Acta Cryst E
CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

# A cuboidal $[Cu_4(SO_4)_4]$ structure supported by $\beta$-picoline ligands

**Ava M. Park,[a] James A. Golen[b] and David R. Manke[b]***

[a]Portsmouth Abbey School, 285 Cory's Lane, Portsmouth, RI, 02871, USA, and [b]University of Massachusetts Dartmouth, 285 Old Westport Road, North Dartmouth, MA 02747, USA. *Correspondence e-mail: dmanke@umassd.edu

Received 15 January 2022
Accepted 23 January 2022

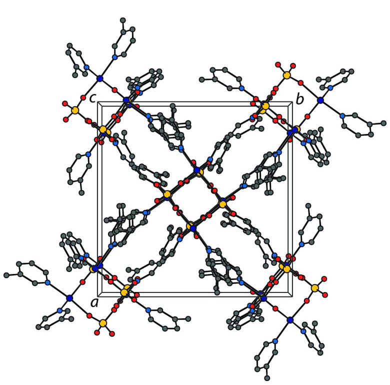
Edited by M. Zeller, Purdue University, USA

**Keywords:** crystal structure; picoline; sulfate; transition metal; coordination chemistry; cobalt complexes.

**CCDC reference**: 2143864

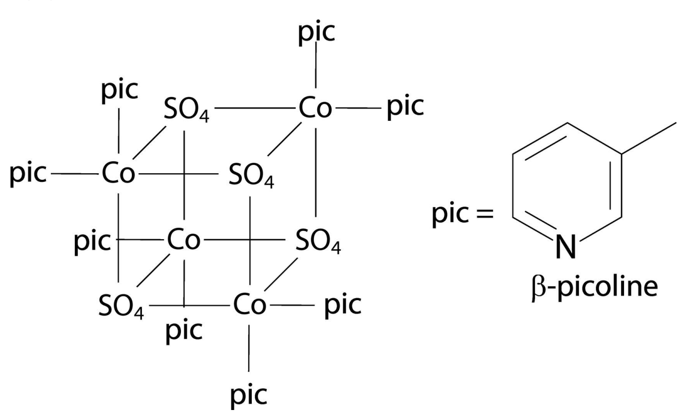
**Supporting information**: this article has supporting information at journals.iucr.org/e

The solid-state structure of the cobalt–$\beta$-picoline–sulfate complex tetra-$\mu_3$-sulfato-tetrakis[bis(3-methylpyridine)cobalt(II)], $[Co_4(SO_4)_4(C_6H_7N)_8]$, is reported. The tetrameric cobalt cluster contains a cuboidal core comprised of four cobalt(II) cations and four sulfate anions at alternate cube vertices. The cobalt corners are each capped with two $\beta$-picoline ligands. The sulfate anions adopt a rare [3.2110] bridging motif, and the cuboidal cluster is unprecedented in coordination chemistry.




## 1. Chemical context

For the past few years, our lab has examined the solid-state structures of first-row transition-metal–pyridine–sulfate complexes (Park *et al.*, 2019; Pham *et al.*, 2018; Roy *et al.*, 2018). Despite the first such compound being reported in 1886 (Jørgensen, 1886; Manke, 2021), the structures of only two had been described in the literature when we started exploring this class of compounds. A series of these structures including Fe, Co, Ni, and Zn, showed one-dimensional coordination polymers exhibiting sulfate dianions bridging in $\mu$-sulfato-$\kappa^2O$:$O'$ modes. Interestingly, by modifying growth conditions, cobalt demonstrated two additional crystalline forms with variation in the bridging mode of sulfate ions that was not observed for the other metals. We have also explored the structural chemistry of such complexes with substituted pyridines, including $\gamma$-picoline, which showed similar structural chemistry to that observed with the pyridine ligand (Pham *et al.*, 2019). When we looked at the reaction of cobalt sulfate with $\beta$-picoline, a unique structure was obtained, a tetramer exhibiting an unprecedented cuboidal $Cu_4(SO_4)_4$ core, described herein.



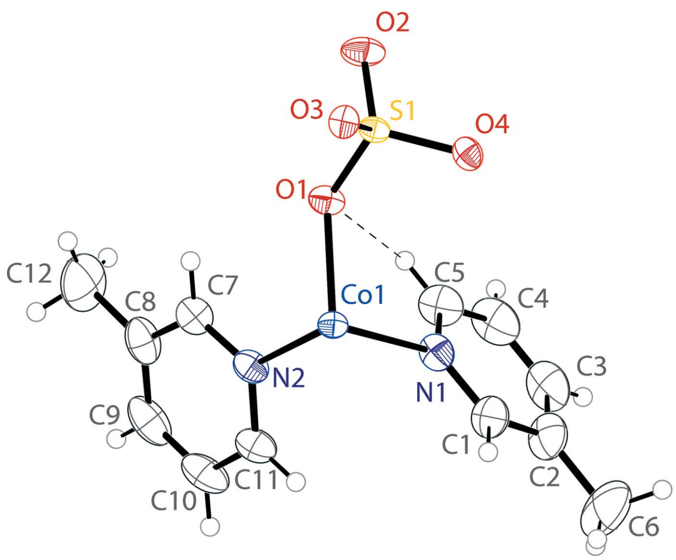



**Figure 1**
The asymmetric unit of the title compound showing the atomic labeling. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.

## 2. Structural commentary

The asymmetric unit of the title compound contains one cobalt cation, one sulfate anion, and two $\beta$-picoline ligands (Fig. 1). When grown out, the cobalt center demonstrates a pseudo-octahedral coordination environment. This consists of two $\beta$-picoline nitrogen atoms, two oxygen atoms of a chelating sulfate ligand, one oxygen atom of a second sulfate anion, which bridges to another metal, and one terminal oxygen atom of a third sulfate ligand. The grown-out structure forms a tetramer of ($\beta$-pic)$_2$CoSO$_4$ units, demonstrating a cuboidal core in which four vertices are occupied by cobalt cations, and the other four vertices are occupied by sulfate anions (Fig. 2). The sulfate anions all bridge three $Co^{2+}$ cations, demonstrating [3.2110] bridging by Harris notation (Fig. 3). Harris notation is written as [$X{\cdot}YYYY$] where $X$ is the number of metals that a ligand bridges, and the $Y$s are the number of metals connected to each donor atom in the ligand (Papatriantafyllopoulou *et al.*, 2009). The [3.2110] bridging motif is rare in sulfates and has only been observed in 1D coordination polymers of copper (Li *et al.*, 2008) and lanthanide/iron mixed-metal 3D coordination polymers (He *et al.*, 2017). There are two C—H···O interactions between the *ortho* hydrogens of one $\beta$-picoline ligand and the oxygens of two sulfate ions (Table 1). This results in a plane-to-plane angle between the CoN$_3$O plane and the pyridine ring of 16.25 (9)°. These interactions are not present in the second unique picoline ligand, giving a larger plane-to-plane angle of 26.95 (9)°.

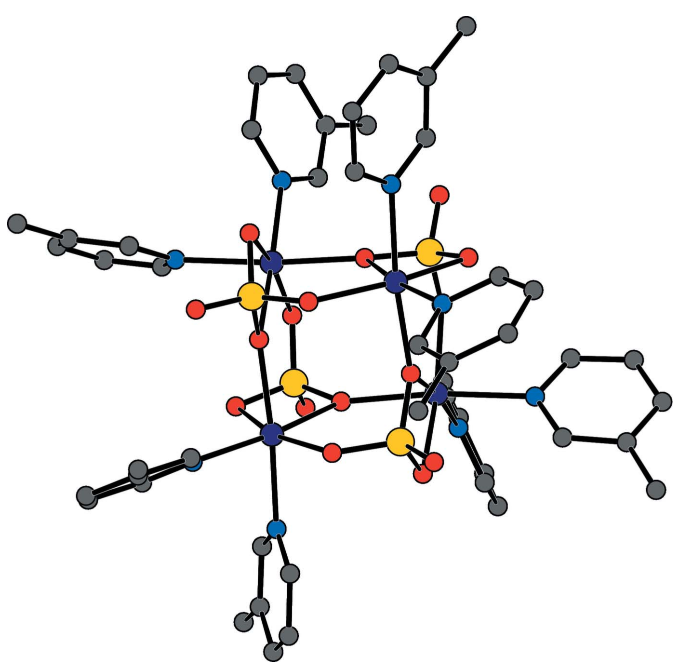


**Figure 2**
The [3.2110] coordination mode of sulfate in the title compound.

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C1—H1···O4$^{i}$ | 0.93 | 2.53 | 3.116 (4) | 121 |
| C3—H3···O2$^{ii}$ | 0.93 | 2.46 | 3.135 (4) | 129 |
| C5—H5···O1 | 0.93 | 2.49 | 3.070 (4) | 121 |

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

## 3. Supramolecular features

The crystal packing for the compound is shown in Fig. 4. The are weak C—H···O interactions between the *trans*-hydrogen atom of one picoline ligand and one of the terminal sulfate oxygens of a neighboring cuboid [C3—H3···O2$^{ii}$; symmetry code: (ii) $\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}-z$, Table 1). This interaction might

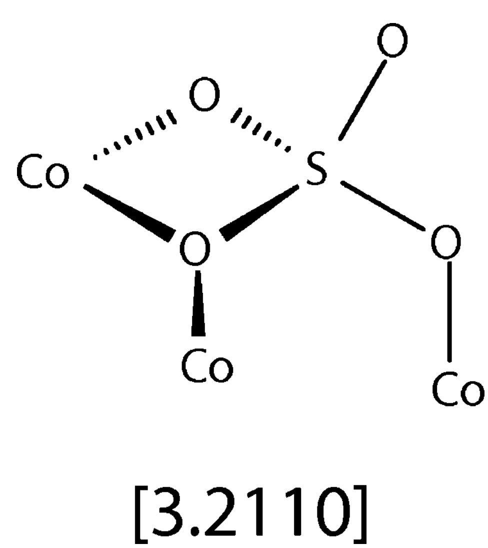



**Figure 3**
The cuboidal tetramer of the title compound. H atoms have been omitted for clarity.

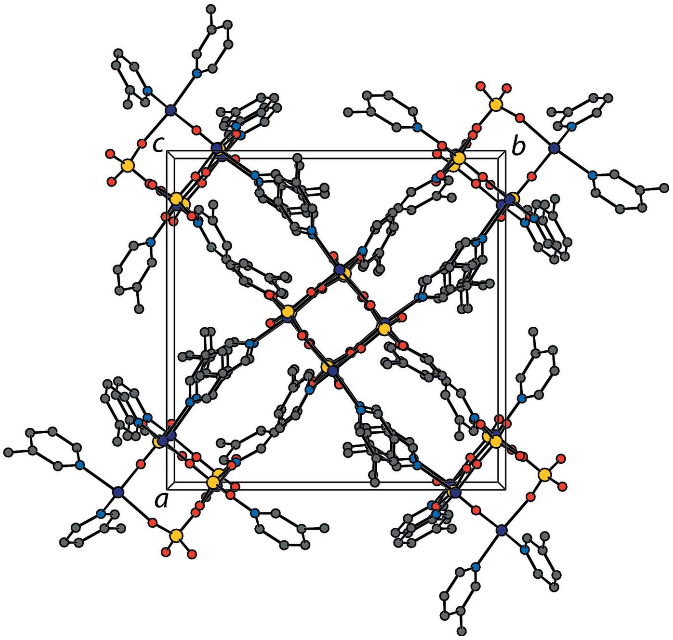



**Figure 4**
The crystal packing of the title compound shown along the *c* axis. H atoms have been omitted for clarity.

assist in the interdigitation of the cuboids in the structure. No significant $\pi$–$\pi$ interactions are observed.

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $[Co_4(SO_4)_4(C_6H_7N)_8]$ |
| $M_r$ | 1364.96 |
| Crystal system, space group | Tetragonal, $P\bar{4}2_1c$ |
| Temperature (K) | 298 |
| $a$, $c$ (Å) | 15.6121 (16), 11.8359 (13) |
| $V$ (Å$^3$) | 2884.9 (7) |
| $Z$ | 2 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 1.35 |
| Crystal size (mm) | 0.24 × 0.22 × 0.20 |
| Data collection | |
| Diffractometer | Bruker D8 Venture CMOS |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2018) |
| $T_{min}$, $T_{max}$ | 0.517, 0.562 |
| No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections | 54595, 2744, 2624 |
| $R_{int}$ | 0.037 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.611 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.019, 0.046, 1.14 |
| No. of reflections | 2744 |
| No. of parameters | 184 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.16, −0.20 |
| Absolute structure | Flack $x$ determined using 1117 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons et al., 2013) |
| Absolute structure parameter | 0.007 (4) |

Computer programs: *APEX3* and *SAINT* (Bruker, 2018), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009), and *publCIF* (Westrip, 2010).

## 4. Database survey

The reported structures demonstrating sulfate ions with [3.2110] bridging modes are with copper (DOHKIV, DOHKIB: Li *et al.*, 2008) or mixtures of lanthanides with iron (He *et al.*, 2017), including dysprosium (DADNOO), erbium (DADPEG), europium (DADNII), gadolinium (DADNUU) and samarium (DADPAC). The prior structures of metal–pyridine sulfate complexes include three variations with pyridine (QIBFOZ: Pham *et al.*, 2018; QOXJAR, QOXJEV: Park *et al.*, 2019) and one with $\gamma$-picoline (ROFMIL: Pham *et al.*, 2019), all of which demonstrate 1D coordination polymers that are structurally quite different than the cuboidal compound reported here.

## 5. Synthesis and crystallization

32 mg of $CoSO_4 \cdot 7H_2O$ were dissolved in 2.0 mL of 3-methylpyridine (Aldrich) and heated at 343 K for 24 h. Dark-pink crystals suitable for X-ray analysis were obtained.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms were placed in calculated positions [C—H = 0.93 Å ($sp^2$) and 0.96 Å ($sp^3$)]. Isotropic displacement parameters were set to $1.2U_{eq}$C ($sp^2$) or $1.5U_{eq}$C ($sp^3$).

## Funding information

Funding for this research was provided by: National Science Foundation, Directorate for Mathematical and Physical Sciences (grant No. CHE-1429086).

## References

Bruker (2018). *APEX3*, *SAINT*, and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
He, X., Cheng, W., Lin, Q., Dong, Y. & Xu, Y. (2017). *Cryst. Growth Des.* **17**, 347–354.
Jørgensen, S. M. (1886). *J. Prakt. Chem.* **33**, 489–538.
Li, G., Xing, Y., Song, S., Xu, N., Liu, X. & Su, Z. (2008). *J. Solid State Chem.* **181**, 2406–2411.
Manke, D. R. (2021). *Bull. Hist. Chem.* **46**, 179–185.
Papatriantafyllopoulou, C., Manessi-Zoupa, E., Escuer, A. & Perlepes, S. P. (2009). *Inorg. Chim. Acta*, **362**, 634–650.
Park, A. M., Pham, D. N. K., Golen, J. A. & Manke, D. R. (2019). *Acta Cryst.* E**75**, 1888–1891.
Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B**69**, 249–259.
Pham, D. N. K., Roy, M., Kreider-Mueller, A., Golen, J. A. & Manke, D. R. (2018). *Acta Cryst.* E**74**, 857–861.
Pham, D. N. K., Roy, M., Kreider-Mueller, A., Golen, J. A. & Manke, D. R. (2019). *Acta Cryst.* C**75**, 568–574.
Roy, M., Pham, D. N. K., Kreider-Mueller, A., Golen, J. A. & Manke, D. R. (2018). *Acta Cryst.* C**74**, 263–268.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

# supporting information

*Acta Cryst.* (2022). E**78**, 108-110 [https://doi.org/10.1107/S2056989022000780]

## A cuboidal [$Cu_4(SO_4)_4$] structure supported by *β*-picoline ligands

Ava M. Park, James A. Golen and David R. Manke

### Computing details

Data collection: *APEX3* (Bruker, 2018); cell refinement: *SAINT* (Bruker, 2018); data reduction: *SAINT* (Bruker, 2018); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### Tetra-$\mu_3$-sulfato-tetrakis[bis(3-methylpyridine)cobalt(II)]

*Crystal data*

[$Co_4(SO_4)_4(C_6H_7N)_8$]
$M_r$ = 1364.96
Tetragonal, $P\bar{4}2_1c$
$a$ = 15.6121 (16) Å
$c$ = 11.8359 (13) Å
$V$ = 2884.9 (7) Å$^3$
$Z$ = 2
$F$(000) = 1400
$D_x$ = 1.571 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 9496 reflections
$\theta$ = 2.9–25.7°
$\mu$ = 1.35 mm$^{-1}$
$T$ = 298 K
BLOCK, pink
0.24 × 0.22 × 0.20 mm

*Data collection*

Bruker D8 Venture CMOS diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (SADABS; Bruker, 2018)
$T_{min}$ = 0.517, $T_{max}$ = 0.562
54595 measured reflections
2744 independent reflections
2624 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.037
$\theta_{max}$ = 25.7°, $\theta_{min}$ = 2.9°
$h = -19 \rightarrow 19$
$k = -19 \rightarrow 19$
$l = -14 \rightarrow 14$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.046
$S$ = 1.14
2744 reflections
184 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0165P)^2 + 1.2064P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.16 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.20 e Å$^{-3}$
Extinction correction: SHELXL-2018/3 (Sheldrick 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0049 (4)
Absolute structure: Flack $x$ determined using 1117 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons et al., 2013)
Absolute structure parameter: 0.007 (4)

*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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Co1 | 0.64636 (2) | 0.49053 (2) | 0.41389 (3) | 0.02066 (11) |
| S1 | 0.52522 (4) | 0.64004 (4) | 0.35520 (5) | 0.02043 (15) |
| O1 | 0.58168 (12) | 0.57205 (12) | 0.30908 (15) | 0.0267 (4) |
| O2 | 0.49144 (15) | 0.69145 (13) | 0.26473 (17) | 0.0370 (5) |
| O3 | 0.45605 (11) | 0.59894 (11) | 0.42553 (16) | 0.0240 (4) |
| O4 | 0.57304 (12) | 0.69234 (11) | 0.43961 (15) | 0.0258 (4) |
| N1 | 0.75982 (14) | 0.57112 (15) | 0.4121 (2) | 0.0319 (5) |
| N2 | 0.70169 (16) | 0.42286 (15) | 0.2775 (2) | 0.0293 (5) |
| C1 | 0.82170 (19) | 0.5691 (2) | 0.4896 (3) | 0.0400 (7) |
| H1 | 0.813680 | 0.534627 | 0.552786 | 0.048* |
| C2 | 0.8976 (2) | 0.6156 (2) | 0.4819 (3) | 0.0489 (8) |
| C3 | 0.9084 (2) | 0.6660 (2) | 0.3863 (3) | 0.0546 (10) |
| H3 | 0.958296 | 0.697697 | 0.376688 | 0.065* |
| C4 | 0.8451 (2) | 0.6690 (2) | 0.3064 (3) | 0.0541 (10) |
| H4 | 0.851466 | 0.702977 | 0.242445 | 0.065* |
| C5 | 0.7719 (2) | 0.6210 (2) | 0.3218 (3) | 0.0434 (8) |
| H5 | 0.729157 | 0.623471 | 0.267110 | 0.052* |
| C6 | 0.9650 (3) | 0.6110 (3) | 0.5724 (4) | 0.0829 (15) |
| H6A | 0.946445 | 0.572676 | 0.630913 | 0.124* |
| H6B | 0.973938 | 0.667009 | 0.603611 | 0.124* |
| H6C | 1.017567 | 0.590328 | 0.540358 | 0.124* |
| C7 | 0.6638 (2) | 0.4183 (2) | 0.1768 (3) | 0.0340 (7) |
| H7 | 0.611734 | 0.446338 | 0.167140 | 0.041* |
| C8 | 0.6978 (2) | 0.3738 (2) | 0.0853 (3) | 0.0422 (7) |
| C9 | 0.7741 (2) | 0.3311 (2) | 0.1032 (3) | 0.0499 (9) |
| H9 | 0.798504 | 0.299413 | 0.045000 | 0.060* |
| C10 | 0.8143 (2) | 0.3351 (2) | 0.2062 (3) | 0.0490 (9) |
| H10 | 0.865907 | 0.306837 | 0.218114 | 0.059* |
| C11 | 0.7766 (2) | 0.3817 (2) | 0.2914 (3) | 0.0386 (8) |
| H11 | 0.803962 | 0.384829 | 0.361126 | 0.046* |
| C12 | 0.6512 (3) | 0.3707 (3) | −0.0255 (3) | 0.0732 (12) |
| H12A | 0.590895 | 0.377919 | −0.012705 | 0.110* |
| H12B | 0.661205 | 0.316328 | −0.061099 | 0.110* |
| H12C | 0.671634 | 0.415746 | −0.073630 | 0.110* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Co1 | 0.01998 (17) | 0.02203 (18) | 0.01997 (16) | 0.00207 (14) | 0.00180 (15) | 0.00176 (14) |

| | | | | | | |
|---|---|---|---|---|---|---|
| S1 | 0.0216 (3) | 0.0201 (3) | 0.0196 (3) | 0.0031 (3) | 0.0031 (2) | 0.0046 (3) |
| O1 | 0.0293 (10) | 0.0290 (10) | 0.0218 (9) | 0.0075 (8) | 0.0056 (8) | 0.0029 (8) |
| O2 | 0.0435 (12) | 0.0380 (11) | 0.0297 (10) | 0.0114 (11) | −0.0007 (10) | 0.0133 (9) |
| O3 | 0.0227 (9) | 0.0272 (9) | 0.0223 (9) | −0.0037 (7) | 0.0042 (8) | 0.0004 (8) |
| O4 | 0.0259 (9) | 0.0213 (9) | 0.0301 (11) | −0.0045 (8) | 0.0048 (8) | 0.0015 (7) |
| N1 | 0.0281 (12) | 0.0299 (12) | 0.0378 (13) | −0.0040 (10) | 0.0080 (12) | 0.0009 (12) |
| N2 | 0.0305 (12) | 0.0272 (12) | 0.0301 (13) | 0.0033 (11) | 0.0070 (11) | 0.0008 (11) |
| C1 | 0.0349 (16) | 0.0417 (17) | 0.0434 (18) | −0.0091 (14) | 0.0040 (14) | 0.0014 (14) |
| C2 | 0.0337 (16) | 0.051 (2) | 0.062 (2) | −0.0128 (14) | 0.0054 (17) | −0.0051 (19) |
| C3 | 0.0408 (19) | 0.043 (2) | 0.080 (3) | −0.0156 (16) | 0.0191 (18) | 0.0026 (18) |
| C4 | 0.052 (2) | 0.042 (2) | 0.068 (3) | −0.0086 (16) | 0.019 (2) | 0.0151 (18) |
| C5 | 0.0396 (18) | 0.0437 (19) | 0.0470 (19) | −0.0036 (15) | 0.0103 (16) | 0.0107 (16) |
| C6 | 0.048 (2) | 0.102 (4) | 0.098 (4) | −0.026 (2) | −0.017 (3) | 0.002 (3) |
| C7 | 0.0376 (17) | 0.0333 (15) | 0.0310 (15) | −0.0005 (13) | 0.0067 (13) | 0.0015 (13) |
| C8 | 0.061 (2) | 0.0340 (16) | 0.0314 (15) | −0.0070 (14) | 0.0115 (17) | −0.0043 (14) |
| C9 | 0.067 (2) | 0.0349 (17) | 0.048 (2) | 0.0039 (16) | 0.0277 (18) | −0.0072 (15) |
| C10 | 0.047 (2) | 0.0364 (18) | 0.063 (2) | 0.0135 (15) | 0.0187 (18) | −0.0001 (16) |
| C11 | 0.0369 (18) | 0.0342 (17) | 0.045 (2) | 0.0085 (14) | 0.0064 (14) | 0.0007 (14) |
| C12 | 0.107 (4) | 0.076 (3) | 0.036 (2) | −0.002 (3) | −0.002 (3) | −0.012 (2) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Co1—S1$^{i}$ | 2.7458 (7) | C3—C4 | 1.368 (6) |
| Co1—O1 | 2.0441 (19) | C4—H4 | 0.9300 |
| Co1—O3$^{i}$ | 2.2037 (19) | C4—C5 | 1.379 (5) |
| Co1—O3$^{ii}$ | 2.1274 (18) | C5—H5 | 0.9300 |
| Co1—O4$^{i}$ | 2.1229 (18) | C6—H6A | 0.9600 |
| Co1—N1 | 2.173 (2) | C6—H6B | 0.9600 |
| Co1—N2 | 2.114 (2) | C6—H6C | 0.9600 |
| S1—O1 | 1.4839 (19) | C7—H7 | 0.9300 |
| S1—O2 | 1.438 (2) | C7—C8 | 1.391 (4) |
| S1—O3 | 1.5069 (18) | C8—C9 | 1.382 (5) |
| S1—O4 | 1.491 (2) | C8—C12 | 1.501 (5) |
| N1—C1 | 1.332 (4) | C9—H9 | 0.9300 |
| N1—C5 | 1.336 (4) | C9—C10 | 1.371 (6) |
| N2—C7 | 1.333 (4) | C10—H10 | 0.9300 |
| N2—C11 | 1.345 (4) | C10—C11 | 1.376 (5) |
| C1—H1 | 0.9300 | C11—H11 | 0.9300 |
| C1—C2 | 1.392 (4) | C12—H12A | 0.9600 |
| C2—C3 | 1.389 (5) | C12—H12B | 0.9600 |
| C2—C6 | 1.503 (5) | C12—H12C | 0.9600 |
| C3—H3 | 0.9300 | | |
| | | | |
| O1—Co1—S1$^{i}$ | 129.94 (5) | N1—C1—H1 | 118.0 |
| O1—Co1—O3$^{ii}$ | 94.41 (7) | N1—C1—C2 | 124.0 (3) |
| O1—Co1—O3$^{i}$ | 97.00 (7) | C2—C1—H1 | 118.0 |
| O1—Co1—O4$^{i}$ | 162.52 (7) | C1—C2—C6 | 121.6 (4) |
| O1—Co1—N1 | 92.08 (9) | C3—C2—C1 | 116.9 (3) |

| | | | |
|---|---|---|---|
| O1—Co1—N2 | 92.84 (9) | C3—C2—C6 | 121.5 (3) |
| O3$^{i}$—Co1—S1$^{i}$ | 33.21 (5) | C2—C3—H3 | 120.2 |
| O3$^{ii}$—Co1—S1$^{i}$ | 81.36 (5) | C4—C3—C2 | 119.7 (3) |
| O3$^{ii}$—Co1—O3$^{i}$ | 86.57 (8) | C4—C3—H3 | 120.2 |
| O3$^{ii}$—Co1—N1 | 173.44 (9) | C3—C4—H4 | 120.4 |
| O4$^{i}$—Co1—S1$^{i}$ | 32.58 (5) | C3—C4—C5 | 119.3 (3) |
| O4$^{i}$—Co1—O3$^{ii}$ | 83.94 (7) | C5—C4—H4 | 120.4 |
| O4$^{i}$—Co1—O3$^{i}$ | 65.55 (7) | N1—C5—C4 | 122.6 (4) |
| O4$^{i}$—Co1—N1 | 90.16 (9) | N1—C5—H5 | 118.7 |
| N1—Co1—S1$^{i}$ | 95.20 (8) | C4—C5—H5 | 118.7 |
| N1—Co1—O3$^{i}$ | 93.61 (8) | C2—C6—H6A | 109.5 |
| N2—Co1—S1$^{i}$ | 136.90 (7) | C2—C6—H6B | 109.5 |
| N2—Co1—O3$^{i}$ | 170.11 (9) | C2—C6—H6C | 109.5 |
| N2—Co1—O3$^{ii}$ | 91.63 (8) | H6A—C6—H6B | 109.5 |
| N2—Co1—O4$^{i}$ | 104.59 (8) | H6A—C6—H6C | 109.5 |
| N2—Co1—N1 | 87.07 (9) | H6B—C6—H6C | 109.5 |
| O1—S1—Co1$^{iii}$ | 116.43 (7) | N2—C7—H7 | 118.2 |
| O1—S1—O3 | 108.92 (10) | N2—C7—C8 | 123.6 (3) |
| O1—S1—O4 | 109.93 (11) | C8—C7—H7 | 118.2 |
| O2—S1—Co1$^{iii}$ | 133.48 (9) | C7—C8—C12 | 120.8 (3) |
| O2—S1—O1 | 110.07 (11) | C9—C8—C7 | 116.8 (3) |
| O2—S1—O3 | 112.71 (12) | C9—C8—C12 | 122.4 (3) |
| O2—S1—O4 | 112.15 (12) | C8—C9—H9 | 119.7 |
| O3—S1—Co1$^{iii}$ | 53.22 (7) | C10—C9—C8 | 120.6 (3) |
| O4—S1—Co1$^{iii}$ | 50.06 (7) | C10—C9—H9 | 119.7 |
| O4—S1—O3 | 102.82 (11) | C9—C10—H10 | 120.6 |
| S1—O1—Co1 | 121.04 (10) | C9—C10—C11 | 118.7 (3) |
| Co1$^{ii}$—O3—Co1$^{iii}$ | 124.11 (9) | C11—C10—H10 | 120.6 |
| S1—O3—Co1$^{ii}$ | 141.48 (12) | N2—C11—C10 | 122.3 (3) |
| S1—O3—Co1$^{iii}$ | 93.57 (9) | N2—C11—H11 | 118.9 |
| S1—O4—Co1$^{iii}$ | 97.36 (9) | C10—C11—H11 | 118.9 |
| C1—N1—Co1 | 124.8 (2) | C8—C12—H12A | 109.5 |
| C1—N1—C5 | 117.5 (3) | C8—C12—H12B | 109.5 |
| C5—N1—Co1 | 117.4 (2) | C8—C12—H12C | 109.5 |
| C7—N2—Co1 | 121.9 (2) | H12A—C12—H12B | 109.5 |
| C7—N2—C11 | 118.1 (3) | H12A—C12—H12C | 109.5 |
| C11—N2—Co1 | 120.0 (2) | H12B—C12—H12C | 109.5 |

| | | | |
|---|---|---|---|
| Co1$^{iii}$—S1—O1—Co1 | −1.75 (15) | O4—S1—O3—Co1$^{iii}$ | −7.25 (10) |
| Co1$^{iii}$—S1—O3—Co1$^{ii}$ | −168.6 (2) | N1—C1—C2—C3 | −0.5 (5) |
| Co1—N1—C1—C2 | 173.9 (3) | N1—C1—C2—C6 | 179.7 (4) |
| Co1—N1—C5—C4 | −174.0 (3) | N2—C7—C8—C9 | 1.5 (5) |
| Co1—N2—C7—C8 | −179.4 (2) | N2—C7—C8—C12 | 179.5 (3) |
| Co1—N2—C11—C10 | 178.4 (2) | C1—N1—C5—C4 | 0.4 (5) |
| O1—S1—O3—Co1$^{iii}$ | 109.34 (9) | C1—C2—C3—C4 | 0.8 (5) |
| O1—S1—O3—Co1$^{ii}$ | −59.3 (2) | C2—C3—C4—C5 | −0.6 (6) |
| O1—S1—O4—Co1$^{iii}$ | −108.29 (10) | C3—C4—C5—N1 | −0.1 (6) |
| O2—S1—O1—Co1 | 176.64 (13) | C5—N1—C1—C2 | −0.1 (5) |

| | | | |
|---|---|---|---|
| O2—S1—O3—Co1$^{iii}$ | −128.20 (11) | C6—C2—C3—C4 | −179.4 (4) |
| O2—S1—O3—Co1$^{ii}$ | 63.1 (2) | C7—N2—C11—C10 | −0.6 (4) |
| O2—S1—O4—Co1$^{iii}$ | 128.92 (11) | C7—C8—C9—C10 | −1.5 (5) |
| O3—S1—O1—Co1 | −59.31 (15) | C8—C9—C10—C11 | 0.6 (5) |
| O3—S1—O4—Co1$^{iii}$ | 7.57 (11) | C9—C10—C11—N2 | 0.5 (5) |
| O4—S1—O1—Co1 | 52.63 (15) | C11—N2—C7—C8 | −0.5 (4) |
| O4—S1—O3—Co1$^{ii}$ | −175.90 (17) | C12—C8—C9—C10 | −179.4 (3) |

Symmetry codes: (i) *y*, −*x*+1, −*z*+1; (ii) −*x*+1, −*y*+1, *z*; (iii) −*y*+1, *x*, −*z*+1.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C1—H1···O4$^{i}$ | 0.93 | 2.53 | 3.116 (4) | 121 |
| C3—H3···O2$^{iv}$ | 0.93 | 2.46 | 3.135 (4) | 129 |
| C5—H5···O1 | 0.93 | 2.49 | 3.070 (4) | 121 |

Symmetry codes: (i) *y*, −*x*+1, −*z*+1; (iv) *x*+1/2, −*y*+3/2, −*z*+1/2.