Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Synthesis, crystal structure and Hirshfeld analysis of a novel supramolecular compound $[Co(tsc)_3]_2[Co(cit)_2](NO_3)_4\cdot 4H_2O$

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Received 23 December 2024
Accepted 6 February 2025

Edited by J. Ellena, Universidade de São Paulo, Brazil

Keywords: crystal structure; cobalt; thiosemicarbazide; citric acid; hydrogen bonding; Hirshfeld analysis.

CCDC reference: 2364098

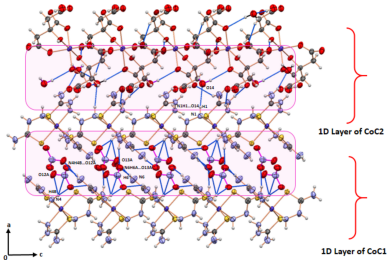
Supporting information: this article has supporting information at journals.iucr.org/e

A new cobalt complex, bis[tris(aminothiourea)cobalt(III)] bis[2-(carboxymethyl)-2-hydroxybutanedioato]cobalt(II) tetranitrate tetrahydrate, $[Co(CH_5N_3S)_3]_2[Co(C_6H_6O_7)_2]_{0.5}(NO_3)_2\cdot 2H_2O$, designated as $[Co(tsc)_3]_2[Co(cit)_2](NO_3)_4\cdot 4H_2O$, was synthesized. Two crystallographically independent cobalt centers are present. In the first, the central metal atom is chelated by three thiosemicarbazide ligands in a bidentate fashion whereas the second, positioned on a crystallographic inversion center, is hexacoordinated by two citrate anions in a distorted octahedral geometry. Additionally, two water molecules and two nitrate anions are present in the asymmetric unit. Hirshfeld surface analysis revealed that the presence of numerous donor and acceptor groups in the complex, which facilitate hydrogen-bonding interactions that contribute significantly to the overall cohesion of the crystal structure.

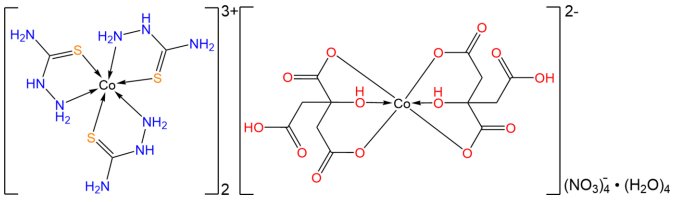
1. Chemical context

Thiosemicarbazide is a widely used ligand in coordination chemistry because of its strong complex-forming ability, attributed to the presence of sulfur and nitrogen donor atoms, which enables it to act as a bidentate ligand (Ibrahim & Bekheit, 1988). Its coordination with transition metals is particularly interesting, as these metals can adopt diverse geometries such as tetrahedral, square-planar, and octahedral depending on the surrounding ligands, enhancing the stability and versatility of the resulting complexes (Hussain, 1994; Yang *et al.*, 2006; Burrows *et al.*, 1997). Citric acid, a tricarboxylic acid, is another versatile molecule known for its role in both chemistry and biology. The citrate dianion acts as a multidentate ligand, coordinating with metals through carboxylate ($-COO^-$) and hydroxyl (–OH) groups, allowing for the formation of robust metal complexes. The applications of complexes formed from thiosemicarbazide and citric acid can be found in catalysis, biomedicine, and environmental remediation (Koolivand *et al.*, 2021; Wakizaka *et al.*, 2024; Andres *et al.*, 2020; Singh *et al.*, 2023).

Although extensive research has been conducted on thiosemicarbazide complexes with metals such as nickel, cobalt, and zinc, systems containing two crystallographically independent centers remain underexplored (Konarev *et al.*, 2004; Antsyshkina *et al.*, 2014). In this work, cobalt was selected as the central metal ion, and citric acid was utilized as a multifunctional ligand to construct a supramolecular framework.



This combination provides an excellent model to study the interplay of metal–ligand coordination and hydrogen-bonding networks. We report the synthesis and crystal structure of a new cobalt complex, $[Co(tsc)_3]_2[Co(cit)_2](NO_3)_4{\cdot}4H_2O$, and highlight the role of citric acid as a key component in the assembly of hybrid materials.



2. Structural commentary

The structure of $[Co(tsc)_3]_2[Co(cit)_2](NO_3)_4{\cdot}4H_2O$ is shown in Fig. 1. The complex crystallizes in the monoclinic system with a $P2_1/c$ space group with two crystallographically independent cobalt centers, namely, $[Co(tsc)_3]$ and $[Co(cit)_2]$, designated as CoC1 and CoC2, respectively. The asymmetric unit of $[Co(tsc)_3]_2[Co(cit)_2](NO_3)_4{\cdot}4H_2O$ comprises one molecule of CoC1, a half-molecule of CoC2, two water molecules, and two nitrate anions (CoC1 and CoC2 are in a 2:1 ratio). The cobalt centers exhibit different oxidation states, with the cobalt atom in CoC1 being in the +3 oxidation state, while in CoC2, it is in the +2 oxidation state. In the first cobalt center (CoC1), the cobalt(III) atom is coordinated by three thiosemicarbazide ligands in a bidentate manner, involving nitrogen and sulfur donor atoms and resulting in the formation of three five-membered rings. The Co—N bond lengths are in the range 1.991 (3)–2.002 (4) Å, while the Co—S bond length are 2.1967 (11)–2.2265 (11) Å. The cobalt(II) atom in the second cobalt center (CoC2) is tridentately chelated by the two citrate ligand through three oxygen atoms from each ligand, *i.e.* two from carboxylate groups and one from a hydroxyl group of the citrate dianion, forming two five-membered and two six-membered rings around the central metal atom. The central cobalt atom exhibits a distorted octahedral geometry and occupies special position on the inversion center. The Co—O (carboxylate) bond lengths are in the range 2.081 (3)–2.084 (4) Å, and the Co—O (hydroxyl) bond length is 2.060 (3) Å. Two molecules of water and a nitrate anion remain uncoordinated in the asymmetric unit but are involved in interactions with both the cobalt centers and assist in the formation of supramolecular construct.

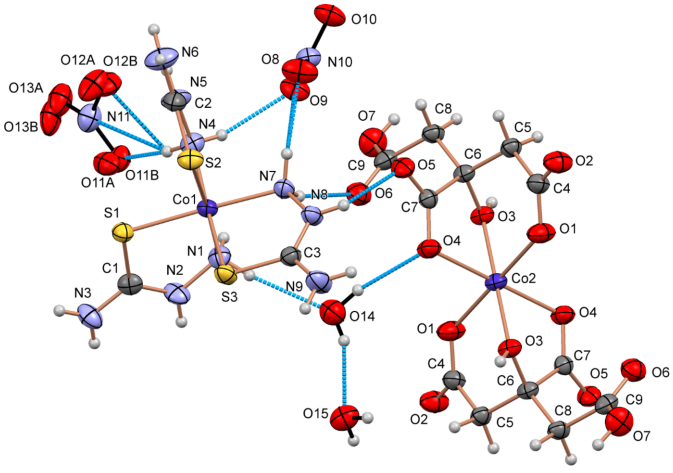


Figure 1
$[Co(tsc)_3]_2[Co(cit)_2](NO_3)_4{\cdot}4H_2O$ with displacement ellipsoids drawn at the 50% probability level and hydrogen atoms shown as small spheres. Intramolecular hydrogen bonds are indicated by dotted lines.

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

D—H···A	D—H	H···A	D···A	D—H···A
O14—H14B···O15	0.85	2.00	2.798 (5)	157
N7—H7A···O6	0.89	2.25	3.100 (5)	159
N7—H7B···O8	0.89	2.10	2.983 (5)	172
O7—H7···O14^{i}	0.82	1.85	2.648 (5)	163
O15—H15A···O2^{ii}	0.85	1.92	2.730 (5)	158
O15—H15B···O4^{iii}	0.85	2.50	2.902 (5)	110
N1—H1A···O9^{iv}	0.89	2.20	2.912 (5)	137
N1—H1A···O10^{iv}	0.89	2.26	3.128 (5)	165
N1—H1B···O14	0.89	2.30	3.185 (5)	172
N8—H8···O5	0.86	1.98	2.670 (5)	136
N4—H4A···O9	0.89	2.19	3.000 (5)	152
N4—H4A···O10^{iv}	0.89	2.45	3.024 (5)	122
N4—H4B···O11A	0.89	2.09	2.96 (3)	166
N4—H4B···O12A	0.89	2.48	3.06 (3)	123
N4—H4B···O12B	0.89	2.56	3.13 (2)	122
N4—H4B···O11B	0.89	2.15	3.04 (3)	175
N2—H2···O10^{ii}	0.86	2.32	3.032 (5)	140
N5—H5···O11A^{i}	0.86	2.28	2.96 (3)	136
N5—H5···O12A	0.86	2.47	2.92 (3)	114
N5—H5···O12B	0.86	2.45	2.88 (2)	112
N5—H5···O11B^{i}	0.86	2.27	3.02 (3)	145
N3—H3A···O8^{ii}	0.86	2.08	2.913 (5)	161
N3—H3B···O13A^{v}	0.86	2.01	2.86 (3)	170
N3—H3B···O13B^{v}	0.86	2.13	2.94 (3)	157
N9—H9A···O15^{vi}	0.86	2.06	2.883 (6)	161
N9—H9B···O5^{iii}	0.86	2.15	2.844 (5)	137
N6—H6A···O13A^{i}	0.86	2.00	2.85 (3)	170
N6—H6A···O13B^{i}	0.86	2.03	2.86 (3)	161
N6—H6B···O12A^{vii}	0.86	2.35	2.93 (3)	125
N6—H6B···O12B^{vii}	0.86	2.32	2.99 (3)	134

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

3. Supramolecular features

In the title complex, the complex cations and the water molecule have proton-donor hydrogen-bonding groups, whereas the oxygen atoms of the nitrate anion and citrate ligands act as proton acceptors in an intricate network of hydrogen bonds (Table 1). The nitrate anions participate in strong hydrogen bonding with the amine hydrogen atoms (N4—H4B···O12A and N7—H7A···O6) of the coordinated thiosemicarbazide ligands. Furthermore, hydrogen bonding is observed between the two cobalt centers. This involves interactions between the amine hydrogens (N7—H7A···O6 and N8—H8···O5) of the thiosemicarbazide ligands from CoC1 and the oxygen atoms of the citrate ligand in the adjacent CoC2 center.

The two uncoordinated water molecules form hydrogen bonds with each other, while also interacting with the amine nitrogen (N1—H1B···O14) of the thiosemicarbazide ligand

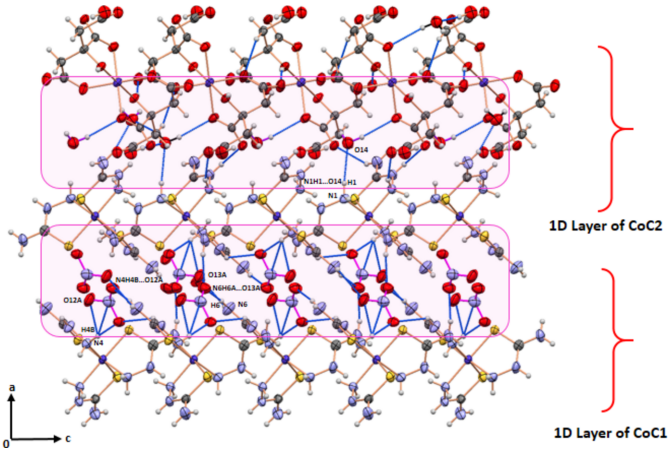


Figure 2
View of the packing of molecules in $[Co(tsc)_3]_2[Co(cit)_2](NO_3)_4{\cdot}4H_2O$ along the *b* axis.

and a neighboring oxygen atom (O14—H14*A*···O4) of the citrate dianion in the second cobalt center (Fig. 1). The nitrate anions are located between two CoC1 layers, whereas the water molecules placed between the CoC1 and CoC2 layers. Thus, both the nitrate anions and the water molecules contribute significantly to the structure of the complex by forming an extensive hydrogen-bond network and form a 1D layered assembly parallel to the *c*-axis direction. Although the hydrogen bonds are relatively weak, all potential donors and acceptors participate, providing notable cohesion to the overall structure (Fig. 2).

4. Hirshfeld Surface Analysis

Hirshfeld surface (Spackman & Jayatilaka, 2009) analysis and fingerprint plot analysis (Spackman & McKinnon, 2002) were performed using *CrystalExplorer21.5* (Wolff *et al.*, 2012) to investigate the intermolecular interactions. These were both performed separately for CoC1 and CoC2, as shown in Figs. 3 and 4. The red spots on the Hirshfeld surface are due to short O···H interactions, which are mapped on the 2D fingerprint plots. The molecule exhibits a significant number of hydrogen-

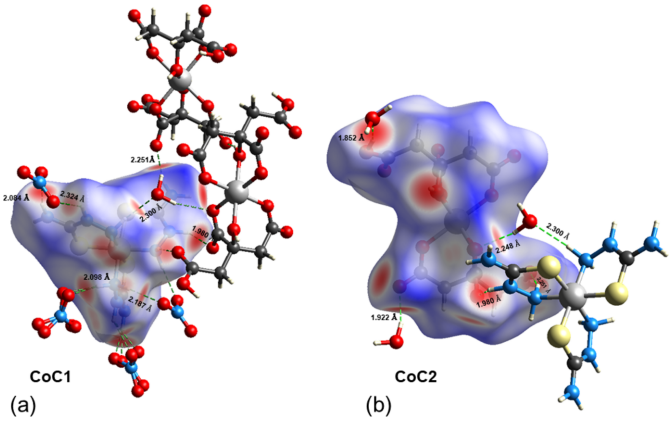


Figure 3
The three-dimensional Hirshfeld surfaces for (*a*) CoC1 and (*b*) CoC2 in $[Co(tsc)_3]_2[Co(cit)_2](NO_3)_4{\cdot}4H_2O$.

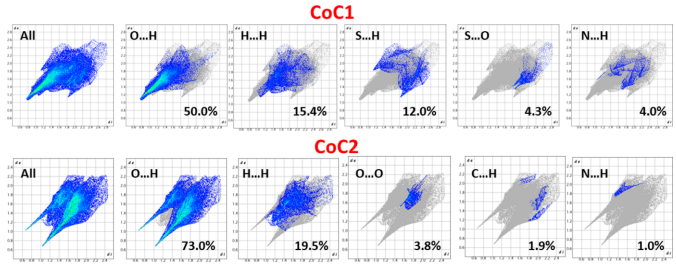


Figure 4
Two-dimensional fingerprint plots of the Hirshfeld surfaces showing contributions of various contacts for CoC1 (upper row) and CoC2 (lower row) in $[Co(tsc)_3]_2[Co(cit)_2](NO_3)_4{\cdot}4H_2O$.

bonding interactions, with O···H/H···O, H···H, S···H/H···S, S···O/O···S, and N···H/H···N interactions accounting for 85.7% of the total interactions in CoC1. In contrast, interactions such as C···S, N···S, and S···S, play a minor role in the crystal cohesion. However, O···H/H···O, H···H, O···O, C···H/H···C and N···H/H···N contacts represent 99.2% of the total interactions in CoC2 (Figs. 3, 4).

5. Database survey

A survey of the Cambridge Structural Database (CSD, Version 5.45, last updated March 2024; Groom *et al.*, 2016) revealed that seven crystal structures for cobalt complexes with three thiosemicarbazide ligands have been reported [AZILOL (Liu *et al.*, 2009); BAYGUD (Rusanovskii *et al.*, 1981); GEWNIF (Larsen *et al.*, 1988); KAZBAP (Bulimestru *et al.*, 2005); THSMCB (Samus *et al.*, 1981); WEWFUZ (Hussain, 1994); YUNTUW (Zhang *et al.*, 1994)]. The CSD includes around 40 structures where citric acid is directly bonded to a cobalt atom, in only three of which [ADENAY, (Herynek *et al.*, 2000); IDANOR (Galloway *et al.*, 2006); QEQVAJ (Shvelashvili *et al.*, 2000)] are two citric acid ligands bonded tridentately to form a hexacoordinated complex. However, no complexes containing both citric acid and thiosemicarbazide with two different coordination centers have been reported.

6. Synthesis and crystallization

$Co(NO_3)_2{\cdot}6H_2O$ (0. 291 g, 1 mmol), thiosemicarbazide (0.091 g, 1 mmol) and citric acid (0.192 g, 1 mmol) were dissolved separately in 70% ethanol (5 ml), mixed together and stirred for 2 h at 333 K. The obtained pink solution was filtered and left for crystallization. Single crystals of the title complex suitable for X-ray analysis were obtained by slow evaporation of the solution over a period of 10 days (yield: 60%).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All the hydrogen atoms were

located in difference-Fourier maps and refined using an isotropic approximation.

Acknowledgements

BT is grateful to the Frank H. Allen International Research and Education (FAIRE) programme, provided by the Cambridge Crystallographic Data Centre (CCDC), for the opportunity to use the Cambridge Structural Database (CSD).

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supporting information

Acta Cryst. (2025). E**81** [https://doi.org/10.1107/S2056989025001136]

Synthesis, crystal structure and Hirshfeld analysis of a novel supramolecular compound $[Co(tsc)_3]_2[Co(cit)_2](NO_3)_4{\cdot}4H_2O$

Guzal Nuralieva, Oydinoy Umirzakova, Batirbay Torambetov, Abdusamat Rasulov, Jamshid Ashurov and Shakhnoza Kadirova

Computing details

Bis[tris(aminothiourea)cobalt(III)] bis[2-(carboxymethyl)-2-hydroxybutanedioato]cobalt(II) tetranitrate tetrahydrate

Crystal data

$[Co(CH_5N_3S)_3][Co(C_6H_6O_7)_2]_{0.5}(NO_3)_2{\cdot}2H_2O$
M_r = 711.97
Monoclinic, $P2_1/c$
a = 22.8868 (7) Å
b = 10.7978 (3) Å
c = 10.1946 (3) Å
β = 95.359 (3)°
V = 2508.35 (13) Å^3
Z = 4
$F(000)$ = 1458
D_x = 1.885 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 6201 reflections
θ = 3.9–71.3°
μ = 11.05 mm^{-1}
T = 293 K
Block, red
0.12 × 0.08 × 0.06 mm

Data collection

XtaLAB Synergy, Single source at home/near, HyPix3000 diffractometer
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2021)
T_{min} = 0.419, T_{max} = 1.000
23912 measured reflections
4582 independent reflections
3715 reflections with $I > 2\sigma(I)$
R_{int} = 0.113
θ_{max} = 68.2°, θ_{min} = 3.9°
h = −27→27
k = −13→12
l = −12→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.150
S = 1.00
4582 reflections
395 parameters
3 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1005P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.92 e Å^{-3}
$\Delta\rho_{min}$ = −0.80 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Co1	0.82571 (3)	0.55594 (6)	0.44027 (6)	0.02392 (19)	
Co2	0.500000	0.500000	0.500000	0.0268 (2)	
S1	0.89780 (4)	0.57221 (10)	0.31121 (9)	0.0299 (3)	
S3	0.78409 (5)	0.72745 (10)	0.35381 (9)	0.0307 (3)	
S2	0.87457 (5)	0.67648 (10)	0.58544 (9)	0.0320 (3)	
O5	0.65342 (13)	0.5523 (3)	0.7133 (3)	0.0348 (7)	
O3	0.53844 (12)	0.3496 (3)	0.5979 (3)	0.0283 (6)	
H3	0.5312 (16)	0.2737 (14)	0.612 (4)	0.042*	
O4	0.58648 (13)	0.5588 (3)	0.5413 (3)	0.0350 (7)	
O6	0.66999 (14)	0.3281 (3)	0.5325 (3)	0.0405 (8)	
O9	0.78502 (15)	0.3036 (3)	0.7225 (3)	0.0419 (8)	
O2	0.50796 (15)	0.6243 (3)	0.8904 (3)	0.0423 (8)	
O14	0.64703 (16)	0.5248 (4)	0.2882 (4)	0.0476 (8)	
H14A	0.633007	0.515855	0.361958	0.071*	
H14B	0.624476	0.577204	0.247038	0.071*	
O1	0.48489 (15)	0.5703 (3)	0.6839 (3)	0.0441 (8)	
N7	0.75933 (15)	0.5446 (3)	0.5529 (3)	0.0285 (7)	
H7A	0.736707	0.480694	0.526268	0.034*	
H7B	0.773626	0.530122	0.635701	0.034*	
O7	0.67078 (16)	0.1366 (3)	0.6050 (4)	0.0467 (8)	
H7	0.659469	0.098157	0.667227	0.070*	
O10	0.78848 (16)	0.3037 (3)	0.9341 (3)	0.0463 (8)	
O15	0.59049 (15)	0.6770 (3)	0.0937 (4)	0.0476 (8)	
H15A	0.567869	0.641229	0.034498	0.071*	
H15B	0.571066	0.730415	0.132922	0.071*	
N1	0.78272 (16)	0.4563 (3)	0.2980 (3)	0.0321 (8)	
H1A	0.783710	0.376846	0.321444	0.038*	
H1B	0.745317	0.480000	0.288731	0.038*	
N8	0.72455 (15)	0.6531 (3)	0.5496 (3)	0.0306 (8)	
H8	0.699347	0.662336	0.606306	0.037*	
N4	0.86476 (15)	0.4111 (3)	0.5347 (3)	0.0304 (8)	
H4A	0.837443	0.363299	0.565348	0.037*	
H4B	0.883111	0.366516	0.477627	0.037*	
N10	0.79107 (16)	0.3600 (3)	0.8299 (3)	0.0332 (8)	
O8	0.79974 (18)	0.4753 (3)	0.8299 (3)	0.0488 (9)	
N2	0.80682 (18)	0.4689 (4)	0.1749 (3)	0.0373 (9)	
H2	0.786582	0.447700	0.103111	0.045*	
O11A	0.9175 (10)	0.224 (2)	0.368 (3)	0.039 (4)	0.5
N11	0.96695 (17)	0.2055 (4)	0.4343 (4)	0.0420 (9)	

N5	0.90574 (18)	0.4465 (4)	0.6407 (4)	0.0391 (9)	
H5	0.926274	0.390669	0.683767	0.047*	
O12A	0.9715 (11)	0.240 (2)	0.542 (2)	0.061 (6)	0.5
N3	0.88378 (19)	0.5169 (4)	0.0582 (4)	0.0404 (9)	
H3A	0.864128	0.490335	−0.012262	0.048*	
H3B	0.918646	0.545588	0.054621	0.048*	
C7	0.60992 (17)	0.5090 (4)	0.6455 (4)	0.0255 (8)	
C6	0.58052 (17)	0.3947 (4)	0.6997 (4)	0.0254 (8)	
O13A	0.9996 (14)	0.114 (3)	0.4205 (19)	0.054 (5)	0.5
N9	0.69505 (18)	0.8363 (4)	0.4571 (4)	0.0452 (10)	
H9A	0.668771	0.842184	0.511769	0.054*	
H9B	0.698370	0.893546	0.399600	0.054*	
N6	0.94963 (19)	0.5926 (5)	0.7769 (4)	0.0523 (12)	
H6A	0.968543	0.534943	0.820948	0.063*	
H6B	0.954741	0.668702	0.799993	0.063*	
C4	0.51204 (19)	0.5526 (4)	0.7954 (4)	0.0313 (9)	
C8	0.62522 (18)	0.2924 (4)	0.7339 (4)	0.0289 (9)	
H8A	0.653819	0.320826	0.803691	0.035*	
H8B	0.605428	0.220686	0.766118	0.035*	
C1	0.86049 (19)	0.5134 (4)	0.1715 (4)	0.0309 (9)	
C9	0.65656 (18)	0.2557 (4)	0.6148 (4)	0.0318 (9)	
C5	0.55003 (18)	0.4372 (4)	0.8193 (4)	0.0284 (9)	
H5A	0.525603	0.370103	0.846255	0.034*	
H5B	0.579699	0.453559	0.891480	0.034*	
C3	0.73011 (18)	0.7399 (4)	0.4613 (4)	0.0295 (9)	
C2	0.91294 (19)	0.5643 (4)	0.6744 (4)	0.0349 (10)	
O12B	0.9840 (10)	0.269 (2)	0.539 (3)	0.052 (5)	0.5
O11B	0.9289 (11)	0.247 (2)	0.353 (3)	0.048 (5)	0.5
O13B	1.0011 (14)	0.134 (3)	0.3756 (19)	0.056 (5)	0.5

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0275 (4)	0.0221 (3)	0.0217 (3)	−0.0001 (2)	−0.0001 (2)	0.0010 (2)
Co2	0.0268 (5)	0.0280 (5)	0.0242 (5)	0.0007 (4)	−0.0048 (4)	0.0018 (4)
S1	0.0301 (5)	0.0346 (6)	0.0247 (5)	−0.0025 (4)	0.0014 (4)	−0.0008 (4)
S3	0.0378 (6)	0.0268 (5)	0.0279 (5)	0.0031 (4)	0.0052 (4)	0.0073 (4)
S2	0.0401 (6)	0.0262 (5)	0.0283 (5)	−0.0023 (4)	−0.0036 (4)	−0.0041 (4)
O5	0.0328 (16)	0.0409 (18)	0.0291 (15)	−0.0093 (13)	−0.0050 (12)	−0.0017 (13)
O3	0.0305 (15)	0.0241 (15)	0.0286 (14)	−0.0010 (12)	−0.0057 (11)	0.0024 (12)
O4	0.0317 (16)	0.0369 (18)	0.0345 (16)	−0.0070 (13)	−0.0065 (12)	0.0129 (13)
O6	0.0463 (19)	0.0425 (19)	0.0331 (16)	0.0048 (15)	0.0051 (14)	−0.0001 (15)
O9	0.060 (2)	0.0325 (17)	0.0323 (16)	−0.0073 (15)	0.0012 (14)	−0.0055 (13)
O2	0.056 (2)	0.0397 (19)	0.0302 (16)	0.0132 (16)	−0.0015 (14)	−0.0056 (14)
O14	0.050 (2)	0.050 (2)	0.0435 (19)	−0.0001 (16)	0.0067 (16)	0.0027 (16)
O1	0.052 (2)	0.052 (2)	0.0268 (16)	0.0218 (16)	−0.0045 (14)	−0.0042 (14)
N7	0.0287 (18)	0.0278 (18)	0.0293 (17)	0.0015 (14)	0.0043 (14)	0.0057 (14)
O7	0.057 (2)	0.0302 (18)	0.054 (2)	0.0096 (15)	0.0094 (16)	−0.0059 (15)

O10	0.068 (2)	0.0372 (19)	0.0330 (16)	−0.0033 (16)	0.0030 (15)	0.0072 (14)
O15	0.048 (2)	0.042 (2)	0.051 (2)	0.0017 (16)	−0.0043 (16)	−0.0002 (16)
N1	0.0313 (19)	0.0305 (19)	0.0338 (19)	−0.0047 (15)	−0.0001 (15)	−0.0028 (15)
N8	0.0355 (19)	0.0305 (19)	0.0264 (17)	0.0082 (15)	0.0064 (14)	0.0057 (14)
N4	0.0334 (19)	0.0249 (18)	0.0321 (18)	0.0008 (14)	−0.0019 (14)	−0.0058 (14)
N10	0.036 (2)	0.031 (2)	0.0316 (19)	0.0016 (15)	−0.0021 (15)	0.0011 (16)
O8	0.082 (3)	0.0189 (16)	0.0432 (19)	−0.0046 (16)	−0.0058 (17)	0.0012 (14)
N2	0.048 (2)	0.041 (2)	0.0225 (17)	−0.0086 (17)	−0.0003 (15)	−0.0089 (16)
O11A	0.032 (8)	0.037 (8)	0.047 (8)	−0.006 (6)	0.003 (5)	−0.006 (6)
N11	0.039 (2)	0.036 (2)	0.051 (3)	0.0012 (18)	0.0054 (19)	−0.0076 (19)
N5	0.047 (2)	0.030 (2)	0.037 (2)	0.0117 (17)	−0.0112 (17)	−0.0004 (16)
O12A	0.063 (12)	0.077 (14)	0.038 (7)	0.003 (8)	−0.015 (6)	−0.015 (7)
N3	0.054 (2)	0.040 (2)	0.0283 (19)	−0.0080 (18)	0.0103 (17)	−0.0063 (17)
C7	0.027 (2)	0.027 (2)	0.0228 (19)	0.0032 (16)	0.0032 (16)	−0.0031 (16)
C6	0.0249 (19)	0.025 (2)	0.0254 (19)	−0.0001 (16)	−0.0040 (15)	0.0010 (16)
O13A	0.041 (6)	0.060 (10)	0.061 (12)	0.003 (6)	0.008 (9)	−0.024 (9)
N9	0.055 (3)	0.042 (2)	0.040 (2)	0.021 (2)	0.0136 (18)	0.0125 (18)
N6	0.056 (3)	0.050 (3)	0.047 (2)	0.000 (2)	−0.020 (2)	−0.004 (2)
C4	0.035 (2)	0.032 (2)	0.027 (2)	0.0028 (18)	0.0008 (17)	0.0030 (17)
C8	0.033 (2)	0.028 (2)	0.0257 (19)	0.0080 (17)	−0.0003 (16)	0.0022 (16)
C1	0.038 (2)	0.020 (2)	0.034 (2)	−0.0007 (17)	−0.0008 (18)	0.0002 (16)
C9	0.030 (2)	0.033 (2)	0.031 (2)	0.0044 (17)	−0.0053 (17)	−0.0028 (19)
C5	0.029 (2)	0.027 (2)	0.028 (2)	0.0047 (16)	0.0007 (16)	0.0030 (16)
C3	0.030 (2)	0.032 (2)	0.026 (2)	0.0060 (17)	0.0009 (16)	−0.0007 (17)
C2	0.034 (2)	0.045 (3)	0.025 (2)	0.0021 (19)	0.0003 (17)	−0.0003 (18)
O12B	0.040 (8)	0.048 (8)	0.067 (8)	0.006 (7)	−0.009 (6)	−0.030 (6)
O11B	0.046 (10)	0.056 (10)	0.039 (7)	−0.019 (6)	−0.005 (7)	0.005 (6)
O13B	0.039 (5)	0.064 (12)	0.067 (13)	0.005 (6)	0.021 (10)	−0.029 (10)

Geometric parameters (Å, º)

Co1—S1	2.2112 (12)	N1—N2	1.424 (5)
Co1—S3	2.2265 (11)	N8—H8	0.8600
Co1—S2	2.1967 (11)	N8—C3	1.314 (5)
Co1—N7	1.992 (3)	N4—H4A	0.8900
Co1—N1	1.991 (3)	N4—H4B	0.8900
Co1—N4	2.002 (4)	N4—N5	1.416 (5)
Co2—O3	2.060 (3)	N10—O8	1.260 (5)
Co2—O3^{i}	2.060 (3)	N2—H2	0.8600
Co2—O4	2.084 (3)	N2—C1	1.322 (6)
Co2—O4^{i}	2.084 (3)	O11A—N11	1.28 (3)
Co2—O1	2.081 (3)	N11—O12A	1.15 (2)
Co2—O1^{i}	2.081 (3)	N11—O13A	1.25 (3)
S1—C1	1.712 (4)	N11—O12B	1.30 (2)
S3—C3	1.731 (4)	N11—O11B	1.23 (3)
S2—C2	1.707 (5)	N11—O13B	1.29 (3)
O5—C7	1.249 (5)	N5—H5	0.8600
O3—H3	0.852 (9)	N5—C2	1.324 (6)

O3—C6	1.434 (4)	N3—H3A	0.8600
O4—C7	1.264 (5)	N3—H3B	0.8600
O6—C9	1.207 (5)	N3—C1	1.318 (6)
O9—N10	1.249 (5)	C7—C6	1.533 (6)
O2—C4	1.251 (5)	C6—C8	1.524 (5)
O14—H14A	0.8497	C6—C5	1.530 (6)
O14—H14B	0.8500	N9—H9A	0.8600
O1—C4	1.258 (5)	N9—H9B	0.8600
N7—H7A	0.8900	N9—C3	1.313 (6)
N7—H7B	0.8900	N6—H6A	0.8600
N7—N8	1.414 (5)	N6—H6B	0.8600
O7—H7	0.8200	N6—C2	1.314 (6)
O7—C9	1.333 (5)	C4—C5	1.526 (6)
O10—N10	1.231 (5)	C8—H8A	0.9700
O15—H15A	0.8502	C8—H8B	0.9700
O15—H15B	0.8506	C8—C9	1.520 (6)
N1—H1A	0.8900	C5—H5A	0.9700
N1—H1B	0.8900	C5—H5B	0.9700

S1—Co1—S3	90.79 (4)	N5—N4—H4B	109.0
S2—Co1—S1	89.58 (4)	O9—N10—O8	119.1 (4)
S2—Co1—S3	86.90 (4)	O10—N10—O9	120.3 (4)
N7—Co1—S1	178.29 (11)	O10—N10—O8	120.6 (4)
N7—Co1—S3	87.60 (10)	N1—N2—H2	120.2
N7—Co1—S2	90.89 (11)	C1—N2—N1	119.7 (3)
N7—Co1—N4	90.30 (15)	C1—N2—H2	120.2
N1—Co1—S1	87.42 (11)	O12A—N11—O11A	116.5 (18)
N1—Co1—S3	89.84 (11)	O12A—N11—O13A	111.1 (18)
N1—Co1—S2	175.53 (11)	O13A—N11—O11A	125.0 (18)
N1—Co1—N7	92.01 (15)	O11B—N11—O12B	120.3 (18)
N1—Co1—N4	95.51 (15)	O11B—N11—O13B	109.0 (18)
N4—Co1—S1	91.36 (11)	O13B—N11—O12B	123.4 (17)
N4—Co1—S3	174.32 (10)	N4—N5—H5	119.5
N4—Co1—S2	87.86 (10)	C2—N5—N4	121.0 (3)
O3^{i}—Co2—O3	180.0	C2—N5—H5	119.5
O3^{i}—Co2—O4^{i}	77.75 (11)	H3A—N3—H3B	120.0
O3—Co2—O4	77.75 (11)	C1—N3—H3A	120.0
O3^{i}—Co2—O4	102.25 (11)	C1—N3—H3B	120.0
O3—Co2—O4^{i}	102.25 (11)	O5—C7—O4	124.0 (4)
O3^{i}—Co2—O1^{i}	87.18 (12)	O5—C7—C6	117.1 (3)
O3^{i}—Co2—O1	92.82 (12)	O4—C7—C6	118.6 (3)
O3—Co2—O1^{i}	92.82 (12)	O3—C6—C7	107.5 (3)
O3—Co2—O1	87.18 (12)	O3—C6—C8	108.1 (3)
O4^{i}—Co2—O4	180.0	O3—C6—C5	110.7 (3)
O1^{i}—Co2—O4	93.37 (14)	C8—C6—C7	111.0 (3)
O1^{i}—Co2—O4^{i}	86.63 (14)	C8—C6—C5	112.4 (3)
O1—Co2—O4^{i}	93.36 (14)	C5—C6—C7	107.1 (3)
O1—Co2—O4	86.64 (14)	H9A—N9—H9B	120.0

O1^{i}—Co2—O1	180.0	C3—N9—H9A	120.0
C1—S1—Co1	97.09 (16)	C3—N9—H9B	120.0
C3—S3—Co1	96.78 (14)	H6A—N6—H6B	120.0
C2—S2—Co1	98.16 (16)	C2—N6—H6A	120.0
Co2—O3—H3	139.7 (18)	C2—N6—H6B	120.0
C6—O3—Co2	108.1 (2)	O2—C4—O1	122.6 (4)
C6—O3—H3	109.2 (16)	O2—C4—C5	117.7 (4)
C7—O4—Co2	111.1 (3)	O1—C4—C5	119.6 (4)
H14A—O14—H14B	104.5	C6—C8—H8A	109.4
C4—O1—Co2	130.4 (3)	C6—C8—H8B	109.4
Co1—N7—H7A	108.9	H8A—C8—H8B	108.0
Co1—N7—H7B	108.9	C9—C8—C6	111.3 (3)
H7A—N7—H7B	107.8	C9—C8—H8A	109.4
N8—N7—Co1	113.1 (2)	C9—C8—H8B	109.4
N8—N7—H7A	108.9	N2—C1—S1	120.3 (3)
N8—N7—H7B	108.9	N3—C1—S1	120.5 (3)
C9—O7—H7	109.5	N3—C1—N2	119.1 (4)
H15A—O15—H15B	109.4	O6—C9—O7	119.5 (4)
Co1—N1—H1A	109.1	O6—C9—C8	123.8 (4)
Co1—N1—H1B	109.1	O7—C9—C8	116.7 (4)
H1A—N1—H1B	107.8	C6—C5—H5A	108.7
N2—N1—Co1	112.6 (3)	C6—C5—H5B	108.7
N2—N1—H1A	109.1	C4—C5—C6	114.4 (3)
N2—N1—H1B	109.1	C4—C5—H5A	108.7
N7—N8—H8	119.4	C4—C5—H5B	108.7
C3—N8—N7	121.1 (3)	H5A—C5—H5B	107.6
C3—N8—H8	119.4	N8—C3—S3	119.9 (3)
Co1—N4—H4A	109.0	N9—C3—S3	120.7 (3)
Co1—N4—H4B	109.0	N9—C3—N8	119.4 (4)
H4A—N4—H4B	107.8	N5—C2—S2	119.9 (3)
N5—N4—Co1	113.0 (3)	N6—C2—S2	121.1 (4)
N5—N4—H4A	109.0	N6—C2—N5	119.0 (4)

Co1—S1—C1—N2	−4.9 (4)	O3—C6—C8—C9	59.8 (4)
Co1—S1—C1—N3	172.1 (3)	O3—C6—C5—C4	−68.1 (4)
Co1—S3—C3—N8	−4.3 (4)	O4—C7—C6—O3	14.4 (5)
Co1—S3—C3—N9	174.6 (4)	O4—C7—C6—C8	132.4 (4)
Co1—S2—C2—N5	0.1 (4)	O4—C7—C6—C5	−104.6 (4)
Co1—S2—C2—N6	−179.7 (4)	O2—C4—C5—C6	−147.9 (4)
Co1—N7—N8—C3	12.1 (5)	O1—C4—C5—C6	34.2 (6)
Co1—N1—N2—C1	17.5 (5)	N7—N8—C3—S3	−4.4 (5)
Co1—N4—N5—C2	3.9 (6)	N7—N8—C3—N9	176.6 (4)
Co2—O3—C6—C7	−37.4 (3)	N1—N2—C1—S1	−7.5 (6)
Co2—O3—C6—C8	−157.3 (3)	N1—N2—C1—N3	175.4 (4)
Co2—O3—C6—C5	79.3 (3)	N4—N5—C2—S2	−2.6 (6)
Co2—O4—C7—O5	−158.1 (3)	N4—N5—C2—N6	177.1 (4)
Co2—O4—C7—C6	16.3 (4)	C7—C6—C8—C9	−57.8 (4)
Co2—O1—C4—O2	160.6 (4)	C7—C6—C5—C4	48.8 (4)

Co2—O1—C4—C5	−21.6 (7)	C6—C8—C9—O6	36.7 (6)
O5—C7—C6—O3	−170.8 (3)	C6—C8—C9—O7	−145.1 (4)
O5—C7—C6—C8	−52.8 (5)	C8—C6—C5—C4	170.9 (4)
O5—C7—C6—C5	70.2 (4)	C5—C6—C8—C9	−177.7 (3)

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O14—H14*B*···O15	0.85	2.00	2.798 (5)	157
N7—H7*A*···O6	0.89	2.25	3.100 (5)	159
N7—H7*B*···O8	0.89	2.10	2.983 (5)	172
O7—H7···O14^{ii}	0.82	1.85	2.648 (5)	163
O15—H15*A*···O2^{iii}	0.85	1.92	2.730 (5)	158
O15—H15*B*···O4^{iv}	0.85	2.50	2.902 (5)	110
N1—H1*A*···O9^{v}	0.89	2.20	2.912 (5)	137
N1—H1*A*···O10^{v}	0.89	2.26	3.128 (5)	165
N1—H1*B*···O14	0.89	2.30	3.185 (5)	172
N8—H8···O5	0.86	1.98	2.670 (5)	136
N4—H4*A*···O9	0.89	2.19	3.000 (5)	152
N4—H4*A*···O10^{v}	0.89	2.45	3.024 (5)	122
N4—H4*B*···O11*A*	0.89	2.09	2.96 (3)	166
N4—H4*B*···O12*A*	0.89	2.48	3.06 (3)	123
N4—H4*B*···O12*B*	0.89	2.56	3.13 (2)	122
N4—H4*B*···O11*B*	0.89	2.15	3.04 (3)	175
N2—H2···O10^{iii}	0.86	2.32	3.032 (5)	140
N5—H5···O11*A*^{ii}	0.86	2.28	2.96 (3)	136
N5—H5···O12*A*	0.86	2.47	2.92 (3)	114
N5—H5···O12*B*	0.86	2.45	2.88 (2)	112
N5—H5···O11*B*^{ii}	0.86	2.27	3.02 (3)	145
N3—H3*A*···O8^{iii}	0.86	2.08	2.913 (5)	161
N3—H3*B*···O13*A*^{vi}	0.86	2.01	2.86 (3)	170
N3—H3*B*···O13*B*^{vi}	0.86	2.13	2.94 (3)	157
N9—H9*A*···O15^{vii}	0.86	2.06	2.883 (6)	161
N9—H9*B*···O5^{iv}	0.86	2.15	2.844 (5)	137
N6—H6*A*···O13*A*^{ii}	0.86	2.00	2.85 (3)	170
N6—H6*A*···O13*B*^{ii}	0.86	2.03	2.86 (3)	161
N6—H6*B*···O12*A*^{viii}	0.86	2.35	2.93 (3)	125
N6—H6*B*···O12*B*^{viii}	0.86	2.32	2.99 (3)	134

Symmetry codes: (ii) *x*, −*y*+1/2, *z*+1/2; (iii) *x*, *y*, *z*−1; (iv) *x*, −*y*+3/2, *z*−1/2; (v) *x*, −*y*+1/2, *z*−1/2; (vi) −*x*+2, *y*+1/2, −*z*+1/2; (vii) *x*, −*y*+3/2, *z*+1/2; (viii) −*x*+2, *y*+1/2, −*z*+3/2.