Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Poly[(μ_4-3-pyridylphosphonato-κ^4-*N*:*O*:*O*′:*O*″)cobalt(II)]

Anna E. Wasson and Robert L. LaDuca*

Lyman Briggs School of Science, Department of Chemistry, Michigan State University, East Lansing, MI 48825, USA

Correspondence e-mail: laduca@msu.edu

Received 14 December 2006
Accepted 5 January 2007

Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.005 Å
R factor = 0.033
wR factor = 0.065
Data-to-parameter ratio = 16.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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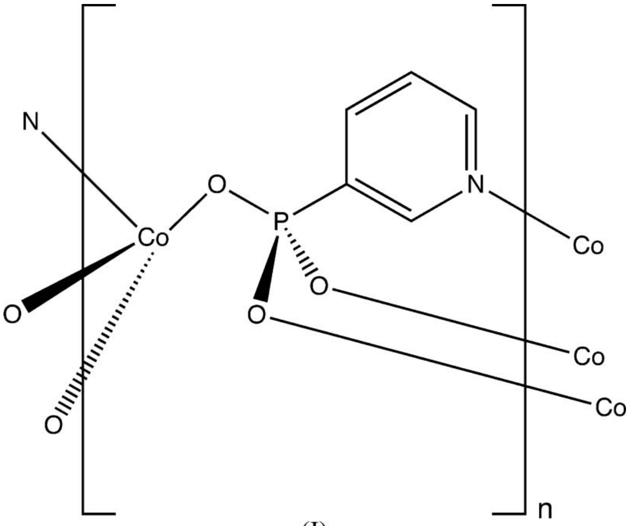
The title compound, $[Co(C_5H_4NPO_3)]_n$, is a three-dimensional network coordination polymer containing tetrahedrally coordinated Co^{II} bound to one N atom from one 3-pyridylphosphonate ligand and three O atoms, each from three other distinct 3-pyridylphosphonate ligands. The structure exhibits two-dimensional cobalt phosphonate layers, parallel to the *ac* crystal plane, constructed from the junction of $Co_3O_6P_3$ 12-membered rings. The inorganic layers are pillared through the N-atom donors of the tethering pyridyl rings to produce the three-dimensional crystal structure of (I).

Comment

Three-dimensional coordination polymers containing pyridylcarboxylate ligands have been shown to possess intriguing luminescent (Wang *et al.*, 2004), nonlinear optical (Lin *et al.*, 1998) and shape-selective absorptive (Chen *et al.*, 2006) properties. In an attempt to prepare a divalent cobalt 3-pyridylphosphonate coordination polymer incorporating the organodiimine 4,4′-bipyridine, blue crystals of the title compound, (I), were produced.



(I)

The asymmetric unit of (I) consists of one divalent Co atom and one 3-pyridylphosphonate ligand (Fig. 1). The Co atom has a distorted tetrahedral coordination environment, with one N donor and three O donors from four distinct exotetradentate 3-pyridylphosphonate ligands. Selected bond lengths and angles for (I) are given in Table 1. Three individual phosphonate ligands connect each Co atom with six

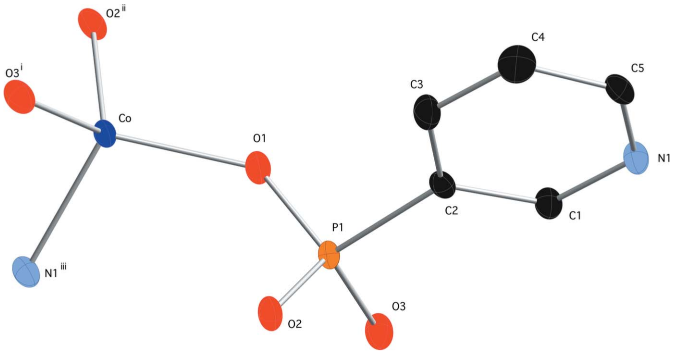


Figure 1
Asymmetric unit of the title compound, with symmetry-equivalent N and O atoms to complete the coordination environment about Co, showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity. The symmetry codes are as in Table 1.

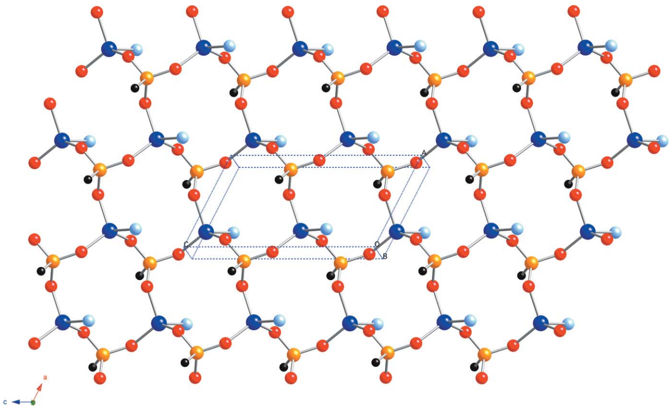


Figure 2
A single layer motif of (I), which lies parallel to the *ac* crystal plane. All H atoms and most C atoms have been omitted for clarity. Color codes: dark-blue Cu, light-blue N, orange P, red O, black C.

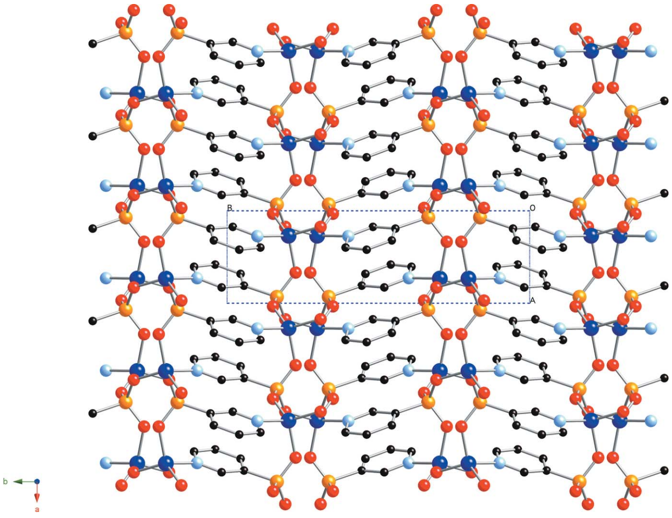


Figure 3
Packing diagram of (I) viewed down *c*, showing the linkage of layer motifs through N donor atoms of 3-pyridylphosphonato ligands.

others through the O donor atoms, to form [$CoPO_3$] layers that lie parallel to the *ac* crystal plane. Each layer is constructed from [$Co_3O_6P_3$] 12-membered fused rings (Fig. 2). The Co$\cdots$Co through-ligand distances within each layer measure 4.99, 5.15 and 5.38 Å. The second of these distances is equal to the lattice parameter *a*.

Each cobalt phosphonate layer lies parallel to the *ac* crystal plane. The layers are covalently conjoined through the N donors of the tethering pyridyl subunits within the 3-pyridylphosphonate ligands along the *b* crystal axis to establish the full three-dimensional crystal structure of (I) (Fig. 3). Non-classical hydrogen bonding (Table 2) also enhances the three-dimensional covalent network connectivity in (I). The Co$\cdots$Co through-ligand distances between adjacent layers are 6.50 and 6.76 Å.

Experimental

All chemicals were obtained commercially, with the exception of diethyl 3-pyridylphosphonate, which was prepared using a published procedure (Ayyappan *et al.*, 2001). A mixture of cobalt(II) chloride hexahydrate (79 mg, 0.33 mmol), diethyl 3-pyridylphosphonate (71 mg, 0.33 mmol), aqueous hydrochloric acid (0.66 ml, 1.0 *M*, 0.66 mmol), 4,4′-bipyridine (52 mg, 0.33 mmol) and 10.0 g water (555 mmol) was placed in a 23 ml Teflon-lined Parr acid digestion bomb, which was then heated under autogenous pressure at 423 K for 72 h. Hydrolysis of the phosphonate ester occurred *in situ*. Blue blocks of the title compound were obtained after facile manual separation from a fine black precipitate *via* repeated washing with water and decantation. The crystals were then washed with acetone and air dried.

Crystal data

[$Co(C_5H_4NO_3P)$]
$M_r = 215.99$
Monoclinic, $P2_1/c$
$a = 5.1510\ (6)$ Å
$b = 15.0236\ (16)$ Å
$c = 9.5778\ (11)$ Å
$\beta = 117.191\ (2)^\circ$
$V = 659.28\ (13)$ Å^3

$Z = 4$
$D_x = 2.176$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 2.79$ mm^{-1}
$T = 173\ (2)$ K
Block, blue
$0.24 \times 0.10 \times 0.08$ mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.554$, $T_{\max} = 0.808$

7832 measured reflections
1600 independent reflections
1368 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.036$
$\theta_{\max} = 28.3^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.065$
$S = 1.13$
1600 reflections
100 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0152P)^2 + 1.4525P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.50$ e Å^{-3}
$\Delta\rho_{\min} = -0.50$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—O1	1.930 (2)	P1—O1	1.517 (2)
Co1—O3^{i}	1.936 (2)	P1—O3	1.518 (2)
Co1—O2^{ii}	1.954 (2)	P1—O2	1.521 (2)
Co1—N1^{iii}	2.051 (2)	P1—C2	1.812 (3)
O1—Co1—O3^{i}	125.50 (9)	O1—Co1—N1^{iii}	106.32 (9)
O1—Co1—O2^{ii}	103.10 (8)	O3^{i}—Co1—N1^{iii}	100.13 (9)
O3^{i}—Co1—O2^{ii}	112.08 (9)	O2^{ii}—Co1—N1^{iii}	108.89 (9)

Symmetry codes: (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $x + 1, -y + \frac{3}{2}, z + \frac{1}{2}$; (iii) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C1—H1$\cdots$O3	0.93	2.53	2.96	108
C5—H5$\cdots$O2^{iv}	0.93	2.34	3.22	157

Symmetry code: (iv) $-x - 1, y + \frac{1}{2}, -z + \frac{1}{2}$.

All H atoms were placed in calculated positions, with C—H = 0.93 Å, and refined in riding mode with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *CrystalMaker* (*CrystalMaker*, 2005); software used to prepare material for publication: *SHELXL97*.

We thank Michigan State University for the financial support of this work.

References

Ayyappan, P., Evans, O. R., Foxman, B. M., Wheeler, K. A., Warren, T. H. & Lin, W. (2001). *Inorg. Chem.* **40**, 5954–5961.

Bruker (2001). *SMART*. Version 5.624. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2003). *SAINT-Plus* (Version 6.25). Bruker AXS Inc., Madison, Wisconsin, USA.

Chen, B., Liang, C., Yang, J., Contreras, D., Clancy, Y. L., Lobkovsky, E. B., Yaghi, O. M. & Dai, S. (2006). *Angew. Chem. Int. Ed.* **45**, 1390–1393.

CrystalMaker (2005). *CrystalMaker*. Version 7.1. CrystalMaker Software, Bicester, Oxfordshire OX26 3TA, England.

Lin, W., Evans, O. R., Xiong, R.-G. & Wang, Z. (1998). *J. Am. Chem. Soc.* **120**, 13272–13273.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. Release 97-2. University of Göttingen, Germany.

Wang, X., Qin, C., Wang, E., Li, Y., Hao, N., Hu, C. & Xu, L. (2004). *Inorg. Chem.* **43**, 1850–1856.