

## catena-Poly[bis[(1,10-phenanthroline)-cobalt(II)]- $\mu_4$ -3,6-dicarboxycyclohexane-1,2,4,5-tetracarboxylato]

**Wei Xu**

Center of Applied Solid State Chemistry Research, Ningbo University, Ningbo 315211, People's Republic of China

Correspondence e-mail: xuwei@nbu.edu.cn

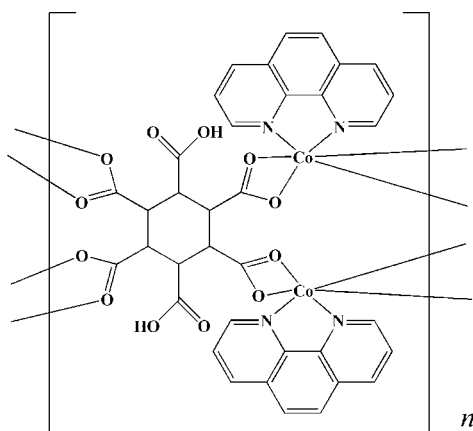
Received 24 May 2011; accepted 26 May 2011

 Key indicators: single-crystal X-ray study;  $T = 295$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.031;  $wR$  factor = 0.083; data-to-parameter ratio = 15.1.

In the title compound,  $[\text{Co}_2(\text{C}_{12}\text{H}_8\text{O}_{12})(\text{C}_{12}\text{H}_8\text{N}_2)_2]_n$ , each 3,6-dicarboxycyclohexane-1,2,4,5-tetracarboxylate ( $\text{H}_2\text{chhc}^{4-}$ ) anion has crystallographically imposed  $C_2$  symmetry and bridges four six-coordinate Co atoms, generating polymeric chains running along [010]. These chains are further extended into a three-dimensional network *via*  $\text{O}-\text{H}\cdots\text{O}$  hydrogen-bonding interactions and interchain  $\pi-\pi$  stacking interactions [centroid-centroid distance = 3.662 (2) Å].

### Related literature

For the design and synthesis of coordination polymer complexes and their potential applications, see: Biradha *et al.* (2006); Bauer *et al.* (2007); Zacher *et al.* (2011). For the 1,2,3,4,5,6-cyclohexanehexacarboxylate ligand, see: Li *et al.* (2006); Wang *et al.* (2008); Thuéry & Masci (2010). For related structures, see: Konar *et al.* (2004); Li *et al.* (2006).



### Experimental

#### Crystal data

$[\text{Co}_2(\text{C}_{12}\text{H}_8\text{O}_{12})(\text{C}_{12}\text{H}_8\text{N}_2)_2]$   
 $M_r = 822.46$   
 Monoclinic,  $C2/c$   
 $a = 22.180$  (4) Å  
 $b = 8.9520$  (18) Å  
 $c = 16.426$  (3) Å  
 $\beta = 93.33$  (3)°

$V = 3256.0$  (11) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 1.10$  mm<sup>-1</sup>  
 $T = 295$  K  
 $0.31 \times 0.23 \times 0.15$  mm

#### Data collection

Siemens P4 diffractometer  
 Absorption correction:  $\psi$  scan  
 (XSCANS; Siemens, 1996)  
 $T_{\min} = 0.702$ ,  $T_{\max} = 0.784$   
 4566 measured reflections  
 3753 independent reflections

3312 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.022$   
 3 standard reflections every 97 reflections  
 intensity decay: none

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$   
 $wR(F^2) = 0.083$   
 $S = 1.03$   
 3753 reflections  
 248 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.38$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.33$  e Å<sup>-3</sup>

**Table 1**

Selected bond lengths (Å).

|                     |             |                     |             |
|---------------------|-------------|---------------------|-------------|
| Co1—O1              | 2.2002 (13) | Co1—O6 <sup>i</sup> | 2.1519 (13) |
| Co1—O2              | 2.0890 (13) | Co1—N1              | 2.1012 (15) |
| Co1—O5 <sup>i</sup> | 2.1211 (13) | Co1—N2              | 2.1016 (15) |

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

**Table 2**

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$                              | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|--------------|--------------------|-------------|----------------------|
| $\text{O4}-\text{H4A}\cdots\text{O2}^{\text{ii}}$ | 0.79 (3)     | 1.89 (3)           | 2.627 (2)   | 156 (2)              |

 Symmetry code: (ii)  $-x, -y + 2, -z$ .

Data collection: XSCANS (Siemens, 1996); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXL97.

This project was supported by the Scientific Research Fund of the Zhejiang Provincial Education Department (grant No. Y201017782) and the Scientific Research Fund of Ningbo University (grant No. XKL09078). Grateful thanks are also extended to the K. C. Wong Magna Fund in Ningbo University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ5153).

## References

- Bauer, C. A., Timofeeva, T. V., Settersten, T. B., Patterson, B. D., Liu, V. H., Simmons, B. A. & Allendorf, M. D. (2007). *J. Am. Chem. Soc.* **129**, 7136–7144.
- Biradha, K., Sarkar, M. & Rajput, L. (2006). *Chem. Commun.* pp. 4169–4179.
- Konar, S., Zangrando, E., Drew, M. G. B., Ribas, J. & Chaudhuri, N. R. (2004). *Dalton Trans.* pp. 260–266.
- Li, Z.-F., Xie, H.-Z. & Zheng, Y.-Q. (2006). *Acta Cryst.* **C62**, m455–m457.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Siemens (1996). *XSCANS*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Thuéry, P. & Masci, B. (2010). *Cryst. Growth Des.* **10**, 3626–3631.
- Wang, J., Lin, Z. J., Ou, Y. C., Shen, Y., Herchel, R. & Tong, M. L. (2008). *Chem. Eur. J.* **14**, 7218–7235.
- Zacher, D., Schmid, R., Wöll, C. & Fischer, R. A. (2011). *Angew. Chem. Int. Ed.* **50**, 176–199.

**supplementary materials**

*Acta Cryst.* (2011). E67, m832-m833 [ doi:10.1107/S1600536811019970 ]

**catena-Poly[bis[(1,10-phenanthroline)cobalt(II)]- $\mu_4$ -3,6-dicarboxycyclohexane-1,2,4,5-tetracarboxylato]**

**W. Xu**

**Comment**

The rational design and construction of metal-organic coordination polymers with flexible multidentate ligands have received more and more attention due to their intriguing structural topologies and novel properties for potential applications (Biradha, *et al.*, 2006; Bauer, *et al.*, 2007; Zacher, *et al.*, 2011). As a typical flexible cycloalkane polycarboxylic acid ligand, we have focused on the 1,2,3,4,5,6-cyclohexanhexacarboxylic acid ( $H_6chhc$ ) whose coordination chemistry remains practically unexplored. We were particularly aware that the greater flexibility of this ligand would make the prediction and control of the final coordination networks that it generates more difficult. (Wang, *et al.*, 2008; Thuéry & Masci, 2010). Herein, we report a new cobalt coordination polymer,  $[Co_2(phen)_2(H_2chhc)]_n$ , resulting from reaction of  $Co^{2+}$  cations, phen and  $H_6chhc$  under hydrothermal conditions. It is isostructural with the previously reported  $[Ni_2(phen)_2(H_2chhc)]_n$  complex (Li, *et al.*, 2006).

The asymmetric unit of the title compound consists of one  $Co^{2+}$  cation, one phen ligand and one-half of a  $H_2chhc^{4-}$  anion lying across a twofold rotation axis. The Co atoms are each in an octahedral environment defined by two N atoms of one phen ligand and four O atoms of two carboxylate groups from different  $H_2chhc^{4-}$  anions. The Co-O bond lengths fall in the range 2.089 (1)-2.200 (1) Å and the two Co-N distances are 2.101 (2) and 2.102 (2) Å (Table 1), thus falling in the expected region (Konar, *et al.*, 2004). The octahedral coordination around the Co atoms are strongly distorted since the diametrical and non-diametrical bond angles indicate significant deviations from 180° and 90°, respectively. The  $H_2chhc^{4-}$  ligands assume an *e,e,e,e,e,e*-conformation with the central ring adopting a chair-shaped configuration, the carboxylate and carboxyl groups being located at the equatorial sites. Each carboxylate group of the  $H_2chhc^{4-}$  anion chelates one Co atom. As a result, the  $H_2chhc^{4-}$  anions are each coordinated to four  $[Co(phen)]^{2+}$  units, leading to polymeric chains  $[Co_2(phen)_2(H_2chhc)]_n$  running along the [010] direction with the phen ligands *exo*-orientated (Fig. 1). The phen ligands of two adjacent supramolecular chains are stacked *via* the quinoline fragments (centroid-centroid distance = 3.662 (2) Å). Obviously, such  $\pi$ - $\pi$  stacking interactions are responsible for the supramolecular assembly of the one-dimensional chains into two-dimensional layers parallel to (001) (Fig. 2). The layers are further connected to form a three-dimensional framework *via* interlayer O-H $\cdots$ O hydrogen bonds ( $d(O4\cdots O2^{\#1}) = 2.627$  (2) Å,  $\angle O4-H4A\cdots O2^{\#1} = 156$  (2)°,  $\#1 = -x, 2-y, -z$ ).

**Experimental**

$CoCl_2 \cdot 6H_2O$  (0.238 g, 1.0 mmol),  $H_6chhc$  (0.173 g, 0.5 mmol), phen (0.200 g, 1.0 mmol) and NaOH 1.5 mL (1 M) were stirred in 20 mL  $H_2O$ . The resulting mixture was placed in a 23 mL Teflon-lined autoclave and heated at 170 °C for 3 days. The reaction system was cooled to room temperature at a rate of 20 °C/h, and small amount of pink crystals of the title complex was obtained.

## Refinement

All H atoms bound to C were position geometrically and refined as riding, with C-H = 0.93 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . H atoms attached to O were located in difference Fourier maps and refined freely with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ .

## Figures

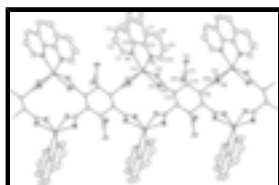


Fig. 1. ORTEP view of the polymer chain  $[\text{Co}_2(\text{phen})_2(\text{H}_2\text{chhc})]_n$  of the title complex. The displacement ellipsoids are drawn at 40% probability level, hydrogen atoms are omitted for clarity.

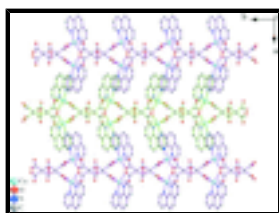


Fig. 2. A view of a single layer of the title complex.

## catena-Poly[bis[(1,10-phenanthroline)cobalt(II)]- $\mu_4$ -3,6-dicarboxycyclohexane-1,2,4,5-tetracarboxylato]

### Crystal data

$[\text{Co}_2(\text{C}_{12}\text{H}_8\text{O}_{12})(\text{C}_{12}\text{H}_8\text{N}_2)_2]$

$M_r = 822.46$

Monoclinic,  $C2/c$

Hall symbol:  $-C\ 2yc$

$a = 22.180(4)\ \text{\AA}$

$b = 8.9520(18)\ \text{\AA}$

$c = 16.426(3)\ \text{\AA}$

$\beta = 93.33(3)^\circ$

$V = 3256.0(11)\ \text{\AA}^3$

$Z = 4$

$F(000) = 1672$

$D_x = 1.678\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 25 reflections

$\theta = 5.0\text{--}12.5^\circ$

$\mu = 1.10\ \text{mm}^{-1}$

$T = 295\ \text{K}$

Block, pink

$0.31 \times 0.23 \times 0.15\ \text{mm}$

### Data collection

Siemens P4  
diffractometer

Radiation source: fine-focus sealed tube

graphite

$\theta/2\theta$  scans

Absorption correction:  $\psi$  scan  
(*XSCANS*; Siemens, 1996)

$T_{\text{min}} = 0.702$ ,  $T_{\text{max}} = 0.784$

4566 measured reflections

3312 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

$\theta_{\text{max}} = 27.5^\circ$ ,  $\theta_{\text{min}} = 2.5^\circ$

$h = -28 \rightarrow 1$

$k = -1 \rightarrow 11$

$l = -21 \rightarrow 21$

3 standard reflections every 97 reflections

3753 independent reflections

intensity decay: none

*Refinement*

Refinement on  $F^2$

Secondary atom site location: difference Fourier map

Least-squares matrix: full

Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.031$

H atoms treated by a mixture of independent and constrained refinement

$wR(F^2) = 0.083$

$$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2 + 2.2781P]$$

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

$S = 1.03$

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

3753 reflections

$$\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$$

248 parameters

$$\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$$

0 restraints

Extinction correction: *SHELXL97* (Sheldrick, 2008),

$$F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$$

Primary atom site location: structure-invariant direct methods

Extinction coefficient: 0.00077 (19)

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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  $F^2 > 2\sigma(F^2)$  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 ( $\text{\AA}^2$ )*

|     | <i>x</i>     | <i>y</i>     | <i>z</i>      | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|---------------|----------------------------------|
| Co1 | 0.098444 (9) | 0.64743 (2)  | 0.140367 (13) | 0.02138 (9)                      |
| O1  | 0.07208 (6)  | 0.79951 (15) | 0.23735 (7)   | 0.0330 (3)                       |
| O2  | 0.04781 (7)  | 0.83776 (14) | 0.10892 (7)   | 0.0327 (3)                       |
| O3  | 0.08305 (7)  | 1.16900 (18) | 0.04746 (9)   | 0.0433 (4)                       |
| O4  | -0.01738 (6) | 1.14637 (17) | 0.04776 (8)   | 0.0363 (3)                       |
| H4A | -0.0159 (12) | 1.148 (3)    | -0.0004 (19)  | 0.054*                           |
| O5  | 0.09100 (5)  | 1.45307 (15) | 0.21296 (8)   | 0.0314 (3)                       |
| O6  | 0.01745 (5)  | 1.51543 (15) | 0.12579 (8)   | 0.0329 (3)                       |
| N1  | 0.13438 (6)  | 0.55177 (17) | 0.03690 (9)   | 0.0277 (3)                       |
| N2  | 0.18993 (7)  | 0.70526 (19) | 0.16045 (9)   | 0.0322 (3)                       |
| C1  | 0.10617 (9)  | 0.4793 (2)   | -0.02411 (11) | 0.0378 (4)                       |
| H1A | 0.0642       | 0.4771       | -0.0272       | 0.045*                           |
| C2  | 0.13708 (13) | 0.4053 (3)   | -0.08457 (14) | 0.0544 (6)                       |
| H2A | 0.1159       | 0.3563       | -0.1272       | 0.065*                           |

## supplementary materials

---

|      |              |              |               |            |
|------|--------------|--------------|---------------|------------|
| C3   | 0.19861 (13) | 0.4065 (3)   | -0.07970 (15) | 0.0591 (7) |
| H3A  | 0.2196       | 0.3561       | -0.1186       | 0.071*     |
| C4   | 0.23052 (10) | 0.4833 (3)   | -0.01624 (14) | 0.0472 (5) |
| C5   | 0.29531 (12) | 0.4955 (4)   | -0.00706 (19) | 0.0673 (8) |
| H5A  | 0.3186       | 0.4468       | -0.0441       | 0.081*     |
| C6   | 0.32300 (10) | 0.5748 (4)   | 0.05321 (19)  | 0.0686 (9) |
| H6A  | 0.3649       | 0.5806       | 0.0569        | 0.082*     |
| C7   | 0.28897 (9)  | 0.6512 (3)   | 0.11216 (16)  | 0.0517 (6) |
| C8   | 0.31442 (11) | 0.7393 (4)   | 0.17623 (18)  | 0.0660 (8) |
| H8A  | 0.3561       | 0.7516       | 0.1821        | 0.079*     |
| C9   | 0.27855 (12) | 0.8067 (4)   | 0.22961 (17)  | 0.0658 (8) |
| H9A  | 0.2954       | 0.8650       | 0.2719        | 0.079*     |
| C10  | 0.21599 (11) | 0.7875 (3)   | 0.22011 (14)  | 0.0487 (5) |
| H10A | 0.1917       | 0.8338       | 0.2568        | 0.058*     |
| C11  | 0.22540 (8)  | 0.6391 (2)   | 0.10648 (12)  | 0.0339 (4) |
| C12  | 0.19595 (8)  | 0.5557 (2)   | 0.04106 (11)  | 0.0318 (4) |
| C13  | 0.00497 (7)  | 1.00717 (17) | 0.20407 (9)   | 0.0213 (3) |
| H13A | -0.0344      | 0.9985       | 0.1741        | 0.026*     |
| C14  | 0.03623 (7)  | 1.15052 (16) | 0.17600 (9)   | 0.0205 (3) |
| H14A | 0.0778       | 1.1519       | 0.1998        | 0.025*     |
| C15  | 0.00349 (7)  | 1.29201 (17) | 0.20377 (9)   | 0.0194 (3) |
| H15A | -0.0367      | 1.2958       | 0.1758        | 0.023*     |
| C16  | 0.04335 (8)  | 0.87293 (17) | 0.18323 (10)  | 0.0234 (3) |
| C17  | 0.03790 (8)  | 1.15477 (18) | 0.08330 (10)  | 0.0256 (3) |
| C18  | 0.03920 (7)  | 1.42928 (17) | 0.17948 (9)   | 0.0209 (3) |

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

|     | $U^{11}$     | $U^{22}$     | $U^{33}$     | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|-----|--------------|--------------|--------------|--------------|--------------|--------------|
| Co1 | 0.02179 (13) | 0.01718 (13) | 0.02545 (13) | -0.00066 (8) | 0.00385 (8)  | -0.00008 (8) |
| O1  | 0.0451 (7)   | 0.0284 (6)   | 0.0258 (6)   | 0.0125 (6)   | 0.0031 (5)   | 0.0002 (5)   |
| O2  | 0.0497 (8)   | 0.0259 (6)   | 0.0228 (6)   | 0.0115 (6)   | 0.0048 (5)   | -0.0013 (5)  |
| O3  | 0.0426 (8)   | 0.0505 (9)   | 0.0389 (7)   | 0.0011 (7)   | 0.0212 (6)   | 0.0015 (6)   |
| O4  | 0.0402 (7)   | 0.0477 (9)   | 0.0209 (6)   | 0.0031 (6)   | 0.0014 (5)   | -0.0005 (6)  |
| O5  | 0.0286 (6)   | 0.0283 (6)   | 0.0368 (6)   | -0.0066 (5)  | -0.0040 (5)  | 0.0084 (5)   |
| O6  | 0.0274 (6)   | 0.0276 (6)   | 0.0431 (7)   | -0.0037 (5)  | -0.0031 (5)  | 0.0141 (6)   |
| N1  | 0.0265 (7)   | 0.0298 (7)   | 0.0272 (7)   | 0.0006 (6)   | 0.0044 (5)   | -0.0008 (6)  |
| N2  | 0.0299 (7)   | 0.0335 (8)   | 0.0328 (7)   | -0.0094 (6)  | -0.0004 (6)  | 0.0029 (7)   |
| C1  | 0.0407 (10)  | 0.0412 (11)  | 0.0313 (9)   | -0.0015 (8)  | 0.0005 (7)   | -0.0037 (8)  |
| C2  | 0.0764 (17)  | 0.0522 (14)  | 0.0353 (11)  | -0.0025 (13) | 0.0089 (10)  | -0.0145 (10) |
| C3  | 0.0742 (17)  | 0.0589 (15)  | 0.0469 (13)  | 0.0132 (14)  | 0.0256 (12)  | -0.0108 (12) |
| C4  | 0.0444 (11)  | 0.0513 (13)  | 0.0479 (12)  | 0.0140 (10)  | 0.0206 (9)   | 0.0045 (10)  |
| C5  | 0.0411 (13)  | 0.086 (2)    | 0.0782 (18)  | 0.0230 (14)  | 0.0307 (13)  | 0.0099 (17)  |
| C6  | 0.0245 (10)  | 0.096 (2)    | 0.087 (2)    | 0.0121 (13)  | 0.0166 (11)  | 0.0225 (18)  |
| C7  | 0.0236 (9)   | 0.0692 (17)  | 0.0620 (14)  | -0.0055 (9)  | 0.0005 (9)   | 0.0216 (12)  |
| C8  | 0.0310 (11)  | 0.092 (2)    | 0.0729 (17)  | -0.0238 (13) | -0.0132 (11) | 0.0211 (16)  |
| C9  | 0.0571 (15)  | 0.081 (2)    | 0.0564 (15)  | -0.0368 (15) | -0.0180 (12) | 0.0040 (14)  |
| C10 | 0.0505 (13)  | 0.0511 (13)  | 0.0438 (11)  | -0.0208 (11) | -0.0043 (9)  | -0.0023 (10) |

|     |            |             |             |             |            |             |
|-----|------------|-------------|-------------|-------------|------------|-------------|
| C11 | 0.0229 (8) | 0.0386 (10) | 0.0404 (10) | -0.0019 (7) | 0.0025 (7) | 0.0106 (8)  |
| C12 | 0.0278 (8) | 0.0337 (9)  | 0.0348 (9)  | 0.0038 (7)  | 0.0091 (7) | 0.0062 (8)  |
| C13 | 0.0275 (7) | 0.0155 (7)  | 0.0213 (7)  | -0.0008 (6) | 0.0037 (6) | -0.0001 (6) |
| C14 | 0.0228 (7) | 0.0161 (7)  | 0.0227 (7)  | -0.0001 (6) | 0.0036 (5) | 0.0001 (6)  |
| C15 | 0.0209 (7) | 0.0157 (7)  | 0.0217 (7)  | 0.0000 (5)  | 0.0020 (5) | 0.0003 (6)  |
| C16 | 0.0302 (8) | 0.0168 (7)  | 0.0238 (7)  | -0.0003 (6) | 0.0051 (6) | 0.0008 (6)  |
| C17 | 0.0342 (8) | 0.0179 (7)  | 0.0252 (8)  | 0.0015 (6)  | 0.0077 (6) | 0.0009 (6)  |
| C18 | 0.0238 (7) | 0.0167 (7)  | 0.0228 (7)  | 0.0008 (6)  | 0.0058 (6) | -0.0014 (6) |

*Geometric parameters (Å, °)*

|                        |             |                        |             |
|------------------------|-------------|------------------------|-------------|
| Co1—O1                 | 2.2002 (13) | C3—H3A                 | 0.9300      |
| Co1—O2                 | 2.0890 (13) | C4—C12                 | 1.406 (3)   |
| Co1—O5 <sup>i</sup>    | 2.1211 (13) | C4—C5                  | 1.440 (3)   |
| Co1—O6 <sup>i</sup>    | 2.1519 (13) | C5—C6                  | 1.338 (5)   |
| Co1—N1                 | 2.1012 (15) | C5—H5A                 | 0.9300      |
| Co1—N2                 | 2.1016 (15) | C6—C7                  | 1.435 (4)   |
| Co1—C18 <sup>i</sup>   | 2.4599 (16) | C6—H6A                 | 0.9300      |
| Co1—C16                | 2.4827 (16) | C7—C8                  | 1.407 (4)   |
| O1—C16                 | 1.250 (2)   | C7—C11                 | 1.412 (3)   |
| O2—C16                 | 1.270 (2)   | C8—C9                  | 1.359 (4)   |
| O3—C17                 | 1.198 (2)   | C8—H8A                 | 0.9300      |
| O4—C17                 | 1.329 (2)   | C9—C10                 | 1.398 (3)   |
| O4—H4A                 | 0.79 (3)    | C9—H9A                 | 0.9300      |
| O5—C18                 | 1.263 (2)   | C10—H10A               | 0.9300      |
| O5—Co1 <sup>ii</sup>   | 2.1211 (13) | C11—C12                | 1.435 (3)   |
| O6—C18                 | 1.247 (2)   | C13—C16                | 1.523 (2)   |
| O6—Co1 <sup>ii</sup>   | 2.1519 (13) | C13—C13 <sup>iii</sup> | 1.538 (3)   |
| N1—C1                  | 1.321 (2)   | C13—C14                | 1.542 (2)   |
| N1—C12                 | 1.364 (2)   | C13—H13A               | 0.9800      |
| N2—C10                 | 1.330 (3)   | C14—C17                | 1.526 (2)   |
| N2—C11                 | 1.355 (3)   | C14—C15                | 1.542 (2)   |
| C1—C2                  | 1.405 (3)   | C14—H14A               | 0.9800      |
| C1—H1A                 | 0.9300      | C15—C18                | 1.528 (2)   |
| C2—C3                  | 1.363 (4)   | C15—C15 <sup>iii</sup> | 1.535 (3)   |
| C2—H2A                 | 0.9300      | C15—H15A               | 0.9800      |
| C3—C4                  | 1.405 (4)   | C18—Co1 <sup>ii</sup>  | 2.4599 (16) |
| O2—Co1—N1              | 110.87 (6)  | C5—C6—C7               | 121.0 (2)   |
| O2—Co1—N2              | 109.77 (6)  | C5—C6—H6A              | 119.5       |
| N1—Co1—N2              | 79.58 (6)   | C7—C6—H6A              | 119.5       |
| O2—Co1—O5 <sup>i</sup> | 138.57 (6)  | C8—C7—C11              | 116.6 (2)   |
| N1—Co1—O5 <sup>i</sup> | 99.55 (6)   | C8—C7—C6               | 124.6 (2)   |
| N2—Co1—O5 <sup>i</sup> | 102.70 (6)  | C11—C7—C6              | 118.8 (2)   |
| O2—Co1—O6 <sup>i</sup> | 89.26 (5)   | C9—C8—C7               | 120.5 (2)   |
| N1—Co1—O6 <sup>i</sup> | 92.27 (6)   | C9—C8—H8A              | 119.8       |
| N2—Co1—O6 <sup>i</sup> | 160.89 (6)  | C7—C8—H8A              | 119.8       |



## supplementary materials

---

|                                       |             |                              |             |
|---------------------------------------|-------------|------------------------------|-------------|
| O5 <sup>i</sup> —Co1—O6 <sup>i</sup>  | 61.34 (5)   | C8—C9—C10                    | 119.2 (2)   |
| O2—Co1—O1                             | 60.84 (5)   | C8—C9—H9A                    | 120.4       |
| N1—Co1—O1                             | 165.26 (6)  | C10—C9—H9A                   | 120.4       |
| N2—Co1—O1                             | 91.64 (6)   | N2—C10—C9                    | 122.4 (2)   |
| O5 <sup>i</sup> —Co1—O1               | 93.89 (5)   | N2—C10—H10A                  | 118.8       |
| O6 <sup>i</sup> —Co1—O1               | 99.50 (6)   | C9—C10—H10A                  | 118.8       |
| O2—Co1—C18 <sup>i</sup>               | 115.12 (6)  | N2—C11—C7                    | 122.6 (2)   |
| N1—Co1—C18 <sup>i</sup>               | 96.96 (6)   | N2—C11—C12                   | 117.47 (15) |
| N2—Co1—C18 <sup>i</sup>               | 132.85 (6)  | C7—C11—C12                   | 119.9 (2)   |
| O5 <sup>i</sup> —Co1—C18 <sup>i</sup> | 30.88 (5)   | N1—C12—C4                    | 122.56 (19) |
| O6 <sup>i</sup> —Co1—C18 <sup>i</sup> | 30.46 (5)   | N1—C12—C11                   | 117.50 (16) |
| O1—Co1—C18 <sup>i</sup>               | 97.68 (5)   | C4—C12—C11                   | 119.94 (18) |
| O2—Co1—C16                            | 30.74 (5)   | C16—C13—C13 <sup>iii</sup>   | 109.53 (11) |
| N1—Co1—C16                            | 140.98 (6)  | C16—C13—C14                  | 108.82 (12) |
| N2—Co1—C16                            | 104.00 (6)  | C13 <sup>iii</sup> —C13—C14  | 112.70 (10) |
| O5 <sup>i</sup> —Co1—C16              | 116.86 (6)  | C16—C13—H13A                 | 108.6       |
| O6 <sup>i</sup> —Co1—C16              | 93.24 (6)   | C13 <sup>iii</sup> —C13—H13A | 108.6       |
| O1—Co1—C16                            | 30.20 (5)   | C14—C13—H13A                 | 108.6       |
| C18 <sup>i</sup> —Co1—C16             | 106.99 (5)  | C17—C14—C13                  | 110.89 (13) |
| C16—O1—Co1                            | 87.50 (10)  | C17—C14—C15                  | 108.29 (12) |
| C16—O2—Co1                            | 92.02 (10)  | C13—C14—C15                  | 111.56 (12) |
| C17—O4—H4A                            | 110 (2)     | C17—C14—H14A                 | 108.7       |
| C18—O5—Co1 <sup>ii</sup>              | 89.55 (10)  | C13—C14—H14A                 | 108.7       |
| C18—O6—Co1 <sup>ii</sup>              | 88.55 (10)  | C15—C14—H14A                 | 108.7       |
| C1—N1—C12                             | 118.65 (16) | C18—C15—C15 <sup>iii</sup>   | 109.99 (10) |
| C1—N1—Co1                             | 128.96 (13) | C18—C15—C14                  | 108.86 (12) |
| C12—N1—Co1                            | 112.02 (12) | C15 <sup>iii</sup> —C15—C14  | 111.64 (10) |
| C10—N2—C11                            | 118.66 (18) | C18—C15—H15A                 | 108.8       |
| C10—N2—Co1                            | 128.76 (15) | C15 <sup>iii</sup> —C15—H15A | 108.8       |
| C11—N2—Co1                            | 112.44 (12) | C14—C15—H15A                 | 108.8       |
| N1—C1—C2                              | 122.6 (2)   | O1—C16—O2                    | 119.22 (15) |
| N1—C1—H1A                             | 118.7       | O1—C16—C13                   | 121.57 (14) |
| C2—C1—H1A                             | 118.7       | O2—C16—C13                   | 119.17 (14) |
| C3—C2—C1                              | 118.9 (2)   | O1—C16—Co1                   | 62.30 (9)   |
| C3—C2—H2A                             | 120.6       | O2—C16—Co1                   | 57.23 (8)   |
| C1—C2—H2A                             | 120.6       | C13—C16—Co1                  | 174.86 (12) |
| C2—C3—C4                              | 120.5 (2)   | O3—C17—O4                    | 124.52 (17) |
| C2—C3—H3A                             | 119.8       | O3—C17—C14                   | 124.24 (17) |
| C4—C3—H3A                             | 119.8       | O4—C17—C14                   | 111.20 (14) |
| C3—C4—C12                             | 116.8 (2)   | O6—C18—O5                    | 120.56 (15) |
| C3—C4—C5                              | 124.8 (2)   | O6—C18—C15                   | 119.79 (14) |
| C12—C4—C5                             | 118.3 (2)   | O5—C18—C15                   | 119.64 (14) |
| C6—C5—C4                              | 122.0 (2)   | O6—C18—Co1 <sup>ii</sup>     | 60.99 (9)   |
| C6—C5—H5A                             | 119.0       | O5—C18—Co1 <sup>ii</sup>     | 59.57 (8)   |

C4—C5—H5A 119.0 C15—C18—Co1<sup>ii</sup> 178.92 (11)  
 Symmetry codes: (i)  $x, y-1, z$ ; (ii)  $x, y+1, z$ ; (iii)  $-x, y, -z+1/2$ .

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

| $D-H\cdots A$                    | $D-H$    | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------------------------|----------|-------------|-------------|---------------|
| O4—H4A $\cdots$ O2 <sup>iv</sup> | 0.79 (3) | 1.89 (3)    | 2.627 (2)   | 156 (2)       |

Symmetry codes: (iv)  $-x, -y+2, -z$ .

Fig. 1

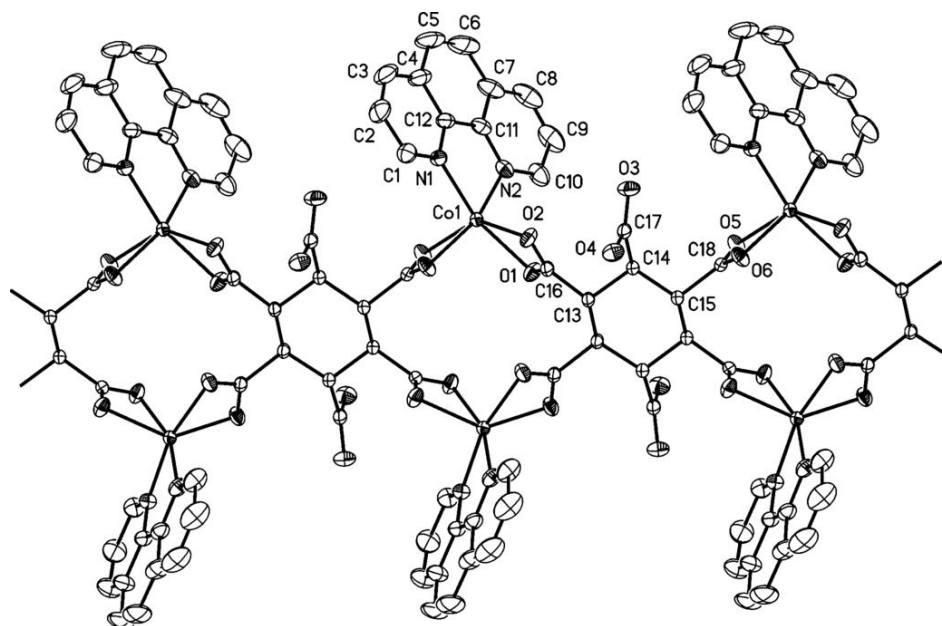


Fig. 2

