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Poly[*diaqua-μ₄-oxalato-di-μ₆-phosphato-tetracobalt(II)*]Wen-Yuan Wu^{a*} and Li-Xin Zhai^b

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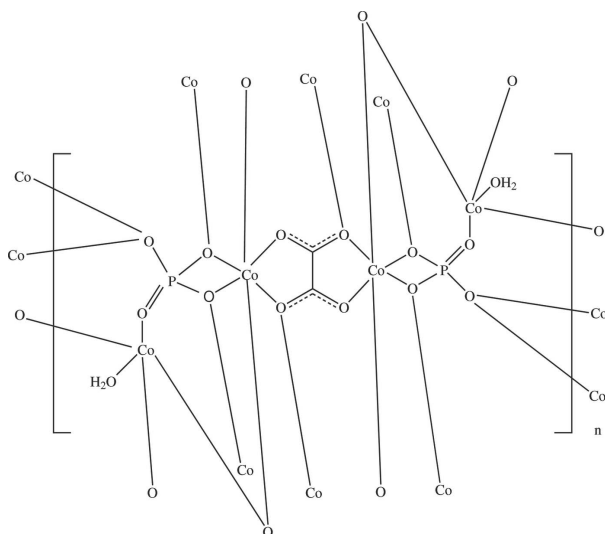
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.041; wR factor = 0.095; data-to-parameter ratio = 10.6.

In the structure of the title compound, $[\text{Co}_4(\text{C}_2\text{O}_4)(\text{PO}_4)_2(\text{H}_2\text{O})_2]_n$, there are layers composed of the phosphate anions and two independent Co^{II} cations. These layers are parallel to (001) and are bridged by the oxalate anions that are situated in special positions on centres of symmetry. One independent Co atom has an octahedral coordination, while the second independent Co atom is coordinated in a trigonal-bipyramidal coordination that includes the water molecule. The crystal packing is stabilized by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds between the coordinated water molecules and oxalate O atoms.

Related literature

For general background, see Lethbridge *et al.* (2004). For the related structure $(\text{C}_4\text{N}_2\text{H}_{12})_{0.5}[\text{Co}_2(\text{HPO}_4)(\text{C}_2\text{O}_4)_{1.5}]$, which also contains the unusual CoO_5 trigonal-bipyramidal configuration, see Choudhury & Natarajan (2000). For the $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding, see Desiraju & Steiner (1999).



Experimental

Crystal data

$[\text{Co}_4(\text{C}_2\text{O}_4)(\text{PO}_4)_2(\text{H}_2\text{O})_2]$
 $M_r = 549.72$

Monoclinic, $P2_1/n$ $a = 7.8541$ (17) Å $b = 4.7829$ (10) Å $c = 14.057$ (3) Å $\beta = 95.937$ (4)° $V = 525.2$ (2) Å³ $Z = 2$ Mo $K\alpha$ radiation $\mu = 6.60$ mm⁻¹ $T = 293$ (2) K $0.32 \times 0.20 \times 0.10$ mm

Data collection

Bruker SMART APEX CCD

area-detector diffractometer

Absorption correction: multi-scan

(SADABS; Bruker, 2000)

 $T_{\text{min}} = 0.22$, $T_{\text{max}} = 0.52$

2798 measured reflections

1133 independent reflections

913 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.034$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.040$ $wR(F^2) = 0.094$ $S = 1.09$

1133 reflections

107 parameters

3 restraints

All H-atom parameters refined

 $\Delta\rho_{\text{max}} = 0.90$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.81$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O7}-\text{H2}\cdots\text{O6}^i$	0.84 (2)	1.94 (3)	2.665 (5)	144 (5)
$\text{O7}-\text{H1}\cdots\text{O6}^{ii}$	0.84 (2)	2.46 (4)	3.188 (5)	145 (5)

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

Data collection: SMART (Bruker, 2000); cell refinement: SMART; data reduction: SAINT-Plus (Bruker, 2000); program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FB2073).

References

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supplementary materials

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Poly[*diaqua-μ*₄-oxalato-di-*μ*₆-phosphato-tetracobalt(II)]

W.-Y. Wu and L.-X. Zhai

Comment

A new class of metal phosphate-oxalates framework structures has been discovered in recent years. In this new class the anions $[\text{PO}_4]^{3-}$ (or $[\text{HPO}_4]^{2-}$) and $[\text{C}_2\text{O}_4]^{2-}$ act as bridging groups that link up with the metal atoms. Both main-group metals (Al, Ga, In, Sn) and transition metals (V, Mn, Fe, Co, Mo) are reported in these systems (Lethbridge *et al.*, 2004). Among these, to the best of our knowledge there is only one example containing Co^{II} : $[\text{C}_4\text{N}_2\text{H}_{12}]_{0.5}[\text{Co}_2(\text{HPO}_4)(\text{C}_2\text{O}_4)_{1.5}]$ (Choudhury & Natarajan, 2000). Here we report the synthesis and the crystal structure of a new oxalate phosphate framework structure containing Co^{II} , $[\text{Co}_4(\text{C}_2\text{O}_4)(\text{PO}_4)_2(\text{H}_2\text{O})_2]$.

The asymmetric unit of the title structure contains two independent Co cations (Fig. 1). Co1 is octahedrally coordinated by six oxygen atoms and Co2 is coordinated by 5 O atoms in a trigonal-bipyramidal configuration. Each phosphate acts as a multiple bridging group, binding six Co atoms to compose the inorganic layer structure. The oxalate group is situated on an inversion centre and links up with two adjacent inorganic layers. The water molecule is coordinated to Co2 (Fig. 2).

Experimental

A mixture of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.1830 g, 0.5 mmol), $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (0.2521 g, 2 mmol), $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ (0.8921 g, 2 mmol) and distilled water (10 ml) was placed into a 23 ml teflon-lined autoclave. The mixture was then heated for 72 h at 425 K. The insoluble purple crystals of the title structure were separated by filtration. The crystals were of rectangular plate-like shape with the average size of $0.4 \times 0.3 \times 0.1$ mm.

Refinement

The H atoms from the water molecule were located in the difference Fourier map and refined with the distance restraints $\text{O}-\text{H}=0.84$ (1), $\text{H}-\text{H}=1.33$ (2) Å, and with $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{O})$.

Figures

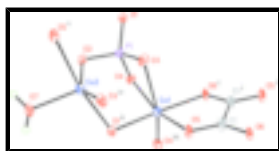


Fig. 1. Coordination environment of Co and P atoms in the title structure. The displacement ellipsoids are shown at the 50% probability level. [Symmetry codes: (i) $1-x, 1-y, 2-z$; (ii) $x, 1+y, z$; (iii) $1/2-x, 1/2+y, 3/2-z$; (iv) $3/2-x, 1/2+y, 3/2-z$; (v) $3/2-x, -1/2+y, 3/2-z$.]

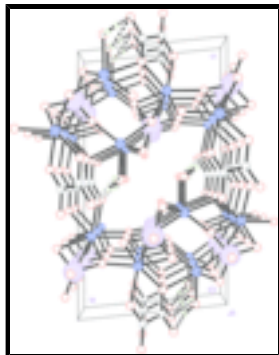


Fig. 2. The packing of the title structure viewed down the *b* axis, showing the cobalt phosphate layers bridged by the oxalate ligands. The hydrogen bonds are shown as dashed lines.

Poly[diaqua- μ_4 -oxalato-di- μ_6 -phosphato-tetracobalt(II)]

Crystal data

[Co₄(C₂O₄)(PO₄)₂(H₂O)₂]

M_r = 549.72

Monoclinic, *P*2₁/*n*

Hall symbol: -*P* 2yn

a = 7.8541 (17) Å

b = 4.7829 (10) Å

c = 14.057 (3) Å

β = 95.937 (4)°

V = 525.2 (2) Å³

Z = 2

*F*₀₀₀ = 532

D_x = 3.476 Mg m⁻³

Mo *K* α radiation

λ = 0.71073 Å

Cell parameters from 897 reflections

θ = 2.9–27.0°

μ = 6.60 mm⁻¹

T = 293 (2) K

Plate, purple

0.32 × 0.20 × 0.10 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 293(2) K

φ and ω scans

Absorption correction: multi-scan (SADABS; Bruker, 2000)

T_{min} = 0.22, *T_{max}* = 0.52

2798 measured reflections

1133 independent reflections

913 reflections with *I* > 2 σ (*I*)

R_{int} = 0.034

θ_{max} = 27.0°

θ_{min} = 2.9°

h = -9→10

k = -6→6

l = -10→17

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2 σ (*F*²)] = 0.040

wR(*F*²) = 0.094

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2]$

where *P* = (*F_o*² + 2*F_c*²)/3

$S = 1.09$	$(\Delta/\sigma)_{\max} < 0.001$
1133 reflections	$\Delta\rho_{\max} = 0.90 \text{ e } \text{\AA}^{-3}$
107 parameters	$\Delta\rho_{\min} = -0.81 \text{ e } \text{\AA}^{-3}$
3 restraints	Extinction correction: SHELXTL (Sheldrick, 2008), $F_c^* = kF_c[1+0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0094 (17)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.40849 (8)	0.46997 (13)	0.80563 (5)	0.0130 (2)
Co2	0.70451 (8)	0.47453 (13)	0.63392 (5)	0.0122 (2)
P1	0.50343 (17)	0.0223 (3)	0.69630 (10)	0.0139 (3)
O1	0.5074 (4)	-0.2997 (7)	0.6975 (2)	0.0126 (7)
O2	0.5646 (4)	0.1346 (7)	0.6038 (2)	0.0155 (7)
O3	0.6187 (4)	0.1571 (8)	0.7802 (2)	0.0158 (7)
O4	0.3244 (4)	0.1379 (7)	0.7118 (2)	0.0148 (7)
C1	0.5588 (6)	0.6255 (11)	0.9925 (4)	0.0171 (10)
O5	0.5694 (4)	0.7013 (8)	0.9079 (2)	0.0183 (8)
O6	0.6373 (4)	0.7274 (7)	1.0660 (2)	0.0134 (7)
O7	0.7066 (4)	0.6605 (9)	0.5068 (2)	0.0197 (8)
H2	0.782 (4)	0.584 (4)	0.478 (3)	0.030*
H1	0.733 (4)	0.830 (4)	0.512 (3)	0.030*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0123 (4)	0.0124 (4)	0.0136 (4)	-0.0042 (2)	-0.0026 (3)	-0.0010 (2)
Co2	0.0129 (4)	0.0118 (4)	0.0109 (4)	-0.0044 (2)	-0.0034 (3)	-0.0011 (2)
P1	0.0132 (6)	0.0138 (6)	0.0146 (7)	0.0006 (4)	0.0005 (5)	-0.0003 (4)
O1	0.0105 (15)	0.0154 (17)	0.0116 (17)	-0.0009 (13)	-0.0003 (13)	0.0001 (13)
O2	0.0181 (17)	0.0162 (18)	0.0126 (18)	0.0010 (13)	0.0039 (13)	-0.0023 (13)
O3	0.0123 (16)	0.0203 (18)	0.0143 (18)	-0.0014 (13)	-0.0008 (14)	-0.0047 (14)
O4	0.0136 (16)	0.0171 (17)	0.0136 (16)	0.0010 (13)	0.0001 (12)	-0.0011 (14)
C1	0.019 (2)	0.022 (3)	0.012 (2)	-0.003 (2)	0.0089 (19)	0.0024 (19)

supplementary materials

O5	0.0235 (19)	0.0231 (19)	0.0074 (17)	-0.0043 (14)	-0.0018 (14)	-0.0004 (14)
O6	0.0164 (17)	0.0176 (17)	0.0054 (16)	-0.0056 (13)	-0.0033 (12)	0.0010 (12)
O7	0.0190 (19)	0.028 (2)	0.0119 (19)	0.0034 (15)	0.0019 (14)	0.0053 (15)

Geometric parameters (\AA , $^\circ$)

Co1—O4 ⁱ	1.989 (3)	P1—O4	1.547 (3)
Co1—O1 ⁱⁱ	2.090 (3)	P1—O3	1.551 (3)
Co1—O6 ⁱⁱⁱ	2.101 (3)	O1—Co1 ^{vi}	2.090 (3)
Co1—O5	2.124 (4)	O1—Co2 ^{vi}	2.156 (3)
Co1—O4	2.126 (4)	O3—Co2 ^v	1.950 (3)
Co1—O3	2.284 (3)	O4—Co1 ^{vii}	1.989 (3)
Co2—O3 ^{iv}	1.950 (3)	C1—O6	1.246 (6)
Co2—O2	1.983 (4)	C1—O5	1.254 (6)
Co2—O7	1.997 (4)	C1—C1 ⁱⁱⁱ	1.542 (10)
Co2—O1 ⁱⁱ	2.156 (3)	O5—Co2 ^{iv}	2.329 (4)
Co2—O5 ^v	2.329 (4)	O6—Co1 ⁱⁱⁱ	2.101 (3)
P1—O2	1.530 (4)	O7—H2	0.84 (2)
P1—O1	1.541 (4)	O7—H1	0.84 (2)
O4 ⁱ —Co1—O1 ⁱⁱ	95.97 (14)	O2—P1—O4	111.3 (2)
O4 ⁱ —Co1—O6 ⁱⁱⁱ	92.87 (14)	O1—P1—O4	111.9 (2)
O1 ⁱⁱ —Co1—O6 ⁱⁱⁱ	166.14 (13)	O2—P1—O3	106.9 (2)
O4 ⁱ —Co1—O5	110.36 (15)	O1—P1—O3	113.4 (2)
O1 ⁱⁱ —Co1—O5	88.72 (13)	O4—P1—O3	102.26 (19)
O6 ⁱⁱⁱ —Co1—O5	78.19 (13)	P1—O1—Co1 ^{vi}	121.8 (2)
O4 ⁱ —Co1—O4	90.16 (9)	P1—O1—Co2 ^{vi}	120.69 (19)
O1 ⁱⁱ —Co1—O4	93.29 (13)	Co1 ^{vi} —O1—Co2 ^{vi}	111.99 (15)
O6 ⁱⁱⁱ —Co1—O4	97.35 (14)	P1—O2—Co2	108.8 (2)
O5—Co1—O4	159.08 (14)	P1—O3—Co2 ^v	127.4 (2)
O4 ⁱ —Co1—O3	156.31 (14)	P1—O3—Co1	90.96 (15)
O1 ⁱⁱ —Co1—O3	84.41 (13)	Co2 ^v —O3—Co1	132.59 (17)
O6 ⁱⁱⁱ —Co1—O3	91.76 (13)	P1—O4—Co1 ^{vii}	132.5 (2)
O5—Co1—O3	93.33 (13)	P1—O4—Co1	97.21 (17)
O4—Co1—O3	66.20 (12)	Co1 ^{vii} —O4—Co1	126.90 (16)
O3 ^{iv} —Co2—O2	147.43 (15)	O6—C1—O5	126.7 (4)
O3 ^{iv} —Co2—O7	106.46 (15)	O6—C1—C1 ⁱⁱⁱ	116.3 (5)
O2—Co2—O7	103.26 (16)	O5—C1—C1 ⁱⁱⁱ	117.0 (6)
O3 ^{iv} —Co2—O1 ⁱⁱ	90.85 (14)	C1—O5—Co1	113.4 (3)
O2—Co2—O1 ⁱⁱ	95.36 (13)	C1—O5—Co2 ^{iv}	121.9 (3)
O7—Co2—O1 ⁱⁱ	102.74 (14)	Co1—O5—Co2 ^{iv}	122.52 (15)
O3 ^{iv} —Co2—O5 ^v	83.95 (13)	C1—O6—Co1 ⁱⁱⁱ	115.0 (3)
O2—Co2—O5 ^v	84.61 (13)	Co2—O7—H2	108 (2)

O7—Co2—O5 ^v	86.98 (14)	Co2—O7—H1	113 (5)
O1 ⁱⁱ —Co2—O5 ^v	169.97 (13)	H2—O7—H1	107 (3)
O2—P1—O1	110.7 (2)		
O2—P1—O1—Co1 ^{vi}	-173.41 (19)	O3—P1—O4—Co1 ^{vii}	-142.9 (3)
O4—P1—O1—Co1 ^{vi}	-48.6 (3)	O2—P1—O4—Co1	-97.2 (2)
O3—P1—O1—Co1 ^{vi}	66.5 (3)	O1—P1—O4—Co1	138.41 (17)
O2—P1—O1—Co2 ^{vi}	35.0 (3)	O3—P1—O4—Co1	16.7 (2)
O4—P1—O1—Co2 ^{vi}	159.81 (19)	O4 ⁱ —Co1—O4—P1	166.4 (2)
O3—P1—O1—Co2 ^{vi}	-85.1 (3)	O1 ⁱⁱ —Co1—O4—P1	70.39 (18)
O1—P1—O2—Co2	-141.52 (19)	O6 ⁱⁱⁱ —Co1—O4—P1	-100.71 (18)
O4—P1—O2—Co2	93.3 (2)	O5—Co1—O4—P1	-24.6 (5)
O3—P1—O2—Co2	-17.6 (2)	O3—Co1—O4—P1	-12.03 (15)
O3 ^{iv} —Co2—O2—P1	42.8 (4)	O4 ⁱ —Co1—O4—Co1 ^{vii}	-32.3 (2)
O7—Co2—O2—P1	-161.77 (19)	O1 ⁱⁱ —Co1—O4—Co1 ^{vii}	-128.3 (2)
O1 ⁱⁱ —Co2—O2—P1	-57.3 (2)	O6 ⁱⁱⁱ —Co1—O4—Co1 ^{vii}	60.6 (2)
O5 ^v —Co2—O2—P1	112.6 (2)	O5—Co1—O4—Co1 ^{vii}	136.7 (3)
O2—P1—O3—Co2 ^v	-108.5 (3)	O3—Co1—O4—Co1 ^{vii}	149.3 (3)
O1—P1—O3—Co2 ^v	13.8 (3)	O6—C1—O5—Co1	-179.2 (4)
O4—P1—O3—Co2 ^v	134.4 (2)	C1 ⁱⁱⁱ —C1—O5—Co1	2.9 (7)
O2—P1—O3—Co1	101.70 (17)	O6—C1—O5—Co2 ^{iv}	17.1 (7)
O1—P1—O3—Co1	-136.07 (17)	C1 ⁱⁱⁱ —C1—O5—Co2 ^{iv}	-160.8 (4)
O4—P1—O3—Co1	-15.39 (19)	O4 ⁱ —Co1—O5—C1	86.3 (4)
O4 ⁱ —Co1—O3—P1	7.9 (4)	O1 ⁱⁱ —Co1—O5—C1	-177.8 (4)
O1 ⁱⁱ —Co1—O3—P1	-84.19 (17)	O6 ⁱⁱⁱ —Co1—O5—C1	-2.4 (3)
O6 ⁱⁱⁱ —Co1—O3—P1	109.16 (17)	O4—Co1—O5—C1	-82.0 (5)
O5—Co1—O3—P1	-172.57 (17)	O3—Co1—O5—C1	-93.5 (4)
O4—Co1—O3—P1	11.90 (15)	O4 ⁱ —Co1—O5—Co2 ^{iv}	-110.0 (2)
O4 ⁱ —Co1—O3—Co2 ^v	-139.2 (3)	O1 ⁱⁱ —Co1—O5—Co2 ^{iv}	-14.1 (2)
O1 ⁱⁱ —Co1—O3—Co2 ^v	128.6 (2)	O6 ⁱⁱⁱ —Co1—O5—Co2 ^{iv}	161.3 (2)
O6 ⁱⁱⁱ —Co1—O3—Co2 ^v	-38.0 (2)	O4—Co1—O5—Co2 ^{iv}	81.7 (4)
O5—Co1—O3—Co2 ^v	40.3 (2)	O3—Co1—O5—Co2 ^{iv}	70.2 (2)
O4—Co1—O3—Co2 ^v	-135.3 (3)	O5—C1—O6—Co1 ⁱⁱⁱ	-177.6 (4)
O2—P1—O4—Co1 ^{vii}	103.2 (3)	C1 ⁱⁱⁱ —C1—O6—Co1 ⁱⁱⁱ	0.3 (7)
O1—P1—O4—Co1 ^{vii}	-21.2 (4)		

Symmetry codes: (i) $-x+1/2, y+1/2, -z+3/2$; (ii) $x, y+1, z$; (iii) $-x+1, -y+1, -z+2$; (iv) $-x+3/2, y+1/2, -z+3/2$; (v) $-x+3/2, y-1/2, -z+3/2$; (vi) $x, y-1, z$; (vii) $-x+1/2, y-1/2, -z+3/2$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O7—H2 \cdots O6 ^v	0.84 (2)	1.94 (3)	2.665 (5)	144 (5)
O7—H1 \cdots O6 ^{iv}	0.84 (2)	2.46 (4)	3.188 (5)	145 (5)

Symmetry codes: (v) $-x+3/2, y-1/2, -z+3/2$; (iv) $-x+3/2, y+1/2, -z+3/2$.

Fig. 1

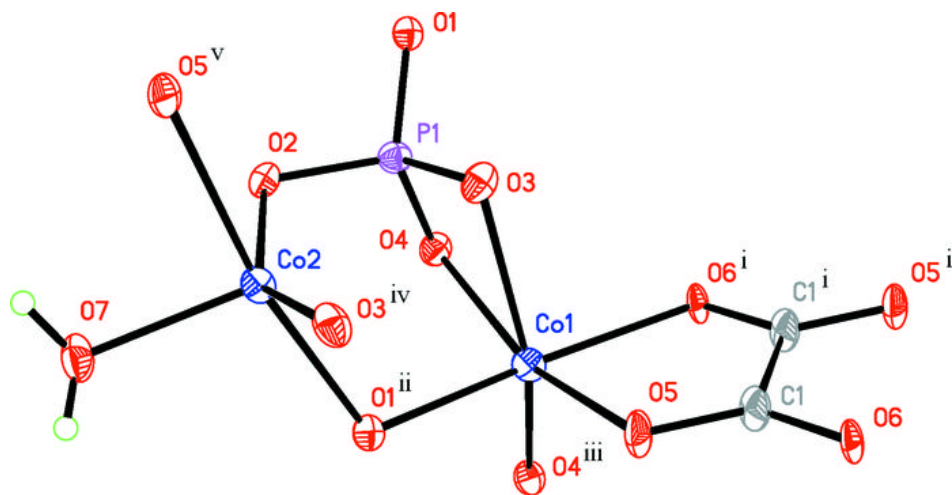


Fig. 2

