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Crystal structure of tris{*N*,*N*-diethyl-*N*′-[(4-nitrophenyl)(oxo)methyl]carbamimidothioato}-cobalt(III)

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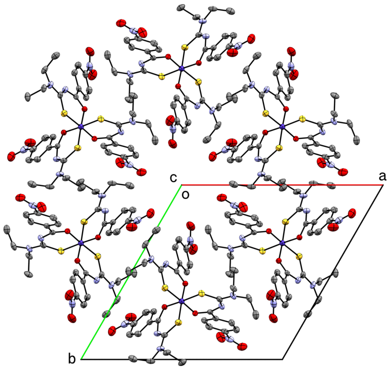
The synthesis, crystal structure, and a Hirshfeld surface analysis of tris{*N*,*N*-diethyl-*N*′-[(4-nitrophenyl)(oxo)methyl]carbamimidothioato}cobalt(III) conducted at 180 K are presented. The complex consists of three *N*,*N*-diethyl-*N*′-[(4-nitrobenzene)(oxo)methyl]carbamimidothioato ligands, threefold symmetrically bonded about the Co^{III} ion, in approximately octahedral coordination, which generates a triple of individually near planar metallacyclic (Co—S—C—N—C—O) rings. The overall geometry of the complex is determined by the mutual orientation of each metallacycle about the crystallographically imposed threefold axis [dihedral angles = 81.70 (2)°] and by the dihedral angles between the various planar groups within each asymmetric unit [metallacycle to benzene ring = 13.83 (7)°; benzene ring to nitro group = 17.494 (8)°]. The complexes stack in anti-parallel columns about the $\overline{3}$ axis of the space group ($P\overline{3}$), generating solvent-accessible channels along [001]. These channels contain ill-defined, multiply disordered, partial-occupancy solvent. Atom–atom contacts in the crystal packing predominantly (∼96%) involve hydrogen, the most abundant types being H⋯H (36.6%), H⋯O (31.0%), H⋯C (19.2%), H⋯N (4.8%), and H⋯S (4.4%).

1. Chemical context

Thiourea derivatives and their metal complexes have been of interest for the past two decades. Recent reviews have highlighted current trends in their chemistry (Zahra *et al.*, 2022; Saeed *et al.*, 2014) including medical and chemosensing applications (Khan *et al.*, 2021). One older study evaluated the potential of *N*-benzoyl-*N*′-dialkyl derivatives and their Co^{III} complexes as antifungal agents (Wiequn *et al.*, 2003, 2005). The synthesis of these later complexes are straightforward: mixing three equivalents of the ligand with $CoCl_2{\cdot}6H_2O$ in water and stirring for an hour results in deposition of the neutral, dark-green Co^{III} complexes. Making the analogous tris-coordinated complexes was not our original intention. In the course of preparing Co^{III} complexes coordinated by a single $\kappa^{2-}S,O$ ligand, the neutral tris product was invariably formed as a side product when reacting the labile Co^{III} starting material $[(en)_2Co(OSO_2CF_3)]CF_3SO_3$ (Dixon *et al.*, 1981) with one equivalent of ligand. This paper presents the synthesis and crystal structure of tris{*N*,*N*-diethyl-*N*′-[(4-nitrophenyl)(oxo)methyl]carbamimidothioato}cobalt(III), **I**.



2. Structural commentary

The molecule of **I** consists of three *N*,*N*-diethyl-*N*′-[(4-nitrobenzene)(oxo)methyl]carbamimidothioato ligands, each bound to a single Co^{III} centre by their sulfur and carbonyl

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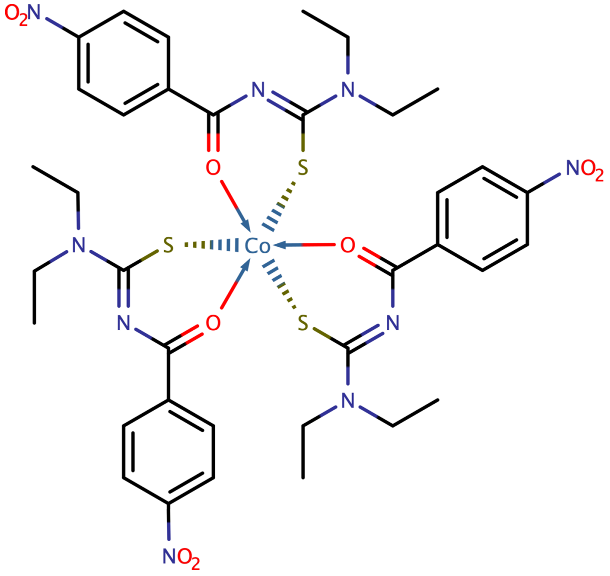
Table 1
Selected geometric parameters (Å, °) for **I**.

Distances		Angles	
Co1—S1^{sym}	2.2082 (5)	(S1—Co1—S1)^{sym}	88.35 (2)
Co1—O1^{sym}	1.9202 (11)	(O1—Co1—O1)^{sym}	84.68 (5)
		O1—Co1—S1	95.09 (3)
		O1—Co1—S1^{i}	91.87 (4)
		O1—Co1—S1^{ii}	176.56 (3)

Symmetry codes: (i) $-y+1, x-y+1, z$; (ii) $-x+y, -x+1, z$; here '*sym*' refers to all crystallographic equivalents about the threefold axis, *i.e.*, (i), (ii), and x, y, z.

oxygen atoms. The complex has crystallographic threefold symmetry, with the Co$^{\rm III}$ atom (Fig. 1) occupying Wyckoff position *d* (1/3, 2/3, *z*) in the space group of type $P\overline{3}$. The coordination geometry about Co1 is moderately distorted octahedral. Due to the threefold symmetry, all Co—S bonds are equivalent [$d_{\rm Co1-S1}$ = 2.2082 (5) Å], as are all Co—O bonds [$d_{\rm Co1-O1}$ = 1.9202 (11) Å]. The bond-valence sum for Co1 amounts to 3.20 v.u. (v.u. = valence units; Brese & O'Keeffe, 1991). Deviations from octahedral geometry are especially apparent in the bond angles subtended at Co1. All S1—Co1—S1 [88.35 (2)°] and O1—Co1—O1 [84.68 (5)°] type bond angles are acute, while equatorial bond angles of type S1—Co—O1 [91.87 (4), 95.09 (3)] are obtuse. The axial S1—Co—O1 bond angles are 176.56 (3)°. These are summarized in Table 1.



Within the asymmetric unit, the metallacyclic (Co1–S1–C1–N1–C2–O1) ring is almost planar [mean plane r.m.s. deviation = 0.0300 Å, largest = 0.0614 (12) Å at N1]. The dihedral angle between this metallacycle and the benzene ring is 13.83 (7)°, while that of the nitro group relative to the benzene ring is 17.494 (8)°. The mean plane through atoms N2–C1–C9–C11 [r.m.s. deviation = 0.0141 Å, largest = 0.0244 (14) Å at N2] forms a dihedral with the metallacycle mean plane of 6.21 (11)°. Lastly, the torsion angles of the two ethyl groups (C1—N2—C9—C10 and C1—N2—C11—C12) are the same at 90.7 (2)°. The overall geometry of the complex is then determined by the dihedral angles between the metallacycles in each asymmetric unit about the crystallographic threefold axis, which are all symmetrically equivalent at 81.70 (2)°.

Table 2
Close contacts (Å, °) for **I**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12*B*···S1	0.98	3.03	3.510 (2)	111.6
C7—H7*A*···S1^{iii}	0.95	2.91	3.8362 (19)	166.4
C9—H9*B*···O3^{iv}	0.99	2.53	3.213 (2)	126.3

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

3. Supramolecular features

There are no conventional hydrogen bonds in the in the crystal structure of **I**. There are, however, three weak hydrogen-bond-type interactions with C—H donors and S or O acceptors (Table 2). Of these, only the C9—H9*B*···O3^{iv} [$d_{D\cdots A}$ = 3.213 (2) Å] and C7—H7*A*···S1^{iii} [$d_{D\cdots A}$ = 3.8362 (19) Å] (symmetry codes as per Table 2) contacts are intermolecular. The former (and their $\overline{3}$-symmetric equivalents) link groups of six molecules into puckered ring assemblies about the *c*-axis, which create and confine the solvent-accessible channels that extend along [001] (Fig. 2). Attempts to create an unambiguous model for the solvent within these channels were unsatisfactory (see section 6, below). Individual molecules loosely stack into columns that propagate parallel to [001] *via* the C7—H7*A*···S1^{iii} (and their symmetry equivalent) interactions (Fig. 3). Adjacent columns are antiparallel (*i.e.*, along [001] and [00$\overline{1}$]). Two-dimensional fingerprint plots from a Hirshfeld surface analysis conducted using *CrystalExplorer*

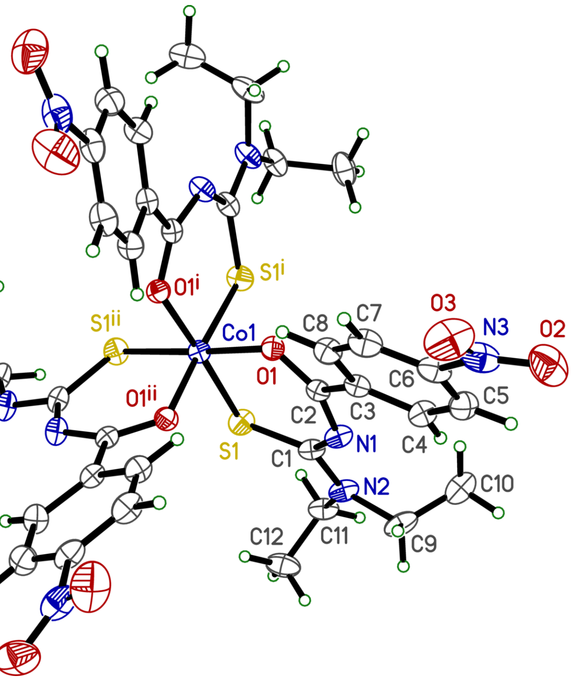


Figure 1
An ellipsoid plot (30% probability) of **I**. Unlabelled atoms correspond to symmetry codes: (i) $-y+1, x-y+1, z$; (ii) $-x+y, -x+1, z$, as indicated by the superscripts on the O and S atoms of the symmetry-equivalent ligands.

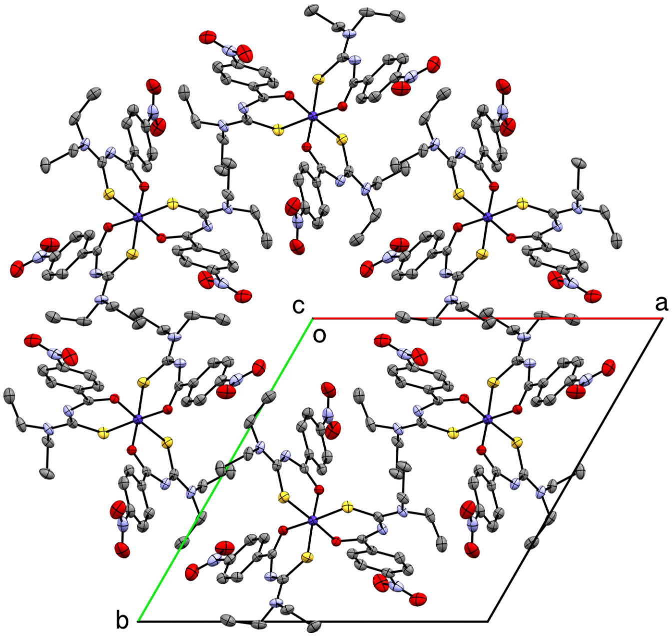


Figure 2
A packing plot of **I** viewed down [001], showing the extended channels running through the crystal along the *c*-axis direction.

(Spackman *et al.*, 2021) show that almost all intermolecular contacts (∼96% of the total) involve hydrogen. These are shown in Fig. 4, separated into H⋯H (36.6%), H⋯O (31.0%), H⋯C (19.2%), H⋯N (4.8%), and H⋯S (4.4%), including reciprocal contacts. All other types, *i.e.* those not involving hydrogen, have negligible coverage.

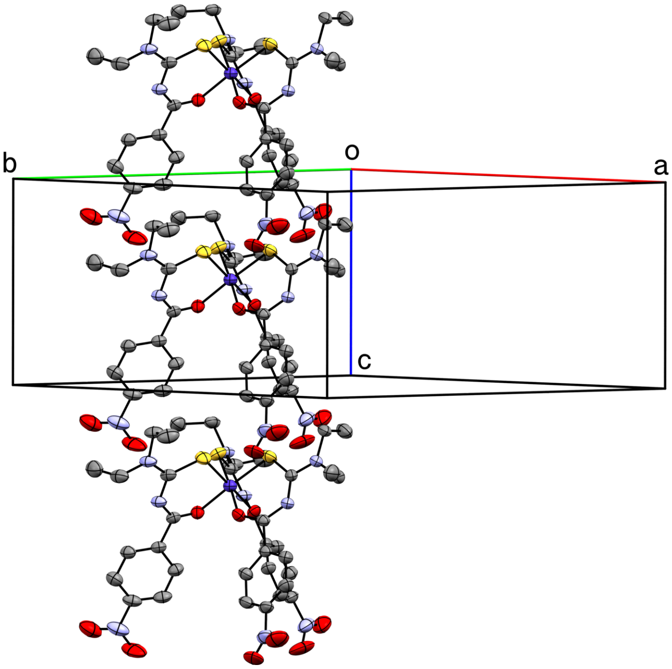


Figure 3
A partial packing plot of **I** viewed approximately along [110] showing a column of molecules extending parallel to [001].

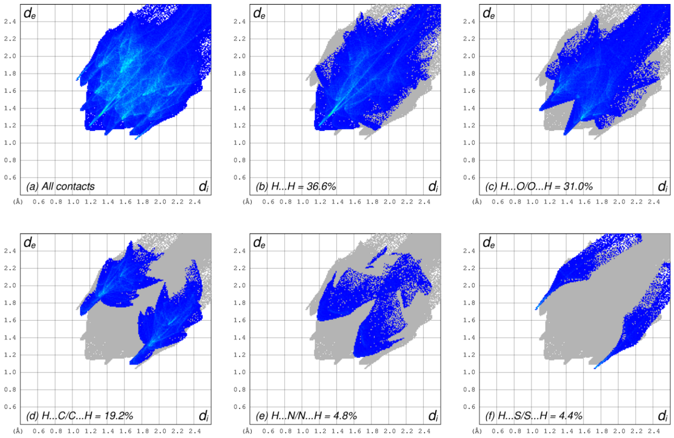


Figure 4
Two-dimensional fingerprint plots from a Hirshfeld surface analysis of **I** showing: (*a*) all contacts; (*b*) H⋯H (36.6%); (*c*) H⋯O/O⋯H (31.0%); (*d*) H⋯C/C⋯H (19.2%); (*e*) H⋯N/N⋯H (4.8%); (*f*) H⋯S/S⋯H (4.4%).

4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.45, update of March 2024; Groom *et al.*, 2016) using a search fragment consisting of just the organic ligand, returned two hits: ZIMNOA (Saeed *et al.*, 2013), a square-planar Ni^{II} complex that contains two of the ligands and NOJWIV (Kuchar *et al.*, 2019), a gold complex that has little else in common with **I**. A modified search with the NO$_2$ group replaced by 'any atom' gave 75 matches. A combined search using this same fragment, but restricted to only trigonal or hexagonal crystal systems resulted in four matches: DOVDOK (Barnard & Koch, 2019), YUFBIK (Bensch & Schuster, 1995), YIVROM (Mandal & Ray, 2014), and VEMKIH (Sieler *et al.*, 1990). These four structures are isotypic to **I**, and share the same space-group symmetry ($P\overline{3}$). The most similar to **I** are entries DOVDOK and YUFBIK; each have cobalt as the metal centre, with –OMe and –H, respectively, in place of NO$_2$. Structures YIVROM and VEMKIH contain iron and ruthenium, respectively, and similar to YUFBIK, have H at the 4-position of the benzene ring. Structures DOVDOK and YIVROM include water in the channels along [001].

5. Synthesis and crystallization

Cis-(en)$_2$Co(OSO$_2$CF$_3$)]CF$_3$SO$_3$ (0.993 g, 1.57 mmol) and *N*,*N*-diethyl-*N*′-[(4-nitrobenzene)(oxo)methyl]carbamimidothioate (Weiqun *et al.*, 2003) (0.524 g, 1.93 mmol) were added to 10 g of sulfolane, stoppered and stirred at room temperature (4 days) resulting in a dark-green solution. Extraction with one 100 mL portion of diethyl ether followed by two 100 mL portions of chloroform resulted in the formation of a maroon precipitate and dark-green solution. Evaporation of the diethyl ether/chloroform mixture resulted in deposition of dark-green crystals of the title complex (0.129 g, 9%).

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Co(C_{12}H_{14}N_3O_3S)_3]$
M_r	899.89
Crystal system, space group	Trigonal, $P\overline{3}$
Temperature (K)	180
a, c (Å)	16.6906 (3), 9.1346 (2)
V (Å^3)	2203.76 (9)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	4.89
Crystal size (mm)	0.12 × 0.11 × 0.04
Data collection	
Diffractometer	Bruker X8 Proteum diffractometer
Absorption correction	Multi-scan [*SADABS* (Krause *et al.*, 2015), *XABS2* (Parkin *et al.*, 1995)]
T_{min}, T_{max}	0.580, 0.753
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	30546, 2682, 2571
R_{int}	0.038
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.602
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.083, 1.08
No. of reflections	2682
No. of parameters	179
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.20, −0.25

Computer programs: *APEX2* (Bruker, 2006), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2019/3* (Sheldrick, 2015*b*), *XP* in *SHELXTL* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2020), *SHELX* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

6. Data collection, structure solution and refinement

On standard cold-N_2 gas stream cooling below about 100 K, all crystals of **I** could be indexed as primitive monoclinic, giving cell dimensions of approximately $a = 16.6$, $b = 9.1$, $c = 44.1$ Å, $\beta = 100.6°$, but many reflections were split and/or streaked, the severity of which varied from crystal to crystal. At room temperature, however, the symmetry was clearly trigonal or hexagonal, with sharp diffraction maxima. Attempts to 'lock in' the room-temperature structure by rapid cooling in liquid N_2 and mounting using cryotongs (Parkin & Hope, 1998) were unsuccessful. One such crystal, however, was monitored on slow warming at about 10° per minute. By 180 K, all splitting/streaking had disappeared. This crystal was used for data collection; details are given in Table 3.

Structure solution (*SHELXT;* Sheldrick, 2015*a*) and refinement (*SHELXL;* Sheldrick, 2015*b*) were straightforward aside from the presence of severely disordered electron density in the channels running along [001]. Modelling of this diffuse electron density as fractional-occupancy chloroform was less than satisfactory, perhaps because the presence of other species (*e.g.* water) could not be ruled out [water was modelled in the channels of DOVDOK and YIVROM (see section 4, above)]. For this reason, the *SQUEEZE* routine (van der Sluis & Spek, 1990; Spek, 2015) in *PLATON* (Spek, 2020) was used to factor out the solvent contribution, which amounted to ∼12.5 electrons per asymmetric unit.

All H atoms were found in difference-Fourier maps, but subsequently included in the refinement using riding models, with constrained distances set to 0.95 Å (Csp^2—H), 0.98 Å (R—CH_3) and 0.99 Å (R_2—CH_2). U_{iso}(H) parameters were set to values of either $1.2U_{eq}$ or $1.5U_{eq}$ (R—CH_3 only) of the attached atom.

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Crystal structure of tris{*N*,*N*-diethyl-*N*′-[(4-nitrophenyl)(oxo)methyl]-carbamimidothioato}cobalt(III)

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Computing details

Tris{*N*,*N*-diethyl-*N*′-[(4-nitrophenyl)(oxo)methyl]carbamimidothioato}cobalt(III)

Crystal data

$[Co(C_{12}H_{14}N_3O_3S)_3]$
M_r = 899.89
Trigonal, $P\overline{3}$
a = 16.6906 (3) Å
c = 9.1346 (2) Å
V = 2203.76 (9) Å^3
Z = 2
F(000) = 936
D_x = 1.356 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 9548 reflections
θ = 3.1–68.1°
μ = 4.89 mm^{-1}
T = 180 K
Shard, dark green
0.12 × 0.11 × 0.04 mm

Data collection

Bruker X8 Proteum diffractometer
Radiation source: fine-focus rotating anode
Detector resolution: 5.6 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan [*SADABS* (Krause *et al.*, 2015), *XABS2* (Parkin *et al.*, 1995)]
T_{min} = 0.580, T_{max} = 0.753
30546 measured reflections
2682 independent reflections
2571 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 68.1°, θ_{min} = 3.1°
h = −20→14
k = −20→20
l = −10→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.083
S = 1.08
2682 reflections
179 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2 + 0.5678P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: *SHELXL2019/3* (Sheldrick, 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00080 (18)

Special details

Experimental. The crystal was mounted using polyisobutene oil on the tip of a fine glass fibre, which was fastened in a copper mounting pin with electrical solder. It was placed directly into the cold gas stream of a liquid-nitrogen based cryostat (Hope, 1994; Parkin & Hope, 1998).

The crystals underwent a reversible phase transition to a triply twinned incommensurately modulated phase when cooled to 90K. Visual inspection of crystal integrity and diffraction quality vs temperature established a safe temperature for data collection of -93° C.

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 progress was checked using *PLATO* (Spek, 2020) and by an *R*-tensor (Parkin, 2000). The final model was further checked with the IUCr utility *checkCIF*.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Co1	0.333333	0.666667	0.48360 (4)	0.03514 (14)
S1	0.21178 (3)	0.58999 (3)	0.34007 (5)	0.04670 (15)
O1	0.30064 (7)	0.56544 (7)	0.61574 (12)	0.0381 (3)
N1	0.14855 (9)	0.45396 (10)	0.55380 (14)	0.0397 (3)
N2	0.06185 (9)	0.42651 (11)	0.35035 (14)	0.0446 (3)
N3	0.20338 (13)	0.32053 (16)	1.18453 (19)	0.0637 (5)
O2	0.16284 (15)	0.23576 (15)	1.18709 (19)	0.0855 (5)
O3	0.24204 (13)	0.36914 (15)	1.28994 (17)	0.0922 (6)
C1	0.13955 (11)	0.48454 (12)	0.42182 (16)	0.0385 (4)
C2	0.22264 (10)	0.49475 (11)	0.63716 (16)	0.0337 (3)
C3	0.21352 (11)	0.44836 (11)	0.78216 (16)	0.0355 (3)
C4	0.14649 (12)	0.35663 (13)	0.80514 (18)	0.0442 (4)
H4A	0.102965	0.323122	0.730224	0.053*
C5	0.14277 (13)	0.31379 (14)	0.9367 (2)	0.0506 (4)
H5A	0.098657	0.250373	0.951941	0.061*
C6	0.20480 (13)	0.36553 (15)	1.04516 (18)	0.0475 (4)
C7	0.26939 (13)	0.45713 (14)	1.02840 (19)	0.0501 (4)
H7A	0.309495	0.491487	1.106539	0.060*
C8	0.27465 (12)	0.49831 (13)	0.89451 (18)	0.0437 (4)
H8A	0.320351	0.561190	0.879134	0.052*
C9	−0.00988 (12)	0.34040 (15)	0.4202 (2)	0.0567 (5)
H9A	−0.071422	0.325873	0.383010	0.068*
H9B	−0.009034	0.350294	0.527181	0.068*
C10	0.00396 (16)	0.25957 (16)	0.3914 (3)	0.0696 (6)
H10A	−0.046291	0.203954	0.437066	0.104*
H10B	0.063308	0.272139	0.432840	0.104*
H10C	0.003909	0.249866	0.285617	0.104*
C11	0.03874 (12)	0.44629 (14)	0.20525 (18)	0.0477 (4)
H11A	0.002515	0.387563	0.150922	0.057*
H11B	0.096499	0.485334	0.150052	0.057*
C12	−0.01665 (15)	0.49554 (18)	0.2149 (2)	0.0637 (6)
H12A	−0.033471	0.504856	0.116135	0.096*

H12B	0.020665	0.555658	0.262676	0.096*
H12C	−0.072966	0.457932	0.272089	0.096*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.03772 (18)	0.03772 (18)	0.0300 (2)	0.01886 (9)	0.000	0.000
S1	0.0477 (2)	0.0531 (3)	0.0353 (2)	0.0221 (2)	−0.00973 (17)	0.00513 (17)
O1	0.0392 (6)	0.0374 (6)	0.0367 (6)	0.0184 (5)	−0.0083 (4)	−0.0005 (4)
N1	0.0343 (7)	0.0538 (8)	0.0258 (6)	0.0180 (6)	−0.0017 (5)	0.0002 (6)
N2	0.0341 (7)	0.0661 (9)	0.0272 (7)	0.0203 (7)	−0.0042 (5)	−0.0021 (6)
N3	0.0647 (11)	0.0996 (15)	0.0439 (10)	0.0539 (11)	0.0078 (8)	0.023 (1)
O2	0.1145 (15)	0.1025 (14)	0.0634 (10)	0.0722 (12)	0.018 (1)	0.0327 (10)
O3	0.0829 (12)	0.1351 (17)	0.0430 (9)	0.0427 (11)	−0.0153 (8)	0.0233 (10)
C1	0.0334 (8)	0.0541 (9)	0.0284 (8)	0.0220 (7)	−0.0003 (6)	−0.0029 (6)
C2	0.0372 (8)	0.0409 (8)	0.0282 (7)	0.0233 (7)	−0.0021 (6)	−0.0047 (6)
C3	0.0381 (8)	0.0475 (9)	0.0274 (7)	0.0262 (7)	−0.0014 (6)	−0.0024 (6)
C4	0.0418 (9)	0.0528 (10)	0.0331 (8)	0.0201 (8)	−0.0019 (7)	0.0004 (7)
C5	0.0493 (10)	0.0576 (11)	0.0435 (10)	0.0256 (9)	0.0060 (8)	0.0114 (8)
C6	0.0507 (10)	0.0752 (13)	0.0309 (8)	0.0421 (10)	0.0030 (7)	0.0095 (8)
C7	0.0539 (10)	0.0723 (13)	0.0316 (9)	0.0372 (10)	−0.0099 (7)	−0.0056 (8)
C8	0.0472 (9)	0.0519 (10)	0.0354 (9)	0.0273 (8)	−0.0082 (7)	−0.0050 (7)
C9	0.0336 (9)	0.0778 (14)	0.0365 (9)	0.0112 (9)	−0.0016 (7)	−0.0002 (8)
C10	0.0578 (12)	0.0661 (14)	0.0576 (13)	0.0105 (10)	0.0003 (10)	0.0028 (10)
C11	0.0418 (9)	0.0761 (12)	0.0287 (8)	0.0321 (9)	−0.0069 (7)	−0.0065 (8)
C12	0.0608 (12)	0.1016 (17)	0.0469 (11)	0.0541 (13)	−0.0111 (9)	−0.0114 (11)

Geometric parameters (Å, º)

Co1—O1^{i}	1.9202 (11)	C4—H4A	0.9500
Co1—O1^{ii}	1.9202 (11)	C5—C6	1.380 (3)
Co1—O1	1.9202 (11)	C5—H5A	0.9500
Co1—S1	2.2082 (5)	C6—C7	1.369 (3)
Co1—S1^{i}	2.2082 (5)	C7—C8	1.384 (2)
Co1—S1^{ii}	2.2082 (5)	C7—H7A	0.9500
S1—C1	1.7284 (17)	C8—H8A	0.9500
O1—C2	1.2606 (19)	C9—C10	1.501 (3)
N1—C2	1.316 (2)	C9—H9A	0.9900
N1—C1	1.347 (2)	C9—H9B	0.9900
N2—C1	1.338 (2)	C10—H10A	0.9800
N2—C11	1.464 (2)	C10—H10B	0.9800
N2—C9	1.478 (2)	C10—H10C	0.9800
N3—O3	1.216 (3)	C11—C12	1.516 (3)
N3—O2	1.226 (3)	C11—H11A	0.9900
N3—C6	1.472 (2)	C11—H11B	0.9900
C2—C3	1.503 (2)	C12—H12A	0.9800
C3—C4	1.388 (2)	C12—H12B	0.9800
C3—C8	1.392 (2)	C12—H12C	0.9800

C4—C5	1.384 (2)

O1^{i}—Co1—O1^{ii}	84.68 (5)	C5—C4—H4A	119.9
O1^{i}—Co1—O1	84.68 (5)	C3—C4—H4A	119.9
O1^{ii}—Co1—O1	84.68 (5)	C6—C5—C4	118.31 (18)
O1^{i}—Co1—S1	91.87 (4)	C6—C5—H5A	120.8
O1^{ii}—Co1—S1	176.56 (3)	C4—C5—H5A	120.8
O1—Co1—S1	95.09 (3)	C7—C6—C5	122.94 (16)
O1^{i}—Co1—S1^{i}	95.09 (3)	C7—C6—N3	117.99 (18)
O1^{ii}—Co1—S1^{i}	91.87 (4)	C5—C6—N3	119.06 (19)
O1—Co1—S1^{i}	176.56 (4)	C6—C7—C8	118.19 (17)
S1—Co1—S1^{i}	88.35 (2)	C6—C7—H7A	120.9
O1^{i}—Co1—S1^{ii}	176.56 (3)	C8—C7—H7A	120.9
O1^{ii}—Co1—S1^{ii}	95.09 (3)	C7—C8—C3	120.56 (17)
O1—Co1—S1^{ii}	91.87 (4)	C7—C8—H8A	119.7
S1—Co1—S1^{ii}	88.35 (2)	C3—C8—H8A	119.7
S1^{i}—Co1—S1^{ii}	88.35 (2)	N2—C9—C10	112.60 (16)
C1—S1—Co1^{ii}	107.73 (5)	N2—C9—H9A	109.1
C1—S1—Co1	107.73 (5)	C10—C9—H9A	109.1
C1—S1—Co1^{i}	107.73 (5)	N2—C9—H9B	109.1
C2—O1—Co1^{ii}	128.85 (10)	C10—C9—H9B	109.1
C2—O1—Co1^{i}	128.85 (10)	H9A—C9—H9B	107.8
C2—O1—Co1	128.85 (10)	C9—C10—H10A	109.5
C2—N1—C1	125.19 (14)	C9—C10—H10B	109.5
C1—N2—C11	123.23 (15)	H10A—C10—H10B	109.5
C1—N2—C9	120.92 (14)	C9—C10—H10C	109.5
C11—N2—C9	115.69 (14)	H10A—C10—H10C	109.5
O3—N3—O2	123.89 (19)	H10B—C10—H10C	109.5
O3—N3—C6	118.5 (2)	N2—C11—C12	111.76 (15)
O2—N3—C6	117.7 (2)	N2—C11—H11A	109.3
N2—C1—N1	114.46 (15)	C12—C11—H11A	109.3
N2—C1—S1	117.16 (12)	N2—C11—H11B	109.3
N1—C1—S1	128.28 (12)	C12—C11—H11B	109.3
O1—C2—N1	131.15 (14)	H11A—C11—H11B	107.9
O1—C2—C3	114.22 (13)	C11—C12—H12A	109.5
N1—C2—C3	114.62 (14)	C11—C12—H12B	109.5
C4—C3—C8	119.62 (15)	H12A—C12—H12B	109.5
C4—C3—C2	121.31 (14)	C11—C12—H12C	109.5
C8—C3—C2	119.07 (15)	H12A—C12—H12C	109.5
C5—C4—C3	120.29 (16)	H12B—C12—H12C	109.5

C11—N2—C1—N1	−179.82 (15)	N1—C2—C3—C4	19.9 (2)
C9—N2—C1—N1	4.9 (2)	O1—C2—C3—C8	19.8 (2)
C11—N2—C1—S1	3.5 (2)	N1—C2—C3—C8	−161.13 (15)
C9—N2—C1—S1	−171.79 (14)	C8—C3—C4—C5	−2.7 (3)
C2—N1—C1—N2	173.13 (15)	C2—C3—C4—C5	176.26 (15)
C2—N1—C1—S1	−10.6 (2)	C3—C4—C5—C6	2.5 (3)
Co1^{ii}—S1—C1—N2	−178.97 (11)	C4—C5—C6—C7	0.2 (3)

Co1—S1—C1—N2	−178.97 (11)	C4—C5—C6—N3	−178.52 (16)
Co1^{i}—S1—C1—N2	−178.97 (11)	O3—N3—C6—C7	17.8 (3)
Co1^{ii}—S1—C1—N1	4.85 (17)	O2—N3—C6—C7	−162.28 (18)
Co1—S1—C1—N1	4.85 (17)	O3—N3—C6—C5	−163.37 (19)
Co1^{i}—S1—C1—N1	4.85 (17)	O2—N3—C6—C5	16.5 (3)
Co1^{ii}—O1—C2—N1	22.6 (2)	C5—C6—C7—C8	−2.5 (3)
Co1^{i}—O1—C2—N1	22.6 (2)	N3—C6—C7—C8	176.20 (16)
Co1—O1—C2—N1	22.6 (2)	C6—C7—C8—C3	2.2 (3)
Co1^{ii}—O1—C2—C3	−158.52 (10)	C4—C3—C8—C7	0.3 (3)
Co1^{i}—O1—C2—C3	−158.52 (10)	C2—C3—C8—C7	−178.67 (15)
Co1—O1—C2—C3	−158.52 (10)	C1—N2—C9—C10	−90.7 (2)
C1—N1—C2—O1	−3.4 (3)	C11—N2—C9—C10	93.7 (2)
C1—N1—C2—C3	177.75 (14)	C1—N2—C11—C12	−90.7 (2)
O1—C2—C3—C4	−159.17 (15)	C9—N2—C11—C12	84.8 (2)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12*B*···S1	0.98	3.03	3.510 (2)	112
C7—H7*A*···S1^{iii}	0.95	2.91	3.8362 (19)	166
C9—H9*B*···O3^{iv}	0.99	2.53	3.213 (2)	126

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