-axis), are connected by aminoethyl groups that are bound via nitrogen to the adjacent layer. The CoO_3N tetrahedra are shown in dark gray and the PO_3C tetrahedra are light gray. Hydrogen atoms are omitted for clarity.

Co^{2+} forms mostly octahedral and tetrahedral complexes, although 5-coordinate species are also known. Most cobalt containing phosphonates, including other *n*-alkylaminophosphonate compounds [27], contain Co^{2+} in an octahedral environment. In contrast to cobalt(II) phosphates where tetrahedral coordination is common [28], there are few examples of tetrahedral Co^{2+} in cobalt phosphonate systems [21–23]. A search of the Cambridge Structural Database reveals that only three of the 40 cobalt(II) phosphonates contain tetrahedral cobalt [29]. Many of the phosphonate ligands are more bulky than 2-(aminoethyl)phosphonic acid, so it is somewhat surprising that with this ligand, Co^{2+} is found with tetrahedral coordination.

3.3. Magnetic properties

Fig. 4 shows the temperature-dependant molar magnetic susceptibility of $Co(O_3PCH_2CH_2NH_2)$ between 2 and 300 K at 10 kG. The FC and ZFC data overlay in all cases over the temperature range investigated and therefore only the ZFC data are shown. Using the inverse susceptibility data between 100 and 300 K, the effective magnetic moment and Weiss constant were obtained and found to be 4.78 μ_B, $\theta = -1$ K. The room temperature effective magnetic moment of 4.78 μ_B is much higher than the predicted spin-only value of 3.87 μ_B for a spin $S = 3/2$ cobalt(II) ion. This is consistent with experimental values observed for other systems at room temperature and is attributed to the orbital contribution of the cobalt(II) ion. Deviations from the Curie–Weiss Law at low temperature and the continuous decrease of $\chi_M T$ upon cooling below 50 K further indicate weak anti-ferromagnetic ordering between the magnetic centers in the compound.

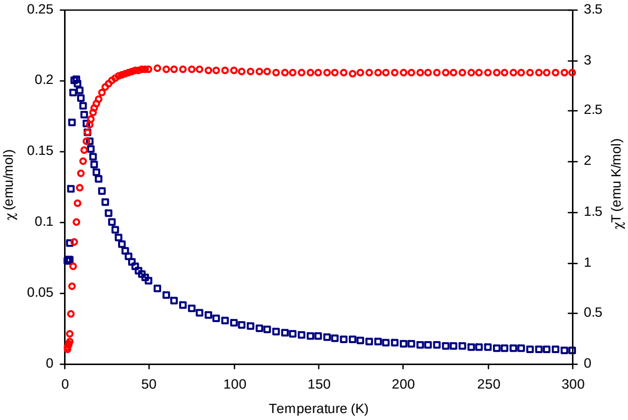

Fig. 4. Temperature dependence of the ZFC magnetic susceptibility (squares) and $\chi_M T$ (circles) of $Co(O_3PCH_2CH_2NH_2)$.

3.4. Thermal properties

The TGA curve indicates that $Co(O_3PCH_2CH_2NH_2)$ undergoes rapid weight loss just above 400 °C and then undergoes a complex decomposition process (Fig. 5). Similar to the chromium(II) phosphonate derived from 2-(aminoethyl)phosphonic acid [15], the transition metal containing coordination polymers exhibit greater thermal stability than the uncoordinated acid [30]. The NH---O hydrogen bonding in this compound likely helps to increase its thermal stability. Powder X-ray diffraction data indicate that the decomposition residue is $Co_2P_2O_7$ (PDF card 49-1091). The calculated mass loss for complete decomposition of the organic component in $Co(O_3PCH_2CH_2NH_2)$ to yield the inorganic pyrophosphate is 19.8% and the observed mass loss was 16.6%. Thus, at 800 °C, decomposition is incomplete. This can be seen both in the shape of the TGA curve and the blue-gray color of the residue. It is apparent from the TGA curve that decomposition of the phosphonic acid continues above the maximum temperature studied. The gray color is indicative of unoxidized carbon trapped in the solid matrix. Heating the residue to 1000 °C produced a blue solid whose color is consistent

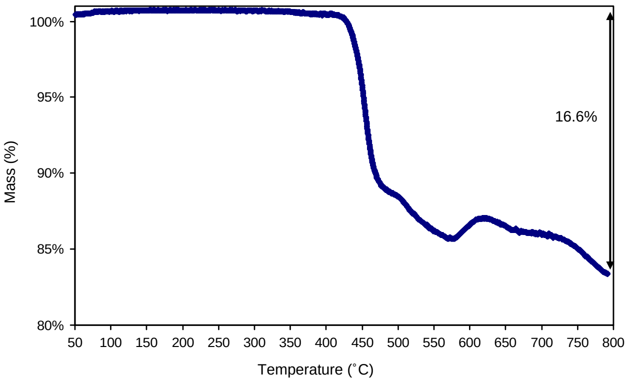

Fig. 5. TGA curve for $Co(O_3PCH_2CH_2NH_2)$.

with $Co_2P_2O_7$. The weight gain during sample decomposition can be attributed to partial oxidation of cobalt(II) ions.

4. Conclusions

The inorganic–organic hybrid compound $Co(O_3PCH_2CH_2NH_2)$ has been hydrothermally synthesized and characterized by single crystal X-ray analysis. The compound crystallizes in a three-dimensional framework containing one-dimensional channels; the magnetic cobalt(II) ion has a tetrahedral coordination geometry, which is rare for known cobalt phosphonates. We are not yet certain if the cobalt(II) compound will serve as a prototype from other divalent magnetic ions. To date, our efforts to incorporate other divalent magnetic ions into this structure type have not been successful.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 264871. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 44 1223 336 033; e-mail:deposit@ccdc.cam.ac.uk).

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