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Poly[[{μ_2-5-[(dimethylamino)(thioxo)methoxy]-benzene-1,3-dicarboxylato-$\kappa^4O^1,O^{1'}:O^3,O^{3'}$}($\mu_2$-4,4′-dipyridylamine-$\kappa^2N^4:N^{4'}$)cobalt(II)] dimethylformamide hemisolvate monohydrate]

Hui-Yu Qin,[a] Bing-Guang Zhang[a]* and Qiao-Zhen Sun[b]

[a]Key Laboratory of Catalysis and Materials Sciences of the State Ethnic Affairs Commission & Ministry of Education, College of Chemistry and Material Science, South-Central Minzu University, Wuhan, 430074, People's Republic of China, and [b]School of Materials Science and Engineering, Central South University, Changsha, 410083, People's Republic of China. *Correspondence e-mail: 3092809@mail.scuec.edu.cn

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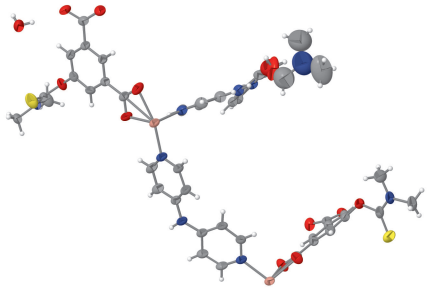
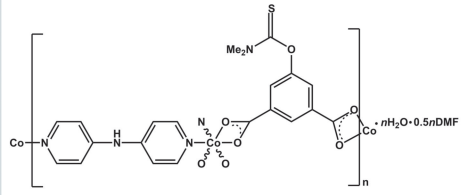
Structural data: full structural data are available from iucrdata.iucr.org

In the crystal structure of the title compound, {[Co($C_{11}H_9NSO_5$)($C_{10}H_9N_3$)]-0.5C_3H_7NO·H_2O}$_n$ or {[Co(dmtb)(dpa)]·0.5DMF·H_2O}$_n$ (dmtb^{2-} = 5-[(dimethylamino)thioxomethoxy]-1,3-benzenedicarboxylate and dpa = 4,4′-dipyridylamine), an assembly of periodic [Co($C_{11}H_9NSO_5$)($C_{10}H_9N_3$)]$_n$ layers extending parallel to the *bc* plane is present. Each layer is constituted by distorted [CoO_4N_2] octahedra, which are connected through the μ_2-coordination modes of both dmtb^{2-} and dpa ligands. Occupationally disordered water and dimethylformamide (DMF) solvent molecules are located in the voids of the network to which they are connected through hydrogen-bonding interactions.

3D view



Chemical scheme



Structure description

The controllable synthesis of coordination polymers with desired structures is always a challenging subject in crystal engineering (Chung *et al.*, 2023; Li *et al.*, 2021; Yang *et al.*, 2021). In many cases, it is difficult to achieve due to the complex interplay of different factors and synthesis parameters such as the preferred coordination environment of the central metal atom, the nature of ligand(s), reaction/incorporation of solvents, temperature, metal-to-ligand ratio, pH value, pressure *etc.* (Sun *et al.*, 2016, 2017, 2018; Vornholt *et al.*, 2017).

According to our previous studies (Gu *et al.*, 2023; Sun *et al.*, 2019), the configuration of the secondary ligand can effectively adjust the steric hindrance within the crystal structure. When Zn^{2+} is coordinated by dmtb^{2-} {5-[(dimethylamino)thioxomethoxy]-1,3-benzenedicarboxylate} and bipy (4,4′-bipyridine), the (dimethylamino)thioxomethoxy

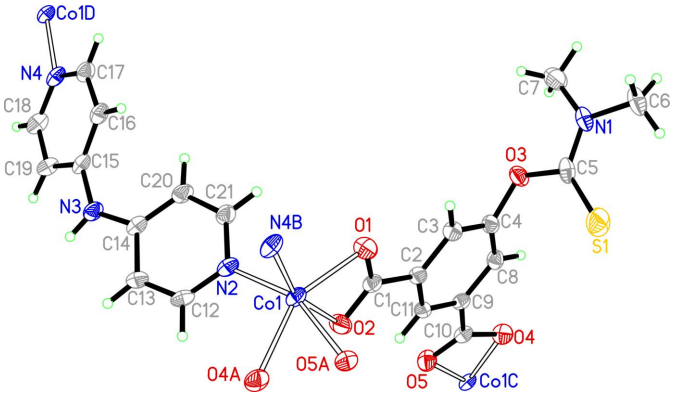


Figure 1
The extended asymmetric unit of (**1**) showing the coordination environment of the Co^{2+} cation. Displacement ellipsoids are drawn at the 30% probability level. The solvent water and DMF molecules are not shown for clarity. [Symmetry codes: (A) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (B) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (C) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (D) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$.]

group of the $dmtb^{2-}$ ligand increases the steric hindrance, and a di-periodic, *i.e.* layered, arrangement results. The rigid bipy ligand acts as a pillar in the structural organization (Gu *et al.*, 2023). In this context and in comparison with the former synthesis, we used the slightly larger Co^{2+} cation and the more flexible 4,4′-dipyridylamine (dpa) ligand for the current study. As a result, the title compound, (**1**), with a likewise layered structural arrangement, was obtained.

The asymmetric unit of (**1**) (Fig. 1) comprises one cobalt(II) cation, one $dmtb^{2-}$ anion, one dpa ligand, two occupationally disordered solvent water and one DMF (dimethylformamide) solvent molecules, with occupancies of 0.5 for the water molecules and of 0.25 for the DMF solvent molecule. The Co—O/N bond lengths are in the range 2.094 (3)–2.216 (3) Å, comparable with those reported for other related Co^{2+}-polycarboxylate compounds (Gu *et al.*, 2022, 2023; Zhao *et al.*, 2024). The Co^{2+} cation is six-coordinated by four oxygen atoms from two different $dmtb^{2-}$ anions and two nitrogen atoms from two different dpa ligands, forming a distorted octahedral environment. The mean deviation of the equatorial plane constructed by atoms O1, O4*A*, O5*A* and N2 is 0.13 Å. The $dmtb^{2-}$ ligand bridges two Co^{2+} cations in a μ_2-κ_2: κ_2 coordination mode, so that each carboxylate group of the $dmtb^{2-}$ anion chelates one Co^{2+} cation. The dpa ligands connect the Co^{2+} cations as a ditopic linker. Accordingly, two $dmtb^{2-}$ and two dpa ligands bridge the Co^{2+} cations into four different directions into a layered arrangement extending parallel to the *bc* plane (Fig. 2). The 5-(dimethylamino)-thioxomethoxy groups dangling above and below a layer protrude into adjacent layers to display an interdigitated motif (Fig. 3). The disordered water and DMF molecules are located in the voids of this arrangement. Without these solvent mol-

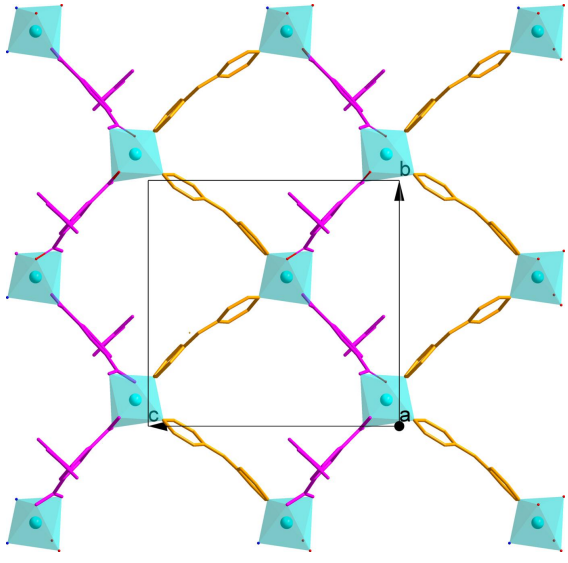


Figure 2
The layered arrangement extending parallel to the *bc* plane in the crystal structure of (**1**).

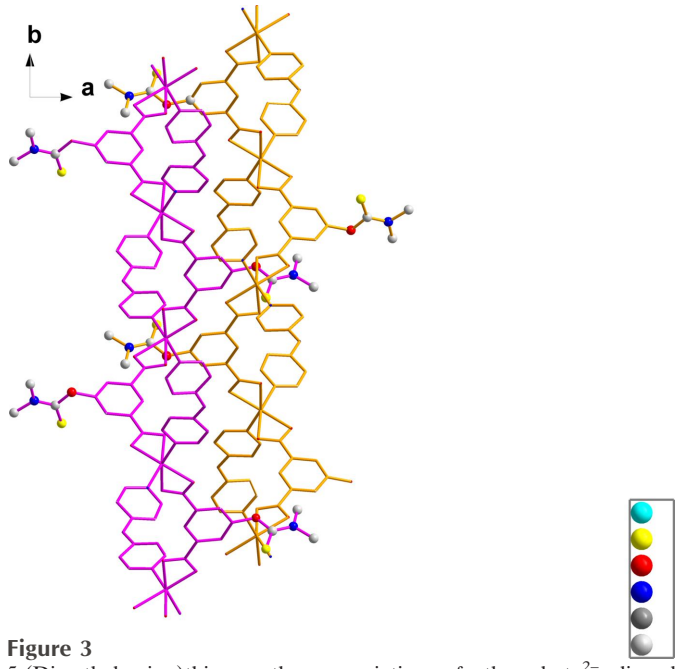


Figure 3
5-(Dimethylamino)thioxomethoxy moieties of the $dmtp^{2-}$ ligand protruding into an adjacent layer.

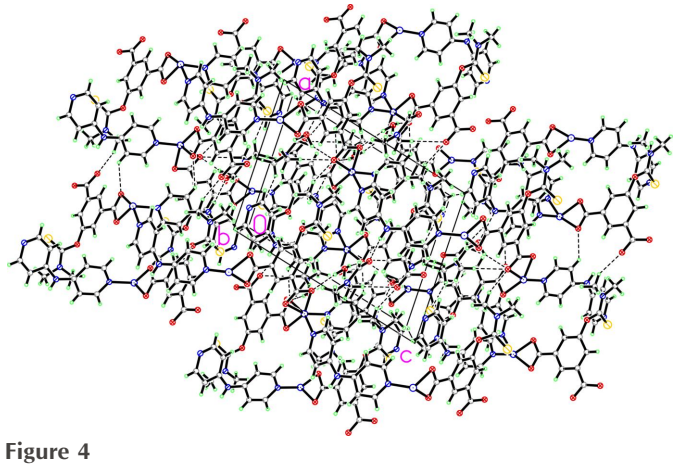


Figure 4
Packing diagram of (**1**), showing hydrogen-bonding interactions (dashed lines).

ecules, the void volume in (**1**) is 19.4%. The solvent molecules are linked to the layers by classical hydrogen-bonding interactions, which includes the amino group of the dpa ligand (entries 1 and 2 in Table 1) and the water molecules (entries 4–7 in Table 1) as donor groups, and the O atoms of the DMF solvent, of the water molecules and the carboxylate O atoms as acceptor groups. A weaker non-classical hydrogen bond between a CH group of a pyridyl ring and a carboxyate O atom consolidates the crystal packing (Fig. 4).

Synthesis and crystallization

A mixture of $Co(NO_3)_2{\cdot}6H_2O$ (29 mg, 0.1 mmol), H_2dmtb (20 mg, 0.07 mmol) and dpa (17 mg, 0.1 mmol) in 4 ml DMF/H_2O (*v*/*v* = 1:1) was sealed in a Teflon-lined autoclave and heated to 423 K for 72 h, then gradually cooled down to room temperature. Pink prismatic crystals were obtained. Yield: 24 mg (71%, based on H_2dmtb).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The DMF molecule was located near a symmetry center and its occupancy was fixed at 0.5. After refinement, some residual electron density peaks still existed near the DMF molecule. They were assigned to the O atoms of water molecules, both refined with occupancies of 0.5. ISOR and SIMU instructions in *SHELXL* (Sheldrick, 2015*b*) were used for these solvent molecules. Hydrogen atoms of the water molecules were included in calculated positions for obtaining reasonable hydrogen bonds and were refined in a riding-model approximation with $U_{iso}(H) = 1.5_{eq}(O)$.

Funding information

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O6	0.86	1.86	2.700 (19)	164
N3—H3···O8	0.86	2.13	2.979 (17)	170
C13—H13···O2^{i}	0.93	2.44	3.174 (5)	135
O7—H7*D*···O4	0.84	2.16	2.992 (7)	174
O7—H7*E*···O2^{ii}	0.88	2.26	3.136 (7)	173
O8—H8*A*···O7^{iii}	0.88	2.33	3.10 (2)	146
O8—H8*B*···O5^{iv}	0.85	2.28	3.102 (17)	163

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Co(C_{11}H_9NO_5S)(C_{10}H_9N_3)]{\cdot}0.5C_3H_7NO{\cdot}H_2O$
M_r	551.95
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	298
a, *b*, *c* (Å)	11.2451 (14), 14.4734 (17), 15.232 (2)
β (°)	103.485 (4)
V (Å^3)	2410.7 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.85
Crystal size (mm)	0.32 × 0.20 × 0.18
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan *(SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.643, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21131, 4711, 3216
R_{int}	0.069
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.053, 0.150, 1.04
No. of reflections	4711
No. of parameters	355
No. of restraints	64
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.76, −0.42

Computer programs: *APEX2* and *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009), *XP* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

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full crystallographic data

IUCrData (2024). **9**, x240489 [https://doi.org/10.1107/S2414314624004899]

Poly[[{μ_2-5-[(dimethylamino)(thioxo)methoxy]benzene-1,3-dicarboxylato-$\kappa^4O^1,O^{1'}:O^3,O^{3'}$}($\mu_2$-4,4′-dipyridylamine-$\kappa^2N^4:N^{4'}$)cobalt(II)] dimethylformamide hemisolvate monohydrate]

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Crystal data

$[Co(C_{11}H_9NO_5S)(C_{10}H_9N_3)]\cdot 0.5C_3H_7NO\cdot H_2O$
M_r = 551.95
Monoclinic, $P2_1/n$
a = 11.2451 (14) Å
b = 14.4734 (17) Å
c = 15.232 (2) Å
β = 103.485 (4)°
V = 2410.7 (5) Å^3
Z = 4
$F(000)$ = 1140
D_x = 1.521 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4852 reflections
θ = 2.9–26.3°
μ = 0.85 mm^{-1}
T = 298 K
Prism, purple
0.32 × 0.20 × 0.18 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min} = 0.643, T_{max} = 0.745
21131 measured reflections
4711 independent reflections
3216 reflections with $I > 2\sigma(I)$
R_{int} = 0.069
θ_{max} = 26.0°, θ_{min} = 2.5°
h = −13→13
k = −17→17
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.150
S = 1.04
4711 reflections
355 parameters
64 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0742P)^2 + 2.1129P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.76 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 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	0.73927 (5)	0.60696 (3)	0.44875 (3)	0.03359 (18)	
S1	0.21293 (14)	0.44589 (10)	0.06254 (10)	0.0733 (4)	
O1	0.5793 (2)	0.53436 (19)	0.38364 (19)	0.0461 (7)	
O2	0.7529 (3)	0.4927 (2)	0.3548 (2)	0.0535 (8)	
O3	0.2652 (2)	0.32239 (19)	0.19296 (19)	0.0456 (7)	
O4	0.5950 (3)	0.18067 (18)	0.05399 (18)	0.0460 (7)	
O5	0.7602 (3)	0.2134 (2)	0.15532 (19)	0.0510 (8)	
N1	0.0682 (3)	0.3554 (2)	0.1501 (2)	0.0469 (9)	
N2	0.8119 (3)	0.5239 (2)	0.5610 (2)	0.0372 (7)	
N3	0.9644 (3)	0.3791 (2)	0.8000 (2)	0.0412 (8)	
H3	1.042657	0.385181	0.814726	0.049*	
N4	0.8350 (3)	0.2025 (2)	0.9750 (2)	0.0393 (8)	
C1	0.6393 (4)	0.4844 (2)	0.3406 (2)	0.0349 (8)	
C2	0.5745 (3)	0.4151 (2)	0.2733 (2)	0.0327 (8)	
C3	0.4479 (4)	0.4062 (2)	0.2574 (3)	0.0366 (9)	
H3A	0.403355	0.444495	0.286860	0.044*	
C4	0.3893 (3)	0.3402 (3)	0.1975 (3)	0.0372 (9)	
C5	0.1790 (4)	0.3741 (3)	0.1362 (3)	0.0440 (10)	
C6	−0.0385 (4)	0.4035 (3)	0.0981 (3)	0.0567 (12)	
H6A	−0.061594	0.451505	0.134299	0.085*	
H6B	−0.104911	0.360578	0.080358	0.085*	
H6C	−0.019640	0.430104	0.045232	0.085*	
C7	0.0470 (4)	0.2900 (4)	0.2157 (4)	0.0664 (14)	
H7A	0.071609	0.229571	0.200946	0.100*	
H7B	−0.038419	0.289331	0.215602	0.100*	
H7C	0.093632	0.307415	0.274533	0.100*	
C8	0.4527 (4)	0.2843 (3)	0.1506 (3)	0.0376 (9)	
H8	0.411067	0.242145	0.108353	0.045*	
C9	0.5783 (3)	0.2916 (2)	0.1671 (2)	0.0331 (8)	
C10	0.6488 (4)	0.2256 (2)	0.1232 (2)	0.0359 (9)	
C11	0.6394 (3)	0.3569 (2)	0.2289 (2)	0.0328 (8)	
H11	0.724132	0.361467	0.240303	0.039*	
C12	0.9316 (4)	0.5240 (3)	0.6018 (3)	0.0432 (10)	
H12	0.983755	0.557585	0.574663	0.052*	
C13	0.9820 (4)	0.4786 (3)	0.6798 (3)	0.0419 (9)	
H13	1.065719	0.482183	0.704535	0.050*	
C14	0.9069 (4)	0.4261 (2)	0.7228 (2)	0.0359 (9)	
C15	0.9165 (4)	0.3234 (2)	0.8576 (2)	0.0374 (9)	
C16	0.7984 (4)	0.3275 (3)	0.8688 (2)	0.0418 (9)	
H16	0.743752	0.371028	0.837599	0.050*	
C17	0.7625 (4)	0.2660 (3)	0.9269 (2)	0.0418 (9)	
H17	0.682131	0.269181	0.932704	0.050*	
C18	0.9509 (4)	0.2020 (3)	0.9670 (3)	0.0459 (10)	
H18	1.004311	0.159659	1.001410	0.055*	
C19	0.9959 (4)	0.2596 (3)	0.9116 (3)	0.0441 (10)	

H19	1.077847	0.256815	0.909575	0.053*	
C20	0.7837 (4)	0.4238 (3)	0.6808 (3)	0.0439 (10)	
H20	0.729663	0.389357	0.705490	0.053*	
C21	0.7419 (4)	0.4728 (3)	0.6025 (3)	0.0414 (9)	
H21	0.658501	0.470415	0.576267	0.050*	
O6	1.2102 (17)	0.3656 (14)	0.8304 (14)	0.116 (6)	0.5
O7	0.3470 (7)	0.2021 (5)	−0.0692 (5)	0.090 (3)	0.5
H7D	0.414831	0.198915	−0.032112	0.135*	0.5
H7E	0.317801	0.146795	−0.086502	0.135*	0.5
C23	1.4935 (17)	0.4546 (13)	0.9452 (13)	0.199 (8)	0.5
H23A	1.466619	0.517120	0.949026	0.298*	0.5
H23B	1.561309	0.453770	0.916886	0.298*	0.5
H23C	1.518269	0.428940	1.004746	0.298*	0.5
N5	1.4060 (15)	0.4024 (12)	0.8994 (13)	0.189 (6)	0.5
C22	1.2767 (15)	0.4296 (13)	0.8683 (16)	0.166 (6)	0.5
H22	1.247808	0.488525	0.876167	0.199*	0.5
C24	1.424 (2)	0.3087 (13)	0.8792 (19)	0.237 (9)	0.5
H24A	1.509290	0.297487	0.884281	0.356*	0.5
H24B	1.379160	0.295245	0.818744	0.356*	0.5
H24C	1.394999	0.269661	0.920830	0.356*	0.5
O8	1.2362 (15)	0.3812 (15)	0.8331 (9)	0.109 (6)	0.5
H8A	1.283550	0.349024	0.876365	0.164*	0.5
H8B	1.255520	0.363564	0.785015	0.164*	0.5

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0496 (3)	0.0268 (3)	0.0268 (3)	−0.0025 (2)	0.0137 (2)	−0.0018 (2)
S1	0.0705 (9)	0.0671 (9)	0.0750 (9)	0.0037 (7)	0.0023 (7)	0.0295 (7)
O1	0.0447 (16)	0.0435 (16)	0.0524 (17)	−0.0023 (13)	0.0158 (14)	−0.0207 (13)
O2	0.0431 (18)	0.071 (2)	0.0508 (18)	−0.0167 (15)	0.0189 (14)	−0.0265 (15)
O3	0.0296 (15)	0.0517 (16)	0.0523 (17)	0.0015 (12)	0.0033 (13)	0.0137 (13)
O4	0.0552 (18)	0.0390 (15)	0.0452 (16)	−0.0038 (13)	0.0146 (14)	−0.0154 (13)
O5	0.0505 (19)	0.0645 (19)	0.0398 (16)	0.0128 (15)	0.0140 (14)	−0.0109 (14)
N1	0.035 (2)	0.049 (2)	0.049 (2)	0.0063 (16)	−0.0050 (16)	−0.0034 (17)
N2	0.053 (2)	0.0305 (16)	0.0321 (16)	−0.0019 (15)	0.0178 (15)	0.0024 (13)
N3	0.055 (2)	0.0375 (18)	0.0328 (17)	−0.0046 (15)	0.0133 (15)	0.0085 (14)
N4	0.062 (2)	0.0301 (16)	0.0278 (16)	−0.0028 (15)	0.0155 (15)	0.0016 (13)
C1	0.044 (2)	0.0323 (19)	0.0303 (19)	−0.0057 (17)	0.0131 (17)	−0.0028 (15)
C2	0.035 (2)	0.0322 (19)	0.0317 (19)	−0.0007 (15)	0.0100 (16)	−0.0002 (15)
C3	0.040 (2)	0.033 (2)	0.039 (2)	0.0070 (16)	0.0119 (17)	−0.0028 (16)
C4	0.034 (2)	0.039 (2)	0.037 (2)	0.0013 (17)	0.0052 (17)	0.0078 (17)
C5	0.046 (3)	0.037 (2)	0.040 (2)	0.0086 (18)	−0.0076 (19)	−0.0092 (17)
C6	0.043 (3)	0.057 (3)	0.059 (3)	0.015 (2)	−0.010 (2)	−0.011 (2)
C7	0.045 (3)	0.078 (3)	0.076 (3)	0.000 (2)	0.013 (2)	0.015 (3)
C8	0.042 (2)	0.034 (2)	0.034 (2)	−0.0048 (17)	0.0021 (17)	−0.0014 (16)
C9	0.039 (2)	0.0337 (19)	0.0284 (18)	−0.0011 (16)	0.0120 (16)	−0.0033 (15)
C10	0.046 (2)	0.0316 (19)	0.033 (2)	−0.0005 (17)	0.0148 (18)	0.0021 (16)

C11	0.032 (2)	0.0368 (19)	0.0307 (19)	−0.0009 (16)	0.0091 (15)	−0.0024 (16)
C12	0.052 (3)	0.042 (2)	0.043 (2)	−0.0035 (19)	0.025 (2)	0.0106 (18)
C13	0.046 (2)	0.043 (2)	0.042 (2)	−0.0049 (18)	0.0210 (19)	0.0059 (18)
C14	0.053 (2)	0.0265 (18)	0.0313 (19)	0.0003 (17)	0.0167 (18)	−0.0002 (15)
C15	0.058 (3)	0.0304 (19)	0.0250 (18)	−0.0051 (18)	0.0122 (17)	−0.0012 (15)
C16	0.059 (3)	0.036 (2)	0.031 (2)	−0.0003 (19)	0.0096 (18)	0.0046 (16)
C17	0.051 (3)	0.040 (2)	0.034 (2)	−0.0045 (19)	0.0088 (18)	0.0073 (17)
C18	0.066 (3)	0.034 (2)	0.040 (2)	0.015 (2)	0.018 (2)	0.0077 (17)
C19	0.057 (3)	0.041 (2)	0.040 (2)	0.007 (2)	0.022 (2)	0.0036 (18)
C20	0.058 (3)	0.041 (2)	0.036 (2)	−0.014 (2)	0.0167 (19)	0.0061 (17)
C21	0.049 (2)	0.039 (2)	0.036 (2)	−0.0113 (18)	0.0098 (18)	0.0028 (17)
O6	0.134 (10)	0.108 (8)	0.110 (9)	0.001 (7)	0.031 (7)	−0.003 (6)
O7	0.085 (6)	0.075 (5)	0.084 (5)	0.023 (4)	−0.034 (4)	−0.032 (4)
C23	0.166 (13)	0.206 (13)	0.211 (14)	−0.064 (11)	0.018 (11)	0.087 (11)
N5	0.190 (8)	0.193 (8)	0.179 (8)	0.003 (7)	0.031 (7)	0.030 (7)
C22	0.168 (9)	0.169 (8)	0.161 (8)	0.002 (7)	0.040 (7)	0.020 (7)
C24	0.233 (14)	0.249 (15)	0.219 (14)	0.067 (13)	0.034 (12)	−0.036 (13)
O8	0.100 (9)	0.192 (16)	0.034 (5)	−0.055 (9)	0.013 (5)	0.020 (7)

Geometric parameters (Å, º)

Co1—O1	2.119 (3)	C8—C9	1.380 (5)
Co1—O2	2.216 (3)	C9—C10	1.496 (5)
Co1—O4^{i}	2.156 (3)	C9—C11	1.395 (5)
Co1—O5^{i}	2.211 (3)	C11—H11	0.9300
Co1—N2	2.094 (3)	C12—H12	0.9300
Co1—N4^{ii}	2.100 (3)	C12—C13	1.361 (5)
Co1—C1	2.502 (4)	C13—H13	0.9300
S1—C5	1.638 (5)	C13—C14	1.406 (5)
O1—C1	1.271 (4)	C14—C20	1.385 (6)
O2—C1	1.251 (5)	C15—C16	1.378 (6)
O3—C4	1.404 (4)	C15—C19	1.409 (5)
O3—C5	1.363 (4)	C16—H16	0.9300
O4—C10	1.266 (4)	C16—C17	1.380 (5)
O5—C10	1.247 (5)	C17—H17	0.9300
N1—C5	1.339 (6)	C18—H18	0.9300
N1—C6	1.451 (5)	C18—C19	1.364 (6)
N1—C7	1.437 (6)	C19—H19	0.9300
N2—C12	1.345 (5)	C20—H20	0.9300
N2—C21	1.341 (5)	C20—C21	1.373 (5)
N3—H3	0.8600	C21—H21	0.9300
N3—C14	1.382 (5)	O6—C22	1.245 (17)
N3—C15	1.390 (5)	O7—H7D	0.8380
N4—C17	1.330 (5)	O7—H7E	0.8812
N4—C18	1.337 (5)	C23—H23A	0.9598
C1—C2	1.496 (5)	C23—H23B	0.9600
C2—C3	1.393 (5)	C23—H23C	0.9595
C2—C11	1.390 (5)	C23—N5	1.306 (14)

C3—H3A	0.9300	N5—C22	1.474 (15)
C3—C4	1.379 (5)	N5—C24	1.416 (15)
C4—C8	1.381 (5)	C22—H22	0.9300
C6—H6A	0.9600	C22—O8	0.93 (3)
C6—H6B	0.9600	C24—H24A	0.9600
C6—H6C	0.9600	C24—H24B	0.9600
C7—H7A	0.9600	C24—H24C	0.9600
C7—H7B	0.9600	O8—H8A	0.8784
C7—H7C	0.9600	O8—H8B	0.8500
C8—H8	0.9300		

O1—Co1—O2	60.43 (10)	C4—C8—H8	120.3
O1—Co1—O4^{i}	151.57 (11)	C9—C8—C4	119.4 (3)
O1—Co1—O5^{i}	98.85 (11)	C9—C8—H8	120.3
O1—Co1—C1	30.50 (11)	C8—C9—C10	119.8 (3)
O2—Co1—C1	29.96 (11)	C8—C9—C11	119.8 (3)
O4^{i}—Co1—O2	99.60 (11)	C11—C9—C10	120.3 (3)
O4^{i}—Co1—O5^{i}	59.65 (10)	O4—C10—C9	120.0 (4)
O4^{i}—Co1—C1	126.57 (12)	O5—C10—O4	119.7 (4)
O5^{i}—Co1—O2	92.57 (12)	O5—C10—C9	120.3 (3)
O5^{i}—Co1—C1	95.62 (11)	C2—C11—C9	120.4 (3)
N2—Co1—O1	102.95 (12)	C2—C11—H11	119.8
N2—Co1—O2	91.51 (12)	C9—C11—H11	119.8
N2—Co1—O4^{i}	97.23 (12)	N2—C12—H12	117.6
N2—Co1—O5^{i}	156.87 (12)	N2—C12—C13	124.9 (4)
N2—Co1—N4^{ii}	93.24 (12)	C13—C12—H12	117.6
N2—Co1—C1	99.22 (12)	C12—C13—H13	120.2
N4^{ii}—Co1—O1	100.46 (12)	C12—C13—C14	119.6 (4)
N4^{ii}—Co1—O2	160.89 (13)	C14—C13—H13	120.2
N4^{ii}—Co1—O4^{i}	98.15 (12)	N3—C14—C13	116.7 (4)
N4^{ii}—Co1—O5^{i}	90.30 (11)	N3—C14—C20	126.9 (4)
N4^{ii}—Co1—C1	130.93 (14)	C20—C14—C13	116.3 (4)
C1—O1—Co1	91.7 (2)	N3—C15—C19	117.5 (4)
C1—O2—Co1	87.8 (2)	C16—C15—N3	125.5 (4)
C5—O3—C4	118.8 (3)	C16—C15—C19	117.0 (3)
C10—O4—Co1^{iii}	91.3 (2)	C15—C16—H16	120.5
C10—O5—Co1^{iii}	89.3 (2)	C15—C16—C17	119.1 (4)
C5—N1—C6	119.9 (4)	C17—C16—H16	120.5
C5—N1—C7	123.6 (3)	N4—C17—C16	124.5 (4)
C7—N1—C6	116.4 (4)	N4—C17—H17	117.8
C12—N2—Co1	122.3 (2)	C16—C17—H17	117.8
C21—N2—Co1	122.8 (3)	N4—C18—H18	117.9
C21—N2—C12	114.6 (3)	N4—C18—C19	124.3 (4)
C14—N3—H3	114.8	C19—C18—H18	117.9
C14—N3—C15	130.5 (4)	C15—C19—H19	120.5
C15—N3—H3	114.8	C18—C19—C15	119.0 (4)
C17—N4—Co1^{iv}	119.2 (3)	C18—C19—H19	120.5
C17—N4—C18	116.0 (3)	C14—C20—H20	120.3

C18—N4—Co1^{iv}	124.7 (3)	C21—C20—C14	119.5 (4)
O1—C1—Co1	57.84 (18)	C21—C20—H20	120.3
O1—C1—C2	120.2 (3)	N2—C21—C20	125.1 (4)
O2—C1—Co1	62.2 (2)	N2—C21—H21	117.5
O2—C1—O1	120.0 (3)	C20—C21—H21	117.5
O2—C1—C2	119.8 (3)	H7D—O7—H7E	111.7
C2—C1—Co1	176.8 (3)	H23A—C23—H23B	109.5
C3—C2—C1	119.7 (3)	H23A—C23—H23C	109.5
C11—C2—C1	120.9 (3)	H23B—C23—H23C	109.5
C11—C2—C3	119.4 (3)	N5—C23—H23A	111.7
C2—C3—H3A	120.3	N5—C23—H23B	109.3
C4—C3—C2	119.4 (3)	N5—C23—H23C	107.3
C4—C3—H3A	120.3	C23—N5—C22	125.5 (15)
C3—C4—O3	118.4 (3)	C23—N5—C24	122.9 (15)
C3—C4—C8	121.6 (4)	C24—N5—C22	111.4 (13)
C8—C4—O3	119.6 (3)	O6—C22—N5	113.0 (15)
O3—C5—S1	122.5 (3)	O6—C22—H22	123.5
N1—C5—S1	127.6 (3)	N5—C22—H22	123.5
N1—C5—O3	109.9 (4)	O8—C22—O6	10.1 (19)
N1—C6—H6A	109.5	O8—C22—N5	107 (2)
N1—C6—H6B	109.5	O8—C22—H22	128.6
N1—C6—H6C	109.5	N5—C24—H24A	109.5
H6A—C6—H6B	109.5	N5—C24—H24B	109.5
H6A—C6—H6C	109.5	N5—C24—H24C	109.5
H6B—C6—H6C	109.5	H24A—C24—H24B	109.5
N1—C7—H7A	109.5	H24A—C24—H24C	109.5
N1—C7—H7B	109.5	H24B—C24—H24C	109.5
N1—C7—H7C	109.5	C22—O8—H8A	80.7
H7A—C7—H7B	109.5	C22—O8—H8B	122.1
H7A—C7—H7C	109.5	H8A—O8—H8B	104.8
H7B—C7—H7C	109.5		

Co1—O1—C1—O2	3.4 (4)	C5—O3—C4—C3	87.8 (4)
Co1—O1—C1—C2	−177.0 (3)	C5—O3—C4—C8	−100.0 (4)
Co1—O2—C1—O1	−3.2 (4)	C6—N1—C5—S1	−1.8 (6)
Co1—O2—C1—C2	177.2 (3)	C6—N1—C5—O3	179.0 (3)
Co1^{iii}—O4—C10—O5	2.2 (4)	C7—N1—C5—S1	179.1 (4)
Co1^{iii}—O4—C10—C9	−176.6 (3)	C7—N1—C5—O3	−0.1 (6)
Co1^{iii}—O5—C10—O4	−2.1 (4)	C8—C9—C10—O4	19.2 (5)
Co1^{iii}—O5—C10—C9	176.7 (3)	C8—C9—C10—O5	−159.6 (4)
Co1—N2—C12—C13	173.3 (3)	C8—C9—C11—C2	−0.5 (5)
Co1—N2—C21—C20	−173.9 (3)	C10—C9—C11—C2	−176.6 (3)
Co1^{iv}—N4—C17—C16	−174.6 (3)	C11—C2—C3—C4	−0.3 (5)
Co1^{iv}—N4—C18—C19	174.4 (3)	C11—C9—C10—O4	−164.7 (3)
O1—C1—C2—C3	0.7 (5)	C11—C9—C10—O5	16.5 (5)
O1—C1—C2—C11	−176.9 (3)	C12—N2—C21—C20	0.5 (6)
O2—C1—C2—C3	−179.7 (4)	C12—C13—C14—N3	177.7 (4)
O2—C1—C2—C11	2.7 (5)	C12—C13—C14—C20	0.6 (6)

O3—C4—C8—C9	−169.0 (3)	C13—C14—C20—C21	−1.2 (6)
N2—C12—C13—C14	0.6 (6)	C14—N3—C15—C16	−23.9 (6)
N3—C14—C20—C21	−178.0 (4)	C14—N3—C15—C19	158.4 (4)
N3—C15—C16—C17	178.3 (4)	C14—C20—C21—N2	0.6 (6)
N3—C15—C19—C18	−178.0 (4)	C15—N3—C14—C13	178.9 (4)
N4—C18—C19—C15	−1.1 (6)	C15—N3—C14—C20	−4.3 (6)
C1—C2—C3—C4	−177.9 (3)	C15—C16—C17—N4	1.0 (6)
C1—C2—C11—C9	179.1 (3)	C16—C15—C19—C18	4.1 (6)
C2—C3—C4—O3	170.1 (3)	C17—N4—C18—C19	−2.0 (6)
C2—C3—C4—C8	−2.0 (6)	C18—N4—C17—C16	2.0 (6)
C3—C2—C11—C9	1.5 (5)	C19—C15—C16—C17	−4.0 (5)
C3—C4—C8—C9	3.1 (6)	C21—N2—C12—C13	−1.2 (6)
C4—O3—C5—S1	8.9 (5)	C23—N5—C22—O6	−176 (2)
C4—O3—C5—N1	−171.9 (3)	C23—N5—C22—O8	175 (2)
C4—C8—C9—C10	174.4 (3)	C24—N5—C22—O6	−1 (3)
C4—C8—C9—C11	−1.8 (5)	C24—N5—C22—O8	−9 (3)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O6	0.86	1.86	2.700 (19)	164
N3—H3···O8	0.86	2.13	2.979 (17)	170
C13—H13···O2^{v}	0.93	2.44	3.174 (5)	135
O7—H7*D*···O4	0.84	2.16	2.992 (7)	174
O7—H7*E*···O2^{vi}	0.88	2.26	3.136 (7)	173
O8—H8*A*···O7^{vii}	0.88	2.33	3.10 (2)	146
O8—H8*B*···O5^{viii}	0.85	2.28	3.102 (17)	163

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