Acta Crystallographica Section C
Crystal Structure Communications

ISSN 0108-2701

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

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

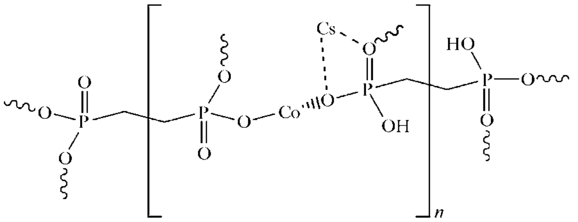
Department of Chemistry, National Chung Hsing University, 250 Kuo Kuang Rd, Taichung 402, Taiwan
Correspondence e-mail: kjlin@dragon.nchu.edu.tw

Received 15 May 2007
Accepted 13 June 2007
Online 14 July 2007

The structure of poly[caesium(I) [(μ_4-ethylenediphosphonato)cobalt(II)]], $\{Cs[Co(C_2H_5O_6P_2)]\}_n$, reveals a three-dimensional polymeric open framework consisting of tetrahedral Co^{II} atoms coordinated by four different ethylenediphosphonate O atoms and intermolecular O—H$\cdots$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) × 4.684 (4) Å^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 $[Ga_2(VO)_3K_2(OH_2)_3(C_2H_4P_2O_6)_4(H_2O)_{13}]$ (Cheng *et al.*, 2003), containing a three-dimensional open framework with multidimensional channels, and a redox copper(I/II)-based coordination polymer, $[Cu(C_{12}H_8N_2)(HO_3P–C_2H_4–PO_3H)(OH_2)_2]$ (Lin *et al.*, 2004), which exhibits supramolecular device behavior. In contrast to Co^{II}–phosphate systems, relatively few examples of tetrahedral 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.



(I)

$\{Cs[Co(C_2H_5P_2O_6)]\}_n$ 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, O4*B*, O3*A* and O6) from different ethylenediphosphonate anions. The Co—O bond lengths [1.934 (3)–1.965 (2) Å] and O—Co—O angles [103.99 (11)–113.09 (11)°] 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 Cs^I–Co^{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

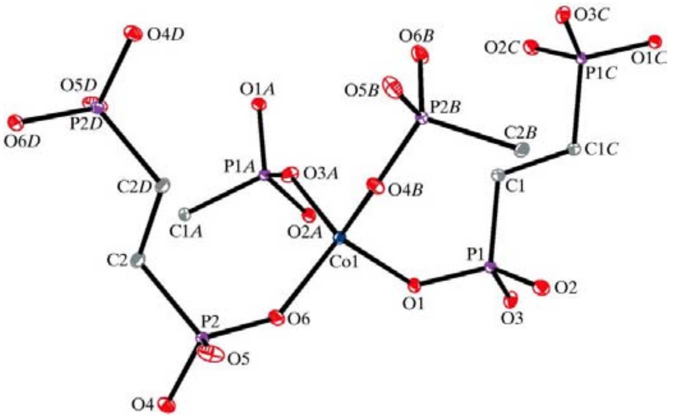


Figure 1
A view of the Co atom coordinated by four phosphonate anions in a slightly distorted tetrahedral environment. [Symmetry codes: (*A*) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (*B*) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (*C*) $-x + 1, -y, -z + 1$; (*D*) $-x, -y + 1, -z$.]

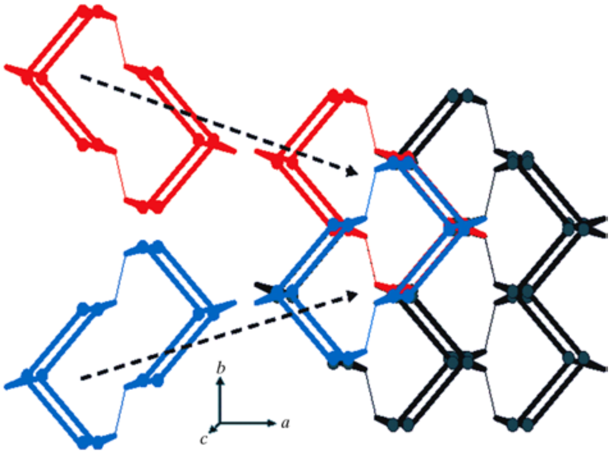


Figure 2
A schematic presentation of the structural building units of bicyclic rings. CoO_4 tetrahedra, phosphonate ligands (PO_3C) and ethylene groups [$-CH_2-CH_2-$] are denoted as dots, bold lines and narrow lines, respectively.

DOI: 10.1107/S0108270107029113

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.

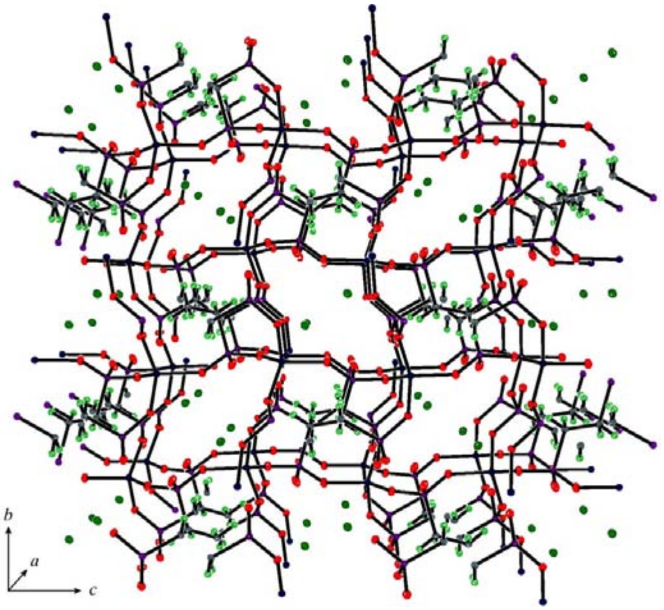


Figure 3
The crystal packing viewed along the *a* axis. Channels containing the Cs^+ cations are clearly visible.

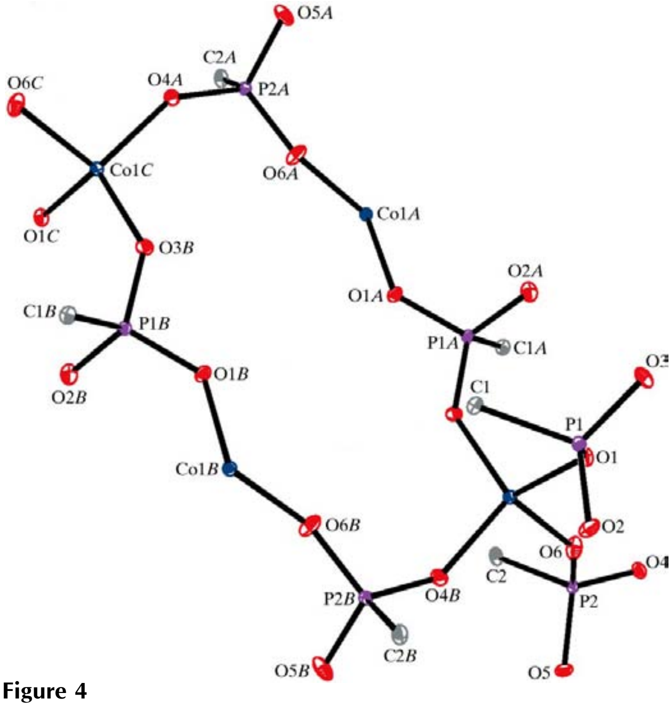


Figure 4
A detailed view of the 16-membered ring that forms the boundary of the channel running along the *a* axis. The dimensions are 9.677 (5) (O4*A*···O4*B*) × 4.684 (4) Å (O1*A*···O1*B*). [Symmetry codes: (*A*) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (*B*) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (*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 CoO_4 and PO_3C tetrahedra to form polymeric $[(\text{–Co}^{II}\text{—PO}_3\text{C—Co}^{II}\text{–})]_n$ 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 CoO_4 and PO_3C tetrahedra to give 16-membered rings (Fig. 4) in which the effective dimensions are *ca* 9.677 (5) (O4*A*···O4*B*) × 4.684 (4) Å (O1*A*···O1*B*). 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 $CoCl_2 \cdot 6H_2O$ (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

$Cs[Co(C_2H_5O_6P_2)]$
$M_r = 378.84$
Monoclinic, $P2_1/c$
$a = 8.2580$ (6) Å
$b = 9.6225$ (7) Å
$c = 10.7899$ (7) Å
$\beta = 101.382$ (1)°

$V = 840.53$ (10) $Å^3$
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 6.68$ mm^{-1}
$T = 293$ (2) K
0.28 × 0.23 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: empirical (using intensity measurements) (*SADABS*; Bruker, 2000)
$T_{min} = 0.172$, $T_{max} = 0.263$

5135 measured reflections
1913 independent reflections
1801 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.080$
$S = 1.19$
1913 reflections

109 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.67$ e $Å^{-3}$
$\Delta\rho_{min} = -2.45$ 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 (CH_2) 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, °).

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
$\mathrm{O2}-\mathrm{H2}\cdots\mathrm{O5}^{\mathrm{i}}$	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: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

This study was supported by the National Science Council of Taiwan (grant No. NSC-95-2627-M-005-001).

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.

References

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.
Bruker (1999). *SMART*. Version 5.059. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2000). *SADABS* (Version 2.01) and *SAINT* (Version 6.02A). Bruker AXS Inc., Madison, Wisconsin, USA.
Cheng, C. Y., Fu, S. J., Yang, C. J., Chen, W. H., Lin, K. J., Lee, G. H. & Wang, Y. (2003). *Angew. Chem. Int. Ed.* **115**, 1981–1984.
Distler, A., Lohse, D. L. & Sevov, S. C. (1999). *J. Chem. Soc. Dalton Trans.* pp. 1805–1812.
Gemmill, W. R., Smith, M. D. & Reisner, B. A. (2005). *J. Solid State Chem.* **178**, 2658–2662.
Gustschke, O. H. S., Price, D. J., Powell, A. K. & Wood, P. T. (1999). *Angew. Chem. Int. Ed.* **38**, 1088–1090.
LaDuca, R., Rose, D., DeBord, J. R. D., Haushalter, R. C., O'Connor, C. J. & Zubieta, J. (1996). *J. Solid State Chem.* **123**, 408–412.
Lin, K. J., Fu, S. J., Cheng, C. Y., Chen, W. H. & Kao, H. M. (2004). *Angew. Chem. Int. Ed.* **43**, 4186–4189.
Lohse, D. L. & Sevov, S. C. (1997). *Angew. Chem. Int. Ed.* **36**, 1619–1621.
Pothiraja, R., Sathiyendiran, M., Butcher, R. J. & Murugavel, R. (2004). *Inorg. Chem.* **43**, 7585–7587.
Rabu, P., Janvier, P. & Bujol, B. (1999). *J. Mater. Chem.* **9**, 1323–1326.
Sheldrick, G. M. (1997*a*). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Turner, A., Jaffres, P. A., MacLean, E. J., Villemin, D., McKee, V. & Hix, G. B. (2003). *Dalton Trans.* pp. 1314–1319.