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Tris(ethylenediamine)cobalt(II) dichloride

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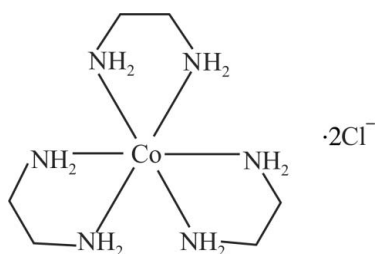
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Key indicators: single-crystal X-ray study; $T = 90$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.024; wR factor = 0.059; data-to-parameter ratio = 11.6.

The title compound, $[\text{Co}^{\text{II}}(\text{C}_2\text{H}_8\text{N}_2)_3]\text{Cl}_2$, was obtained unexpectedly as the product of an attempted solvothermal synthesis of cobalt selenide from the elements in the presence of NH_4Cl in ethylenediamine solvent. The three chelate rings of the distorted octahedral $[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_3]^{2+}$ complex cation adopt twisted conformations about their C—C bonds. The spread of *cis*-N—Co—N bond angles $[80.17(6)–98.10(6)^\circ]$ in the title compound is considerably greater than the equivalent data for $[\text{Co}^{\text{III}}(\text{C}_2\text{H}_8\text{N}_2)_3]\text{Cl}_3$ [Takamizawa *et al.* (2008). *Angew. Chem. Int. Ed.* **47**, 1689–1692]. In the crystal, the components are linked by numerous N—H...Cl hydrogen bonds, generating a three-dimensional network in which the cationic complexes are stacked in columns along [010] and separated by columns of chloride anions.

Related literature

The corresponding Co^{III} -tris-ethylenediamine complex with chloride counter-anions has been reported by Takamizawa *et al.* (2008).



Experimental

Crystal data

$[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_3]\text{Cl}_2$

$M_r = 310.14$

Orthorhombic, *Pbca*

$a = 8.1590(8)$ Å

$b = 17.047(3)$ Å

$c = 20.3974(14)$ Å

$V = 2837.0(6)$ Å³

$Z = 8$

Cu $K\alpha$ radiation

$\mu = 12.81$ mm⁻¹

$T = 90$ K

$0.31 \times 0.17 \times 0.15$ mm

Data collection

Bruker APEXII CCD

diffractometer

Absorption correction: multi-scan

(*SADABS*; Bruker, 2003)

$T_{\text{min}} = 0.109$, $T_{\text{max}} = 0.243$

17930 measured reflections

2700 independent reflections

2437 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.042$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$

$wR(F^2) = 0.059$

$S = 1.06$

2700 reflections

232 parameters

All H-atom parameters refined

$\Delta\rho_{\text{max}} = 0.26$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.37$ e Å⁻³

Table 1

Selected bond lengths (Å).

| | | | |
|-------|-------------|-------|-------------|
| Co—N1 | 2.1540 (15) | Co—N5 | 2.1748 (15) |
| Co—N3 | 2.1558 (15) | Co—N4 | 2.1767 (15) |
| Co—N2 | 2.1635 (15) | Co—N6 | 2.1791 (16) |

Table 2

Hydrogen-bond geometry (Å, °).

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| N1—H1B...Cl2 | 0.82 (2) | 2.48 (3) | 3.2839 (17) | 167 (2) |
| N1—H1A...Cl2 ⁱ | 0.86 (2) | 2.57 (2) | 3.3056 (16) | 145.4 (18) |
| N2—H2A...Cl1 ⁱⁱ | 0.83 (2) | 2.92 (2) | 3.5494 (16) | 133.6 (17) |
| N2—H2B...Cl1 | 0.83 (2) | 2.94 (2) | 3.5887 (17) | 135.8 (17) |
| N2—H2B...Cl1 | 0.88 (2) | 2.65 (2) | 3.4566 (17) | 152.5 (18) |
| N5—H5B...Cl1 ⁱⁱⁱ | 0.87 (2) | 2.51 (2) | 3.3770 (16) | 173.1 (19) |
| N5—H5A...Cl1 ^{iv} | 0.82 (2) | 2.70 (2) | 3.4514 (18) | 152.4 (19) |
| N6—H6B...Cl1 | 0.88 (3) | 2.66 (3) | 3.4552 (18) | 150.3 (19) |
| N6—H6A...Cl1 ^v | 0.83 (2) | 2.71 (2) | 3.4653 (16) | 152.9 (19) |
| N3—H3A...Cl1 ^{iv} | 0.88 (2) | 2.59 (2) | 3.4075 (17) | 154.2 (17) |
| N3—H3B...Cl2 ⁱ | 0.82 (2) | 2.49 (2) | 3.2560 (16) | 156 (2) |
| N4—H4A...Cl2 | 0.85 (2) | 2.68 (2) | 3.5003 (17) | 161 (2) |
| N4—H4B...Cl2 ⁱⁱⁱ | 0.87 (2) | 2.55 (2) | 3.2919 (16) | 143.5 (19) |

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

Data collection: *APEX2* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB7079).

References

- Bruker (2003). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Takamizawa, S., Akatsuka, T. & Ueda, T. (2008). *Angew. Chem. Int. Ed.* **47**, 1689–1692.

supporting information

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Tris(ethylenediamine)cobalt(II) dichloride

Kristin Cooke, Andrei V. Olenov and Kirill Kovnir

S1. Comment

In the chiral Co(II)(en)₃ cationic complex (Fig. 1) N atoms form distorted octahedron around central Co atom, *cis* angles deviate from 90° by less than 10°. Both Λ and Δ isomers are present in equal amounts in the centrosymmetric crystal structure.

Co(en)₃ cationic complexes are stacked in columns along [010] direction (Figure 2) and separated by the columns of Cl anions. There two types of chlorine anions in the crystal structure. Cl1 has distorted octahedral coordination by 6 hydrogen atoms from 4 different Co(en)₃ complexes. Cl2 has distorted trigonal bipyramid coordination by 5 hydrogen atoms from 2 different Co(en)₃ complexes. H···Cl distances vary from 2.45 to 2.70 Å.

The corresponding Co(III) trisethylenediamine complex with chloride counter-anions has been reported. (Takamizawa *et al.*, 2008). The Co(III)(en)₃ cationic complex is more regular: *cis* angles deviate from 90° by less than 4°.

S2. Experimental

The title compound, [Co(C₂N₂H₈)₃]Cl₂, was obtained unintentionally as the product of an attempted synthesis of cobalt selenide. Co (64 mg), Se (86 mg), and NH₄Cl (100 mg) were reacted in ethylenediamine (en) solvent (30 ml). Reaction was performed in closed hydrothermal vessel at 180°C for 48 h. Degree of the vessel filling was 70%. Irregular moisture-sensitive yellow crystals of the title compound were recovered.

S3. Refinement

H atoms bonded to N and C atoms were located in a difference Fourier maps and refined without any restraints.

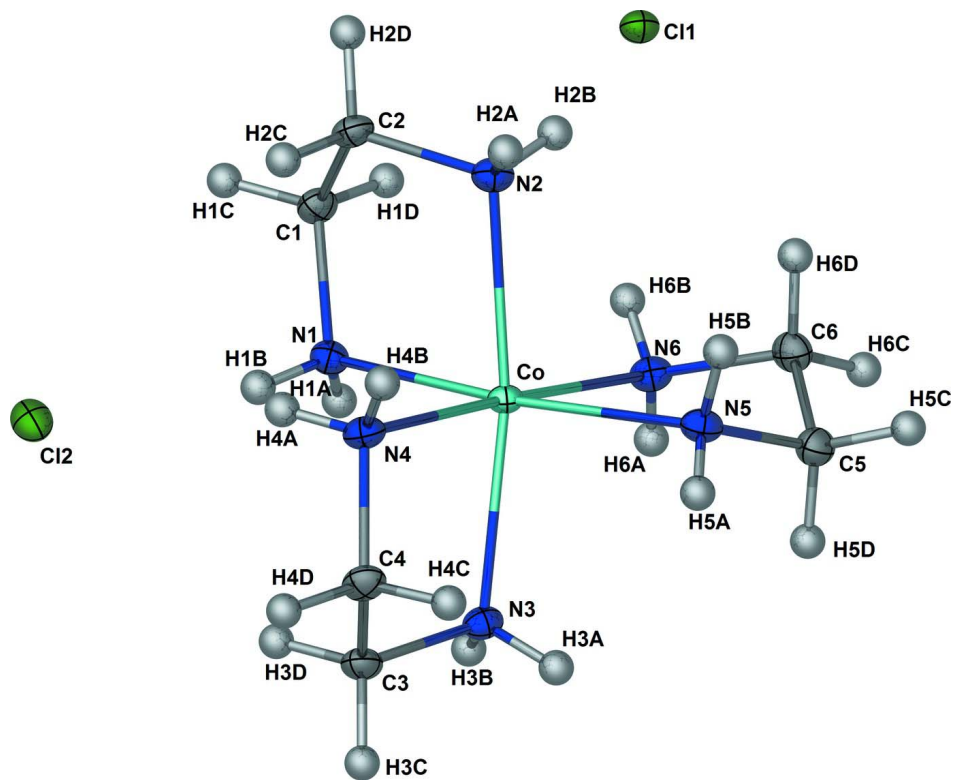


Figure 1

The molecular structure of (I) with 50% probability displacement ellipsoids for non-H atoms.

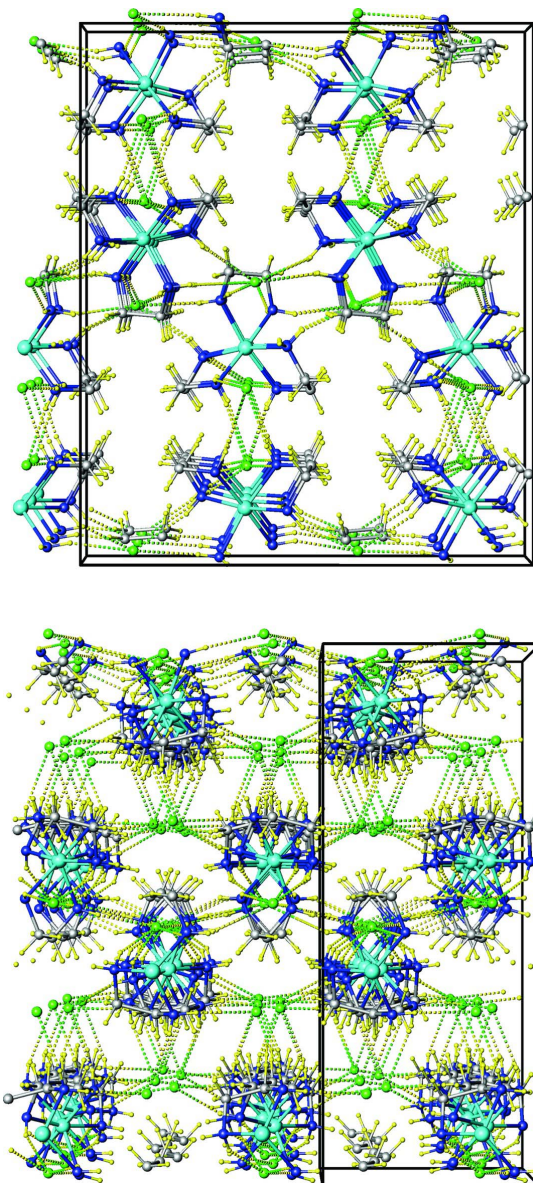


Figure 2

Packing of the molecules in the crystal structure of (I) along (top) [100] and (bottom) [010] crystallographic directions. Cl–H distances in the range from 2.45 to 2.70 Å are shown with dashed lines.

Tris(ethylenediamine)cobalt(II) dichloride'

Crystal data

$[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_3]\text{Cl}_2$

$M_r = 310.14$

Orthorhombic, *Pbca*

$a = 8.1590$ (8) Å

$b = 17.047$ (3) Å

$c = 20.3974$ (14) Å

$V = 2837.0$ (6) Å³

$Z = 8$

$F(000) = 1304$

$D_x = 1.451$ Mg m⁻³

Melting point: not measured K

Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å

Cell parameters from 6618 reflections

$\theta = 4.3\text{--}71.0^\circ$

$\mu = 12.81$ mm⁻¹

$T = 90$ K

Irregular, yellow

$0.31 \times 0.17 \times 0.15$ mm

Data collection

Bruker APEXII CCD
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
 φ and ω scans
Absorption correction: multi-scan
(*SADABS*; Bruker, 2003)
 $T_{\min} = 0.109$, $T_{\max} = 0.243$

17930 measured reflections
2700 independent reflections
2437 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.042$
 $\theta_{\max} = 72.0^\circ$, $\theta_{\min} = 4.3^\circ$
 $h = -9 \rightarrow 9$
 $k = -19 \rightarrow 20$
 $l = -24 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.059$
 $S = 1.06$
2700 reflections
232 parameters
0 restraints
Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map
Hydrogen site location: inferred from
neighbouring sites
All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0273P)^2 + 1.3198P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.26 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.37 \text{ e } \text{\AA}^{-3}$

Special details

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.

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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|---------------|---------------|----------------------------------|
| Co | 0.22206 (3) | 0.636475 (16) | 0.101937 (14) | 0.01130 (9) |
| Cl1 | 0.22916 (5) | 0.38557 (2) | 0.02211 (2) | 0.01517 (10) |
| Cl2 | 0.19514 (5) | 0.63342 (2) | 0.32464 (2) | 0.01878 (11) |
| N1 | 0.31525 (19) | 0.56644 (9) | 0.18154 (8) | 0.0144 (3) |
| H1A | 0.419 (3) | 0.5613 (12) | 0.1780 (10) | 0.021 (6)* |
| H1B | 0.297 (3) | 0.5888 (15) | 0.2164 (12) | 0.023 (6)* |
| N2 | 0.04364 (19) | 0.54264 (9) | 0.09943 (8) | 0.0155 (3) |
| H2A | -0.051 (3) | 0.5597 (13) | 0.0934 (10) | 0.019 (6)* |
| H2B | 0.068 (3) | 0.5088 (13) | 0.0683 (11) | 0.023 (6)* |
| C1 | 0.2324 (2) | 0.48967 (10) | 0.18119 (9) | 0.0169 (4) |
| H1C | 0.238 (2) | 0.4648 (12) | 0.2236 (10) | 0.014 (5)* |
| H1D | 0.285 (2) | 0.4581 (12) | 0.1472 (10) | 0.016 (5)* |
| C2 | 0.0533 (2) | 0.50142 (11) | 0.16281 (9) | 0.0167 (4) |
| H2C | 0.003 (2) | 0.5343 (12) | 0.1971 (10) | 0.020 (5)* |
| H2D | 0.001 (2) | 0.4511 (12) | 0.1614 (10) | 0.018 (5)* |
| N6 | 0.37572 (19) | 0.57543 (9) | 0.03100 (8) | 0.0156 (3) |

| | | | | |
|-----|--------------|--------------|--------------|------------|
| H5B | 0.044 (3) | 0.6765 (13) | 0.0010 (10) | 0.023 (6)* |
| H5A | 0.135 (3) | 0.7409 (15) | 0.0172 (10) | 0.024 (6)* |
| N5 | 0.14074 (19) | 0.69328 (9) | 0.01218 (8) | 0.0152 (3) |
| H6A | 0.474 (3) | 0.5868 (13) | 0.0328 (10) | 0.020 (5)* |
| H6B | 0.372 (3) | 0.5247 (15) | 0.0387 (11) | 0.029 (6)* |
| C5 | 0.2573 (2) | 0.67473 (11) | −0.04124 (9) | 0.0179 (4) |
| H5D | 0.351 (2) | 0.7073 (12) | −0.0344 (9) | 0.016 (5)* |
| H5C | 0.211 (2) | 0.6829 (13) | −0.0850 (11) | 0.021 (5)* |
| C6 | 0.3113 (2) | 0.59006 (11) | −0.03548 (9) | 0.0182 (4) |
| H6D | 0.217 (2) | 0.5559 (11) | −0.0402 (9) | 0.008 (4)* |
| H6C | 0.391 (3) | 0.5790 (12) | −0.0690 (10) | 0.019 (5)* |
| N3 | 0.38406 (18) | 0.73377 (9) | 0.12091 (8) | 0.0146 (3) |
| H3A | 0.385 (2) | 0.7681 (13) | 0.0886 (10) | 0.016 (5)* |
| H3B | 0.478 (3) | 0.7190 (13) | 0.1278 (11) | 0.023 (6)* |
| N4 | 0.07178 (18) | 0.70245 (9) | 0.17074 (8) | 0.0155 (3) |
| H4B | −0.032 (3) | 0.7045 (13) | 0.1610 (10) | 0.027 (6)* |
| H4A | 0.079 (3) | 0.6796 (14) | 0.2080 (11) | 0.026 (6)* |
| C3 | 0.3253 (2) | 0.77480 (11) | 0.17991 (9) | 0.0175 (4) |
| H3D | 0.353 (2) | 0.7452 (12) | 0.2186 (9) | 0.011 (5)* |
| H3C | 0.374 (2) | 0.8260 (12) | 0.1837 (9) | 0.016 (5)* |
| C4 | 0.1402 (2) | 0.78212 (10) | 0.17682 (10) | 0.0178 (4) |
| H4C | 0.109 (2) | 0.8107 (12) | 0.1386 (10) | 0.018 (5)* |
| H4D | 0.097 (3) | 0.8110 (12) | 0.2159 (10) | 0.020 (5)* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|---------------|---------------|---------------|
| Co | 0.00953 (15) | 0.00972 (15) | 0.01465 (16) | −0.00031 (10) | −0.00038 (10) | 0.00023 (10) |
| Cl1 | 0.0154 (2) | 0.0123 (2) | 0.0178 (2) | −0.00106 (14) | −0.00053 (15) | 0.00024 (15) |
| Cl2 | 0.0122 (2) | 0.0245 (2) | 0.0197 (2) | 0.00031 (15) | 0.00082 (16) | −0.00254 (17) |
| N1 | 0.0125 (8) | 0.0140 (7) | 0.0166 (8) | 0.0004 (6) | −0.0007 (6) | −0.0010 (6) |
| N2 | 0.0127 (8) | 0.0134 (8) | 0.0204 (9) | 0.0004 (6) | −0.0011 (6) | −0.0001 (6) |
| C1 | 0.0196 (9) | 0.0125 (9) | 0.0186 (9) | −0.0005 (7) | −0.0005 (7) | 0.0022 (7) |
| C2 | 0.0176 (9) | 0.0119 (8) | 0.0207 (10) | −0.0024 (7) | 0.0022 (7) | 0.0013 (7) |
| N6 | 0.0120 (8) | 0.0138 (8) | 0.0211 (8) | 0.0009 (6) | 0.0007 (6) | 0.0007 (6) |
| N5 | 0.0133 (7) | 0.0118 (8) | 0.0204 (8) | 0.0009 (6) | −0.0020 (6) | −0.0005 (6) |
| C5 | 0.0184 (9) | 0.0175 (9) | 0.0177 (10) | −0.0011 (7) | −0.0012 (7) | 0.0010 (7) |
| C6 | 0.0189 (9) | 0.0177 (9) | 0.0181 (10) | 0.0006 (7) | 0.0022 (8) | −0.0030 (7) |
| N3 | 0.0114 (7) | 0.0136 (7) | 0.0189 (8) | −0.0005 (6) | −0.0006 (6) | 0.0020 (6) |
| N4 | 0.0132 (8) | 0.0129 (7) | 0.0205 (9) | −0.0011 (6) | 0.0019 (6) | 0.0000 (6) |
| C3 | 0.0201 (9) | 0.0125 (9) | 0.0198 (10) | −0.0034 (7) | −0.0015 (7) | 0.0003 (7) |
| C4 | 0.0210 (9) | 0.0106 (8) | 0.0217 (10) | 0.0001 (7) | 0.0023 (8) | −0.0001 (7) |

Geometric parameters (Å, °)

| | | | |
|-------|-------------|--------|-----------|
| Co—N1 | 2.1540 (15) | N5—C5 | 1.480 (2) |
| Co—N3 | 2.1558 (15) | N5—H5B | 0.87 (2) |
| Co—N2 | 2.1635 (15) | N5—H5A | 0.82 (2) |

| | | | |
|------------|-------------|------------|-------------|
| Co—N5 | 2.1748 (15) | C5—C6 | 1.514 (3) |
| Co—N4 | 2.1767 (15) | C5—H5D | 0.95 (2) |
| Co—N6 | 2.1791 (16) | C5—H5C | 0.98 (2) |
| N1—C1 | 1.473 (2) | C6—H6D | 0.967 (19) |
| N1—H1A | 0.86 (2) | C6—H6C | 0.96 (2) |
| N1—H1B | 0.82 (2) | N3—C3 | 1.472 (2) |
| N2—C2 | 1.473 (2) | N3—H3A | 0.88 (2) |
| N2—H2A | 0.83 (2) | N3—H3B | 0.82 (2) |
| N2—H2B | 0.88 (2) | N4—C4 | 1.474 (2) |
| C1—C2 | 1.522 (2) | N4—H4B | 0.87 (2) |
| C1—H1C | 0.96 (2) | N4—H4A | 0.85 (2) |
| C1—H1D | 0.98 (2) | C3—C4 | 1.517 (2) |
| C2—H2C | 0.99 (2) | C3—H3D | 0.963 (19) |
| C2—H2D | 0.96 (2) | C3—H3C | 0.96 (2) |
| N6—C6 | 1.475 (2) | C4—H4C | 0.95 (2) |
| N6—H6A | 0.83 (2) | C4—H4D | 1.00 (2) |
| N6—H6B | 0.88 (3) | | |
| N1—Co—N3 | 94.28 (6) | H6A—N6—H6B | 105 (2) |
| N1—Co—N2 | 81.11 (6) | C5—N5—Co | 109.18 (11) |
| N3—Co—N2 | 170.27 (6) | C5—N5—H5B | 108.7 (14) |
| N1—Co—N5 | 171.51 (6) | Co—N5—H5B | 110.5 (14) |
| N3—Co—N5 | 89.75 (6) | C5—N5—H5A | 109.8 (15) |
| N2—Co—N5 | 95.97 (6) | Co—N5—H5A | 110.6 (15) |
| N1—Co—N4 | 89.95 (6) | H5B—N5—H5A | 108 (2) |
| N3—Co—N4 | 80.33 (6) | N5—C5—C6 | 109.49 (15) |
| N2—Co—N4 | 91.05 (6) | N5—C5—H5D | 106.3 (12) |
| N5—Co—N4 | 98.10 (6) | C6—C5—H5D | 108.2 (12) |
| N1—Co—N6 | 91.88 (6) | N5—C5—H5C | 113.1 (12) |
| N3—Co—N6 | 97.69 (6) | C6—C5—H5C | 108.5 (13) |
| N2—Co—N6 | 91.05 (6) | H5D—C5—H5C | 111.1 (17) |
| N5—Co—N6 | 80.17 (6) | N6—C6—C5 | 109.64 (15) |
| N4—Co—N6 | 177.41 (6) | N6—C6—H6D | 105.8 (11) |
| C1—N1—Co | 109.07 (11) | C5—C6—H6D | 109.6 (11) |
| C1—N1—H1A | 111.3 (14) | N6—C6—H6C | 112.2 (12) |
| Co—N1—H1A | 110.0 (14) | C5—C6—H6C | 109.1 (13) |
| C1—N1—H1B | 109.6 (16) | H6D—C6—H6C | 110.4 (16) |
| Co—N1—H1B | 109.5 (16) | C3—N3—Co | 108.21 (11) |
| H1A—N1—H1B | 107 (2) | C3—N3—H3A | 107.4 (13) |
| C2—N2—Co | 107.21 (11) | Co—N3—H3A | 112.6 (13) |
| C2—N2—H2A | 110.2 (14) | C3—N3—H3B | 108.1 (16) |
| Co—N2—H2A | 111.6 (15) | Co—N3—H3B | 111.7 (15) |
| C2—N2—H2B | 108.0 (14) | H3A—N3—H3B | 109 (2) |
| Co—N2—H2B | 110.4 (14) | C4—N4—Co | 108.49 (11) |
| H2A—N2—H2B | 109 (2) | C4—N4—H4B | 110.5 (15) |
| N1—C1—C2 | 108.96 (14) | Co—N4—H4B | 114.9 (15) |
| N1—C1—H1C | 111.3 (12) | C4—N4—H4A | 108.7 (16) |
| C2—C1—H1C | 109.1 (12) | Co—N4—H4A | 107.5 (15) |

| | | | |
|------------|-------------|------------|-------------|
| N1—C1—H1D | 106.9 (12) | H4B—N4—H4A | 107 (2) |
| C2—C1—H1D | 108.7 (11) | N3—C3—C4 | 109.24 (15) |
| H1C—C1—H1D | 111.9 (16) | N3—C3—H3D | 110.2 (11) |
| N2—C2—C1 | 109.29 (15) | C4—C3—H3D | 108.0 (11) |
| N2—C2—H2C | 109.2 (12) | N3—C3—H3C | 111.2 (12) |
| C1—C2—H2C | 107.6 (12) | C4—C3—H3C | 110.0 (12) |
| N2—C2—H2D | 112.1 (12) | H3D—C3—H3C | 108.2 (16) |
| C1—C2—H2D | 108.4 (12) | N4—C4—C3 | 107.74 (14) |
| H2C—C2—H2D | 110.2 (17) | N4—C4—H4C | 107.6 (12) |
| C6—N6—Co | 108.95 (11) | C3—C4—H4C | 109.8 (12) |
| C6—N6—H6A | 110.3 (15) | N4—C4—H4D | 112.8 (12) |
| Co—N6—H6A | 114.7 (15) | C3—C4—H4D | 110.8 (12) |
| C6—N6—H6B | 108.5 (14) | H4C—C4—H4D | 108.0 (16) |
| Co—N6—H6B | 109.3 (14) | | |

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------------|----------|-------------|-------------|---------------|
| N1—H1B \cdots C12 | 0.82 (2) | 2.48 (3) | 3.2839 (17) | 167 (2) |
| N1—H1A \cdots C12 ⁱ | 0.86 (2) | 2.57 (2) | 3.3056 (16) | 145.4 (18) |
| N2—H2A \cdots C11 ⁱⁱ | 0.83 (2) | 2.92 (2) | 3.5494 (16) | 133.6 (17) |
| N2—H2A \cdots C12 ⁱⁱⁱ | 0.83 (2) | 2.94 (2) | 3.5887 (17) | 135.8 (17) |
| N2—H2B \cdots C11 | 0.88 (2) | 2.65 (2) | 3.4566 (17) | 152.5 (18) |
| N5—H5B \cdots C11 ⁱⁱ | 0.87 (2) | 2.51 (2) | 3.3770 (16) | 173.1 (19) |
| N5—H5A \cdots C11 ^{iv} | 0.82 (2) | 2.70 (2) | 3.4514 (18) | 152.4 (19) |
| N6—H6B \cdots C11 | 0.88 (3) | 2.66 (3) | 3.4552 (18) | 150.3 (19) |
| N6—H6A \cdots C11 ^v | 0.83 (2) | 2.71 (2) | 3.4653 (16) | 152.9 (19) |
| N3—H3A \cdots C11 ^{iv} | 0.88 (2) | 2.59 (2) | 3.4075 (17) | 154.2 (17) |
| N3—H3B \cdots C12 ⁱ | 0.82 (2) | 2.49 (2) | 3.2560 (16) | 156 (2) |
| N4—H4A \cdots C12 | 0.85 (2) | 2.68 (2) | 3.5003 (17) | 161 (2) |
| N4—H4B \cdots C12 ⁱⁱⁱ | 0.87 (2) | 2.55 (2) | 3.2919 (16) | 143.5 (19) |

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