Crystal structure of the tetraaquabis(thiocyanato-κN)cobalt(II)–caffeine–water (1/2/4) co-crystal

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In the structure of the title compound [systematic name: tetraaquabis(thiocyanato-κN)cobalt(II)–1,3,7-trimethyl-1,2,3,6-tetrahydro-7H-purine-2,6-dione–water (1/2/4)], [Co(NCS)$_2$(H$_2$O)$_4$]·2C$_8$H$_{10}$N$_4$O$_2$·4H$_2$O, the cobalt(II) cation lies on an inversion centre and is coordinated in a slightly distorted octahedral geometry by the oxygen atoms of four water molecules and two N atoms of two trans-arranged thiocyanate anions. In the crystal, the complex molecules interact with the caffeine molecules through O—H···N, O—H···O and C—H···S hydrogen bonds and π–π interactions [centroid-to-centroid distance = 3.4715 (5) Å], forming layers parallel to the ab plane, which are further connected into a three-dimensional network by O—H···O and O—H···S hydrogen bonds involving the non-coordinating water molecules.

1. Chemical context

Compounds with supramolecular metal–organic structures, which are diversified by their innovative applications, attract attention in various fields such as non-linear optical activity, catalysis, electrical conductivity, and cooperative magnetic behavior (Fan et al., 2016). In particular, the supramolecular complexes of mixed metals and ligands that possess active pharmaceutical ingredients (APIs) offers an approach to generate crystalline materials that form pharmaceutical co-crystals to effect therapeutic parameters such as solubility and lipophilicity (Ma & Moulton, 2007). The properties of caffeine as a pharmaceutical compound exhibiting moisture instability with the formation of a non-stoichiometric crystalline hydrate have been widely studied. Caffeine is a stimulant of the central nervous system and a smooth muscle relaxant, and is used as a formulation additive to analgesic remedies (Trask et al., 2005). Caffeine has attractive effects on various biological systems, including cardiovascular, gastrointestinal, respiratory and muscle systems (Taşdemir et al., 2016), and forms complexes with transition metals having different coordination and biological properties such as anti-inflammatory and anti-bacterial (Taşdemir et al., 2016). Thiocyanate is a commonly used ligand because of its numerous bonding modes to one or more transition metal ions, and provides useful precursors for numerous coordination complexes. Usually, the thiocyanate anion bonds terminally through the nitrogen atom with first-row transition metals, and can act as a hydrogen-bond acceptor through the nitrogen or sulfur atom (Bie et al., 2005).

4(H₂O)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C2—H21$\cdots$S17^i	0.97	2.83	3.7622 (9)	160.6
O20—H202$\cdots$O21^{ii}	0.86	1.98	2.8119 (11)	161.6
O19—H191$\cdots$O21	0.86	1.91	2.7634 (10)	174.9
O18—H182$\cdots$N3^{iii}	0.85	2.01	2.8671 (11)	178.4
O21—H211$\cdots$S17^{iv}	0.88	2.38	3.2481 (7)	173.3
O21—H212$\cdots$O20^{iv}	0.87	1.97	2.8157 (11)	164.8
O20—H201$\cdots$O12	0.85	2.02	2.8531 (10)	166.8
O19—H192$\cdots$O14^v	0.85	1.89	2.7460 (10)	178.5

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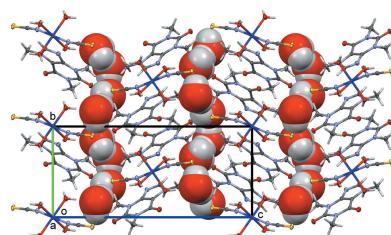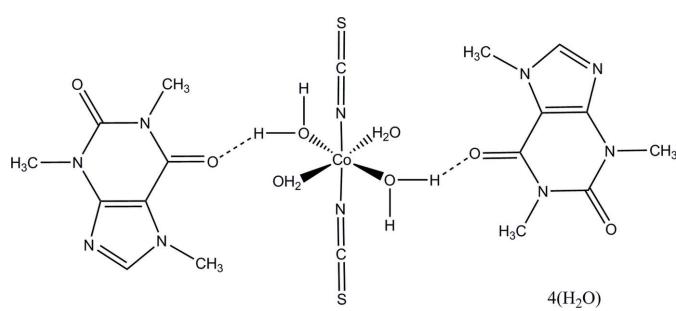
2. Structural commentary

The asymmetric unit of the title compound (Fig. 1) contains half a complex molecule of formula [Co(NCS)₂(H₂O)₄], a caffeine molecule and two free water molecules. The cobalt(II) cation lies on an inversion centre and displays a *trans*-arranged octahedral coordination geometry provided by the N atoms of two thiocyanate anions and four O atoms of coordinating water molecules. The Co1—N15 [2.0981 (8) Å] and Co1—O18 [2.0981 (7) Å] bond lengths are equal within standard uncertainties and significantly longer than the Co1–O19 bond length [2.0732 (7) Å], and therefore the CoN₂O₄ octahedron is slightly axially compressed. This structural feature is typical for related compounds (Shylin *et al.*, 2013, 2015). The thiocyanato ligands are bound through the nitrogen atoms and are nearly linear [N15—C16—S17 = 177.81 (8)°], while the Co—NCS linkage is bent [C16—N15—Co1 = 167.35 (8)°]. Previously reported complexes with an N-bound NCS group possess similar structural features (Petrusenko *et al.*, 1997). The caffeine molecule is nearly planar (r.m.s. deviation = 0.0346 Å), with a maximum deviation from the mean plane of 0.0404 (7) Å for atom N5.

3. Supramolecular features

In the crystal, each complex molecule interacts with four neighboring caffeine molecules through classical O—H$\cdots$N and O—H$\cdots$O hydrogen bonds (Table 1) involving the coordinating water molecules as H-atom donors to form layers parallel to the *ab* plane. These planes are further enforced by C—H$\cdots$S hydrogen bonds and π–π interactions occurring between centrosymmetrically related six-membered rings of the purine ring system [$Cg\cdots Cg^i$ = 3.4715 (5) Å; Cg is the centroid of the N3/N7/C4/C6/C8/C9 ring; symmetry code: (i) $1-x, 2-y, 1-z$; Fig. 2], and are alternated by layers of non-coordinating water molecules linked through O—H$\cdots$O and O—H$\cdots$S hydrogen bonds (Fig. 3), leading to the formation of a three-dimensional network (Fig. 3).

4. Synthesis and crystallization

In a glass tube, a solution of CoCl₂·6H₂O (129 mg, 1 mmol) in 5 ml of water and caffeine (194.19 mg, 1 mmol) in 10 ml of ethanol was added to a solution of potassium thiocyanate (190 mg, 2 mmol) in 5 ml of water. Single crystals of the title compound suitable for X-ray analysis were grown after several months by slow evaporation of the solvent at room temperature.

Figure 1
The asymmetric unit [expanded for the cobalt(II) cation to show the full coordination sphere; primed atoms are related to the non-primed atoms by the symmetry operation $-x+2, -y+1, -z+1$] of the title compound, with displacement ellipsoids drawn at the 50% probability level
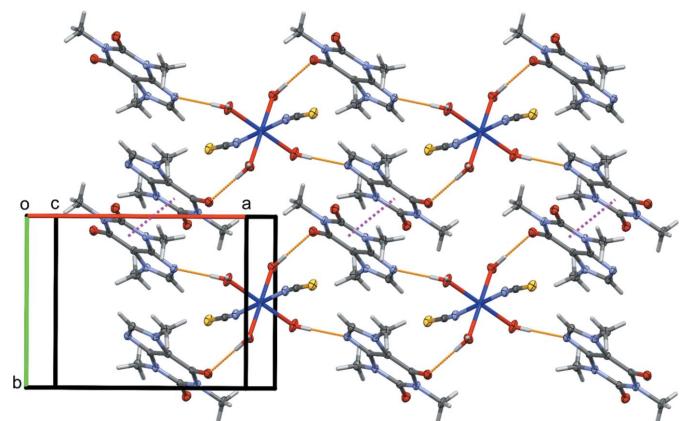

Figure 2
Partial packing diagram of the title compound, showing the network of hydrogen bonds (orange dotted lines) and π–π interactions (purple dotted lines) linking complexes and caffeine molecules into layers parallel to the *ab* plane.
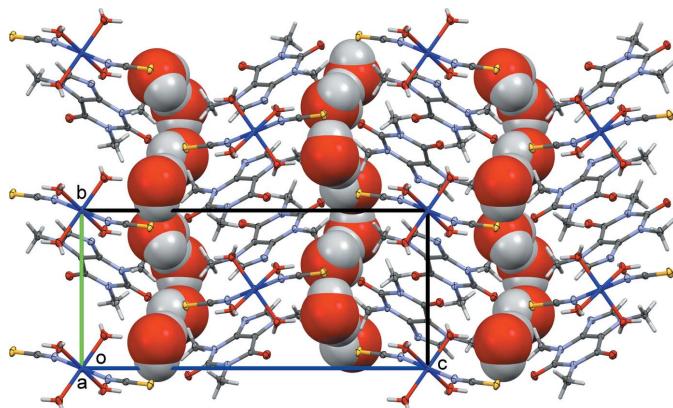
Figure 3
Crystal packing of the title compound viewed down the *a* axis.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms could be located in a difference-Fourier map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H = 0.98, O—H = 0.82 Å) and with U_{iso}(H) set at 1.2–1.5 times of the U_{eq} of the parent atom, after which the positions were refined with riding constraints (Cooper *et al.*, 2010).

Acknowledgements

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Table 2
Experimental details.

Crystal data	
Chemical formula	$[Co(NCS)_2(H_2O)_4]\cdot 2C_8H_{10}N_4O_2\cdot 4H_2O$
M_r	707.61
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	120
a, b, c (Å)	10.65854 (19), 8.16642 (14), 18.0595 (3)
β (°)	96.4701 (15)
V (Å^3)	1561.93 (3)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.75
Crystal size (mm)	$0.25 \times 0.20 \times 0.20$
Data collection	
Diffractometer	Oxford Diffraction Gemini
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2011)
T_{min}, T_{max}	0.78, 0.86
No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	62568, 4002, 3693
R_{int}	0.023
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.689
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.023, 0.022, 1.13
No. of reflections	3586
No. of parameters	196
H-atom treatment	H-atom parameters not refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.36, −0.24

Computer programs: *GEMINI* (Oxford Diffraction, 2006), *CrysAlis PRO* (Agilent, 2011), *SIR92* (Altomare *et al.*, 1994), *CRYSTALS* (Betteridge *et al.*, 2003) and *CAMERON* (Watkin *et al.*, 1996). Weighting scheme: Chebychev polynomial, (Watkin, 1994; Prince, 1982).

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supporting information

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Computing details

Data collection: Gemini (Oxford Diffraction, 2006); cell refinement: *CrysAlis PRO* (Agilent, 2011); data reduction: *CrysAlis PRO* (Agilent, 2011); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS* (Betteridge *et al.*, 2003).

(I)

Crystal data
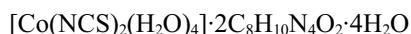
[Co(NCS)$_2$(H$_2$O)$_4$]·2C$_8$H$_{10}$N$_4$O$_2$·4H$_2$O	$F(000) = 738$
$M_r = 707.61$	$D_x = 1.504$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 26895 reflections
$a = 10.65854$ (19) Å	$\theta = 4$–29°
$b = 8.16642$ (14) Å	$\mu = 0.75$ mm^{-1}
$c = 18.0595$ (3) Å	$T = 120$ K
$\beta = 96.4701$ (15)°	Block, orange
$V = 1561.93$ (3) Å^3	$0.25 \times 0.20 \times 0.20$ mm
$Z = 2$	

Data collection

Oxford Diffraction Gemini diffractometer	4002 independent reflections
Graphite monochromator	3693 reflections with $I > 2.0\sigma(I)$
φ & ω scans	$R_{int} = 0.023$
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2011)	$\theta_{max} = 29.3°$, $\theta_{min} = 3.1°$
	$h = -14 \rightarrow 13$
	$k = -10 \rightarrow 10$
$T_{min} = 0.78$, $T_{max} = 0.86$	$l = -24 \rightarrow 24$
62568 measured reflections	

Refinement

Refinement on F	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.023$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.022$	H-atom parameters not refined
$S = 1.13$	
3586 reflections	
196 parameters	
0 restraints	

Method, part 1, Chebychev polynomial, (Watkin, 1994, *P*rince, 1982) [*w*eight] = $1.0/[A_0*T_0(x) + A_1*T_1(x) \cdots + A_{n-1}]*T_{n-1}(x)]$ where A_i are the Chebychev coefficients belo*w* and x = *F* /*F*max Method = Robust Weighting (*P*rince, 1982) W = [*w*eight] * $[1-(deltaF/6*sigmaF)^2]^2$ A_i are: 4.58 -1.83 2.76

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

$\Delta\rho_{max} = 0.36$ e Å^{-3}

$\Delta\rho_{min} = -0.24$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems open-flow nitrogen cryostat (Cosier & Glazer, 1986) with a nominal stability of 0.1K.
Cosier, J. & Glazer, A.M., 1986. J. Appl. Cryst. 105-107.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.52963 (7)	0.70159 (10)	0.44118 (4)	0.0159
N3	0.39238 (7)	0.69668 (10)	0.52732 (4)	0.0165
N5	0.50891 (7)	0.88202 (9)	0.61607 (4)	0.0138
N7	0.70166 (7)	0.97981 (10)	0.57845 (4)	0.0148
N15	0.87722 (7)	0.56972 (10)	0.57738 (4)	0.0177
C2	0.42006 (9)	0.64292 (12)	0.46092 (5)	0.0177
C4	0.49202 (8)	0.79469 (11)	0.55076 (5)	0.0134
C6	0.61761 (8)	0.97269 (11)	0.63265 (5)	0.0145
C8	0.68939 (8)	0.89801 (11)	0.50972 (5)	0.0140
C9	0.57826 (8)	0.80031 (11)	0.49965 (5)	0.0138
C10	0.58693 (10)	0.66144 (13)	0.37365 (5)	0.0214
C11	0.41902 (9)	0.86319 (12)	0.67132 (5)	0.0187
C13	0.81636 (9)	1.07902 (13)	0.59652 (6)	0.0212
C16	0.82097 (8)	0.58619 (11)	0.62832 (5)	0.0146
O12	0.63887 (6)	1.04807 (9)	0.69164 (4)	0.0199
O14	0.76700 (6)	0.91542 (9)	0.46473 (4)	0.0191
O18	1.14207 (7)	0.63274 (10)	0.56379 (4)	0.0243
O19	1.04404 (7)	0.29467 (9)	0.56531 (4)	0.0202
O20	0.85940 (7)	1.15725 (10)	0.78244 (4)	0.0218
O21	1.04346 (7)	0.33657 (9)	0.71711 (4)	0.0227
S17	0.73704 (2)	0.60472 (3)	0.699098 (13)	0.0206
Co1	1.0000	0.5000	0.5000	0.0133
H21	0.3674	0.5683	0.4293	0.0226*
H103	0.6697	0.6105	0.3874	0.0339*
H102	0.5958	0.7614	0.3446	0.0343*
H101	0.5302	0.5835	0.3448	0.0347*
H111	0.4397	0.9420	0.7112	0.0299*
H112	0.3339	0.8828	0.6471	0.0298*
H113	0.4258	0.7533	0.6921	0.0310*
H131	0.8546	1.0964	0.5513	0.0326*
H132	0.7942	1.1847	0.6172	0.0322*

H133	0.8741	1.0211	0.6328	0.0327*
H181	1.1398	0.6463	0.6098	0.0378*
H202	0.9034	1.2295	0.7618	0.0364*
H191	1.0428	0.3014	0.6127	0.0336*
H182	1.2164	0.6538	0.5531	0.0384*
H211	1.1073	0.2809	0.7394	0.0376*
H212	1.0591	0.4409	0.7176	0.0382*
H201	0.7920	1.1412	0.7538	0.0355*
H192	1.1020	0.2292	0.5552	0.0330*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0180 (4)	0.0155 (4)	0.0136 (3)	0.0004 (3)	0.0001 (3)	−0.0018 (3)
N3	0.0150 (3)	0.0163 (4)	0.0178 (4)	−0.0018 (3)	0.0000 (3)	−0.0004 (3)
N5	0.0130 (3)	0.0168 (4)	0.0119 (3)	−0.0009 (3)	0.0028 (3)	−0.0008 (3)
N7	0.0127 (3)	0.0175 (4)	0.0140 (3)	−0.0031 (3)	0.0010 (3)	0.0002 (3)
N15	0.0152 (3)	0.0229 (4)	0.0155 (3)	−0.0010 (3)	0.0039 (3)	−0.0018 (3)
C2	0.0164 (4)	0.0178 (4)	0.0185 (4)	−0.0015 (3)	−0.0005 (3)	−0.0012 (3)
C4	0.0133 (4)	0.0136 (4)	0.0132 (4)	0.0012 (3)	0.0007 (3)	0.0012 (3)
C6	0.0140 (4)	0.0156 (4)	0.0135 (4)	0.0007 (3)	0.0002 (3)	0.0007 (3)
C8	0.0137 (4)	0.0141 (4)	0.0140 (4)	0.0024 (3)	0.0012 (3)	0.0023 (3)
C9	0.0149 (4)	0.0146 (4)	0.0120 (4)	0.0011 (3)	0.0011 (3)	0.0000 (3)
C10	0.0269 (5)	0.0228 (5)	0.0152 (4)	0.0007 (4)	0.0058 (4)	−0.0028 (4)
C11	0.0177 (4)	0.0244 (5)	0.0152 (4)	−0.0010 (4)	0.0067 (3)	−0.0006 (3)
C13	0.0154 (4)	0.0269 (5)	0.0208 (4)	−0.0084 (4)	0.0000 (3)	−0.0009 (4)
C16	0.0139 (4)	0.0147 (4)	0.0146 (4)	−0.0021 (3)	−0.0005 (3)	−0.0003 (3)
O12	0.0199 (3)	0.0232 (3)	0.0163 (3)	−0.0028 (3)	0.0006 (2)	−0.0052 (3)
O14	0.0172 (3)	0.0224 (3)	0.0190 (3)	0.0006 (3)	0.0071 (2)	0.0021 (3)
O18	0.0175 (3)	0.0413 (4)	0.0147 (3)	−0.0121 (3)	0.0044 (2)	−0.0074 (3)
O19	0.0212 (3)	0.0232 (3)	0.0173 (3)	0.0041 (3)	0.0063 (2)	0.0018 (3)
O20	0.0203 (3)	0.0300 (4)	0.0146 (3)	−0.0021 (3)	−0.0004 (2)	0.0011 (3)
O21	0.0241 (3)	0.0246 (4)	0.0195 (3)	0.0044 (3)	0.0020 (3)	0.0047 (3)
S17	0.01944 (11)	0.02902 (12)	0.01456 (10)	−0.00462 (9)	0.00757 (8)	−0.00446 (9)
Co1	0.01068 (8)	0.01859 (9)	0.01093 (8)	−0.00186 (6)	0.00259 (5)	−0.00104 (6)

Geometric parameters (Å, º)

N1—C2	1.3469 (12)	C10—H102	0.980
N1—C9	1.3820 (11)	C10—H101	0.985
N1—C10	1.4616 (12)	C11—H111	0.972
N3—C2	1.3407 (12)	C11—H112	0.975
N3—C4	1.3588 (12)	C11—H113	0.972
N5—C4	1.3727 (11)	C13—H131	0.963
N5—C6	1.3792 (11)	C13—H132	0.980
N5—C11	1.4672 (11)	C13—H133	0.969
N7—C6	1.4006 (11)	C16—S17	1.6476 (9)
N7—C8	1.4027 (11)	O18—Co1	2.0981 (7)

N7—C13	1.4723 (11)	O18—H181	0.842
N15—C16	1.1610 (12)	O18—H182	0.853
N15—Co1	2.0981 (8)	O19—Co1	2.0732 (7)
C2—H21	0.969	O19—H191	0.860
C4—C9	1.3749 (12)	O19—H192	0.853
C6—O12	1.2291 (11)	O20—H202	0.864
C8—C9	1.4226 (12)	O20—H201	0.846
C8—O14	1.2314 (11)	O21—H211	0.877
C10—H103	0.982	O21—H212	0.868
C2—N1—C9	105.49 (7)	H111—C11—H112	110.1
C2—N1—C10	126.68 (8)	N5—C11—H113	109.5
C9—N1—C10	127.76 (8)	H111—C11—H113	109.0
C2—N3—C4	103.21 (8)	H112—C11—H113	110.5
C4—N5—C6	119.42 (7)	N7—C13—H131	108.3
C4—N5—C11	119.83 (7)	N7—C13—H132	109.8
C6—N5—C11	120.37 (7)	H131—C13—H132	109.6
C6—N7—C8	126.55 (7)	N7—C13—H133	109.2
C6—N7—C13	116.65 (7)	H131—C13—H133	110.3
C8—N7—C13	116.77 (7)	H132—C13—H133	109.6
C16—N15—Co1	167.35 (8)	N15—C16—S17	177.81 (8)
N1—C2—N3	113.89 (8)	Co1—O18—H181	120.7
N1—C2—H21	122.0	Co1—O18—H182	127.7
N3—C2—H21	124.1	H181—O18—H182	109.1
N5—C4—N3	126.58 (8)	Co1—O19—H191	119.2
N5—C4—C9	121.78 (8)	Co1—O19—H192	120.6
N3—C4—C9	111.64 (8)	H191—O19—H192	110.2
N7—C6—N5	117.28 (8)	H202—O20—H201	107.9
N7—C6—O12	120.99 (8)	H211—O21—H212	111.4
N5—C6—O12	121.70 (8)	O18^{i}—Co1—O18	179.995
N7—C8—C9	111.93 (7)	O18^{i}—Co1—N15^{i}	87.69 (3)
N7—C8—O14	121.76 (8)	O18—Co1—N15^{i}	92.31 (3)
C9—C8—O14	126.29 (8)	O18^{i}—Co1—N15	92.31 (3)
C8—C9—N1	131.30 (8)	O18—Co1—N15	87.69 (3)
C8—C9—C4	122.88 (8)	N15^{i}—Co1—N15	179.995
N1—C9—C4	105.77 (8)	O18^{i}—Co1—O19	89.86 (3)
N1—C10—H103	109.4	O18—Co1—O19	90.14 (3)
N1—C10—H102	109.5	N15^{i}—Co1—O19	92.36 (3)
H103—C10—H102	110.5	N15—Co1—O19	87.64 (3)
N1—C10—H101	107.3	O18^{i}—Co1—O19^{i}	90.14 (3)
H103—C10—H101	109.9	O18—Co1—O19^{i}	89.86 (3)
H102—C10—H101	110.2	N15^{i}—Co1—O19^{i}	87.64 (3)
N5—C11—H111	108.8	N15—Co1—O19^{i}	92.36 (3)
N5—C11—H112	108.9	O19—Co1—O19^{i}	179.994

Symmetry code: (i) −x+2, −y+1, −z+1.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C2—H21···S17[ii]	0.97	2.83	3.7622 (9)	160.6
O20—H202···O21[iii]	0.86	1.98	2.8119 (11)	161.6
O19—H191···O21	0.86	1.91	2.7634 (10)	174.9
O18—H182···N3[iv]	0.85	2.01	2.8671 (11)	178.4
O21—H211···S17[v]	0.88	2.38	3.2481 (7)	173.3
O21—H212···O20[v]	0.87	1.97	2.8157 (11)	164.8
O20—H201···O12	0.85	2.02	2.8531 (10)	166.8
O19—H192···O14[i]	0.85	1.89	2.7460 (10)	178.5

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