Bis[benzyl 2-(heptan-4-ylidene)hydrazine-1-carboxylate]bis(thiocyanato)cobalt(II)

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The title compound, [Co(NCS)2(C15H22N2O2)2] or C32H44CoN6O4S2, was prepared from cobalt(II) nitrate, benzyl carbazate and ammonium thiocyanate in the presence of 4-heptanone. The compound crystallizes with two centrosymmetric complexes in which the cobalt(II) atoms have a trans-CoO2N4 octahedral coordination geometry. In the crystal, N—H···S, C—H···S and C—H···π contacts stack the complex molecules along the b-axis direction.

Structure description

Our previous work involving Schiff-base complexes derived from benzyl carbazate and carbonyl compounds was limited to short-chain dialkyl ketones (Nithya et al., 2016, 2017). In order to investigate and compare the coordinating ability of benzyl carbazate Schiff bases derived from higher homologues, we have prepared the title cobalt complex from benzyl carbazate with 4-heptanone with thiocyanate as the charge-balancing anionic ligand. We report the molecular and crystal structure of the complex here. Neither the structure of the bidentate ligand used here, nor of its complexes, have been reported previously.

The title compound, Co(C15H22N2O2)2(NCS)2, crystallizes with two centrosymmetric, octahedral cobalt(II) complexes (1) and (2) in the monoclinic unit cell. These are differentiated in the numbering scheme by leading 1 and 2 characters, respectively (Fig. 1). The molecules overlay with an r.m.s. deviation of 0.602 Å (Fig. 2), with the greatest conformational differences in the vicinity of the n-propyl substituents on C12 and C22 (Macrae et al., 2008). The benzyl-2-(heptan-4-ylidene)hydrazine-1-carboxylate ligand is N,O-bidentate with two such ligands in the equatorial plane, binding through the imine N and carbonyl O atoms. The N bound thiocyanato ligands occupy trans-axial positions and are slightly kinked, with N—C—S and Co—N—C bond angles of 177.3 (6)

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data reports
and 169.8 (5)^\circ \text{, respectively, in (1) and 178.9 (6) and 165.6 (6)^\circ \text{, respectively, in (2). With the exception of the di-n-propyl substituents on the C12 and C22 carbon atoms, the non-hydrogen atoms of the bidentate ligands lie close to the equatorial planes of both complexes with r.m.s. deviations from the best-fit plane through N11, N12, O11, C11, O12, C13 \ldots C19 of 0.079 Å for (1) and 0.094 Å for the corresponding plane in (2). Pairs of intramolecular C—H—O hydrogen bonds form in both molecules, Table 1, Fig. 1. In the crystal, N—H—S and weaker C—H—S hydrogen bonds combine with a C—H— \pi contact between molecules (1) and (2), Table 1, to stack the complexes along the b-axis direction, Fig. 3.

Synthesis and crystallization

Cobalt(II) nitrate (0.146 g, 0.50 mmol) dissolved in 10 ml of doubly distilled water was added to a methanolic solution (10 ml) of benzyl carbazate (0.166 g, 1.00 mmol) and ammonium thiocyanate (0.076 g, 1.00 mmol). The solution was then layered with 4-heptanone (0.1 ml, 1 mmol) and the colour changed from pink to blue. The resulting mixture was retained for slow evaporation at room temperature, resulting in olive-green crystals, which were collected, washed with water and air-dried. Yield 81.5% (0.119 g) with respect to the metal.

Figure 1
The molecular structure of the title compound with ellipsoids drawn at the 50% probability level. Intramolecular hydrogen bonds are drawn as dashed lines. Labelled atom are related to unlabelled atoms by the symmetry operations \(-x, -y, -z\) for molecule (1) and \(-x + 1, -y, -z + 1\) for molecule (2).

Figure 2
An overlay of the two unique molecules of the title compound (r.m.s. deviation = 0.602 Å).
Table 1
Hydrogen-bond geometry (Å, °).

| D—H⋯A | D—H | H⋯A | D⋯A | D—H⋯A |
|--------|------|-----|-----|-------|
| N12—H12⋯S1i | 0.85 (8) | 2.47 (8) | 3.298 (6) | 166 (7) |
| C121—H12B⋯S1i | 0.99 | 2.93 | 3.786 (7) | 146 |
| N22—H22⋯S2ii | 0.96 (8) | 2.55 (8) | 3.480 (6) | 164 (6) |
| C25—H25⋯Cg6 | 0.95 | 2.94 | 3.811 (7) | 153 |
| C124—H12I⋯O11iii | 0.99 | 2.48 | 3.259 (9) | 153 |
| C221—H22A⋯O21iv | 0.99 | 2.38 | 3.229 (8) | 144 |
| C13—H13B⋯Cg6 | 0.99 | 2.60 | 3.464 (7) | 145 |

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

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Crystals of this compound were not of good quality and, despite several data collections on different samples with both Cu and Mo radiation, the residuals reported here were the best that could be obtained.

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Table 2
Experimental details.

| Crystal data | Chemical formula | [Co(NCS)2(C15H22N2O2)2] |
|--------------|-------------------|-------------------------|
| Crystal system, space group | Monoclinic, P21/c |
| Temperature (K) | 100 |
| a, b, c (Å) | 23.194 (3), 9.825 (1), 16.475 (2) |
| V (Å³) | 3606.1 (8) |
| Z | 4 |
| Radiation type | Cu Kα |
| μ (mm⁻¹) | 5.16 |
| Crystal size (mm) | 0.21 × 0.15 × 0.11 |

Data collection

Diffractometer | Agilent SuperNova, Dual, Cu at zero, Atlas |
Absorption correction | Gaussian (CrysAlis PRO: Agilent, 2014) |
Tmin, Tmax | 0.839, 0.912 |
No. of measured, independent and observed [I > 2σ(I)] reflections | 34985, 7198, 4299 |
Rint | 0.153 |
(Sin θ/λ)max | 0.625 |
Reflecton | 0.094, 0.263, 1.07 |
No. of reflections | 7198 |
No. of parameters | 419 |
H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
Δρmax, Δρmin (e Å⁻³) | 1.19, −0.62 |

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**Bis[benzyl 2-(heptan-4-ylidene)hydrazine-1-carboxylate]bis(thiocyanato)cobalt(II)**

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Crystal data

$[\text{Co(NCS)}_2(\text{C}_{15}\text{H}_{22}\text{N}_2\text{O}_2)_2]$

$M_r = 699.78$

Monoclinic, $P2_1/c$

$\alpha = 23.194 (3)$ Å

$b = 9.825 (1)$ Å

$c = 16.475 (2)$ Å

$\beta = 106.154 (13)^\circ$

$V = 3606.1 (8)$ Å$^3$

$Z = 4$

Data collection

Agilent SuperNova, Dual, Cu at zero, Atlas diffractometer

Radiation source: sealed X-ray tube, SuperNova (Cu) X-ray Source

Detector resolution: 5.1725 pixels mm$^{-1}$

$\omega$ scans

Absorption correction: gaussian

(CrysAlis PRO; Agilent, 2014)

$T_{\text{min}} = 0.839, T_{\text{max}} = 0.912$

Refinement

Refinement on $F^2$

Least-squares matrix: full

$\sum w(F^2 - F)^2 / \sigma(F^2) = 0.094$

$\sum wR(F^2) = 0.263$

$S = 1.07$

7198 reflections

419 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F^2) + (0.0923P)^2 + 14.0183P]$

where $P = (\text{Fo}^2 + 2Fc^2)/3$

$\Delta \rho_{\text{max}} = 1.19$ e Å$^{-3}$

$\Delta \rho_{\text{min}} = -0.62$ 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.

**Refinement.** 1 reflection with $\text{Fo} >>> \text{Fc}$ was omitted from the final refinement cycles.
### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|   | x        | y        | z        | Uiso*/Ueq |
|---|----------|----------|----------|-----------|
| Co1 | 0.000000 | 0.000000 | 0.000000 | 0.0298   |
| N11 | 0.0137 (2)| —1.1536 (6)| 0.1013 (3)| 0.0322   |
| C12 | —0.0084 (3)| —0.2731 (7)| 0.1072 (4)| 0.0323   |
| C121| 0.0110 (3)| —0.3609 (7)| 0.1846 (4)| 0.0341   |
| H12A| —0.021053| —0.427640| 0.184426 | 0.041*    |
| H12B| 0.016911 | —0.303327| 0.235640 | 0.041*    |
| C122| 0.0698 (3)| —0.4373 (8)| 0.1883 (5)| 0.0419   |
| H12C| 0.065812 | —0.483492| 0.133592 | 0.050*    |
| H12D| 0.103087 | —0.370939| 0.197190 | 0.050*    |
| C123| 0.0847 (4)| —0.5416 (9)| 0.2586 (5)| 0.052 (2) |
| H12E| 0.083817 | —0.498159| 0.311823 | 0.078*    |
| H12F| 0.124762 | —0.578869| 0.264194 | 0.078*    |
| H12G| 0.055024 | —0.615241| 0.245368 | 0.078*    |
| C124| —0.0538 (3)| —0.3287 (8)| 0.0323 (4)| 0.0364   |
| H12H| —0.045942| —0.426947| 0.027124 | 0.044*    |
| H12I| —0.049392| —0.282823| —0.019149| 0.044*    |
| C125| —0.1180 (3)| —0.3104 (8)| 0.0371 (5)| 0.0441   |
| H12J| —0.128347| —0.212379| 0.032133 | 0.053*    |
| H12K| —0.120808| —0.342201| 0.092904 | 0.053*    |
| C126| —0.1631 (3)| —0.3887 (8)| —0.0324 (5)| 0.0448   |
| H12L| —0.157943| —0.363491| —0.087509| 0.067*    |
| H12M| —0.203926| —0.366375| —0.030912| 0.067*    |
| H12N| —0.156212| —0.486701| —0.023340| 0.067*    |
| N12 | 0.0573 (3)| —0.1037 (6)| 0.1712 (4)| 0.0327   |
| H12 | 0.070 (3)| —0.136 (8)| 0.221 (5)| 0.039*    |
| O11 | 0.0806 (2)| 0.0600 (5)| 0.0883 (3)| 0.0323   |
| C11 | 0.0897 (3)| 0.0026 (7)| 0.1561 (4)| 0.0298   |
| O12 | 0.1327 (2)| 0.0389 (5)| 0.2253 (3)| 0.0330   |
| C13 | 0.1703 (3)| 0.1503 (7)| 0.2106 (4)| 0.0333   |
| H13A| 0.145852 | 0.234005 | 0.196051 | 0.040*    |
| H13B| 0.186039 | 0.127334 | 0.162198 | 0.040*    |
| C14 | 0.2213 (3)| 0.1757 (7)| 0.2867 (4)| 0.0347   |
| C15 | 0.2366 (3)| 0.0952 (8)| 0.3578 (5)| 0.0392   |
| H15 | 0.212777 | 0.017778 | 0.360963 | 0.047*    |
| C16 | 0.2865 (3)| 0.1251 (8)| 0.4254 (5)| 0.0438   |
| H16 | 0.296721 | 0.068016 | 0.473807 | 0.053*    |
| C17 | 0.3209 (3)| 0.2383 (8)| 0.4212 (5)| 0.0408   |
| H17 | 0.355073 | 0.258792 | 0.466877 | 0.049*    |
| C18 | 0.3058 (3)| 0.3213 (9)| 0.3514 (5)| 0.0468   |
| H18 | 0.329365 | 0.399711 | 0.349200 | 0.056*    |
| C19 | 0.2563 (3)| 0.2911 (8)| 0.2838 (5)| 0.0402   |
| H19 | 0.246196 | 0.348720 | 0.235564 | 0.048*    |
| N13 | —0.0433 (2)| 0.1289 (6)| 0.0627 (4)| 0.0333   |
| C110| —0.0677 (3)| 0.2137 (7)| 0.0880 (4)| 0.0323   |
| S1  | —0.10507 (8)| 0.33019 (19)| 0.12477 (11)| 0.0400   |

IUCrData (2019). 4, x190812
| Atom | x      | y      | z      | Uiso  |
|------|--------|--------|--------|-------|
| Co2  | 0.50000| 0.00000| 0.50000| 0.0305 |
| N21  | 0.4960 (2) | 0.1867 (6) | 0.4197 (3) | 0.0317 (12) |
| C22  | 0.5324 (3) | 0.2874 (7) | 0.4219 (5) | 0.0362 (16) |
| C221 | 0.5867 (3) | 0.2997 (7) | 0.4961 (5) | 0.0353 (15) |
| H22A | 0.579237 | 0.2414 (8) | 0.4786 (5) | 0.0474 (19) |
| H22B | 0.593417 | 0.2414 (8) | 0.4786 (5) | 0.0474 (19) |
| C222 | 0.6438 (3) | 0.142286 | 0.468111 | 0.057* |
| H22D | 0.649752 | 0.284469 | 0.427178 | 0.057* |
| C223 | 0.6985 (4) | 0.2666 (11) | 0.5525 (6) | 0.065 (3) |
| H22E | 0.703882 | 0.364756 | 0.562330 | 0.097* |
| H22F | 0.734119 | 0.228732 | 0.539771 | 0.097* |
| H22G | 0.692954 | 0.222654 | 0.603170 | 0.097* |
| C224 | 0.5242 (3) | 0.3964 (7) | 0.3546 (5) | 0.0363 (15) |
| H22H | 0.504172 | 0.356725 | 0.298601 | 0.044* |
| H22I | 0.563979 | 0.431013 | 0.353031 | 0.044* |
| C225 | 0.4860 (3) | 0.5153 (7) | 0.3730 (5) | 0.0381 (16) |
| H22J | 0.445356 | 0.481693 | 0.370723 | 0.046* |
| H22K | 0.504616 | 0.550544 | 0.430677 | 0.046* |
| C226 | 0.4811 (4) | 0.6303 (7) | 0.3089 (5) | 0.0420 (17) |
| H22L | 0.512139 | 0.664875 | 0.311985 | 0.063* |
| H22M | 0.456602 | 0.704064 | 0.321719 | 0.063* |
| H22N | 0.462394 | 0.595675 | 0.251870 | 0.063* |
| N22  | 0.4473 (3) | 0.1744 (6) | 0.3494 (4) | 0.0353 (13) |
| H22  | 0.435 (3) | 0.238 (8) | 0.304 (5) | 0.042* |
| O21  | 0.4248 (2) | −0.0321 (5) | 0.3958 (3) | 0.0343 (11) |
| C21  | 0.4151 (3) | 0.0578 (7) | 0.3420 (4) | 0.0327 (14) |
| O22  | 0.3730 (2) | 0.0517 (5) | 0.2689 (3) | 0.0371 (11) |
| C23  | 0.3364 (2) | −0.0692 (7) | 0.2566 (5) | 0.0393 (16) |
| H23A | 0.317866 | −0.079440 | 0.303634 | 0.047* |
| H23B | 0.361459 | −0.150441 | 0.255731 | 0.047* |
| C24  | 0.2882 (3) | −0.0577 (7) | 0.1742 (4) | 0.0351 (15) |
| C25  | 0.2887 (3) | 0.0403 (7) | 0.1141 (4) | 0.0339 (15) |
| H25  | 0.320617 | 0.104275 | 0.124184 | 0.041* |
| C26  | 0.2432 (3) | 0.0459 (7) | 0.0395 (4) | 0.0363 (15) |
| H26  | 0.243128 | 0.115637 | −0.000417 | 0.044* |
| C27  | 0.1972 (3) | −0.0505 (8) | 0.0226 (5) | 0.0415 (17) |
| H27  | 0.166382 | −0.048600 | −0.029316 | 0.050* |
| C28  | 0.1970 (3) | −0.1493 (8) | 0.0828 (5) | 0.0430 (17) |
| H28  | 0.165563 | −0.214556 | 0.072367 | 0.052* |
| C29  | 0.2422 (3) | −0.1534 (8) | 0.1576 (5) | 0.0410 (17) |
| H29  | 0.241882 | −0.222004 | 0.198078 | 0.049* |
| N23  | 0.5525 (3) | −0.0819 (6) | 0.4321 (4) | 0.0357 (13) |
| C210 | 0.5825 (3) | −0.1012 (7) | 0.3862 (4) | 0.0320 (14) |
| S2   | 0.62538 (8) | −0.1277 (2) | 0.32411 (12) | 0.0406 (4) |
Atomic displacement parameters (Å²)

|     | $U_{11}$   | $U_{22}$   | $U_{33}$   | $U_{12}$   | $U_{13}$   | $U_{23}$   |
|-----|------------|------------|------------|------------|------------|------------|
| Co  | 0.0294 (7) | 0.0330 (9) | 0.0297 (8) | -0.0011 (7)| 0.0125 (6) | 0.0001 (7) |
| N1  | 0.035 (3)  | 0.035 (3)  | 0.031 (3)  | -0.001 (2) | 0.015 (2)  | -0.001 (2) |
| C1  | 0.034 (3)  | 0.036 (4)  | 0.032 (3)  | -0.002 (3) | 0.018 (3)  | -0.002 (3) |
| C11 | 0.040 (4)  | 0.027 (4)  | 0.039 (4)  | -0.006 (3) | 0.018 (3)  | -0.002 (3) |
| C12 | 0.043 (4)  | 0.048 (5)  | 0.038 (4)  | 0.009 (3)  | 0.016 (3)  | -0.001 (3) |
| C13 | 0.064 (5)  | 0.050 (5)  | 0.046 (5)  | 0.021 (4)  | 0.021 (4)  | 0.000 (4)  |
| C14 | 0.037 (4)  | 0.037 (4)  | 0.039 (4)  | -0.001 (3)| 0.0125 (6) | 0.0001 (7) |
| C15 | 0.037 (4)  | 0.045 (5)  | 0.052 (5)  | 0.003 (3)  | 0.015 (3)  | 0.007 (4)  |
| C16 | 0.043 (4)  | 0.048 (5)  | 0.043 (4)  | -0.009 (4) | 0.012 (3)  | 0.009 (4)  |
| C17 | 0.034 (3)  | 0.035 (3)  | 0.028 (3)  | -0.004 (2) | 0.008 (2)  | 0.006 (2)  |
| C18 | 0.035 (2)  | 0.034 (3)  | 0.030 (2)  | -0.003 (2) | 0.0119 (19)| -0.001 (2) |
| C19 | 0.031 (3)  | 0.035 (4)  | 0.026 (3)  | 0.002 (3)  | 0.013 (3)  | 0.000 (3)  |
| C20 | 0.032 (2)  | 0.036 (3)  | 0.032 (2)  | -0.0044 (19)| 0.0096 (19)| 0.002 (2)  |
| C21 | 0.032 (3)  | 0.035 (4)  | 0.035 (4)  | -0.007 (3) | 0.013 (3)  | 0.001 (3)  |
| C22 | 0.032 (3)  | 0.039 (4)  | 0.038 (4)  | -0.001 (3) | 0.017 (3)  | -0.006 (3) |
| C23 | 0.039 (4)  | 0.043 (4)  | 0.038 (4)  | -0.005 (3) | 0.014 (3)  | -0.007 (3) |
| N2  | 0.034 (3)  | 0.032 (3)  | 0.036 (3)  | 0.000 (2)  | 0.013 (2)  | 0.000 (2)  |
| C24 | 0.035 (3)  | 0.028 (4)  | 0.031 (3)  | -0.005 (3) | 0.005 (3)  | 0.001 (3)  |
| S1  | 0.0469 (10)| 0.0344 (10)| 0.0380 (9) | 0.0061 (8) | 0.0108 (8) | -0.0038 (7)|
| Co2 | 0.0319 (8) | 0.0302 (8) | 0.0331 (8) | -0.0011 (7)| 0.0152 (6) | 0.0002 (7) |
| N21 | 0.038 (3)  | 0.028 (3)  | 0.033 (3)  | -0.001 (2) | 0.017 (2)  | 0.000 (2)  |
| C22 | 0.041 (4)  | 0.030 (4)  | 0.042 (4)  | 0.000 (3)  | 0.020 (3)  | -0.003 (3) |
| C23 | 0.031 (3)  | 0.027 (4)  | 0.052 (4)  | -0.005 (3) | 0.019 (3)  | 0.006 (3)  |
| C24 | 0.042 (4)  | 0.040 (5)  | 0.063 (5)  | -0.001 (3) | 0.021 (4)  | 0.003 (4)  |
| C25 | 0.044 (5)  | 0.073 (7)  | 0.076 (7)  | -0.012 (5) | 0.016 (4)  | 0.023 (5)  |
| C26 | 0.041 (4)  | 0.031 (4)  | 0.044 (4)  | -0.002 (3) | 0.021 (3)  | -0.001 (3) |
| C27 | 0.050 (4)  | 0.030 (4)  | 0.041 (4)  | 0.003 (3)  | 0.023 (3)  | 0.004 (3)  |
| C28 | 0.060 (5)  | 0.024 (4)  | 0.047 (4)  | -0.005 (3) | 0.024 (4)  | -0.002 (3)|
| N22 | 0.041 (3)  | 0.031 (3)  | 0.036 (3)  | 0.000 (3)  | 0.015 (3)  | 0.006 (3)  |
| O21 | 0.038 (3)  | 0.034 (3)  | 0.033 (3)  | -0.001 (2) | 0.014 (2)  | 0.005 (2)  |
| C29 | 0.037 (3)  | 0.032 (3)  | 0.039 (3)  | 0.000 (2)  | 0.013 (3)  | -0.001 (2) |
| C210| 0.033 (3)  | 0.031 (4)  | 0.035 (4)  | 0.000 (3)  | 0.013 (3)  | -0.009 (3) |
Geometric parameters (Å, º)

|          |        |        |        |        |        |        |
|----------|--------|--------|--------|--------|--------|--------|
| Co1—N13  | 2.064  | Co2—N23| 2.036  |
| Co1—N13i | 2.064  | Co2—N23ii| 2.036  |
| Co1—O11  | 2.109  | Co2—O21 | 2.103  |
| Co1—O11i | 2.109  | Co2—O21ii| 2.103  |
| N11—C12  | 1.295  | N21—C22 | 1.293  |
| N11—N12  | 1.393  | N21—N22 | 1.380  |
| C12—C124 | 1.486  | C22—C221| 1.496  |
| C12—C121 | 1.501  | C22—C224| 1.515  |
| C121—C122 | 1.544  | C221—C222| 1.542  |
| C121—H12A | 0.9900 | C221—H22A| 0.9900  |
| C121—H12B | 0.9900 | C221—H22B| 0.9900  |
| N12—C11  | 1.350  | N22—C21 | 1.354  |
| N12—H12  | 0.85   | N22—H22 | 0.96   |
| O11—C11  | 1.216  | O21—C21 | 1.227  |
| C11—O12  | 1.338  | C21—O22 | 1.325  |
| O12—C13  | 1.462  | O22—C23 | 1.442  |
| C13—C14  | 1.487  | C23—C24 | 1.503  |
| C13—H13A | 0.9900 | C23—H23A| 0.9900  |
| C13—H13B | 0.9900 | C23—H23B| 0.9900  |
| C14—C15  | 1.375  | C24—C25 | 1.383  |
| C14—C19  | 1.403  | C24—C29 | 1.392  |
| C15—C16  | 1.395  | C25—C26 | 1.380  |
| C15—H15  | 0.9500 | C25—H25 | 0.9500  |
| C16—C17  | 1.381  | C26—C27 | 1.396  |
| C16—H16  | 0.9500 | C26—H26 | 0.9500  |
| C17—C18  | 1.375  | C27—C28 | 1.388  |
| C17—H17  | 0.9500 | C27—H27 | 0.9500  |
| Bond          | Distance (Å) | Bond          | Distance (Å) | Bond          | Distance (Å) |
|---------------|--------------|---------------|--------------|---------------|--------------|
| C18—C19       | 1.391 (11)   | C28—C29       | 1.378 (11)   | C18—H18      | 0.9500       |
| C18—H18      | 0.9500       | C28—H28      | 0.9500       | C19—H19      | 0.9500       |
| N13—C110     | 1.148 (9)    | N23—C210     | 1.176 (8)    | C110—S1      | 1.649 (7)    |
| N13—C10—N11  | 91.7 (2)     | N23—Co2—N21i | 86.1 (2)     | N13—Co1—N11  | 88.4 (2)     |
| N13—Co1—O11  | 86.8 (2)     | N23—Co2—O21  | 91.2 (2)     | N13—Co1—O11  | 93.2 (2)     |
| N13—Co1—O11i | 86.8 (2)     | N23—Co2—O21i | 91.2 (2)     | O11—Co1—O11i | 180.0        |
| N13—Co1—O11ii| 86.8 (2)     | N23—Co2—O21ii| 88.8 (2)     | O11—Co1—O11  | 180.0 (3)    |
| N13—Co1—N11  | 91.7 (2)     | N23—Co2—N21i | 86.1 (2)     | N13—Co1—N11  | 91.7 (2)     |
| N13—Co1—N11i | 91.7 (2)     | N23—Co2—N21ii| 104.29 (19)  | N13—Co1—N11i| 88.4 (2)     |
| N13—Co1—N11ii| 91.7 (2)     | N23—Co2—N21i | 93.9 (2)     | N13—Co1—N11ii| 75.87 (19)  |
| N13—Co1—N11iii| 91.7 (2)    | N23—Co2—N21ii| 93.9 (2)     | N13—Co1—N11iii| 91.7 (2)  |
| N13—Co1—N11iv| 91.7 (2)    | N23—Co2—N21iv| 108.2 (4)    | N11—Co1—N11iv| 75.87 (19)  |
| N13—Co1—N11v | 91.7 (2)     | N23—Co2—N21i | 104.29 (19)  | N11—Co1—N11v| 75.87 (19)  |
| C12—N11—N12  | 117.9 (6)    | C22—N21—N22  | 117.7 (6)    | C12—N11—N12i| 180.0        |
| C12—N11—Co1  | 134.5 (5)    | C22—N21—Co2  | 133.5 (5)    | C12—N11—Co1  | 107.7 (4)    |
| N12—N11—Co1  | 107.7 (4)    | N22—N21—Co2  | 108.2 (4)    | N11—C12—C124 | 118.3 (6)    |
| N11—C12—C124 | 118.3 (6)    | N21—C22—C221 | 118.6 (6)    | N11—C12—C124 | 123.6 (6)    |
| C12—C12—H12A | 111.3 (5)    | C22—C21—C222 | 116.5 (6)    | C12—C12—H12A | 111.1 (7)    |
| C12—C12—H12A | 111.3 (5)    | C22—C21—C222 | 116.5 (6)    | C12—C12—H12A | 111.1 (7)    |
| C12—C12—H12B | 111.3 (5)    | C22—C21—C222 | 116.5 (6)    | C12—C12—H12B | 111.3 (5)    |
| C12—C12—H12B | 111.3 (5)    | C22—C21—C222 | 116.5 (6)    | C12—C12—H12B | 111.3 (5)    |
| H12A—C12—H12B| 111.3 (5)    | C22—C21—C222 | 116.5 (6)    | H12A—C12—H12B| 111.3 (5)    |
| C12—C12—H12A | 111.3 (5)    | C22—C21—C222 | 116.5 (6)    | C12—C12—H12A | 111.3 (5)    |
| C12—C12—H12B | 111.3 (5)    | C22—C21—C222 | 116.5 (6)    | C12—C12—H12B | 111.3 (5)    |
| H12C—C12—H12D| 111.3 (5)    | C22—C21—C222 | 116.5 (6)    | H12C—C12—H12D| 111.3 (5)    |
| C12—C12—H12C | 111.3 (5)    | C22—C21—C222 | 116.5 (6)    | C12—C12—H12C | 111.3 (5)    |
| C12—C12—H12D | 111.3 (5)    | C22—C21—C222 | 116.5 (6)    | C12—C12—H12D | 111.3 (5)    |
| H12E—C12—H12F| 111.3 (5)    | C22—C21—C222 | 116.5 (6)    | H12E—C12—H12F| 111.3 (5)    |
| C12—C12—H12C | 111.3 (5)    | C22—C21—C222 | 116.5 (6)    | C12—C12—H12C | 111.3 (5)    |
| C12—C12—H12D | 111.3 (5)    | C22—C21—C222 | 116.5 (6)    | C12—C12—H12D | 111.3 (5)    |
| H12F—C12—H12G| 111.3 (5)    | C22—C21—C222 | 116.5 (6)    | H12F—C12—H12G| 111.3 (5)    |
| C12—C12—H12C | 111.3 (5)    | C22—C21—C222 | 116.5 (6)    | C12—C12—H12C | 111.3 (5)    |
| C12—C12—H12D | 111.3 (5)    | C22—C21—C222 | 116.5 (6)    | C12—C12—H12D | 111.3 (5)    |
| C12—C12—H12C | 111.3 (5)    | C22—C21—C222 | 116.5 (6)    | C12—C12—H12C | 111.3 (5)    |
| C12—C12—H12D | 111.3 (5)    | C22—C21—C222 | 116.5 (6)    | C12—C12—H12D | 111.3 (5)    |
| C12—C12—H12C | 111.3 (5)    | C22—C21—C222 | 116.5 (6)    | C12—C12—H12C | 111.3 (5)    |
| C12—C12—H12D | 111.3 (5)    | C22—C21—C222 | 116.5 (6)    | C12—C12—H12D | 111.3 (5)    |
| C12—C12—H12C | 111.3 (5)    | C22—C21—C222 | 116.5 (6)    | C12—C12—H12C | 111.3 (5)    |
| C12—C12—H12D | 111.3 (5)    | C22—C21—C222 | 116.5 (6)    | C12—C12—H12D | 111.3 (5)    |
| Bond                  | Angle (°) | Bond                  | Angle (°) |
|----------------------|-----------|----------------------|-----------|
| C12—C124—H12I       | 109.0     | C22—C224—H22I       | 109.5     |
| C125—C124—H12I      | 109.0     | C225—C224—H22I      | 109.5     |
| H12H—C124—H12I      | 107.8     | H22H—C224—H22I      | 108.1     |
| C124—C125—C126      | 112.1 (6) | C226—C225—C224      | 111.0 (6) |
| C124—C125—H12J      | 109.2     | C226—C225—H22J      | 109.4     |
| C126—C125—H12J      | 109.2     | C224—C225—H22J      | 109.4     |
| C124—C125—H12K      | 109.2     | C226—C225—H22K      | 109.4     |
| C126—C125—H12K      | 109.2     | C224—C225—H22K      | 109.4     |
| H12J—C125—H12K      | 107.9     | H22J—C225—H22K      | 108.0     |
| C125—C126—H12L      | 109.5     | C225—C226—H22L      | 109.5     |
| C125—C126—H12M      | 109.5     | C225—C226—H22M      | 109.5     |
| H12L—C126—H12M      | 109.5     | H22L—C226—H22M      | 109.5     |
| C125—C126—H12N      | 109.5     | C225—C226—H22N      | 109.5     |
| H12L—C126—H12N      | 109.5     | H22L—C226—H22N      | 109.5     |
| H12M—C126—H12N      | 109.5     | H22M—C226—H22N      | 109.5     |
| C11—N12—N11         | 115.7 (5) | C11—N12—H12         | 114 (5)   |
| C11—N12—H12         | 114 (5)   | N11—N12—H12         | 114 (5)   |
| N11—N12—H12         | 130 (5)   | C1—O11—Co1          | 113.4 (4) |
| C11—O11—Co1         | 113.4 (4) | O11—C11—O12         | 123.8 (6) |
| O11—C11—O12         | 123.8 (6) | O11—C11—N12         | 124.4 (6) |
| O11—C11—N12         | 124.4 (6) | O11—C11—N12         | 124.4 (6) |
| O12—C11—N12         | 111.7 (5) | O12—C11—N12         | 111.6 (6) |
| C11—O12—C13         | 113.3 (5) | C1—O12—C13          | 110.9 (5) |
| O12—C13—C14         | 110.9 (5) | O12—C13—C14         | 110.9 (5) |
| O12—C13—C14         | 110.9 (5) | O12—C13—C14         | 110.9 (5) |
| C13—C14—H13A        | 119.5     | C13—C14—H13B        | 119.5     |
| C14—C13—H13A        | 119.5     | C14—C13—H13B        | 119.5     |
| C14—C13—H13B        | 119.5     | C14—C13—H13B        | 119.5     |
| H13A—C13—H13B       | 108.0     | H13A—C13—H13B       | 108.3     |
| C15—C14—C19         | 118.7 (7) | C15—C14—C19         | 118.7 (7) |
| C15—C14—C13         | 125.3 (6) | C15—C14—C13         | 125.3 (6) |
| C19—C14—C13         | 116.0 (6) | C19—C14—C13         | 116.0 (6) |
| C14—C15—C16         | 121.2 (7) | C14—C15—C16         | 121.2 (7) |
| C14—C15—H15         | 119.4     | C14—C15—H15         | 119.4     |
| C16—C15—C15         | 119.5 (7) | C16—C15—C15         | 119.5 (7) |
| C17—C16—C15         | 120.2     | C17—C16—C15         | 120.2     |
| C15—C16—H16         | 120.2     | C15—C16—H16         | 120.2     |
| C18—C17—C16         | 120.2 (7) | C18—C17—C16         | 120.2 (7) |
| C18—C17—H17         | 119.9     | C18—C17—H17         | 119.9     |
| C16—C17—H17         | 119.9     | C16—C17—H17         | 119.9     |
| C17—C18—C19         | 120.3 (8) | C17—C18—C19         | 120.3 (8) |
| C17—C18—H18         | 119.9     | C17—C18—H18         | 119.9     |
| C19—C18—H18         | 119.9     | C19—C18—H18         | 119.9     |
| C18—C19—C14         | 120.1 (7) | C18—C19—C14         | 120.1 (7) |
| C18—C19—H19         | 120.0     | C18—C19—H19         | 120.0     |
| C14—C19—H19         | 120.0     | C14—C19—H19         | 120.0     |
| C110—N13—Co1        | 169.8 (5) | C110—N13—Co1        | 169.8 (5) |
| N13—C110—S1 | 177.3 (6) | N23—C210—S2 | 178.9 (6) |
| N12—N11—C12—C124 | −178.5 (5) | N22—N21—C22—C221 | −177.7 (6) |
| Co1—N11—C12—C124 | −0.2 (9) | Co2—N21—C22—C221 | −8.0 (9) |
| N12—N11—C12—C121 | −0.8 (9) | N22—N21—C22—C224 | 2.6 (10) |
| Co1—N11—C12—C121 | 177.6 (4) | Co2—N21—C22—C224 | 172.3 (5) |
| N11—C12—C121—C122 | −81.0 (8) | N21—C22—C221—C222 | 97.9 (7) |
| C124—C12—C121—C122 | 96.8 (7) | C224—C22—C221—C222 | −82.4 (8) |
| C12—C121—C122—C123 | −171.4 (6) | C22—C221—C222—C223 | 175.2 (7) |
| N11—C12—C124—C125 | −98.8 (7) | N21—C22—C224—C225 | 88.3 (8) |
| C121—C12—C124—C125 | 83.3 (8) | C221—C22—C224—C225 | −91.4 (7) |
| C12—C124—C125—C126 | −170.3 (6) | C22—C224—C225—C226 | 176.1 (6) |
| C12—N11—N12—C11 | 163.7 (6) | C22—N21—N22—C21 | 170.0 (6) |
| Co1—N11—N12—C11 | −15.0 (6) | Co2—N21—N22—C21 | −2.1 (6) |
| Co1—O11—C11—O12 | −169.3 (5) | Co2—O21—C21—O22 | 174.5 (5) |
| Co1—O11—C11—N12 | 9.6 (8) | Co2—O21—C21—N22 | −3.8 (8) |
| N11—N12—C11—O11 | 4.6 (10) | N21—N22—C21—O21 | 4.1 (10) |
| N11—N12—C11—O12 | −176.3 (5) | N21—N22—C21—O22 | −174.3 (5) |
| O11—C11—O12—C13 | −3.3 (9) | O21—C21—C22—C23 | 2.1 (10) |
| N12—C11—O12—C13 | 177.7 (5) | N22—C21—C22—C23 | −179.5 (6) |
| C11—O12—C13—C14 | −173.5 (5) | C21—O22—C23—C24 | 176.2 (6) |
| O12—C13—C14—C15 | 8.2 (9) | O22—C23—C24—C25 | 12.5 (9) |
| O12—C13—C14—C19 | −172.4 (6) | O22—C23—C24—C29 | −169.4 (6) |
| C19—C14—C15—C16 | −1.3 (10) | C29—C24—C25—C26 | 1.9 (10) |
| C13—C14—C15—C16 | 178.1 (7) | C29—C24—C25—C26 | −180.0 (7) |
| C14—C15—C16—C17 | 0.6 (11) | C24—C25—C26—C27 | −2.3 (10) |
| C15—C16—C17—C18 | 0.4 (11) | C24—C25—C26—C27 | 1.8 (11) |
| C16—C17—C18—C19 | −0.8 (11) | C26—C27—C28—C29 | −1.0 (11) |
| C17—C18—C19—C14 | 0.2 (11) | C27—C28—C29—C24 | 0.7 (12) |
| C15—C14—C19—C18 | 0.9 (10) | C25—C24—C29—C28 | −1.1 (11) |
| C13—C14—C19—C18 | −178.5 (7) | C23—C24—C29—C28 | −179.3 (7) |

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

Hydrogen-bond geometry (Å, °)

*Cg6* is the centroid of the C24–C29 phenyl ring.

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|----------|
| N12—H12···S1iii | 0.85 (8) | 2.47 (8) | 3.298 (6) | 166 (7) |
| C121—H12B···S1iii | 0.99 | 2.93 | 3.786 (7) | 146 |
| N22—H22···S2wii | 0.96 (8) | 2.55 (8) | 3.480 (6) | 164 (6) |
| C25—H25···S2wii | 0.95 | 2.94 | 3.811 (7) | 153 |
| C124—H12F···O11i | 0.99 | 2.48 | 3.259 (9) | 135 |
| C221—H22A···O21ii | 0.99 | 2.38 | 3.229 (8) | 144 |
| C13—H13B···Cg6 | 0.99 | 2.60 | 3.464 (7) | 145 |

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