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A tetrahedrally coordinated cobalt(II)
phosphonate with a three-dimensional
framework containing two-dimen-
sional channels

Shu-Juan Fu, Ching-Yuan Cheng and Kuan-Jiuh Lin*

Department of Chemistry, National Chung Hsing University, 250 Kuo Kuang Rd,
Taichung 402, TaiwanCorrespondence e-mail: kjlin@dragon.nchu.edu.tw

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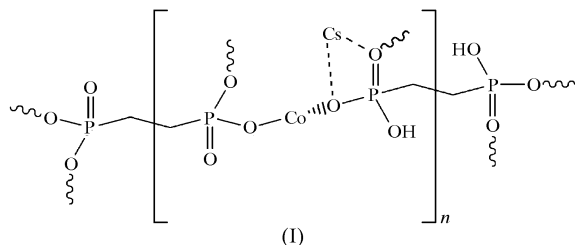
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The structure of poly[caesium(I) $[(\mu_4\text{-ethylenediphosphonato})\text{cobalt(II)}]]$, $[\text{Cs}[\text{Co}(\text{C}_2\text{H}_5\text{O}_6\text{P}_2)]_n]$, reveals a three-dimensional polymeric open framework consisting of tetrahedral Co^{II} atoms coordinated by four different ethylenediphosphonate O atoms and intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds. The largest open window is made of corner-sharing CoO_4 and PO_3C tetrahedra, giving 16-membered rings of dimensions $9.677(5) \times 4.684(4) \text{ \AA}^2$. There are two independent ethylenediphosphonate ligands, each lying about an inversion centre.

Comment

Metal phosphonates are currently the subject of intense interest as open-framework materials because of their distinct catalytic, magnetic and electric properties. Multifunctional diphosphonate ligands, such as simple ethylenediphosphonate, have been used to produce inorganic-organic hybrid materials with a wide range of dimensions and structures. Examples from our laboratory include $[\text{Ga}_2(\text{VO})_3\text{K}_2(\text{OH}_2)_3(\text{C}_2\text{H}_4\text{P}_2\text{O}_6)_4(\text{H}_2\text{O})_{13}]$ (Cheng *et al.*, 2003), containing a three-dimensional open framework with multidimensional channels, and a redox copper(I/II)-based coordination polymer, $[\text{Cu}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{HO}_3\text{P}-\text{C}_2\text{H}_4-\text{PO}_3\text{H})(\text{OH}_2)_2]$ (Lin *et al.*, 2004), which exhibits supramolecular device behavior. In contrast to Co^{II} -phosphate systems, relatively few examples of tetra-



hedral geometry in Co^{II} -phosphonate systems have been reported. This paper reports what is, to our knowledge, the

first structural characterization of a tetrahedrally coordinated cobalt(II) ethylenediphosphonate with an open-framework structure.

$[\text{Cs}[\text{Co}(\text{C}_2\text{H}_5\text{P}_2\text{O}_6)]]_n$ adopts a three-dimensional framework with two-dimensional channels. The Co atom has a distorted tetrahedral geometry (Fig. 1) composed of four O atoms (O1, O4B, O3A and O6) from different ethylenediphosphonate anions. The Co–O bond lengths [$1.934(3)$ – $1.965(2) \text{ \AA}$] and O–Co–O angles [$103.99(11)$ – $113.09(11)^\circ$] are comparable to those found in other cobalt(II) phosphonates (Gemmill *et al.*, 2005; LaDuca *et al.*, 1996; Turner *et al.*, 2003; Distler *et al.*, 1999; Rabu *et al.*, 1999; Gustschke *et al.*, 1999; Lohse & Sevov, 1997) containing cobalt in a tetrahedral environment. Moreover, a bond-valence calculation gives a value of 2.00 for the cobalt ions (Brown & Altermatt, 1985). Owing to the $\text{Cs}^{\text{I}}-\text{Co}^{\text{II}}$ -ethylenediphosphonate ratio of 1:1:1 in the asymmetric unit, the diphosphonate anions should be monoprotonated. Analysis of tetrahedral coordination of cobalt ions in related systems (Pothiraja *et al.*, 2004; Gemmill

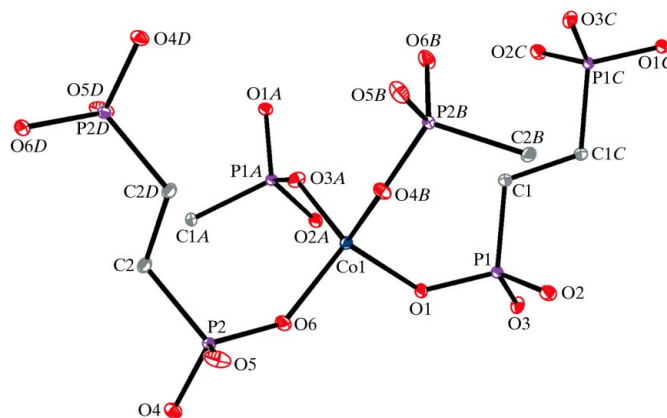


Figure 1

A view of the Co atom coordinated by four phosphonate anions in a slightly distorted tetrahedral environment. [Symmetry codes: (A) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (B) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (C) $-x + 1, -y, -z + 1$; (D) $-x, -y + 1, -z$.]

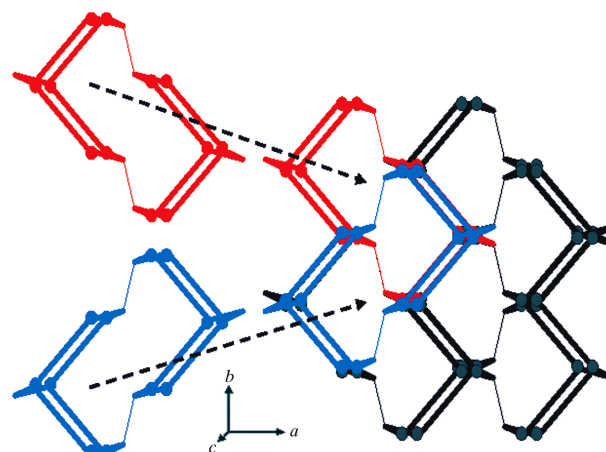


Figure 2

A schematic presentation of the structural building units of bicyclic rings. CoO_4 tetrahedra, phosphonate ligands (PO_3C) and ethylene groups $[-\text{CH}_2-\text{CH}_2-]$ are denoted as dots, bold lines and narrow lines, respectively.

et al., 2005) shows that the P—O bonds associated with metal ions [ranging from 1.517 (3) to 1.525 (3) Å in our case] are somewhat shorter than those of noncoordinated P—OH or P=O bonds [1.531 (3) and 1.536 (3) Å]. These noncoordinated O atoms also participate in a short O—H...O hydrogen bond (Table 1), which plays a key role in constructing the robust open framework.

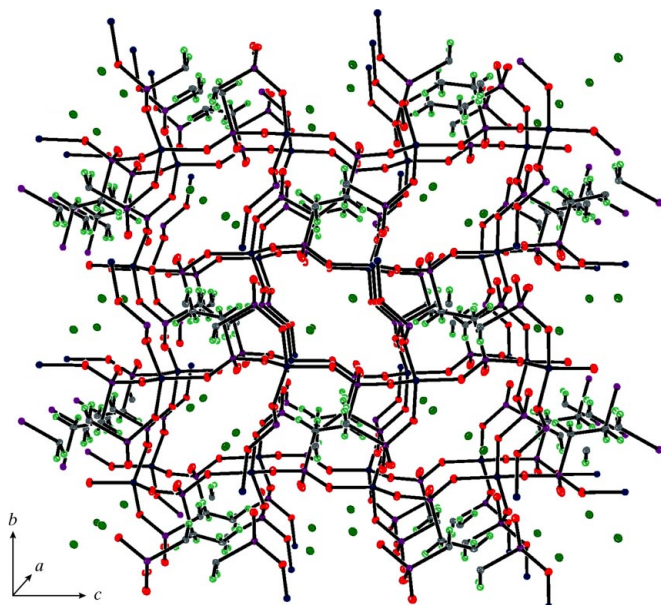


Figure 3
The crystal packing viewed along the *a* axis. Channels containing the Cs⁺ cations are clearly visible.

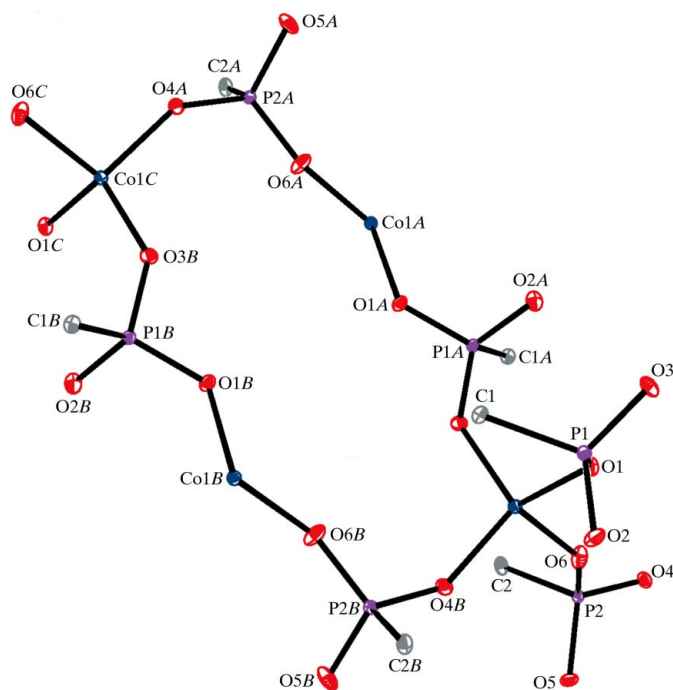


Figure 4
A detailed view of the 16-membered ring that forms the boundary of the channel running along the *a* axis. The dimensions are 9.677 (5) (O4A...O4B) × 4.684 (4) Å (O1A...O1B). [Symmetry codes: (A) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (B) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (C) $-x + 1, -y + 1, -z + 1$.]

The architecture of this material is shown in Fig. 2. The structural building unit may be described as a bicyclic ring (dots and bold lines) that is constructed *via* corner-sharing CoO₄ and PO₃C tetrahedra to form polymeric [(−Co^{II}−PO₃C−Co^{II}−)]_{*n*} open windows comprising 12 Co atoms. The bicyclic rings are stacking upon each other in such a way as to generate two infinite channel systems that run through the entire structure. One has square-like windows that run in the *c* direction, while the largest channels are clearly revealed when viewed along the *a* axis (Fig. 3). The open window is made of eight corner-sharing CoO₄ and PO₃C tetrahedra to give 16-membered rings (Fig. 4) in which the effective dimensions are *ca* 9.677 (5) (O4A...O4B) × 4.684 (4) Å (O1A...O1B). Two symmetry-related Cs⁺ cations occupy these channels. Each caesium ion is coordinated by eight O atoms from the surrounding six phosphonate anions. The Cs—O bond lengths range from 3.030 (3) to 3.573 (3) Å. In conclusion, this three-dimensional open framework can be described as a new type of zeolite-like analog structure in which the framework is composed of tetrahedrally coordinated cobalt phosphonate.

Experimental

A reaction mixture of CoCl₂·6H₂O (0.1189 g, 0.5 mmol), ethylenediphosphonic acid (0.1421 g, 0.75 mmol), 1,10-phenanthroline monohydrate (0.0991 g, 0.5 mmol), CsOH (99%, 50 wt% solution in water, 0.3 ml) and ethanol (8 ml) was placed in a 23 ml Teflon-lined stainless steel autoclave, which was sealed and heated at 373 K for 2 h, then heated at 473 K for 96 h, then cooled to 344 K at a rate of 9 K h^{−1}, and finally allowed to cool to room temperature (final pH < 7). The resulting deep-blue crystals were collected by filtration and washed with ethanol.

Crystal data

Cs[Co(C ₂ H ₅ O ₆ P ₂)]	<i>V</i> = 840.53 (10) Å ³
<i>M_r</i> = 378.84	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 8.2580 (6) Å	<i>μ</i> = 6.68 mm ^{−1}
<i>b</i> = 9.6225 (7) Å	<i>T</i> = 293 (2) K
<i>c</i> = 10.7899 (7) Å	0.28 × 0.23 × 0.20 mm
<i>β</i> = 101.382 (1)°	

Data collection

Bruker SMART CCD area-detector diffractometer	5135 measured reflections
Absorption correction: empirical (using intensity measurements) (SADABS; Bruker, 2000)	1913 independent reflections
<i>T</i> _{min} = 0.172, <i>T</i> _{max} = 0.263	1801 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.025

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.031	109 parameters
<i>wR</i> (<i>F</i> ²) = 0.080	H-atom parameters constrained
<i>S</i> = 1.19	Δ <i>ρ</i> _{max} = 0.67 e Å ^{−3}
1913 reflections	Δ <i>ρ</i> _{min} = −2.45 e Å ^{−3}

H atoms were placed in calculated positions and included as riding atoms, with C—H = 0.97 Å and O—H = 0.82 Å. Displacement parameters were set at 1.2 (CH₂) or 1.5 (OH) times *U*_{eq} of the parent C or O atom. Given the nearly identical P—O distances involving O2 and O5, it was not obvious which O atom should carry the acidic H atom, so it was assigned to O2 arbitrarily. We cannot rule out a

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O2-H2\cdots O5^i$	0.82	1.73	2.432 (3)	143

Symmetry code: (i) $-x, -y, -z$.

symmetrical arrangement, which would be consistent with the equivalent P—O bond lengths.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3080). Services for accessing these data are described at the back of the journal.

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