Crystal structure of a looped-chain CoII coordination polymer: *catena*-poly[[bis(nitrato-κO)cobalt(II)]bis[μ-bis(pyridin-3-ylmethyl)sulfane-κ²*N*:*N*′]]

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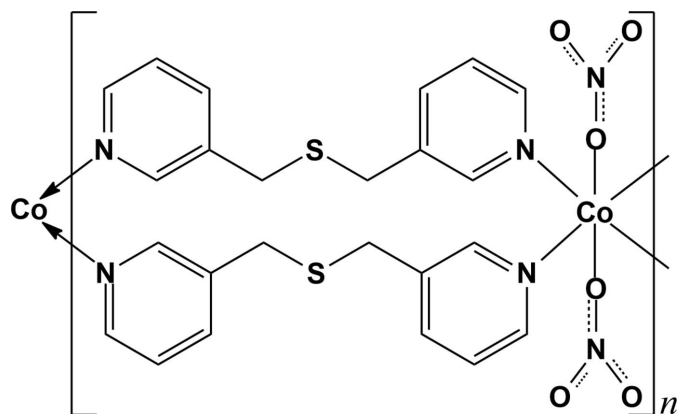
The asymmetric unit of the title compound, $[Co(NO_3)_2(C_{12}H_{12}N_2S)_2]_n$, contains a bis(pyridin-3-ylmethyl)sulfane (*L*) ligand, an NO_3^- anion and half a CoII cation, which lies on an inversion centre. The CoII cation is six-coordinated, being bound to four pyridine N atoms from four symmetry-related *L* ligands. The remaining coordination sites are occupied by two O atoms from two symmetry-related nitrate anions in a monodentate manner. Thus, the CoII centre adopts a distorted octahedral geometry. Two symmetry-related *L* ligands are connected by two symmetry-related CoII cations, forming a 20-membered cyclic dimer, in which the CoII atoms are separated by 10.2922 (7) Å. The cyclic dimers are connected to each other by sharing CoII atoms, giving rise to the formation of an infinite looped chain propagating along the [101] direction. Intermolecular C—H···π (H···ring centroid = 2.89 Å) interactions between one pair of corresponding *L* ligands and C—H···O hydrogen bonds between the *L* ligands and the nitrate anions occur in the looped chain. In the crystal, adjacent looped chains are connected by intermolecular π–π stacking interactions [centroid-to-centroid distance = 3.8859 (14) Å] and C—H···π hydrogen bonds (H···ring centroid = 2.65 Å), leading to the formation of layers parallel to (101). These layers are further connected through C—H···O hydrogen bonds between the layers, resulting in the formation of a three-dimensional supramolecular architecture.

1. Chemical context

Over the last two decades, numerous one-dimensional coordination polymers have been developed, not only because of their fascinating architectures but also their potential applications as functional materials (Furukawa *et al.*, 2014; Silva *et al.*, 2015). In this area of research, dipyridyl-type molecules as organic building blocks have been widely used to construct diverse one-dimensional self-assembled coordination polymers with intriguing structural topologies (Leong & Vittal, 2011; Wang *et al.*, 2012). Our group has also developed several one-dimensional coordination polymers with fascinating topologies such as zigzag (Lee *et al.*, 2013; Moon *et al.*, 2016), helical (Moon *et al.*, 2014, 2015), double helical (Lee *et al.*, 2015), looped chain (Ju *et al.*, 2014) and ribbon-type double-stranded (Moon *et al.*, 2017; Park *et al.*, 2010) structures using dipyridyl-type ligands. In an extension of our research, the title compound was prepared by the reaction of cobalt(II) nitrate with bis(pyridin-3-ylmethyl)sulfane (*L*) as a

flexible dipyridyl-type ligand, synthesized using a literature procedure (Park *et al.*, 2010; Lee *et al.*, 2012). Herein, we report the crystal structure of the title compound, which adopts a one-dimensional looped-chain structure.

2. Structural commentary

As illustrated in Fig. 1, the asymmetric unit of the title compound consists of one Co^{II} cation located on an inversion centre, one (pyridin-3-ylmethyl)sulfane ligand, *L*, and one NO_3^- anion. The Co^{II} cation is coordinated by four pyridine N atoms from four symmetry-related *L* ligands. In addition, the Co^{II} cation binds to two O atoms of two symmetry-related monodentate nitrate anions, forming a distorted octahedral CoN_4O_2 coordination. Selected bond lengths and angles around the Co1 atom are listed in Table 1. The N1- and N2-pyridine rings coordinated to the Co^{II} centre are tilted by 70.75 (7)° with respect to each other (Fig. 1).
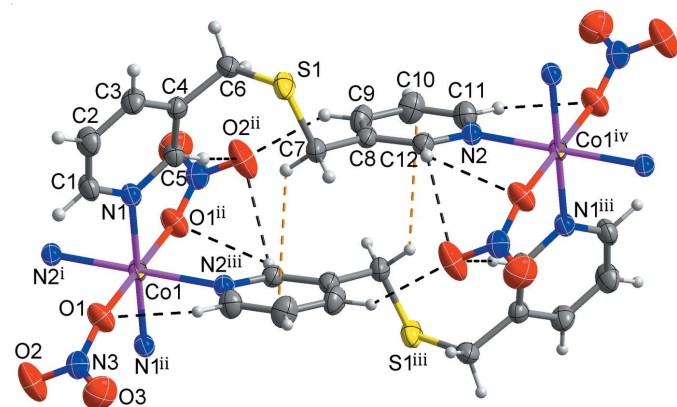

Figure 1
View of the cyclic dimer structure of the title compound, showing the geometry around Co^{II} centre and the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Intermolecular C—H···π and C—H···O hydrogen bonds are represented by yellow and black dashed lines, respectively [symmetry codes: (i) $x + 1, y, z + 1$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x, -y + 1, -z$; (iv) $x - 1, y, z - 1$].

Table 1
Selected geometric parameters (Å, °).

Co1—O1	2.1414 (16)	Co1—N2^i	2.1907 (18)
Co1—N1	2.1571 (17)		
O1^{ii}—Co1—O1	180.0	N1—Co1—N2^i	92.32 (6)
O1—Co1—N1	85.34 (7)	O1—Co1—N2^{iii}	88.21 (7)
O1—Co1—N1^{ii}	94.66 (7)	N1—Co1—N2^{iii}	87.68 (6)
N1—Co1—N1^{ii}	180.0	N2^i—Co1—N2^{iii}	180.0
O1—Co1—N2^i	91.79 (7)		

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

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

*Cg*2 is the centroid of the N2/C8–C12 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···O3^{iv}	0.93	2.60	3.466 (3)	155
C5—H5···O2^{ii}	0.93	2.30	3.171 (3)	157
C9—H9···O2^{ii}	0.93	2.54	3.373 (3)	149
C11—H11···O1^{iii}	0.93	2.43	3.032 (3)	122
C12—H12···O1^v	0.93	2.53	3.134 (3)	123
C12—H12···O2^v	0.93	2.59	3.219 (3)	125
C6—H6A···Cg2^{vi}	0.97	2.65	3.546 (3)	154
C7—H7B···Cg2^{iii}	0.97	2.89	3.565 (3)	127

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

Two symmetry-related *L* ligands bridge two Co^{II} atoms, resulting in the formation of a 20-membered cyclic dimer with a Co···Co separation of 10.2922 (7) Å. The cyclic dimers are connected by sharing Co^{II} atoms, leading to the formation of an infinite looped chain propagating along the [101] direction. An intermolecular C7—H7B···Cg2^i interactions [H···π = 2.89 Å; Table 2; yellow dashed lines in Fig. 1; Cg2 is the centroid of atoms N2/C8–C12; symmetry code: (i) $-x, -y + 1, -z$] between one pair of corresponding *L* ligands and several C—H···O hydrogen bonds between the *L* ligands and the NO_3^- anions (Table 2; black dashed lines in Fig. 1) contribute to the stabilization of the looped chain.

3. Supramolecular features

Adjacent looped chains in the structure are connected by intermolecular π–π stacking interactions between the N1-pyridine rings [Cg1···Cg1^{ii} = 3.8859 (14) Å; yellow dashed lines in Fig. 2; Cg1 is the centroid of atoms N1/C1–C5; symmetry code: (ii) $-x + 1, -y + 2, -z + 1$] together with intermolecular C6—H6A···Cg2^{iii} hydrogen bonds [H···π = 2.65 Å; Table 2; black dashed lines in Fig. 2; symmetry code: (iii) $-x, -y + 2, -z$], generating layers parallel to (101). Neighboring layers are packed by C1—H1···O3^{iv} hydrogen bonds [H···O = 2.60 Å; Table 2; yellow dashed lines in Fig. 3; symmetry code: (iv) $-x + 2, -y + 1, -z + 1$] between pyridine H atoms and nitrogen O atoms, resulting in the formation of a three-dimensional supramolecular architecture.
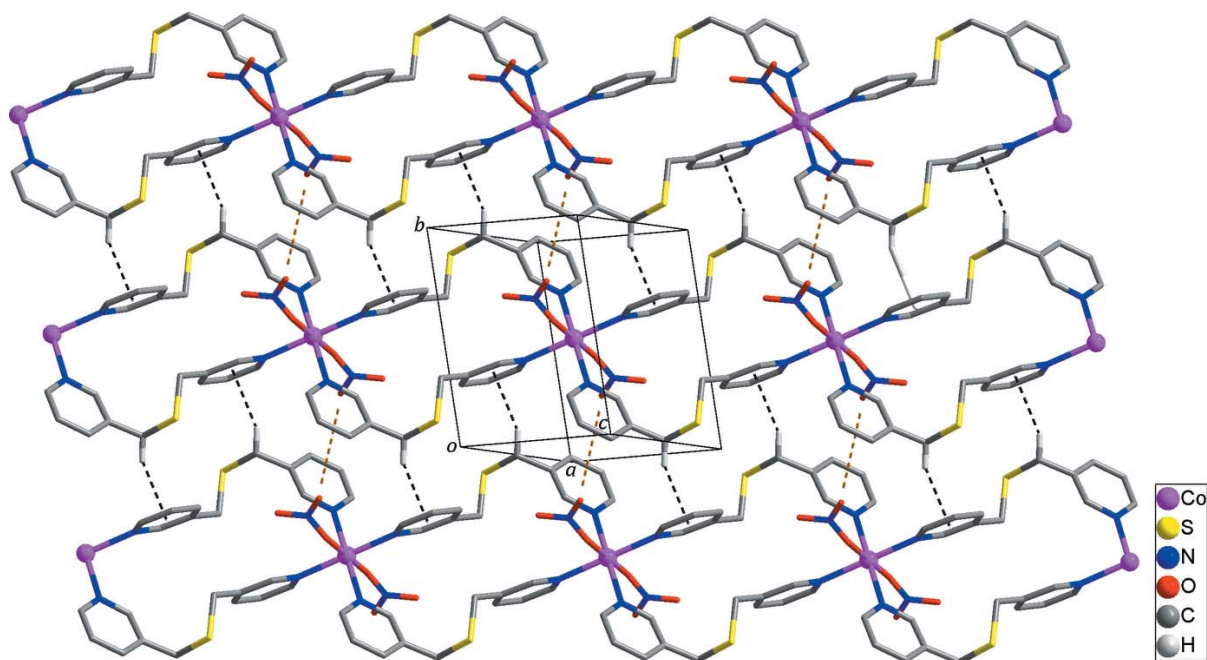
Figure 2
The supramolecular layer formed by intermolecular π–π stacking interactions (yellow dashed lines) and C—H$\cdots\pi$ hydrogen bonds (black dashed lines) between the looped chains. H atoms not involved in intermolecular interactions have been omitted for clarity.

4. Synthesis and crystallization

The *L* ligand was synthesized according to a literature method (Park *et al.*, 2010; Lee *et al.*, 2012). Crystals of the title compound were grown by slow evaporation of a methanol/H$_2$O (2:1) solution of the *L* ligand with Co(NO$_3$)$_2$·6H$_2$O in a 2:1 molar ratio.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms were positioned geometrically and refined as riding: C—H = 0.93 Å for Csp^2—H and 0.97 Å for methylene C—H with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.
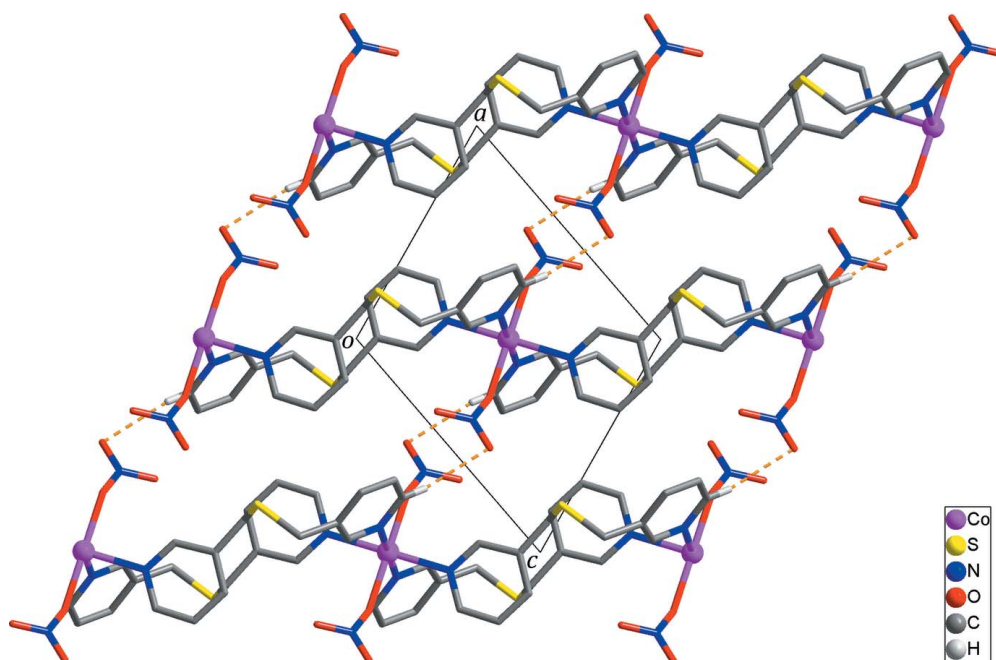

Figure 3
The three-dimensional supramolecular network formed *via* intermolecular C—H$\cdots$O hydrogen bonds (yellow dashed lines) between the layers. H atoms not involved in intermolecular interactions have been omitted for clarity.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Co(NO_3)_2(C_{12}H_{12}N_2S)_2]$
M_r	615.54
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	298
a, b, c (Å)	8.1620 (7), 8.8158 (8), 9.5078 (8)
α, β, γ (°)	98.531 (2), 109.218 (2), 92.062 (2)
V (Å^3)	636.22 (10)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.89
Crystal size (mm)	$0.45 \times 0.30 \times 0.15$
Data collection	
Diffractometer	Bruker APEXII CCD area detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.634, 0.896
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3659, 2456, 2082
R_{int}	0.040
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.033, 0.088, 1.04
No. of reflections	2456
No. of parameters	178
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.33, −0.37

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXS97* and *SHELXTL* (Sheldrick, 2008), *SHELXL2014/7* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 2010) and *publCIF* (Westrip, 2010).

References

Brandenburg, K. (2010). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Bruker (2014). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Furukawa, S., Reboul, J., Diring, S., Sumida, K. & Kitagawa, S. (2014). *Chem. Soc. Rev.* **43**, 5700–5734.

Ju, H., Lee, E., Moon, S.-H., Lee, S. S. & Park, K.-M. (2014). *Bull. Korean Chem. Soc.* **35**, 3658–3660.

Lee, E., Ju, H., Moon, S.-H., Lee, S. S. & Park, K.-M. (2015). *Bull. Korean Chem. Soc.* **36**, 1532–1535.

Lee, E., Ryu, H., Moon, S.-H. & Park, K.-M. (2013). *Bull. Korean Chem. Soc.* **34**, 3477–3480.

Lee, E., Seo, J., Lee, S. S. & Park, K.-M. (2012). *Cryst. Growth Des.* **12**, 3834–3837.

Leong, W. L. & Vittal, J. J. (2011). *Chem. Rev.* **111**, 688–764.

Moon, B., Jeon, Y., Moon, S.-H. & Park, K.-M. (2014). *Acta Cryst.* E**70**, 507–509.

Moon, S.-H., Kang, Y. & Park, K.-M. (2015). *Acta Cryst.* E**71**, 1287–1289.

Moon, S.-H., Kang, D. & Park, K.-M. (2016). *Acta Cryst.* E**72**, 1513–1516.

Moon, S.-H., Kang, Y. & Park, K.-M. (2017). *Acta Cryst.* E**73**, 1587–1589.

Park, K.-M., Seo, J., Moon, S.-H. & Lee, S. S. (2010). *Cryst. Growth Des.* **10**, 4148–4154.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Silva, P., Vilela, S. M. F., Tomé, J. P. C. & Almeida Paz, F. A. (2015). *Chem. Soc. Rev.* **44**, 6774–6803.

Wang, C., Zhang, T. & Lin, W. (2012). *Chem. Rev.* **112**, 1084–1104.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Crystal structure of a looped-chain Co^{II} coordination polymer: *catena*-poly[[bis-(nitrato-*κO*)cobalt(II)]bis[*μ*-bis(pyridin-3-ylmethyl)sulfane-*κ²N:N′*]]

Suk-Hee Moon, Joobeom Seo and Ki-Min Park

Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

***catena*-Poly[[bis(nitrato-*κO*)cobalt(II)]bis[*μ*-bis(pyridin-3-ylmethyl)sulfane-*κ²N:N′*]]**

Crystal data

[Co(NO₃)₂(C₁₂H₁₂N₂S)₂]	$Z = 1$
$M_r = 615.54$	$F(000) = 317$
Triclinic, $P\overline{1}$	$D_x = 1.607$ Mg m⁻³
$a = 8.1620\ (7)$ Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 8.8158\ (8)$ Å	Cell parameters from 3659 reflections
$c = 9.5078\ (8)$ Å	$\theta = 2.3–26.0°$
$\alpha = 98.531\ (2)°$	$\mu = 0.89$ mm⁻¹
$\beta = 109.218\ (2)°$	$T = 298$ K
$\gamma = 92.062\ (2)°$	Plate, violet
$V = 636.22\ (10)$ Å³	$0.45 \times 0.30 \times 0.15$ mm

Data collection

Bruker APEXII CCD area detector diffractometer	2456 independent reflections
	2082 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.040$
Absorption correction: multi-scan (SADABS; Bruker, 2014)	$\theta_{max} = 26.0°$, $\theta_{min} = 2.3°$
	$h = -7 \rightarrow 10$
$T_{min} = 0.634$, $T_{max} = 0.896$	$k = -10 \rightarrow 10$
3659 measured reflections	$l = -11 \rightarrow 7$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.033$	H-atom parameters constrained
$wR(F^2) = 0.088$	$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 0.1617P]$
$S = 1.04$	where $P = (F_o^2 + 2F_c^2)/3$
2456 reflections	$(\Delta/\sigma)_{max} < 0.001$
178 parameters	$\Delta\rho_{max} = 0.33$ e Å⁻³
0 restraints	$\Delta\rho_{min} = -0.37$ e Å⁻³

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 ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.5000	0.5000	0.5000	0.02620 (13)
S1	0.20509 (7)	0.89446 (7)	−0.01804 (7)	0.03834 (17)
N1	0.5427 (2)	0.7131 (2)	0.42595 (19)	0.0294 (4)
N2	−0.3498 (2)	0.5946 (2)	−0.2639 (2)	0.0294 (4)
N3	0.8472 (2)	0.3452 (2)	0.4702 (2)	0.0353 (4)
O1	0.7307 (2)	0.4382 (2)	0.4536 (2)	0.0459 (4)
O2	0.9392 (2)	0.3314 (3)	0.5987 (2)	0.0623 (6)
O3	0.8698 (3)	0.2729 (2)	0.3594 (2)	0.0600 (5)
C1	0.7012 (3)	0.7803 (3)	0.4459 (3)	0.0359 (5)
H1	0.7992	0.7378	0.5020	0.043*
C2	0.7239 (3)	0.9093 (3)	0.3867 (3)	0.0419 (6)
H2	0.8356	0.9533	0.4041	0.050*
C3	0.5807 (3)	0.9731 (3)	0.3014 (3)	0.0377 (5)
H3	0.5945	1.0595	0.2595	0.045*
C4	0.4158 (3)	0.9065 (2)	0.2792 (2)	0.0293 (4)
C5	0.4044 (3)	0.7788 (2)	0.3446 (2)	0.0288 (4)
H5	0.2939	0.7352	0.3316	0.035*
C6	0.2546 (3)	0.9672 (3)	0.1822 (3)	0.0345 (5)
H6A	0.2707	1.0788	0.1994	0.041*
H6B	0.1566	0.9379	0.2119	0.041*
C7	0.1232 (3)	0.6961 (3)	−0.0308 (3)	0.0345 (5)
H7A	0.1544	0.6312	−0.1080	0.041*
H7B	0.1802	0.6624	0.0648	0.041*
C8	−0.0710 (3)	0.6735 (2)	−0.0675 (2)	0.0298 (5)
C9	−0.1533 (3)	0.7008 (3)	0.0387 (3)	0.0390 (5)
H9	−0.0889	0.7344	0.1402	0.047*
C10	−0.3334 (3)	0.6773 (3)	−0.0089 (3)	0.0425 (6)
H10	−0.3915	0.6973	0.0603	0.051*
C11	−0.4259 (3)	0.6242 (3)	−0.1590 (3)	0.0369 (5)
H11	−0.5466	0.6082	−0.1889	0.044*
C12	−0.1752 (3)	0.6202 (2)	−0.2167 (2)	0.0292 (4)
H12	−0.1205	0.6011	−0.2885	0.035*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0226 (2)	0.0291 (2)	0.0237 (2)	0.00094 (15)	0.00236 (16)	0.00769 (16)
S1	0.0360 (3)	0.0407 (3)	0.0324 (3)	−0.0055 (2)	0.0012 (2)	0.0141 (2)
N1	0.0260 (9)	0.0313 (9)	0.0286 (9)	0.0012 (7)	0.0049 (7)	0.0082 (7)

N2	0.0280 (9)	0.0285 (9)	0.0279 (9)	−0.0005 (7)	0.0039 (7)	0.0067 (7)
N3	0.0288 (10)	0.0424 (11)	0.0357 (11)	−0.0022 (8)	0.0122 (8)	0.0074 (9)
O1	0.0323 (9)	0.0589 (11)	0.0496 (10)	0.0161 (8)	0.0135 (8)	0.0168 (9)
O2	0.0407 (10)	0.1040 (17)	0.0441 (11)	0.0230 (11)	0.0094 (9)	0.0258 (11)
O3	0.0686 (13)	0.0642 (13)	0.0510 (12)	0.0086 (10)	0.0314 (10)	−0.0046 (10)
C1	0.0243 (11)	0.0422 (13)	0.0367 (12)	0.0025 (9)	0.0023 (9)	0.0114 (10)
C2	0.0292 (12)	0.0469 (14)	0.0478 (14)	−0.0051 (10)	0.0093 (11)	0.0133 (11)
C3	0.0368 (12)	0.0334 (12)	0.0398 (13)	−0.0066 (9)	0.0077 (10)	0.0113 (10)
C4	0.0308 (11)	0.0282 (10)	0.0247 (10)	0.0002 (8)	0.0044 (9)	0.0040 (8)
C5	0.0238 (10)	0.0331 (11)	0.0274 (10)	−0.0003 (8)	0.0056 (8)	0.0067 (9)
C6	0.0337 (12)	0.0285 (11)	0.0370 (12)	0.0035 (9)	0.0042 (10)	0.0100 (9)
C7	0.0305 (11)	0.0330 (11)	0.0311 (11)	0.0001 (9)	−0.0008 (9)	0.0047 (9)
C8	0.0315 (11)	0.0254 (10)	0.0276 (11)	−0.0008 (8)	0.0027 (9)	0.0071 (8)
C9	0.0440 (13)	0.0419 (13)	0.0249 (11)	−0.0050 (10)	0.0051 (10)	0.0037 (9)
C10	0.0441 (14)	0.0520 (15)	0.0334 (12)	−0.0032 (11)	0.0181 (11)	0.0039 (11)
C11	0.0321 (12)	0.0444 (13)	0.0347 (12)	−0.0005 (10)	0.0117 (10)	0.0083 (10)
C12	0.0294 (11)	0.0279 (10)	0.0282 (11)	0.0004 (8)	0.0072 (9)	0.0052 (8)

Geometric parameters (Å, º)

Co1—O1^i	2.1414 (16)	C2—H2	0.9300
Co1—O1	2.1414 (16)	C3—C4	1.386 (3)
Co1—N1	2.1571 (17)	C3—H3	0.9300
Co1—N1^i	2.1571 (17)	C4—C5	1.378 (3)
Co1—N2^{ii}	2.1907 (18)	C4—C6	1.505 (3)
Co1—N2^{iii}	2.1907 (18)	C5—H5	0.9300
S1—C6	1.820 (2)	C6—H6A	0.9700
S1—C7	1.822 (2)	C6—H6B	0.9700
N1—C1	1.346 (3)	C7—C8	1.505 (3)
N1—C5	1.346 (3)	C7—H7A	0.9700
N2—C11	1.338 (3)	C7—H7B	0.9700
N2—C12	1.345 (3)	C8—C9	1.384 (3)
N2—Co1^{iv}	2.1907 (17)	C8—C12	1.392 (3)
N3—O3	1.219 (3)	C9—C10	1.386 (3)
N3—O2	1.232 (3)	C9—H9	0.9300
N3—O1	1.264 (2)	C10—C11	1.376 (3)
C1—C2	1.374 (3)	C10—H10	0.9300
C1—H1	0.9300	C11—H11	0.9300
C2—C3	1.378 (3)	C12—H12	0.9300
O1^i—Co1—O1	180.0	C4—C3—H3	120.5
O1^i—Co1—N1	94.66 (7)	C5—C4—C3	117.63 (19)
O1—Co1—N1	85.34 (7)	C5—C4—C6	120.95 (19)
O1^i—Co1—N1^i	85.34 (7)	C3—C4—C6	121.38 (19)
O1—Co1—N1^i	94.66 (7)	N1—C5—C4	124.37 (19)
N1—Co1—N1^i	180.0	N1—C5—H5	117.8
O1^i—Co1—N2^{ii}	88.21 (7)	C4—C5—H5	117.8
O1—Co1—N2^{ii}	91.79 (7)	C4—C6—S1	112.23 (16)

N1—Co1—N2ⁱⁱ	92.32 (6)	C4—C6—H6A	109.2
N1ⁱ—Co1—N2ⁱⁱ	87.68 (6)	S1—C6—H6A	109.2
O1ⁱ—Co1—N2ⁱⁱⁱ	91.79 (7)	C4—C6—H6B	109.2
O1—Co1—N2ⁱⁱⁱ	88.21 (7)	S1—C6—H6B	109.2
N1—Co1—N2ⁱⁱⁱ	87.68 (6)	H6A—C6—H6B	107.9
N1ⁱ—Co1—N2ⁱⁱⁱ	92.32 (6)	C8—C7—S1	113.88 (15)
N2ⁱⁱ—Co1—N2ⁱⁱⁱ	180.0	C8—C7—H7A	108.8
C6—S1—C7	101.13 (11)	S1—C7—H7A	108.8
C1—N1—C5	116.71 (18)	C8—C7—H7B	108.8
C1—N1—Co1	123.98 (14)	S1—C7—H7B	108.8
C5—N1—Co1	119.10 (13)	H7A—C7—H7B	107.7
C11—N2—C12	116.94 (19)	C9—C8—C12	117.5 (2)
C11—N2—Co1ⁱᵛ	121.87 (15)	C9—C8—C7	124.0 (2)
C12—N2—Co1ⁱᵛ	121.15 (14)	C12—C8—C7	118.5 (2)
O3—N3—O2	120.9 (2)	C8—C9—C10	118.8 (2)
O3—N3—O1	119.8 (2)	C8—C9—H9	120.6
O2—N3—O1	119.3 (2)	C10—C9—H9	120.6
N3—O1—Co1	145.89 (15)	C11—C10—C9	119.7 (2)
N1—C1—C2	122.6 (2)	C11—C10—H10	120.2
N1—C1—H1	118.7	C9—C10—H10	120.2
C2—C1—H1	118.7	N2—C11—C10	122.9 (2)
C1—C2—C3	119.8 (2)	N2—C11—H11	118.6
C1—C2—H2	120.1	C10—C11—H11	118.6
C3—C2—H2	120.1	N2—C12—C8	124.2 (2)
C2—C3—C4	118.9 (2)	N2—C12—H12	117.9
C2—C3—H3	120.5	C8—C12—H12	117.9
O3—N3—O1—Co1	122.6 (3)	C7—S1—C6—C4	73.67 (17)
O2—N3—O1—Co1	−59.0 (4)	C6—S1—C7—C8	91.15 (17)
C5—N1—C1—C2	−0.2 (3)	S1—C7—C8—C9	−82.8 (2)
Co1—N1—C1—C2	174.55 (18)	S1—C7—C8—C12	98.0 (2)
N1—C1—C2—C3	−0.9 (4)	C12—C8—C9—C10	−1.4 (3)
C1—C2—C3—C4	1.0 (4)	C7—C8—C9—C10	179.4 (2)
C2—C3—C4—C5	0.1 (3)	C8—C9—C10—C11	1.5 (4)
C2—C3—C4—C6	−177.6 (2)	C12—N2—C11—C10	−0.5 (3)
C1—N1—C5—C4	1.4 (3)	Co1ⁱᵛ—N2—C11—C10	177.10 (18)
Co1—N1—C5—C4	−173.66 (16)	C9—C10—C11—N2	−0.6 (4)
C3—C4—C5—N1	−1.3 (3)	C11—N2—C12—C8	0.6 (3)
C6—C4—C5—N1	176.39 (19)	Co1ⁱᵛ—N2—C12—C8	−177.01 (15)
C5—C4—C6—S1	−95.4 (2)	C9—C8—C12—N2	0.4 (3)
C3—C4—C6—S1	82.2 (2)	C7—C8—C12—N2	179.61 (19)

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

Hydrogen-bond geometry (Å, º)

*Cg*2 is the centroid of the N2/C8–C12 ring.

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C1—H1⋯O3ᵛ	0.93	2.60	3.466 (3)	155

C5—H5···O2[i]	0.93	2.30	3.171 (3)	157
C9—H9···O2[i]	0.93	2.54	3.373 (3)	149
C11—H11···O1[iii]	0.93	2.43	3.032 (3)	122
C12—H12···O1[iv]	0.93	2.53	3.134 (3)	123
C12—H12···O2[iv]	0.93	2.59	3.219 (3)	125
C6—H6*A*···*Cg*2[vi]	0.97	2.65	3.546 (3)	154
C7—H7*B*···*Cg*2[iii]	0.97	2.89	3.565 (3)	127

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (iii) −*x*, −*y*+1, −*z*; (iv) *x*−1, *y*, *z*−1; (v) −*x*+2, −*y*+1, −*z*+1; (vi) −*x*, −*y*+2, −*z*.