

## Poly[[tetraqua( $\mu_6$ -benzene-1,2,4,5-tetracarboxylato)dicobalt(II)] dihydrate]

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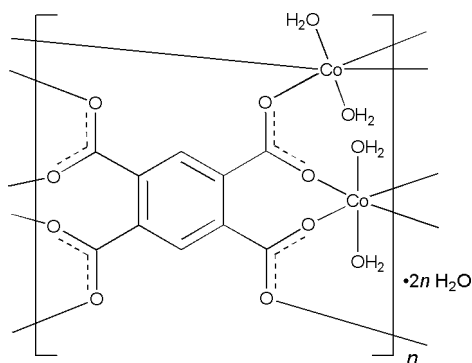
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 Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å; H-atom completeness 72%; disorder in solvent or counterion;  $R$  factor = 0.038;  $wR$  factor = 0.103; data-to-parameter ratio = 14.4.

The asymmetric unit of the title coordination polymer,  $\{[\text{Co}_2(\text{C}_{10}\text{H}_2\text{O}_8)(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}\}_n$ , contains two crystallographically distinct  $\text{Co}^{\text{II}}$  cations, located on inversion centers. Each  $\text{Co}^{\text{II}}$  cation exists in an octahedral coordination environment formed by two water molecules and four carboxylate groups. The deprotonated benzene-1,2,4,5-tetracarboxylic acid ligand, with the center of the benzene ring located on an inversion center, bridges  $\text{Co}^{\text{II}}$  cations to form a (3,4)-connected three-dimensional network that is topologically related to  $\text{Pt}_3\text{O}_4$  (waserite).  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonding between coordinated water molecules and carboxylate groups helps to stabilize the crystal structure. One water molecule is disordered over two positions, with almost equal occupancies.

### Related literature

For related structures, see: Kumagai *et al.* (2002); O'Keeffe *et al.* (2000); Wells (1977); Yang *et al.* (2003).



### Experimental

#### Crystal data

$[\text{Co}_2(\text{C}_{10}\text{H}_2\text{O}_8)(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$   
 $M_r = 238.04$   
 Triclinic,  $P\bar{1}$   
 $a = 6.9362$  (7) Å  
 $b = 7.4559$  (6) Å  
 $c = 8.2797$  (7) Å  
 $\alpha = 90.342$  (8)°  
 $\beta = 109.848$  (7)°

$\gamma = 93.161$  (7)°  
 $V = 402.00$  (6) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 2.14$  mm<sup>-1</sup>  
 $T = 298$  (2) K  
 $0.3 \times 0.1 \times 0.1$  mm

#### Data collection

Bruker P4 diffractometer  
 Absorption correction:  $\psi$  scan  
 (North *et al.*, 1968)  
 $T_{\text{min}} = 0.685$ ,  $T_{\text{max}} = 0.811$   
 2314 measured reflections  
 1883 independent reflections

1570 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.028$   
 3 standard reflections  
 every 24 reflections  
 intensity decay: 1.0%

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$   
 $wR(F^2) = 0.103$   
 $S = 1.05$   
 1883 reflections

131 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.59$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.77$  e Å<sup>-3</sup>

**Table 1**

Selected bond lengths (Å).

Co1—O1	2.065 (2)	Co2—O2	2.083 (2)
Co1—O3	2.046 (2)	Co2—O4 <sup>i</sup>	2.0996 (19)
Co1—O21	2.151 (2)	Co2—O22	2.105 (2)

 Symmetry code: (i)  $x, y + 1, z$ .

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O21—H21A <sup>ii</sup> ···O4 <sup>ii</sup>	0.85	2.03	2.864 (3)	169
O21—H21B <sup>ii</sup> ···O31A	0.82	2.17	2.876 (6)	144
O22—H22A <sup>i</sup> ···O3 <sup>i</sup>	0.84	2.25	2.848 (3)	129
O22—H22B <sup>i</sup> ···O1	0.84	1.99	2.790 (3)	157

 Symmetry codes: (i)  $x, y + 1, z$ ; (ii)  $-x + 1, -y, -z + 1$ .

Data collection: XSCANS (Bruker, 1991); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003) and ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2263).

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**supplementary materials**

*Acta Cryst.* (2007). E63, m1828-m1829 [ doi:10.1107/S1600536807025901 ]

## Poly[[tetraaqua( $\mu_6$ -benzene-1,2,4,5-tetracarboxylato)dicobalt(II)] dihydrate]

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### Comment

As shown in figure 1, a half of the Benzene-1,2,4,5-tetracarboxylic acid ( $H_4btec$ ) is observed in the crystallographic asymmetric unit with center of the benzene ring located on a crystallographic  $\bar{1}$  position. The observation of symmetrical C=O bond lengths ranges from 1.250 (2) to 1.265 (3) Å indicates that all of the carboxyl groups of the  $H_4btec$  are deprotonated to become the  $btec^{4-}$  anion. The asymmetric unit of the title compound contains two crystallographic distinct  $Co^{II}$  cations, located on crystallographic inversion centers with site occupation factor of 0.5. Each Co ion exists in an octahedral coordination environment (Table 1) formed by two water molecules and four carboxylate groups. The  $btec^{4-}$  ligands bridges Co ions to form a three-dimensional metal-organic framework with one-dimensional channels in the [010] direction that are occupied by disordered guest water molecules and coordinated water molecules (Fig. 2). The formula of the compound is assigned to be  $[Co_2(C_{10}H_2O_8)(H_2O)_4 \cdot 2H_2O]_n$ . A  $Ni^{II}$  analogue, and a  $Co^{II}$ - $btec$  coordination polymer with different contents of unit-cell packing were previously reported (Yang *et al.*, 2003; Kumagai *et al.*, 2002).

The network topology of the title compound is analyzed. The carbon atom of the carboxylate group serves as a simple three-connected node linking benzene ring and two Co ions. The benzene ring of the Benzene-1,2,4,5-tetracarboxylate ligand serves as a planar four-connected node. If coordinated water molecules are neglected, each Co ion also serves as a planar four-connected secondary building unit on the basis of four coordinated carboxylate groups. As a result, the title compound represents a new example of a (3,4)-connected net that is topologically related to  $Pt_3O_4$  (waserite) (O'Keeffe *et al.*, 2000; Wells, 1977).

The O—H $\cdots$ O hydroge bonding between coordinated water molecules and carboxyl groups helps to stabilize the crystal structure (Table 2).

### Experimental

All reagents and solvents were used as obtained without further purification.  $CoCl_2 \cdot 6H_2O$  (0.6 mmol),  $H_4btec$  (0.5 mmol) and NaOH (1.0 mmol) were dissolved in 8 ml of distilled water. The mixture was sealed in a Teflon-lined stainless steel vessel and held at 383 K for 72 h. The vessel was gradually cooled to room temperature, and red crystals suitable for crystallographic analysis were obtained after 4 d.

### Refinement

The C-bound H atoms were placed in calculated positions (C—H = 0.93 Å) and refined in the riding-model approximation with  $U_{iso}(H) = 1.2U_{eq}(C)$ . The H atoms of the coordinated water molecules were located in a difference Fourier map, and refined as riding model with O—H distances range from 0.82 to 0.85 Å, and with  $U_{iso}(H) = 1.5U_{eq}(O)$ . The *PLATON SQUEEZE* procedure was used to treat regions of disordered guest molecules that could not be judiciously modeled in terms

## supplementary materials

of atomic sites (Spek, 2003). The number of electrons thus located, 17 per unit cell, is assigned to two molecules of water solvent and is included in the formula, formula weight, calculated density,  $\mu$  and  $F(000)$ . There is difference between the reported and calculated values. Two largest residual densities located from the difference Fourier map separated by 1.93 Å are assigned to two disordered guest water molecules O31A and O31B. The refinement of relative site occupation factor leads to 0.53 and 0.47 for O31A and O31B, respectively. No attempt was made to locate hydrogen atoms of the disordered guest water molecules.

### Figures

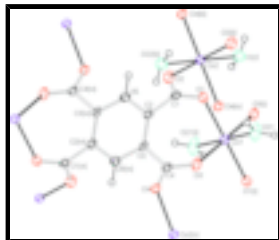


Fig. 1. The asymmetric unit, expanded to show the complete coordination of the Co ions, with displacement ellipsoids drawn at the 50% probability level. Guest water molecules are omitted for clarity. (Symmetry codes are the same as geometric tables.)

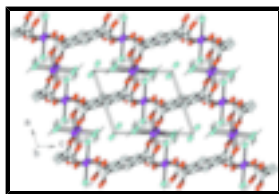


Fig. 2. Solid-state packing diagram of the three-dimensional framework.

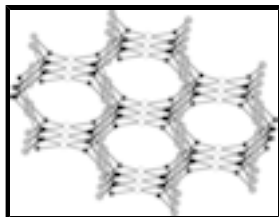


Fig. 3. Topological view of the  $\text{Pt}_3\text{O}_4$  related (3,4)-connected net of the title compound. (black sphere: C atom of carboxylate group; white sphere: center of  $\text{btec}^{4-}$  ligand; grey sphere: Co ion.)

### Poly[[tetraaqua( $\mu_6$ -benzene-1,2,4,5-tetracarboxylato)dicobalt(II)] dihydrate]

#### Crystal data

$[\text{Co}_2(\text{C}_{10}\text{H}_2\text{O}_8)(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$

$M_r = 238.04$

Triclinic,  $P\bar{1}$

Hall symbol:  $-P\ 1$

$a = 6.9362$  (7) Å

$b = 7.4559$  (6) Å

$c = 8.2797$  (7) Å

$\alpha = 90.342$  (8)°

$\beta = 109.848$  (7)°

$\gamma = 93.161$  (7)°

$V = 402.00$  (6) Å<sup>3</sup>

$Z = 2$

$F_{000} = 240$

$D_x = 1.966$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 34 reflections

$\theta = 5.6$ – $12.8$ °

$\mu = 2.14$  mm<sup>-1</sup>

$T = 298$  (2) K

Column, red

$0.3 \times 0.1 \times 0.1$  mm

*Data collection*

Bruker P4 diffractometer	$R_{\text{int}} = 0.028$
Radiation source: sealed tube	$\theta_{\text{max}} = 28.0^\circ$
Monochromator: graphite	$\theta_{\text{min}} = 2.6^\circ$
$T = 298(2)$ K	$h = -9 \rightarrow 1$
$2\theta/\omega$ scans	$k = -9 \rightarrow 9$
Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968)	$l = -10 \rightarrow 10$
$T_{\text{min}} = 0.685$ , $T_{\text{max}} = 0.811$	3 standard reflections
2314 measured reflections	every 24 reflections
1883 independent reflections	intensity decay: 1.0%
1570 reflections with $I > 2\sigma(I)$	

*Refinement*

Refinement on $F^2$	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2 + 0.4406P]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.103$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.59 \text{ e } \text{\AA}^{-3}$
1883 reflections	$\Delta\rho_{\text{min}} = -0.77 \text{ e } \text{\AA}^{-3}$
131 parameters	Extinction correction: none

*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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Co1	0	0	0.5	0.01624 (16)	
Co2	0.5	0.5	0.5	0.01426 (16)	
O1	0.1694 (3)	0.2325 (3)	0.6119 (3)	0.0223 (4)	
O2	0.4875 (3)	0.3576 (3)	0.7123 (3)	0.0227 (4)	
O3	0.2645 (3)	-0.1283 (3)	0.5378 (3)	0.0268 (5)	
O4	0.5570 (3)	-0.2620 (3)	0.6499 (2)	0.0175 (4)	
O21	0.0391 (4)	0.0928 (4)	0.2669 (3)	0.0342 (6)	
H21A	0.151	0.1538	0.2826	0.051*	
H21B	-0.0337	0.0886	0.1656	0.051*	
O22	0.1793 (3)	0.5155 (3)	0.3953 (3)	0.0265 (5)	
H22A	0.1224	0.6092	0.404	0.04*	

## supplementary materials

H22B	0.1421	0.4397	0.4559	0.04*	
O31A	-0.0980 (8)	0.2254 (8)	-0.0766 (7)	0.0469 (18)	0.527 (8)
O31B	-0.1415 (13)	0.4510 (14)	0.0178 (11)	0.089 (4)	0.473 (8)
C1	0.3523 (4)	0.2411 (4)	0.7155 (3)	0.0155 (5)	
C2	0.4193 (4)	0.1081 (4)	0.8574 (3)	0.0150 (5)	
C3	0.4640 (4)	-0.0677 (4)	0.8333 (3)	0.0136 (5)	
C4	0.4246 (4)	-0.1563 (4)	0.6596 (3)	0.0145 (5)	
C5	0.4549 (4)	0.1741 (4)	1.0238 (3)	0.0163 (5)	
H5A	0.4241	0.2912	1.0399	0.02*	

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Co1	0.0143 (3)	0.0151 (3)	0.0165 (3)	0.00031 (19)	0.0018 (2)	-0.00175 (19)
Co2	0.0178 (3)	0.0117 (3)	0.0122 (2)	-0.00056 (19)	0.00392 (19)	-0.00044 (18)
O1	0.0210 (10)	0.0161 (10)	0.0224 (10)	-0.0007 (8)	-0.0018 (8)	0.0031 (8)
O2	0.0236 (11)	0.0234 (11)	0.0181 (9)	-0.0065 (8)	0.0042 (8)	0.0048 (8)
O3	0.0238 (11)	0.0343 (13)	0.0170 (10)	0.0117 (9)	-0.0015 (8)	-0.0091 (9)
O4	0.0177 (9)	0.0163 (9)	0.0170 (9)	0.0033 (7)	0.0035 (8)	-0.0042 (7)
O21	0.0222 (11)	0.0541 (16)	0.0214 (11)	-0.0087 (11)	0.0028 (9)	0.0053 (10)
O22	0.0219 (10)	0.0225 (11)	0.0346 (12)	0.0025 (9)	0.0088 (9)	-0.0006 (9)
O31A	0.038 (3)	0.059 (4)	0.040 (3)	-0.001 (3)	0.009 (2)	0.004 (3)
O31B	0.068 (6)	0.092 (7)	0.067 (5)	-0.026 (5)	-0.023 (4)	0.007 (5)
C1	0.0210 (13)	0.0127 (12)	0.0120 (11)	0.0002 (10)	0.0048 (10)	-0.0032 (9)
C2	0.0143 (12)	0.0158 (12)	0.0127 (11)	-0.0026 (10)	0.0025 (10)	-0.0019 (9)
C3	0.0140 (12)	0.0147 (12)	0.0107 (11)	-0.0023 (9)	0.0032 (9)	-0.0035 (9)
C4	0.0174 (12)	0.0129 (12)	0.0130 (11)	-0.0008 (10)	0.0052 (10)	-0.0026 (9)
C5	0.0201 (13)	0.0131 (12)	0.0158 (12)	0.0007 (10)	0.0062 (10)	-0.0018 (9)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

Co1—O1	2.065 (2)	O3—C4	1.250 (3)
Co1—O1 <sup>i</sup>	2.065 (2)	O4—C4	1.264 (3)
Co1—O3 <sup>i</sup>	2.046 (2)	O4—Co2 <sup>v</sup>	2.0996 (19)
Co1—O3	2.046 (2)	O21—H21A	0.8472
Co1—O21	2.151 (2)	O21—H21B	0.8188
Co1—O21 <sup>i</sup>	2.151 (2)	O22—H22A	0.8359
Co2—O2 <sup>ii</sup>	2.083 (2)	O22—H22B	0.8447
Co2—O2	2.083 (2)	C1—C2	1.508 (4)
Co2—O4 <sup>iii</sup>	2.0996 (19)	C2—C3	1.392 (4)
Co2—O4 <sup>iv</sup>	2.0996 (19)	C2—C5	1.395 (3)
Co2—O22	2.105 (2)	C3—C5 <sup>vi</sup>	1.398 (4)
Co2—O22 <sup>ii</sup>	2.105 (2)	C3—C4	1.511 (3)
O1—C1	1.265 (3)	C5—C3 <sup>vi</sup>	1.398 (4)
O2—C1	1.250 (3)	C5—H5A	0.93
O3 <sup>i</sup> —Co1—O3	180.00 (12)	O4 <sup>iv</sup> —Co2—O22 <sup>ii</sup>	96.15 (8)

O3 <sup>i</sup> —Co1—O1	89.65 (9)	O22—Co2—O22 <sup>ii</sup>	180.0000 (10)
O3—Co1—O1	90.35 (9)	C1—O1—Co1	125.58 (19)
O3 <sup>i</sup> —Co1—O1 <sup>i</sup>	90.35 (9)	C1—O2—Co2	126.83 (18)
O3—Co1—O1 <sup>i</sup>	89.65 (9)	C4—O3—Co1	137.74 (18)
O1—Co1—O1 <sup>i</sup>	180	C4—O4—Co2 <sup>v</sup>	126.45 (17)
O3 <sup>i</sup> —Co1—O21	94.40 (10)	Co1—O21—H21A	113.9
O3—Co1—O21	85.60 (10)	Co1—O21—H21B	134.3
O1—Co1—O21	85.35 (9)	H21A—O21—H21B	111.6
O1 <sup>i</sup> —Co1—O21	94.65 (9)	Co2—O22—H22A	121.8
O3 <sup>i</sup> —Co1—O21 <sup>i</sup>	85.60 (10)	Co2—O22—H22B	99.9
O3—Co1—O21 <sup>i</sup>	94.40 (10)	H22A—O22—H22B	105.4
O1—Co1—O21 <sup>i</sup>	94.65 (9)	O2—C1—O1	124.3 (3)
O1 <sup>i</sup> —Co1—O21 <sup>i</sup>	85.35 (9)	O2—C1—C2	115.2 (2)
O21—Co1—O21 <sup>i</sup>	180.0000 (10)	O1—C1—C2	120.4 (2)
O2 <sup>ii</sup> —Co2—O2	180.0000 (10)	C3—C2—C5	119.3 (2)
O2 <sup>ii</sup> —Co2—O4 <sup>iii</sup>	91.12 (8)	C3—C2—C1	124.0 (2)
O2—Co2—O4 <sup>iii</sup>	88.88 (8)	C5—C2—C1	116.4 (2)
O2 <sup>ii</sup> —Co2—O4 <sup>iv</sup>	88.88 (8)	C2—C3—C5 <sup>vi</sup>	119.4 (2)
O2—Co2—O4 <sup>iv</sup>	91.12 (8)	C2—C3—C4	124.2 (2)
O4 <sup>iii</sup> —Co2—O4 <sup>iv</sup>	180	C5 <sup>vi</sup> —C3—C4	116.4 (2)
O2 <sup>ii</sup> —Co2—O22	86.24 (9)	O3—C4—O4	123.9 (2)
O2—Co2—O22	93.76 (9)	O3—C4—C3	119.9 (2)
O4 <sup>iii</sup> —Co2—O22	96.15 (8)	O4—C4—C3	116.1 (2)
O4 <sup>iv</sup> —Co2—O22	83.85 (8)	C2—C5—C3 <sup>vi</sup>	121.4 (2)
O2 <sup>ii</sup> —Co2—O22 <sup>ii</sup>	93.76 (9)	C2—C5—H5A	119.3
O2—Co2—O22 <sup>ii</sup>	86.24 (9)	C3 <sup>vi</sup> —C5—H5A	119.3
O4 <sup>iii</sup> —Co2—O22 <sup>ii</sup>	83.85 (8)		

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

*Hydrogen-bond geometry* ( $\text{\AA}, ^\circ$ )

<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>
O21—H21A $\cdots$ O4 <sup>iv</sup>	0.85	2.03	2.864 (3)	169
O21—H21B $\cdots$ O31A	0.82	2.17	2.876 (6)	144
O22—H22A $\cdots$ O3 <sup>iii</sup>	0.84	2.25	2.848 (3)	129
O22—H22B $\cdots$ O1	0.84	1.99	2.790 (3)	157

Symmetry codes: (iv)  $-x+1, -y, -z+1$ ; (iii)  $x, y+1, z$ .



Fig. 1

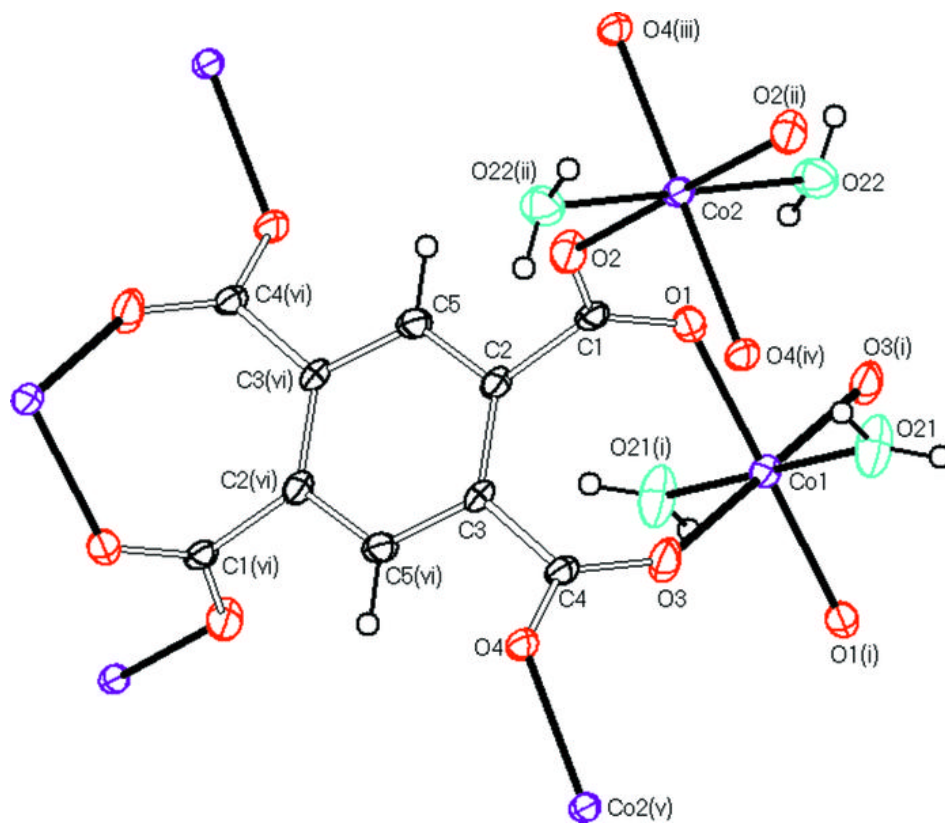


Fig. 2

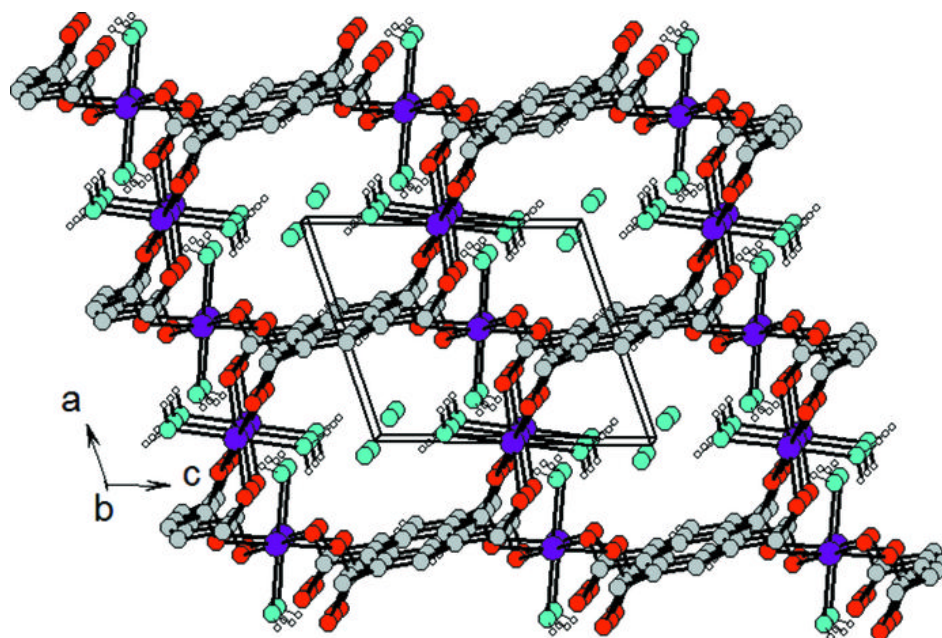


Fig. 3

