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Tris(1,1,5,5-tetramethyl-2-thiobiuretato)cobalt(III)

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(N–C) = 0.003 Å
R factor = 0.033
wR factor = 0.070
Data-to-parameter ratio = 25.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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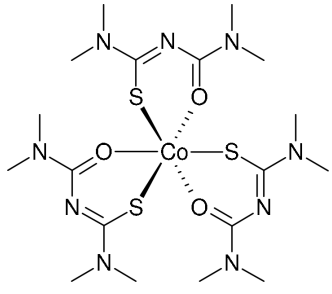
At 150 K, the title compound, $[Co(C_6H_{12}N_3OS)_3]$, comprises an octahedral cobalt(III) ion with three anionic bidentate 1,1,5,5-tetramethyl-2-thiobiuretate ligands. Within the first coordination sphere of the cobalt ion, the disposition of the three S atoms is *fac*.

Comment

The title compound, (I), is the neutral homoleptic cobalt(III) complex of the anionic bidentate 1,1,5,5-tetramethyl-2-thiobiuretate ligand. The cobalt(III) ion is octahedral (Table 1) with an S_3O_3 donor set. The sets of three S and three O atoms are each mutually *fac*, and their respective planes are almost parallel with a dihedral angle of 1.73 (4)°. Within each of the three thiobiuretate ligands, the four atoms of the urea or thiourea groups are close to being coplanar, with the greatest deviation from the least-squares plane of 0.0231 (16) Å for atom C8. However, overall, the three thiobiuretate ligands all show significant deviations from planarity due to twisting about the central N atom; the dihedral angles between the three pairs of urea and thiourea least-squares planes are 18.28 (6), 21.49 (6) and 7.78 (6)°. In all three ligands, the pattern of bond distances indicates that the formal negative charge is predominately localized on the S atom. The relatively long C—S and short C—O average bond lengths of 1.745 (4) and 1.265 (3) Å are consistent with mostly single- and double-bond character, respectively, and this bond localization is also reflected in the average C—N bond distances to the central N atom: 1.318 (3) Å in the (iso)thiourea group and 1.349 (2) Å in the urea group. In contrast, all the C—NMe_2 bond lengths are similar, with an average of 1.353 (2) Å.



(I)

Experimental

The title compound, (I), was prepared by a variation of the method of Koenig *et al.* (1987). Dimethylcarbamyl chloride (1.08 g, 10 mmol)

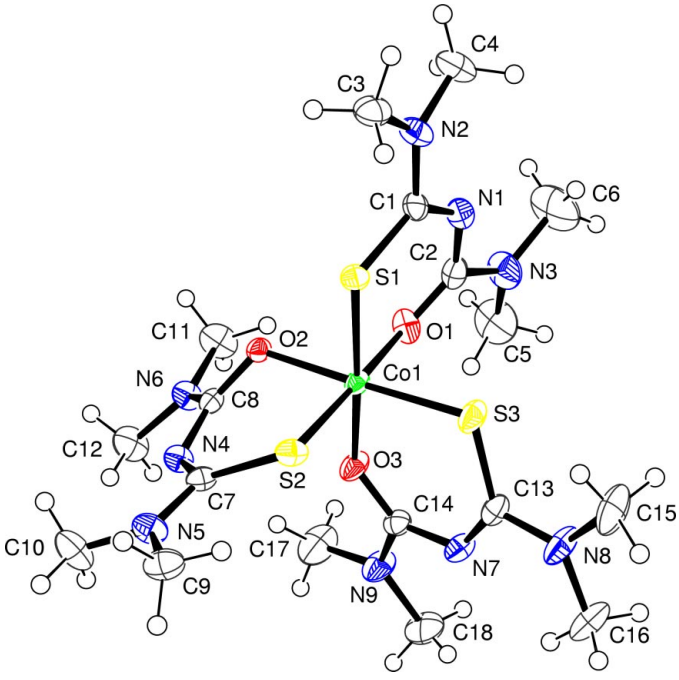


Figure 1
View of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size.

and potassium thiocyanate (0.97 g, 10 mmol) in acetonitrile (40 ml) were heated at reflux for 2 h. The solution was allowed to cool to room temperature and excess 40% aqueous dimethylamine (3.4 ml, 30 mmol) was added with stirring, followed after 15 min by cobalt(II) acetate tetrahydrate (0.87 g, 3.5 mmol) and water (5 ml). After stirring for a further 15 min, the crude product was obtained as a green powder by precipitation with methanol (200 ml), isolation by filtration and washing sequentially with water, methanol and diethyl ether. Suitable crystals were grown by recrystallization from dichloromethane/methanol (yield 1.18 g, 61%). Spectroscopic analysis, IR (KBr disk, ν cm^{-1}): 2916 (*w*), 1533 (*s*), 1473 (*s*), 1387 (*s*), 1355 (*s*), 1269 (*w*), 1198 (*w*), 1115 (*m*), 1027 (*m*), 729 (*m*), 461 (*w*); ^{1}H NMR ($CDCl_3$, p.p.m.): 3.34 (*br s*, 9H), 3.14 (*br s*, 9H), 3.01 (*s*, 18H); ^{13}C NMR ($CDCl_3$, p.p.m.): 173.4, 165.6, 39.7 (2 peaks), 37.5, 36.1; analysis calculated for $C_{18}H_{36}CoN_9O_3S_3$: C 37.17, H 6.24, N 21.67, S 16.54%; found: C 36.90, H 6.34, N 21.49, S 16.24%.

Crystal data

$[Co(C_6H_{12}N_3OS)_3]$
M_r = 581.67
Monoclinic, $P2_1/c$
a = 13.1635 (11) Å
b = 12.1355 (7) Å
c = 18.0309 (16) Å
β = 106.665 (7)°
V = 2759.4 (4) Å^3
Z = 4
D_x = 1.400 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 17 726 reflections
θ = 2.8–30°
μ = 0.89 mm^{-1}
T = 150 (2) K
Plate, green
0.55 × 0.45 × 0.10 mm

Data collection

Stoe IPDS-II area-detector diffractometer
φ and ω scans
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 2001)
T_{min} = 0.533, T_{max} = 0.820
28 286 measured reflections
8038 independent reflections
5023 reflections with $I > 2\sigma(I)$
R_{int} = 0.060
θ_{max} = 30.0°
$h = -18 \rightarrow 18$
$k = -14 \rightarrow 17$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.070
S = 0.80
8038 reflections
319 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0316P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—O1	1.9387 (13)	N1—C1	1.324 (2)
Co1—O2	1.9538 (11)	N1—C2	1.348 (3)
Co1—O3	1.9101 (12)	N2—C1	1.358 (2)
Co1—S1	2.2072 (5)	N3—C2	1.358 (2)
Co1—S2	2.2133 (6)	N4—C7	1.320 (2)
Co1—S3	2.2008 (5)	N4—C8	1.349 (2)
S1—C1	1.7358 (19)	N5—C7	1.351 (2)
S2—C7	1.7530 (18)	N6—C8	1.348 (2)
S3—C13	1.7455 (19)	N7—C13	1.311 (2)
O1—C2	1.262 (2)	N7—C14	1.349 (2)
O2—C8	1.272 (2)	N8—C13	1.355 (2)
O3—C14	1.261 (2)	N9—C14	1.350 (2)
S1—Co1—S2	88.196 (19)	O3—Co1—S1	176.93 (4)
S3—Co1—S1	87.97 (2)	C1—S1—Co1	107.22 (7)
S3—Co1—S2	90.40 (2)	C7—S2—Co1	105.50 (6)
O1—Co1—O2	86.80 (5)	C13—S3—Co1	107.50 (6)
O3—Co1—O1	85.72 (6)	C2—O1—Co1	127.72 (13)
O3—Co1—O2	86.54 (5)	C8—O2—Co1	119.05 (10)
O1—Co1—S1	93.47 (4)	C14—O3—Co1	131.79 (12)
O2—Co1—S2	90.50 (4)	C1—N1—C2	123.39 (16)
O3—Co1—S3	95.02 (4)	C7—N4—C8	122.94 (15)
O1—Co1—S2	176.83 (4)	C13—N7—C14	125.12 (16)
O2—Co1—S3	178.17 (4)		

All H atoms were initially located in a difference Fourier map. They were then constrained to an ideal geometry, with a C—H distance of 0.98 Å and U_{iso}(H) values set at 1.2U_{eq}(C), but each methyl group was allowed to rotate freely about its X—C bond.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2001); program(s) used to solve structure: *X-STEP*32 (Stoe & Cie, 2001) and *WinGX* (Farrugia, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX*.

References

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Koenig, K. H., Kaul, L., Kuge, M. & Schuster, M. (1987). *Liebigs Ann. Chem.* pp. 1115–1116.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Stoe & Cie (2001). *X-AREA*, *X-RED*, *X-SHAPE* and *X-STEP*32. Stoe & Cie, Darmstadt, Germany.

supporting information

Acta Cryst. (2004). E**60**, m350–m351 [https://doi.org/10.1107/S1600536804004696]

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$D_x = 1.400$ Mg m^{-3}
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Cell parameters from 17726 reflections
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$\theta_{max} = 30.0°$, $\theta_{min} = 2.8°$
$h = -18 \rightarrow 18$
$k = -14 \rightarrow 17$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.070$
$S = 0.80$
8038 reflections
319 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0316P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}

Special details

Experimental. The crystal was mounted under the perfluoro-polyether PFO-XR75 (Lancaster Synthesis). A total of 185 frames (1 minute exposure) were collected (phi/omega: 10/40–100, 75/25–150, delta-omega = 1 °.)

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes. Weighted least-squares planes through the starred atoms (Nardelli, Musatti, Domiano & Andreetti Ric·Sci.(1965),15(II—A),807). (1) Thiourea/urea planes Plane 1 Atom d s d/s (d/s)**2 S1 * -0.0001 0.0005 - 0.143 0.021 C1 * 0.0028 0.0017 1.614 2.606 N1 * -0.0009 0.0016 - 0.562 0.316 N2 * -0.0007 0.0016 - 0.463 0.215 Co1 0.2275 0.0002 1230.633 1514457.125 ========== Sum((d/s)**2) for starred atoms 3.156 Chi-squared at 95% for 1 degrees of freedom: 3.84 Plane 2 Atom d s d/s (d/s)**2 O1 * 0.0042 0.0014 3.072 9.440 C2 * -0.0185 0.0018 - 10.596 112.266 N1 * 0.0050 0.0016 3.218 10.355 N3 * 0.0076 0.0021 3.657 13.377 Co1 - 0.8296 0.0002 - 4385.111 19229198.000 ========== Sum((d/s)**2) for starred atoms 145.437 Chi-squared at 95% for 1 degrees of freedom: 3.84 Plane 3 Atom d s d/s (d/s)**2 S2 * -0.0003 0.0005 - 0.566 0.320 C7 * 0.0115 0.0017 6.690 44.760 N4 * -0.0031 0.0014 - 2.146 4.607 N5 * -0.0032 0.0016 - 2.015 4.061 Co1 - 0.1254 0.0002 - 530.478 281407.250 ========== Sum((d/s)**2) for starred atoms 53.748 Chi-squared at 95% for 1 degrees of freedom: 3.84 Plane 4 Atom d s d/s (d/s)**2 O2 * 0.0041 0.0011 3.552 12.619 C8 * -0.0231 0.0016 - 14.023 196.657 N4 * 0.0059 0.0014 4.099 16.801 N6 * 0.0063 0.0016 4.019 16.154 Co1 - 1.3346 0.0002 - 5994.649 35935820.000 ========== Sum((d/s)**2) for starred atoms 242.231 Chi-squared at 95% for 1 degrees of freedom: 3.84 Plane 5 Atom d s d/s (d/s)**2 S3 * 0.0001 0.0005 0.278 0.077 C13 * -0.0072 0.0020 - 3.606 13.002 N7 * 0.0021 0.0017 1.223 1.497 N8 * 0.0025 0.0021 1.208 1.458 Co1 - 0.3392 0.0003 - 1225.555 1501985.250 ========== Sum((d/s)**2) for starred atoms 16.034 Chi-squared at 95% for 1 degrees of freedom: 3.84 Plane 6 Atom d s d/s (d/s)**2 O3 * -0.0013 0.0015 - 0.925 0.855 C14 * 0.0061 0.0019 3.250 10.560 N7 * -0.0018 0.0017 - 1.028 1.056 N9 * -0.0019 0.0020 - 0.988 0.976 Co1 0.0550 0.0003 195.594 38257.027 ========== Sum((d/s)**2) for starred atoms 13.447 Chi-squared at 95% for 1 degrees of freedom: 3.84 Dihedral angles formed by LSQ-planes Plane - plane angle (s.u.) angle (s.u.) 1 2 18.28 (0.06) 161.72 (0.06) 3 4 21.49 (0.06) 158.51 (0.06) 5 6 7.78 (0.06) 172.22 (0.06) (2) Ligand (biureto backbone) planes Plane 1 Atom d s d/s (d/s)**2 S1 * -0.0287 0.0005 - 55.035 3028.829 O1 * 0.2700 0.0014 195.236 38117.277 N1 * -0.1234 0.0016 - 79.289 6286.707 N2 * 0.2141 0.0016 137.595 18932.359 N3 * -0.2712 0.0021 - 130.827 17115.574 C1 * 0.0154 0.0017 8.928 79.710 C2 * -0.0455 0.0017 - 26.281 690.707 Co1 - 0.1403 0.0002 - 764.463 584403.125 ========== Sum((d/s)**2) for starred atoms 84251.164 Chi-squared at 95% for 4 degrees of freedom: 9.49 Plane 2 Atom d s d/s (d/s)**2 S2 * -0.0443 0.0005 - 89.648 8036.834 O2 * 0.3241 0.0012 273.520 74813.164 N4 * -0.0822 0.0014 - 56.876 3234.825 N5 * 0.2852 0.0016 180.971 32750.467 N6 * -0.3306 0.0016 - 209.916 44064.598 C7 * 0.0625 0.0017 36.600 1339.579 C8 * -0.0363 0.0017 - 21.652 468.825 Co1 - 0.5597 0.0002 - 2372.004 5626402.500 ========== Sum((d/s)**2) for starred atoms 164708.297 Chi-squared at 95% for 4 degrees of freedom: 9.49 Plane 3 Atom d s d/s (d/s)**2 S3 * 0.0123 0.0005 23.195 538.001 O3 * -0.0998 0.0014 - 69.940 4891.660 N7 * -0.0306 0.0017 - 17.743 314.800 N8 * -0.0680 0.0021 - 32.802 1075.952 N9 * 0.1499 0.0019 77.610 6023.274 C13 * -0.0390 0.0020 - 19.662 386.589 C14 * 0.0039 0.0019 2.118 4.484 Co1 - 0.2691 0.0003 - 971.474 943761.938 ========== Sum((d/s)**2) for starred atoms 13234.761 Chi-squared at 95% for 4 degrees of freedom: 9.49 Dihedral angles formed by LSQ-planes Plane - plane angle (s.u.) angle (s.u.) 1 2 62.44 (0.03) 117.56 (0.03) 1 3 87.59 (0.04) 92.41 (0.04) 2 3 70.59 (0.04) 109.41 (0.04) (3) Cobalt(III) donor atom square-planes Plane 1 Atom d s d/s (d/s)**2 Co1 * -0.0060 0.0002 - 31.832 1013.277 O1 * 0.0713 0.0014 51.554 2657.807 O3 * 0.0776 0.0012 63.316 4008.918 S1 * 0.0125 0.0005 23.874 569.970 S2 * 0.0091 0.0005 17.332 300.405 O2 1.9473 0.0010 1856.071 3445001.000 S3 - 2.2047 0.0004 - 6068.647 36828484.000 ========== Sum((d/s)**2) for starred atoms 8550.377 Chi-squared at 95% for 2 degrees of freedom: 5.99 Plane 2 Atom d s d/s (d/s)**2 Co1 * -0.0033 0.0003 - 11.855 140.532 S1 * 0.0018 0.0005 3.273 10.715 S3 * 0.0039 0.0005 7.417 55.007 O2 * 0.0229 0.0012 18.794 353.215 O3 * 0.0153 0.0014 10.623 112.845 O1 1.9298 0.0014 1403.278 1969188.000 S2 - 2.2153 0.0005 - 4066.692 16537987.000 ========== Sum((d/s)**2) for starred atoms 672.315 Chi-squared at 95% for 2 degrees of freedom: 5.99 Plane 3 Atom d s d/s (d/s)**2 Co1 * -0.0006 0.0003 - 2.189 4.792 S2 * -0.0059 0.0005 - 11.761 138.325 S3 * 0.0068 0.0005 13.606 185.128 O1 * -0.0493 0.0013 - 36.667 1344.491 O2 * 0.0474 0.0012 38.925 1515.174 O3 - 1.9018 0.0013 - 1488.512 2215666.750 S1 2.2043 0.0005 4385.180 19229800.000 ========== Sum((d/s)**2) for starred atoms 3187.910 Chi-squared at 95% for 2 degrees of freedom: 5.99 Dihedral angles formed by LSQ-planes Plane - plane angle (s.u.) angle (s.u.) 1 2 89.91 (0.02) 90.09 (0.02) 1 3 87.68 (0.02) 92.32 (0.02) 2 3 87.92 (0.02) 92.08 (0.02) (4) Cobalt(III) (S)3 and (O)3 *fac*-planes Plane 1 Atom d s d/s (d/s)**2 S1 * 0.0000 0.0005 0.000 0.000 S2 * 0.0000 0.0005 0.000 0.000 S3 * 0.0000 0.0004 0.000 0.000 Co1 - 1.2992 0.0002 - 5904.329 34861096.000 ========== Sum((d/s)**2) for starred atoms 0.000 Plane 2 Atom d s d/s (d/s)**2 O1 * 0.0000 0.0014 0.000 0.000 O2 * 0.0000 0.0011 0.000 0.000 O3 * 0.0000 0.0012 0.000 0.000 Co1 1.1855 0.0002 5430.405 29489302.000 ========== Sum((d/s)**2) for starred atoms 0.000 Dihedral angles formed by LSQ-planes Plane - plane angle (s.u.) angle (s.u.) 1 2 1.73 (0.04) 178.27 (0.04) ———————————————————————- Ring puckering coordinates following Cremer D. & Pople J·A., JACS (1975).97,1354 Ring 1: S1 C1 N1 C2 O1 Co1 q2 = 0.2887(0.0015) q3 = -0.1317(0.0013) phi2 = 83.80 (0.24) Total puckering amplitude: QT = 0.3173(0.0013) Spherical polar angles: Theta2 = 114.51 (0.26) Ring 2: S2 C7 N4 C8 O2 Co1 q2 = 0.4868(0.0013) q3 = 0.2957(0.0014) phi2 = -84.31 (0.17) Total puckering amplitude: QT = 0.5695(0.0011) Spherical polar angles: Theta2 = 58.73 (0.16) Ring 3: S3 C13 N7 C14 O3 Co1 q2 = 0.1405(0.0014) q3 = -0.0626(0.0015) phi2 = 157.09 (3/4) Total puckering amplitude: QT = 0.1538(0.0012) Spherical polar angles: Theta2 = 114.03 (0.64) ———————————————————————- Interatomic contacts between cobalt(III) donor atoms. (Corrections following Busing & Levy, Acta Cryst.(1964).17,142) uncorrected lower upper riding non-correlated distance bound bound motion motion S2 ···S3 3.1322 (7) 3.1325 3.1626 3.1354 3.1476 S1 ···S2 3.0762 (8) 3.0762 3.1067 3.0770 3.0914 S1 ···S3

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.706899 (19)	0.261083 (18)	−0.084441 (13)	0.01921 (6)
S1	0.77837 (4)	0.42502 (4)	−0.08717 (3)	0.02184 (9)
S2	0.57314 (4)	0.34392 (4)	−0.05581 (3)	0.02404 (10)
S3	0.79454 (4)	0.25205 (4)	0.03928 (2)	0.03102 (11)
O1	0.81847 (10)	0.18509 (11)	−0.11452 (8)	0.0286 (3)
O2	0.63277 (9)	0.27193 (10)	−0.19483 (6)	0.0197 (2)
O3	0.64271 (11)	0.11928 (10)	−0.08800 (7)	0.0280 (3)
N1	0.96002 (12)	0.31143 (14)	−0.09102 (9)	0.0271 (3)
N2	0.95780 (12)	0.49703 (14)	−0.10407 (9)	0.0293 (4)
N3	0.98436 (14)	0.12528 (15)	−0.08977 (12)	0.0406 (4)
N4	0.45459 (11)	0.25483 (12)	−0.19551 (8)	0.0227 (3)
N5	0.36664 (13)	0.34845 (13)	−0.12525 (9)	0.0285 (4)
N6	0.52150 (12)	0.16343 (13)	−0.28135 (9)	0.0256 (3)
N7	0.68597 (13)	0.05734 (13)	0.04170 (9)	0.0274 (3)
N8	0.78406 (16)	0.12897 (15)	0.15585 (9)	0.0378 (4)
N9	0.59087 (15)	−0.04475 (13)	−0.05985 (10)	0.0343 (4)
C1	0.90570 (14)	0.40403 (15)	−0.09424 (10)	0.0235 (4)
C2	0.91533 (16)	0.21063 (16)	−0.09792 (10)	0.0272 (4)
C3	0.91422 (17)	0.60657 (16)	−0.10361 (12)	0.0334 (5)
H3A	0.8857	0.6139	−0.0593	0.040*
H3B	0.8573	0.6184	−0.1517	0.040*
H3C	0.9702	0.6614	−0.0996	0.040*
C4	1.05976 (16)	0.4893 (2)	−0.12032 (14)	0.0395 (5)
H4A	1.0543	0.4371	−0.1627	0.047*
H4B	1.1137	0.4636	−0.0739	0.047*
H4C	1.0799	0.5619	−0.1352	0.047*
C5	0.9440 (2)	0.0133 (2)	−0.10697 (18)	0.0581 (7)
H5A	0.9395	−0.0048	−0.1608	0.070*
H5B	0.8734	0.0080	−0.0994	0.070*
H5C	0.9921	−0.0386	−0.0723	0.070*
C6	1.0961 (2)	0.1429 (2)	−0.0811 (2)	0.0727 (9)
H6A	1.1209	0.2071	−0.0478	0.087*
H6B	1.1066	0.1559	−0.1320	0.087*
H6C	1.1364	0.0776	−0.0575	0.087*
C7	0.46051 (14)	0.31231 (14)	−0.13226 (10)	0.0219 (4)
C8	0.53995 (14)	0.23180 (14)	−0.21999 (9)	0.0199 (3)
C9	0.35364 (17)	0.40958 (17)	−0.05886 (12)	0.0332 (5)
H9A	0.3309	0.4850	−0.0747	0.040*
H9B	0.4213	0.4115	−0.0180	0.040*
H9C	0.3000	0.3733	−0.0393	0.040*

C10	0.26996 (16)	0.3283 (2)	−0.18741 (14)	0.0429 (6)
H10A	0.2571	0.2488	−0.1932	0.052*
H10B	0.2776	0.3586	−0.2359	0.052*
H10C	0.2100	0.3639	−0.1750	0.052*
C11	0.60783 (18)	0.12949 (19)	−0.31128 (13)	0.0376 (5)
H11A	0.6754	0.1388	−0.2710	0.045*
H11B	0.6078	0.1749	−0.3562	0.045*
H11C	0.5986	0.0519	−0.3268	0.045*
C12	0.41716 (17)	0.11911 (19)	−0.32009 (12)	0.0383 (5)
H12A	0.3647	0.1514	−0.2974	0.046*
H12B	0.4180	0.0389	−0.3137	0.046*
H12C	0.3984	0.1372	−0.3753	0.046*
C13	0.74822 (15)	0.13688 (15)	0.07768 (10)	0.0248 (4)
C14	0.64297 (14)	0.05034 (14)	−0.03562 (10)	0.0227 (4)
C15	0.8561 (2)	0.2075 (2)	0.20481 (12)	0.0505 (7)
H15A	0.8447	0.2806	0.1806	0.061*
H15B	0.9295	0.1843	0.2114	0.061*
H15C	0.8427	0.2108	0.2555	0.061*
C16	0.7566 (2)	0.0352 (2)	0.19725 (13)	0.0497 (6)
H16A	0.8202	−0.0093	0.2197	0.060*
H16B	0.7030	−0.0101	0.1611	0.060*
H16C	0.7283	0.0620	0.2386	0.060*
C17	0.5431 (2)	−0.0643 (2)	−0.14191 (14)	0.0517 (7)
H17A	0.5973	−0.0915	−0.1650	0.062*
H17B	0.5132	0.0046	−0.1672	0.062*
H17C	0.4867	−0.1193	−0.1489	0.062*
C18	0.5902 (2)	−0.13590 (18)	−0.00738 (14)	0.0461 (6)
H18A	0.5902	−0.1068	0.0433	0.055*
H18B	0.6534	−0.1815	−0.0017	0.055*
H18C	0.5265	−0.1807	−0.0285	0.055*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.02435 (12)	0.01594 (12)	0.01541 (10)	−0.00310 (10)	0.00262 (8)	0.00065 (9)
S1	0.0229 (2)	0.0176 (2)	0.0248 (2)	−0.00239 (17)	0.00656 (17)	0.00079 (17)
S2	0.0293 (2)	0.0254 (2)	0.0194 (2)	−0.00704 (19)	0.01010 (17)	−0.00579 (17)
S3	0.0392 (3)	0.0296 (3)	0.0176 (2)	−0.0098 (2)	−0.00245 (17)	0.00309 (19)
O1	0.0253 (7)	0.0246 (7)	0.0318 (7)	0.0027 (5)	0.0018 (5)	−0.0055 (6)
O2	0.0211 (6)	0.0221 (6)	0.0150 (5)	−0.0037 (5)	0.0036 (4)	0.0001 (5)
O3	0.0392 (8)	0.0194 (6)	0.0208 (6)	−0.0091 (6)	0.0014 (6)	0.0033 (5)
N1	0.0233 (8)	0.0304 (9)	0.0263 (8)	0.0008 (7)	0.0051 (6)	−0.0010 (7)
N2	0.0241 (8)	0.0305 (9)	0.0337 (9)	−0.0085 (7)	0.0088 (7)	−0.0053 (7)
N3	0.0315 (10)	0.0321 (10)	0.0578 (12)	0.0118 (8)	0.0122 (9)	0.0017 (9)
N4	0.0232 (8)	0.0232 (8)	0.0220 (7)	−0.0034 (6)	0.0069 (6)	−0.0049 (6)
N5	0.0275 (9)	0.0296 (9)	0.0317 (9)	−0.0018 (7)	0.0138 (7)	−0.0072 (7)
N6	0.0259 (8)	0.0279 (8)	0.0228 (8)	−0.0047 (7)	0.0066 (6)	−0.0090 (6)
N7	0.0365 (9)	0.0233 (8)	0.0230 (8)	−0.0003 (7)	0.0095 (7)	0.0047 (6)

N8	0.0600 (12)	0.0338 (10)	0.0171 (8)	−0.0003 (9)	0.0069 (8)	0.0043 (7)
N9	0.0488 (11)	0.0195 (8)	0.0311 (9)	−0.0112 (7)	0.0057 (8)	0.0036 (7)
C1	0.0210 (9)	0.0298 (10)	0.0173 (8)	−0.0048 (7)	0.0017 (7)	−0.0024 (7)
C2	0.0293 (10)	0.0310 (10)	0.0201 (9)	0.0070 (8)	0.0052 (7)	0.0010 (7)
C3	0.0350 (11)	0.0282 (10)	0.0373 (11)	−0.0108 (9)	0.0108 (9)	−0.0026 (8)
C4	0.0286 (11)	0.0462 (13)	0.0469 (13)	−0.0125 (10)	0.0159 (10)	−0.0087 (11)
C5	0.0561 (17)	0.0305 (13)	0.088 (2)	0.0157 (12)	0.0206 (15)	−0.0013 (13)
C6	0.0405 (15)	0.0573 (18)	0.126 (3)	0.0196 (13)	0.0336 (17)	0.0057 (19)
C7	0.0260 (9)	0.0190 (8)	0.0226 (9)	−0.0042 (7)	0.0100 (7)	−0.0002 (7)
C8	0.0244 (9)	0.0182 (8)	0.0161 (7)	−0.0007 (7)	0.0043 (6)	0.0015 (6)
C9	0.0421 (12)	0.0292 (11)	0.0358 (11)	0.0013 (9)	0.0232 (9)	−0.0023 (9)
C10	0.0244 (11)	0.0551 (15)	0.0499 (14)	0.0008 (10)	0.0117 (9)	−0.0132 (11)
C11	0.0398 (12)	0.0404 (12)	0.0365 (12)	−0.0031 (10)	0.0173 (9)	−0.0175 (10)
C12	0.0365 (12)	0.0452 (13)	0.0305 (11)	−0.0116 (10)	0.0053 (9)	−0.0159 (10)
C13	0.0321 (10)	0.0233 (9)	0.0198 (9)	0.0083 (8)	0.0086 (7)	0.0032 (7)
C14	0.0254 (9)	0.0180 (9)	0.0259 (9)	0.0021 (7)	0.0093 (7)	0.0032 (7)
C15	0.0732 (18)	0.0487 (14)	0.0185 (10)	0.0022 (12)	−0.0046 (10)	−0.0022 (9)
C16	0.0736 (18)	0.0499 (15)	0.0279 (11)	0.0052 (13)	0.0181 (11)	0.0167 (10)
C17	0.0749 (18)	0.0317 (12)	0.0387 (13)	−0.0234 (12)	0.0006 (12)	−0.0026 (10)
C18	0.0562 (15)	0.0274 (11)	0.0545 (15)	−0.0105 (10)	0.0153 (12)	0.0143 (10)

Geometric parameters (Å, º)

Co1—O1	1.9387 (13)	C3—H3A	0.9800
Co1—O2	1.9538 (11)	C3—H3B	0.9800
Co1—O3	1.9101 (12)	C3—H3C	0.9800
Co1—S1	2.2072 (5)	C4—H4A	0.9800
Co1—S2	2.2133 (6)	C4—H4B	0.9800
Co1—S3	2.2008 (5)	C4—H4C	0.9800
S1—C1	1.7358 (19)	C5—H5A	0.9800
S2—C7	1.7530 (18)	C5—H5B	0.9800
S3—C13	1.7455 (19)	C5—H5C	0.9800
O1—C2	1.262 (2)	C6—H6A	0.9800
O2—C8	1.272 (2)	C6—H6B	0.9800
O3—C14	1.261 (2)	C6—H6C	0.9800
N1—C1	1.324 (2)	C9—H9A	0.9800
N1—C2	1.348 (3)	C9—H9B	0.9800
N2—C1	1.358 (2)	C9—H9C	0.9800
N2—C3	1.449 (3)	C10—H10A	0.9800
N2—C4	1.457 (3)	C10—H10B	0.9800
N3—C2	1.358 (2)	C10—H10C	0.9800
N3—C6	1.450 (3)	C11—H11A	0.9800
N3—C5	1.460 (3)	C11—H11B	0.9800
N4—C7	1.320 (2)	C11—H11C	0.9800
N4—C8	1.349 (2)	C12—H12A	0.9800
N5—C7	1.351 (2)	C12—H12B	0.9800
N5—C10	1.455 (3)	C12—H12C	0.9800
N5—C9	1.459 (2)	C15—H15A	0.9800

N6—C8	1.348 (2)	C15—H15B	0.9800
N6—C11	1.450 (2)	C15—H15C	0.9800
N6—C12	1.454 (2)	C16—H16A	0.9800
N7—C13	1.311 (2)	C16—H16B	0.9800
N7—C14	1.349 (2)	C16—H16C	0.9800
N8—C13	1.355 (2)	C17—H17A	0.9800
N8—C15	1.452 (3)	C17—H17B	0.9800
N8—C16	1.462 (3)	C17—H17C	0.9800
N9—C14	1.350 (2)	C18—H18A	0.9800
N9—C17	1.452 (3)	C18—H18B	0.9800
N9—C18	1.457 (3)	C18—H18C	0.9800

S1—Co1—S2	88.196 (19)	N3—C6—H6A	109.5
S3—Co1—S1	87.97 (2)	N3—C6—H6B	109.5
S3—Co1—S2	90.40 (2)	H6A—C6—H6B	109.5
O1—Co1—O2	86.80 (5)	N3—C6—H6C	109.5
O3—Co1—O1	85.72 (6)	H6A—C6—H6C	109.5
O3—Co1—O2	86.54 (5)	H6B—C6—H6C	109.5
O1—Co1—S1	93.47 (4)	N4—C7—N5	115.05 (16)
O2—Co1—S2	90.50 (4)	N4—C7—S2	128.47 (14)
O3—Co1—S3	95.02 (4)	N5—C7—S2	116.45 (13)
O1—Co1—S3	92.35 (4)	O2—C8—N6	117.19 (16)
O1—Co1—S2	176.83 (4)	O2—C8—N4	127.51 (16)
O2—Co1—S3	178.17 (4)	N6—C8—N4	115.16 (15)
O3—Co1—S1	176.93 (4)	N5—C9—H9A	109.5
O2—Co1—S1	90.46 (4)	N5—C9—H9B	109.5
O3—Co1—S2	92.47 (5)	H9A—C9—H9B	109.5
C1—S1—Co1	107.22 (7)	N5—C9—H9C	109.5
C7—S2—Co1	105.50 (6)	H9A—C9—H9C	109.5
C13—S3—Co1	107.50 (6)	H9B—C9—H9C	109.5
C2—O1—Co1	127.72 (13)	N5—C10—H10A	109.5
C8—O2—Co1	119.05 (10)	N5—C10—H10B	109.5
C14—O3—Co1	131.79 (12)	H10A—C10—H10B	109.5
C1—N1—C2	123.39 (16)	N5—C10—H10C	109.5
C1—N2—C3	123.10 (16)	H10A—C10—H10C	109.5
C1—N2—C4	120.09 (17)	H10B—C10—H10C	109.5
C3—N2—C4	116.73 (17)	N6—C11—H11A	109.5
C2—N3—C6	121.7 (2)	N6—C11—H11B	109.5
C2—N3—C5	119.72 (19)	H11A—C11—H11B	109.5
C6—N3—C5	117.14 (19)	N6—C11—H11C	109.5
C7—N4—C8	122.94 (15)	H11A—C11—H11C	109.5
C7—N5—C10	119.65 (16)	H11B—C11—H11C	109.5
C7—N5—C9	124.57 (16)	N6—C12—H12A	109.5
C10—N5—C9	115.77 (16)	N6—C12—H12B	109.5
C8—N6—C11	120.28 (15)	H12A—C12—H12B	109.5
C8—N6—C12	123.02 (16)	N6—C12—H12C	109.5
C11—N6—C12	116.70 (15)	H12A—C12—H12C	109.5
C13—N7—C14	125.12 (16)	H12B—C12—H12C	109.5

C13—N8—C15	123.90 (18)	N7—C13—N8	116.37 (17)
C13—N8—C16	121.52 (19)	N7—C13—S3	129.28 (14)
C15—N8—C16	114.50 (18)	N8—C13—S3	114.34 (15)
C14—N9—C17	120.07 (16)	O3—C14—N7	130.00 (17)
C14—N9—C18	122.42 (18)	O3—C14—N9	115.66 (16)
C17—N9—C18	117.14 (17)	N7—C14—N9	114.34 (16)
N1—C1—N2	115.11 (16)	N8—C15—H15A	109.5
N1—C1—S1	129.94 (15)	N8—C15—H15B	109.5
N2—C1—S1	114.95 (14)	H15A—C15—H15B	109.5
O1—C2—N1	129.01 (17)	N8—C15—H15C	109.5
O1—C2—N3	115.95 (18)	H15A—C15—H15C	109.5
N1—C2—N3	114.94 (18)	H15B—C15—H15C	109.5
N2—C3—H3A	109.5	N8—C16—H16A	109.5
N2—C3—H3B	109.5	N8—C16—H16B	109.5
H3A—C3—H3B	109.5	H16A—C16—H16B	109.5
N2—C3—H3C	109.5	N8—C16—H16C	109.5
H3A—C3—H3C	109.5	H16A—C16—H16C	109.5
H3B—C3—H3C	109.5	H16B—C16—H16C	109.5
N2—C4—H4A	109.5	N9—C17—H17A	109.5
N2—C4—H4B	109.5	N9—C17—H17B	109.5
H4A—C4—H4B	109.5	H17A—C17—H17B	109.5
N2—C4—H4C	109.5	N9—C17—H17C	109.5
H4A—C4—H4C	109.5	H17A—C17—H17C	109.5
H4B—C4—H4C	109.5	H17B—C17—H17C	109.5
N3—C5—H5A	109.5	N9—C18—H18A	109.5
N3—C5—H5B	109.5	N9—C18—H18B	109.5
H5A—C5—H5B	109.5	H18A—C18—H18B	109.5
N3—C5—H5C	109.5	N9—C18—H18C	109.5
H5A—C5—H5C	109.5	H18A—C18—H18C	109.5
H5B—C5—H5C	109.5	H18B—C18—H18C	109.5

O1—Co1—S1—C1	−11.81 (7)	C6—N3—C2—O1	171.6 (2)
O2—Co1—S1—C1	−98.64 (7)	C5—N3—C2—O1	5.4 (3)
S3—Co1—S1—C1	80.42 (6)	C6—N3—C2—N1	−5.1 (3)
S2—Co1—S1—C1	170.88 (6)	C5—N3—C2—N1	−171.3 (2)
O3—Co1—S2—C7	−58.62 (7)	C8—N4—C7—N5	166.00 (16)
O2—Co1—S2—C7	27.94 (7)	C8—N4—C7—S2	−16.0 (3)
S3—Co1—S2—C7	−153.66 (6)	C10—N5—C7—N4	−3.6 (3)
S1—Co1—S2—C7	118.38 (6)	C9—N5—C7—N4	177.45 (17)
O3—Co1—S3—C13	−9.91 (8)	C10—N5—C7—S2	178.16 (16)
O1—Co1—S3—C13	−95.81 (8)	C9—N5—C7—S2	−0.8 (2)
S1—Co1—S3—C13	170.79 (7)	Co1—S2—C7—N4	−2.14 (18)
S2—Co1—S3—C13	82.61 (7)	Co1—S2—C7—N5	175.85 (12)
O3—Co1—O1—C2	−149.85 (16)	Co1—O2—C8—N6	−129.30 (14)
O2—Co1—O1—C2	123.39 (16)	Co1—O2—C8—N4	55.2 (2)
S3—Co1—O1—C2	−54.99 (16)	C11—N6—C8—O2	6.1 (2)
S1—Co1—O1—C2	33.12 (16)	C12—N6—C8—O2	−174.66 (17)
O3—Co1—O2—C8	36.87 (13)	C11—N6—C8—N4	−177.83 (17)

O1—Co1—O2—C8	122.77 (13)	C12—N6—C8—N4	1.4 (3)
S1—Co1—O2—C8	−143.78 (12)	C7—N4—C8—O2	−10.6 (3)
S2—Co1—O2—C8	−55.58 (12)	C7—N4—C8—N6	173.88 (16)
O1—Co1—O3—C14	98.05 (17)	C14—N7—C13—N8	−179.65 (18)
O2—Co1—O3—C14	−174.91 (17)	C14—N7—C13—S3	−0.9 (3)
S3—Co1—O3—C14	6.06 (17)	C15—N8—C13—N7	178.0 (2)
S2—Co1—O3—C14	−84.56 (17)	C16—N8—C13—N7	1.5 (3)
C2—N1—C1—N2	−165.51 (17)	C15—N8—C13—S3	−0.9 (3)
C2—N1—C1—S1	15.0 (3)	C16—N8—C13—S3	−177.41 (17)
C3—N2—C1—N1	−175.62 (17)	Co1—S3—C13—N7	10.1 (2)
C4—N2—C1—N1	8.0 (2)	Co1—S3—C13—N8	−171.18 (13)
C3—N2—C1—S1	4.0 (2)	Co1—O3—C14—N7	3.3 (3)
C4—N2—C1—S1	−172.41 (14)	Co1—O3—C14—N9	−177.98 (13)
Co1—S1—C1—N1	−6.50 (19)	C13—N7—C14—O3	−8.0 (3)
Co1—S1—C1—N2	173.98 (12)	C13—N7—C14—N9	173.27 (18)
Co1—O1—C2—N1	−36.0 (3)	C17—N9—C14—O3	2.7 (3)
Co1—O1—C2—N3	147.83 (15)	C18—N9—C14—O3	175.48 (19)
C1—N1—C2—O1	6.5 (3)	C17—N9—C14—N7	−178.4 (2)
C1—N1—C2—N3	−177.27 (18)	C18—N9—C14—N7	−5.6 (3)