



Crystal structure of a looped-chain Co^{II} coordination polymer: *catena*-poly[[bis(nitrato- κ O)cobalt(II)]bis[μ -bis(pyridin-3-ylmethyl)sulfane- κ^2 N:N']]

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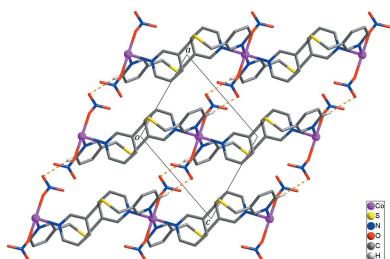
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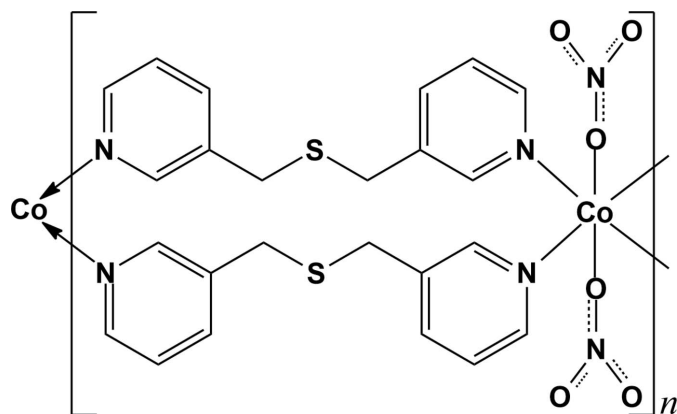
The asymmetric unit of the title compound, [Co(NO₃)₂(C₁₂H₁₂N₂S)₂]_n, contains a bis(pyridin-3-ylmethyl)sulfane (*L*) ligand, an NO₃⁻ anion and half a Co^{II} cation, which lies on an inversion centre. The Co^{II} cation is six-coordinated, being bound to four pyridine N atoms from four symmetry-related *L* ligands. The remaining coordination sites are occupied by two O atoms from two symmetry-related nitrate anions in a monodentate manner. Thus, the Co^{II} centre adopts a distorted octahedral geometry. Two symmetry-related *L* ligands are connected by two symmetry-related Co^{II} cations, forming a 20-membered cyclic dimer, in which the Co^{II} atoms are separated by 10.2922 (7) Å. The cyclic dimers are connected to each other by sharing Co^{II} 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, dipyriddy-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 dipyriddy-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 NO₃[−] 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 CoN₄O₂ 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).

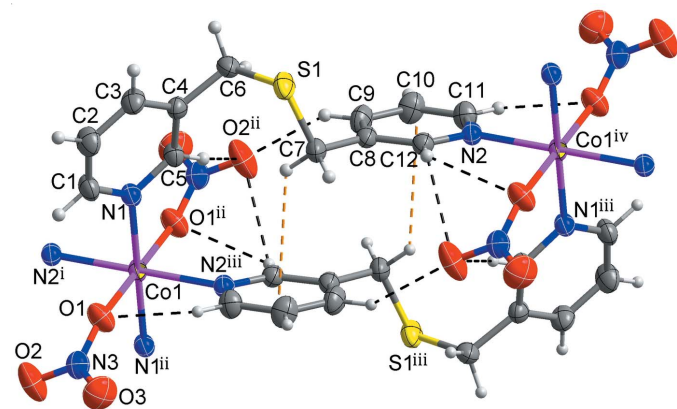


Figure 1

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 ⁱⁱ —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, °).

Cg2 is the centroid of the N2/C8—C12 ring.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
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...Cg2ⁱ interactions [$H \cdots \pi = 2.89$ 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 NO₃[−] 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 [$Cg1 \cdots Cg1^{ii} = 3.8859$ (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...Cg2ⁱⁱⁱ hydrogen bonds [$H \cdots \pi = 2.65$ 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 [$H \cdots O = 2.60$ 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.

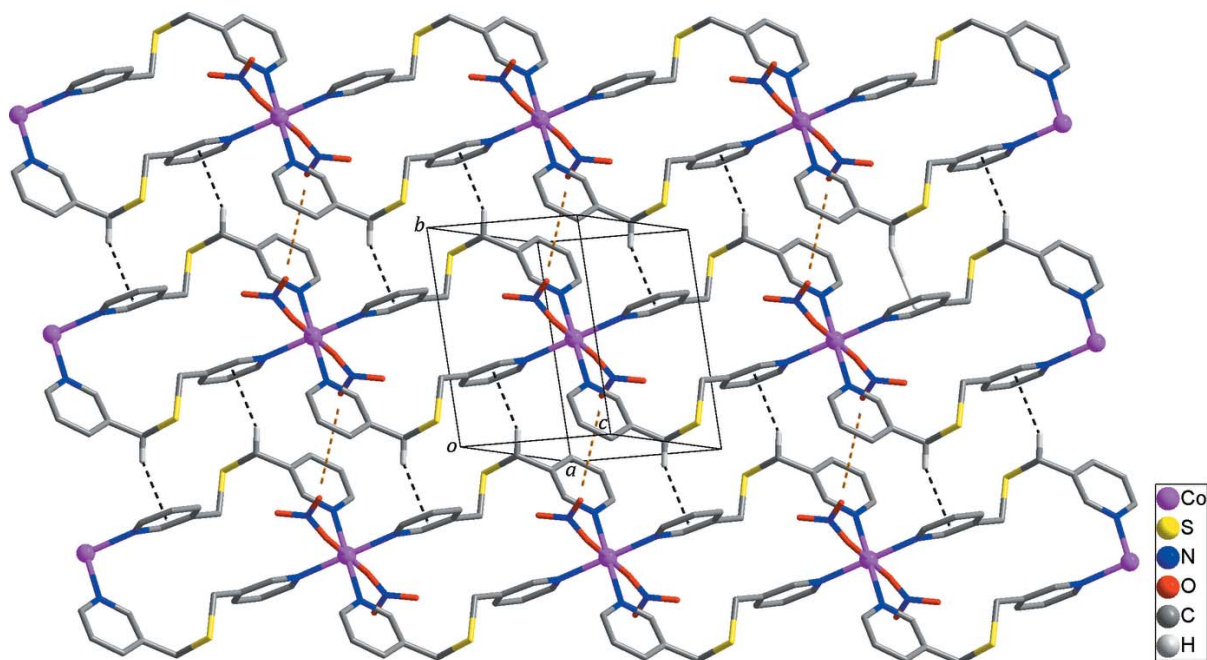


Figure 2
The supramolecular layer formed by intermolecular π - π stacking interactions (yellow dashed lines) and C-H $\cdots\pi$ hydrogen bonds (black dashed lines) between the looped chains. H atoms not involved in intermolecular interactions have been omitted for clarity.

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_2O (2:1) solution of the *L* ligand with $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

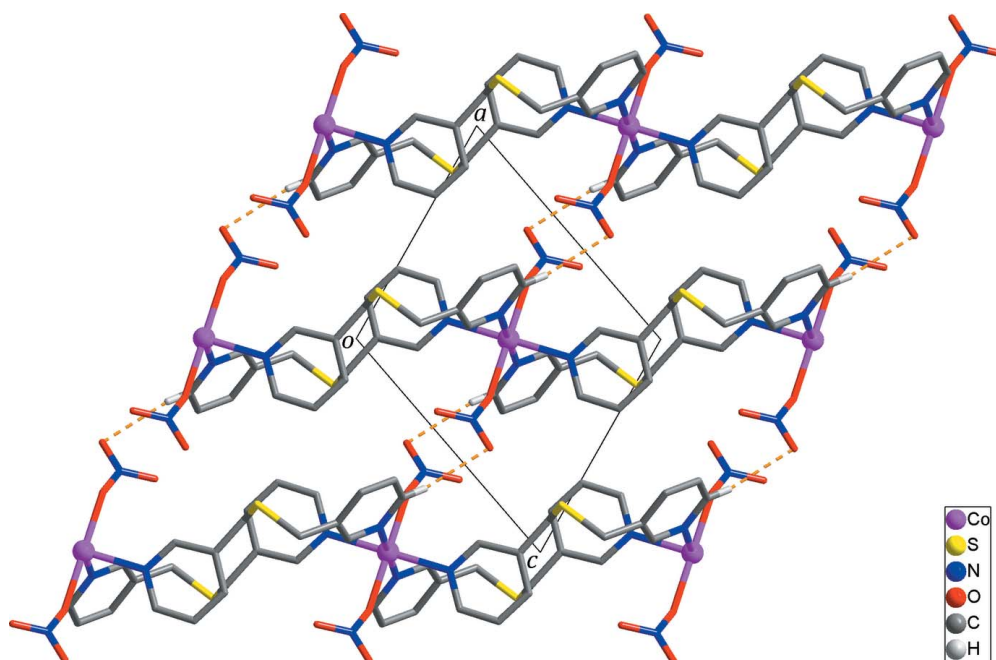


Figure 3
The three-dimensional supramolecular network formed *via* intermolecular C-H $\cdots\text{O}$ hydrogen bonds (yellow dashed lines) between the layers. H atoms not involved in intermolecular interactions have been omitted for clarity.

Table 3
Experimental details.

Crystal data	
Chemical formula	[Co(NO ₃) ₂ (C ₁₂ H ₁₂ N ₂ S) ₂]
<i>M</i> _r	615.54
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	298
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.1620 (7), 8.8158 (8), 9.5078 (8)
α , β , γ (°)	98.531 (2), 109.218 (2), 92.062 (2)
<i>V</i> (Å ³)	636.22 (10)
<i>Z</i>	1
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.89
Crystal size (mm)	0.45 × 0.30 × 0.15
Data collection	
Diffractometer	Bruker APEXII CCD area detector
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2014)
<i>T</i> _{min} , <i>T</i> _{max}	0.634, 0.896
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	3659, 2456, 2082
<i>R</i> _{int}	0.040
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.617
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.033, 0.088, 1.04
No. of reflections	2456
No. of parameters	178
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (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 *pubCIF* (Westrip, 2010).

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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.* **E70**, 507–509.
- Moon, S.-H., Kang, Y. & Park, K.-M. (2015). *Acta Cryst.* **E71**, 1287–1289.
- Moon, S.-H., Kang, D. & Park, K.-M. (2016). *Acta Cryst.* **E72**, 1513–1516.
- Moon, S.-H., Kang, Y. & Park, K.-M. (2017). *Acta Cryst.* **E73**, 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.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 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.

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Acta Cryst. (2017). E73, 1700-1703 [https://doi.org/10.1107/S2056989017014980]

Crystal structure of a looped-chain Co^{II} coordination polymer: *catena*-poly[[bis-(nitrate- κ O)cobalt(II)]bis[μ -bis(pyridin-3-ylmethyl)sulfane- κ^2 N:N']]

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

Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINTE* (Bruker, 2014); data reduction: *SAINTE* (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 *pubCIF* (Westrip, 2010).

catena-Poly[[bis(nitrate- κ O)cobalt(II)]bis[μ -bis(pyridin-3-ylmethyl)sulfane- κ^2 N:N']]

Crystal data

[Co(NO₃)₂(C₁₂H₁₂N₂S)₂]

$M_r = 615.54$

Triclinic, $P\bar{1}$

$a = 8.1620$ (7) Å

$b = 8.8158$ (8) Å

$c = 9.5078$ (8) Å

$\alpha = 98.531$ (2)°

$\beta = 109.218$ (2)°

$\gamma = 92.062$ (2)°

$V = 636.22$ (10) Å³

$Z = 1$

$F(000) = 317$

$D_x = 1.607$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3659 reflections

$\theta = 2.3$ – 26.0 °

$\mu = 0.89$ mm⁻¹

$T = 298$ K

Plate, violet

$0.45 \times 0.30 \times 0.15$ mm

Data collection

Bruker APEXII CCD area detector
diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2014)

$T_{\min} = 0.634$, $T_{\max} = 0.896$

3659 measured reflections

2456 independent reflections

2082 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$

$\theta_{\max} = 26.0$ °, $\theta_{\min} = 2.3$ °

$h = -7 \rightarrow 10$

$k = -10 \rightarrow 10$

$l = -11 \rightarrow 7$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.088$

$S = 1.04$

2456 reflections

178 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 0.1617P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.33$ e Å⁻³

$\Delta\rho_{\min} = -0.37$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (\AA^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, °)

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—N2 ⁱⁱ	92.32 (6)	C4—C6—H6A	109.2
N1 ⁱ —Co1—N2 ⁱⁱ	87.68 (6)	S1—C6—H6A	109.2
O1 ⁱ —Co1—N2 ⁱⁱⁱ	91.79 (7)	C4—C6—H6B	109.2
O1—Co1—N2 ⁱⁱⁱ	88.21 (7)	S1—C6—H6B	109.2
N1—Co1—N2 ⁱⁱⁱ	87.68 (6)	H6A—C6—H6B	107.9
N1 ⁱ —Co1—N2 ⁱⁱⁱ	92.32 (6)	C8—C7—S1	113.88 (15)
N2 ⁱⁱ —Co1—N2 ⁱⁱⁱ	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—Co1 ^{iv}	121.87 (15)	C9—C8—C7	124.0 (2)
C12—N2—Co1 ^{iv}	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)	Co1 ^{iv} —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)	Co1 ^{iv} —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 (\AA , $^\circ$)

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

<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>
C1—H1 \cdots O3 ^v	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—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: (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) $-x, -y+2, -z$.