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## Hexaaquacobalt(II) 3,3'-dicarboxy-biphenyl-4,4'-dicarboxylate

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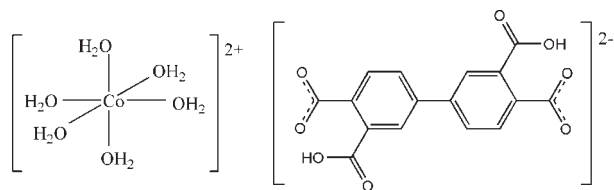
Received 24 June 2010; accepted 19 July 2010

Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å;  $R$  factor = 0.048;  $wR$  factor = 0.169; data-to-parameter ratio = 10.9.

In the crystal structure of the title compound,  $[\text{Co}(\text{H}_2\text{O})_6]-(\text{C}_{16}\text{H}_8\text{O}_8)$ , both the cation and anion are centrosymmetric. The Co cation displays a  $\text{CoO}_6$  octahedral geometry formed by six water molecules. In the anion, the two carboxyl groups are oriented at dihedral angles of 4.8 (5) and 10.4 (7)° with respect to the benzene ring. Very strong  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds between the protonated and deprotonated carboxylate groups occur. Neighbouring cations and anions are connected through  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds into a three-dimensional supramolecular structure.

## Related literature

For related metal complexes with the biphenyl-3,3',4,4'-tetracarboxylate ligand, see: Sun *et al.* (2009); Wang *et al.* (2005, 2006). For the structures containing the 4,4'-dicarboxy-biphenyl-3,3'-dicarboxylate ligand, see: Kang *et al.* (2009a,b); Zhu *et al.* (2008).



## Experimental

## Crystal data

$[\text{Co}(\text{H}_2\text{O})_6](\text{C}_{16}\text{H}_8\text{O}_8)$   
 $M_r = 495.25$   
 Triclinic,  $P\bar{1}$   
 $a = 6.5197$  (14) Å  
 $b = 7.9514$  (17) Å  
 $c = 9.664$  (2) Å

$\alpha = 76.339$  (2)°  
 $\beta = 87.656$  (2)°  
 $\gamma = 86.221$  (2)°  
 $V = 485.57$  (18) Å<sup>3</sup>  
 $Z = 1$   
 Mo  $K\alpha$  radiation

$\mu = 0.96$  mm<sup>-1</sup>  
 $T = 293$  K

0.23 × 0.19 × 0.12 mm

## Data collection

Bruker APEXII CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Bruker, 2001)  
 $T_{\min} = 0.804$ ,  $T_{\max} = 0.895$

2871 measured reflections  
 1590 independent reflections  
 1305 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.028$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$   
 $wR(F^2) = 0.169$   
 $S = 1.00$   
 1590 reflections  
 146 parameters  
 1 restraint

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.47$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.43$  e Å<sup>-3</sup>

**Table 1**  
 Selected bond lengths (Å).

Co1—O5	2.054 (3)	Co1—O7	2.082 (3)
Co1—O6	2.027 (3)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2 $\cdots$ O4	0.85 (2)	1.55 (2)	2.391 (5)	173 (8)
O5—H5B $\cdots$ O4 <sup>i</sup>	0.96	2.17	2.820 (5)	124
O5—H5C $\cdots$ O2 <sup>ii</sup>	0.96	1.97	2.789 (4)	142
O6—H6A $\cdots$ O3 <sup>iii</sup>	0.96	1.84	2.676 (4)	144
O6—H6C $\cdots$ O1 <sup>ii</sup>	0.96	1.79	2.708 (4)	159
O7—H7A $\cdots$ O1 <sup>iv</sup>	0.96	1.83	2.749 (5)	159
O7—H7C $\cdots$ O3	0.96	1.99	2.822 (5)	144

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

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; 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.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2789).

## References

- Bruker (2001). SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Bruker (2007). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Kang, J., Huang, C.-C., Jiang, Z.-Q., Huang, S. & Huang, S.-L. (2009a). *Acta Cryst.* **E65**, m452.  
 Kang, J., Huang, C.-C., Zhai, L.-S., Qin, X.-H. & Liu, Z.-Q. (2009b). *Acta Cryst.* **E65**, m380–m381.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
 Sun, L.-X., Qi, Y., Che, Y.-X., Batten, S. R. & Zheng, J.-M. (2009). *Cryst. Growth Des.* **9**, 2995–2998.  
 Wang, X.-L., Cao, Q. & Wang, E.-B. (2005). *Eur. J. Inorg. Chem.* pp. 3418–3421.  
 Wang, X.-L., Cao, Q. & Wang, E.-B. (2006). *Cryst. Growth Des.* **6**, 439–433.  
 Zhu, S., Zhang, H. & Shao, M. (2008). *Transition Met. Chem.* **33**, 669–680.

**supplementary materials**

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## Hexaaquacobalt(II) 3,3'-dicarboxybiphenyl-4,4'-dicarboxylate

Y.-H. Zhang, J.-M. Han and Z.-Z. Li

### Comment

Biphenyl-3,3',4,4'-tetracarboxylic acid have been used to construct high-dimensional supramolecular networks due to their versatile coordination modes and potential covalent or hydrogen bonding interactions with related parts in the assembly process (Sun *et al.* 2009; Wang *et al.* 2005) such as one-dimensional covalent zigzag chain coexist with one-dimensional hydrogen-bonded ladder (Wang *et al.* 2006). Here we reported a mononuclear complex, containing two ionic components of complex  $[\text{Co}(\text{H}_2\text{O})_6](\text{C}_{16}\text{H}_{18}\text{O}_8)$  (I) in which the two parts are connected *via* O—H $\cdots$ O hydrogen bonds forming a three-dimensional framework. The structure of the compound (I) consists of discrete ionic entities. A labeled diagram of the crystal  $[\text{Co}(\text{H}_2\text{O})_6](\text{C}_{16}\text{H}_{18}\text{O}_{18})$  is shown in Fig. 1. In the cations, the metal atom is surrounded by six aqua ligands, exhibiting a slightly distorted octahedral stereochemistry. The *cis/trans* O—Co—O angles are nearly 90°. The average Co—O distance for compound (I) is 2.077 Å. The anion 3,3',4,4'-biphenyltetralate contain inversion center. The mean plane was calculated throughout the six atoms of the benzene ring. Because of symmetric reason, the two benzene rings of the biphenyl ligand are coplanar. The carboxylate groups are almost coplanar with the benzene ring with the largest deviation of -0.205 (6) Å for O4. As expected, there are considerable hydrogen bonds in the structure. The bond distances and angles are listed in Table 2. A three-dimensional structure was formed *via* three kinds of hydrogen bonds between the coordinated water molecules and carboxyl groups which also help to consolidate the crystal packing (Fig. 2).

### Experimental

A mixture of biphenyl-3,3',4,4'-tetracarboxylic acid (0.2 mmol) and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.4 mmol) in 12 ml methanol/water (8:3) sealed in a 25 ml Teflon-lined stainless steel autoclave was kept at 393 K for three days. Single crystals suitable for the X-ray experiment were obtained.

### Refinement

The carboxyl H atom was located in a difference map and refined isotropically. The H atoms of aromatic ring and water molecules were generated geometrically and were included in the refinement in the riding model approximation with C—H = 0.93 Å,  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$  and O—H = 0.96 Å,  $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$ .

## Figures

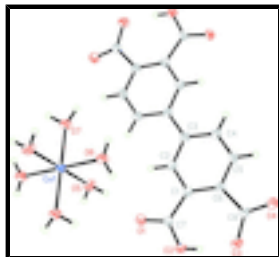


Fig. 1. The molecular structure of the title complex with the atom-numbering diagram. Ellipsoids were drawn at the 30% probability level.

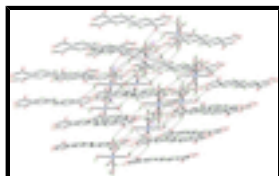


Fig. 2. The packing diagram of (I). Hydrogen bonds are marked by dashed line.

## Hexaaquacobalt(II) 3,3'-dicarboxybiphenyl-4,4'-dicarboxylate

### Crystal data

[Co(H<sub>2</sub>O)<sub>6</sub>](C<sub>16</sub>H<sub>8</sub>O<sub>8</sub>)

*M<sub>r</sub>* = 495.25

Triclinic, *P* $\bar{1}$

*a* = 6.5197 (14) Å

*b* = 7.9514 (17) Å

*c* = 9.664 (2) Å

$\alpha$  = 76.339 (2)°

$\beta$  = 87.656 (2)°

$\gamma$  = 86.221 (2)°

*V* = 485.57 (18) Å<sup>3</sup>

*Z* = 1

*F*(000) = 255

*D<sub>x</sub>* = 1.694 Mg m<sup>-3</sup>

Mo *K*α radiation,  $\lambda$  = 0.71073 Å

Cell parameters from 774 reflections

$\theta$  = 2.2–25.0°

$\mu$  = 0.96 mm<sup>-1</sup>

*T* = 293 K

Block, pink

0.23 × 0.19 × 0.12 mm

### Data collection

Bruker APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (*SADABS*; Bruker, 2001)

*T<sub>min</sub>* = 0.804, *T<sub>max</sub>* = 0.895

2871 measured reflections

1590 independent reflections

1305 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.028

$\theta_{\max}$  = 25.0°,  $\theta_{\min}$  = 2.2°

*h* = -7→7

*k* = -9→9

*l* = -11→10

### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

$$R[F^2 > 2\sigma(F^2)] = 0.048$$

$$wR(F^2) = 0.169$$

$$S = 1.00$$

1590 reflections

146 parameters

1 restraint

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.1263P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.47 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$$

### 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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	1.0000	0.0000	0.5000	0.0281 (3)
O1	0.5091 (5)	0.1808 (4)	1.2457 (3)	0.0408 (8)
O2	0.3077 (5)	0.1278 (4)	1.0880 (4)	0.0396 (8)
O3	0.4682 (5)	0.2634 (5)	0.6417 (4)	0.0494 (10)
O4	0.2791 (5)	0.1755 (4)	0.8356 (3)	0.0417 (8)
O5	1.0135 (5)	-0.0174 (5)	0.2911 (3)	0.0434 (9)
H5B	0.9751	-0.1302	0.2858	0.065*
H5C	1.1512	-0.0002	0.2537	0.065*
O6	1.2248 (5)	0.1707 (5)	0.4594 (4)	0.0444 (9)
H6A	1.3079	0.1541	0.5419	0.067*
H6C	1.3089	0.1508	0.3803	0.067*
O7	0.7843 (5)	0.2081 (4)	0.4461 (4)	0.0441 (9)
H7A	0.6763	0.1760	0.3946	0.066*
H7C	0.7277	0.2372	0.5314	0.066*
C1	0.6112 (6)	0.2899 (5)	1.0027 (4)	0.0255 (9)
C2	0.7719 (6)	0.3637 (5)	1.0551 (5)	0.0257 (9)
H2B	0.7823	0.3463	1.1532	0.031*
C3	0.9157 (6)	0.4613 (5)	0.9679 (5)	0.0267 (9)
C4	0.8945 (7)	0.4888 (6)	0.8216 (5)	0.0336 (10)
H4B	0.9850	0.5580	0.7599	0.040*
C5	0.7413 (7)	0.4147 (6)	0.7674 (5)	0.0358 (11)
H5A	0.7335	0.4324	0.6691	0.043*
C6	0.5974 (6)	0.3144 (5)	0.8535 (5)	0.0279 (9)

## supplementary materials

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C7	0.4682 (6)	0.1923 (5)	1.1202 (5)	0.0288 (10)
C8	0.4405 (7)	0.2462 (6)	0.7705 (5)	0.0311 (10)
H2	0.293 (12)	0.152 (9)	0.999 (2)	0.10 (3)*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Co1	0.0215 (5)	0.0511 (6)	0.0143 (5)	-0.0164 (3)	0.0002 (3)	-0.0092 (4)
O1	0.0359 (17)	0.070 (2)	0.0193 (19)	-0.0237 (16)	0.0020 (14)	-0.0103 (15)
O2	0.0344 (17)	0.062 (2)	0.025 (2)	-0.0271 (15)	0.0024 (15)	-0.0103 (16)
O3	0.046 (2)	0.087 (3)	0.024 (2)	-0.0326 (19)	0.0002 (16)	-0.0224 (17)
O4	0.0316 (17)	0.066 (2)	0.032 (2)	-0.0238 (15)	0.0005 (14)	-0.0133 (16)
O5	0.0368 (18)	0.077 (2)	0.0222 (18)	-0.0290 (16)	0.0048 (14)	-0.0167 (16)
O6	0.0373 (18)	0.074 (2)	0.028 (2)	-0.0310 (16)	0.0045 (15)	-0.0191 (16)
O7	0.0361 (18)	0.070 (2)	0.0301 (19)	-0.0101 (16)	-0.0049 (15)	-0.0162 (16)
C1	0.025 (2)	0.032 (2)	0.022 (2)	-0.0069 (16)	0.0007 (17)	-0.0092 (17)
C2	0.026 (2)	0.034 (2)	0.018 (2)	-0.0103 (17)	-0.0028 (17)	-0.0074 (17)
C3	0.024 (2)	0.033 (2)	0.024 (2)	-0.0054 (17)	-0.0038 (18)	-0.0064 (17)
C4	0.038 (2)	0.045 (2)	0.022 (2)	-0.023 (2)	-0.0027 (19)	-0.0090 (19)
C5	0.042 (3)	0.045 (3)	0.024 (3)	-0.019 (2)	-0.002 (2)	-0.0117 (19)
C6	0.024 (2)	0.034 (2)	0.029 (3)	-0.0078 (17)	-0.0020 (18)	-0.0103 (18)
C7	0.028 (2)	0.037 (2)	0.026 (3)	-0.0109 (18)	0.0014 (19)	-0.0126 (18)
C8	0.029 (2)	0.040 (2)	0.029 (3)	-0.0118 (19)	-0.0047 (19)	-0.0137 (19)

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

Co1—O5	2.054 (3)	O7—H7A	0.9600
Co1—O5 <sup>i</sup>	2.054 (3)	O7—H7C	0.9600
Co1—O6	2.027 (3)	C1—C2	1.401 (6)
Co1—O6 <sup>i</sup>	2.027 (3)	C1—C6	1.415 (6)
Co1—O7	2.082 (3)	C1—C7	1.534 (6)
Co1—O7 <sup>i</sup>	2.082 (3)	C2—C3	1.383 (6)
O1—C7	1.233 (5)	C2—H2B	0.9300
O2—C7	1.276 (5)	C3—C4	1.390 (6)
O2—H2	0.85 (2)	C3—C3 <sup>ii</sup>	1.516 (8)
O3—C8	1.226 (6)	C4—C5	1.374 (6)
O4—C8	1.295 (5)	C4—H4B	0.9300
O5—H5B	0.9600	C5—C6	1.389 (6)
O5—H5C	0.9601	C5—H5A	0.9300
O6—H6A	0.9600	C6—C8	1.526 (6)
O6—H6C	0.9600		
O6—Co1—O6 <sup>i</sup>	180.0	C2—C1—C6	118.3 (4)
O6—Co1—O5	90.40 (13)	C2—C1—C7	113.4 (4)
O6 <sup>i</sup> —Co1—O5	89.60 (13)	C6—C1—C7	128.3 (4)
O6—Co1—O5 <sup>i</sup>	89.60 (13)	C3—C2—C1	123.2 (4)
O6 <sup>i</sup> —Co1—O5 <sup>i</sup>	90.40 (13)	C3—C2—H2B	118.4
O5—Co1—O5 <sup>i</sup>	180.0	C1—C2—H2B	118.4

O6—Co1—O7	88.72 (14)	C2—C3—C4	117.5 (4)
O6 <sup>i</sup> —Co1—O7	91.28 (14)	C2—C3—C3 <sup>ii</sup>	120.3 (5)
O5—Co1—O7	89.16 (14)	C4—C3—C3 <sup>ii</sup>	122.2 (5)
O5 <sup>i</sup> —Co1—O7	90.84 (14)	C5—C4—C3	120.6 (4)
O6—Co1—O7 <sup>i</sup>	91.28 (14)	C5—C4—H4B	119.7
O6 <sup>i</sup> —Co1—O7 <sup>i</sup>	88.72 (14)	C3—C4—H4B	119.7
O5—Co1—O7 <sup>i</sup>	90.83 (14)	C4—C5—C6	122.6 (4)
O5 <sup>i</sup> —Co1—O7 <sup>i</sup>	89.17 (14)	C4—C5—H5A	118.7
O7—Co1—O7 <sup>i</sup>	180.000 (1)	C6—C5—H5A	118.7
C7—O2—H2	111 (5)	C5—C6—C1	117.8 (4)
Co1—O5—H5B	109.3	C5—C6—C8	113.7 (4)
Co1—O5—H5C	109.4	C1—C6—C8	128.5 (4)
H5B—O5—H5C	109.5	O1—C7—O2	120.9 (4)
Co1—O6—H6A	109.3	O1—C7—C1	118.8 (4)
Co1—O6—H6C	109.1	O2—C7—C1	120.3 (4)
H6A—O6—H6C	109.5	O3—C8—O4	121.2 (4)
Co1—O7—H7A	109.1	O3—C8—C6	118.9 (4)
Co1—O7—H7C	109.5	O4—C8—C6	119.9 (4)
H7A—O7—H7C	109.5		
C6—C1—C2—C3	0.9 (6)	C2—C1—C6—C8	179.1 (4)
C7—C1—C2—C3	-178.3 (4)	C7—C1—C6—C8	-1.9 (7)
C1—C2—C3—C4	1.4 (6)	C2—C1—C7—O1	-2.9 (6)
C1—C2—C3—C3 <sup>ii</sup>	179.4 (4)	C6—C1—C7—O1	178.0 (4)
C2—C3—C4—C5	-2.8 (7)	C2—C1—C7—O2	175.6 (4)
C3 <sup>ii</sup> —C3—C4—C5	179.2 (5)	C6—C1—C7—O2	-3.5 (7)
C3—C4—C5—C6	2.0 (7)	C5—C6—C8—O3	9.6 (6)
C4—C5—C6—C1	0.3 (7)	C1—C6—C8—O3	-171.2 (4)
C4—C5—C6—C8	179.6 (4)	C5—C6—C8—O4	-168.7 (4)
C2—C1—C6—C5	-1.8 (6)	C1—C6—C8—O4	10.4 (7)
C7—C1—C6—C5	177.3 (4)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2 $\cdots$ O4	0.85 (2)	1.55 (2)	2.391 (5)	173 (8)
O5—H5B $\cdots$ O4 <sup>iii</sup>	0.96	2.17	2.820 (5)	124
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O6—H6A $\cdots$ O3 <sup>v</sup>	0.96	1.84	2.676 (4)	144
O6—H6C $\cdots$ O1 <sup>iv</sup>	0.96	1.79	2.708 (4)	159
O7—H7A $\cdots$ O1 <sup>vi</sup>	0.96	1.83	2.749 (5)	159
O7—H7C $\cdots$ O3	0.96	1.99	2.822 (5)	144

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

Fig. 1

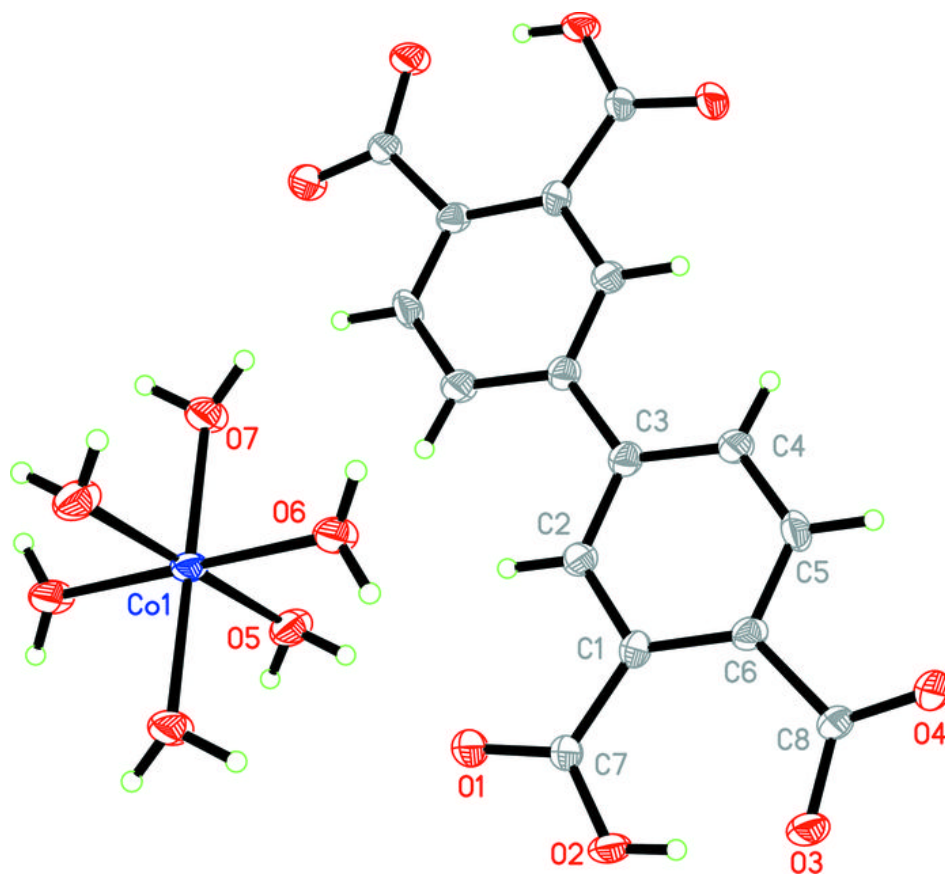




Fig. 2

