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# Tris[(2*E*)-1,3-bis(4-chlorophenyl)triaz-2-en-1-ido-$\kappa^2N^1,N^3$]cobalt(III)

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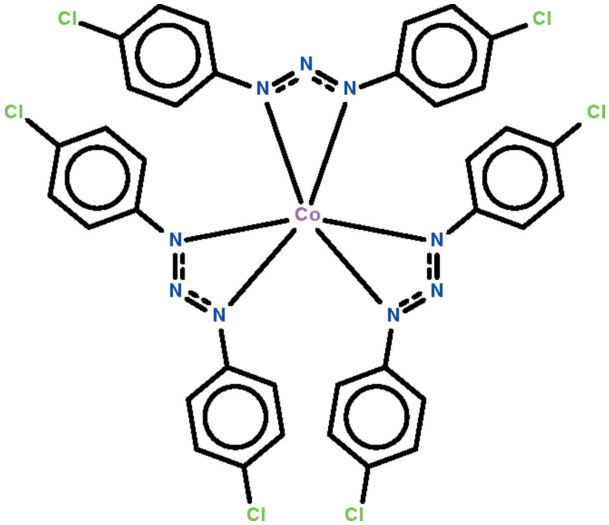
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.006 Å; $R$ factor = 0.053; $wR$ factor = 0.159; data-to-parameter ratio = 18.4.

Molecules of the title compound, $[Co(C_{12}H_8Cl_2N_3)_3]$, lie on a threefold rotation axis. The tris-*N*,*N*′-chelated $Co^{III}$ atom, which is located on the threefold rotation axis, shows a distorted octahedral coordination.

## Related literature

For tris(diphenyltriazenido)cobalt(III), see: Krigbaum & Rubin (1973).




## Experimental

### Crystal data

$[Co(C_{12}H_8Cl_2N_3)_3]$
$M_r$ = 854.27
Trigonal, $R\overline{3}$
$a$ = 19.383 (3) Å
$c$ = 17.546 (2) Å
$V$ = 5708.5 (10) Å$^3$
$Z$ = 6
Mo $K\alpha$ radiation
$\mu$ = 0.91 mm$^{-1}$
$T$ = 293 K
0.30 × 0.25 × 0.20 mm

### Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.771, $T_{max}$ = 0.839
8131 measured reflections
2891 independent reflections
1714 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.053

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.159
$S$ = 1.04
2891 reflections
157 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.35 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.34 e Å$^{-3}$

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5911).

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# supporting information

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## Tris[(2*E*)-1,3-bis(4-chlorophenyl)triaz-2-en-1-ido-$\kappa^2N^1,N^3$]cobalt(III)

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### S1. Comment

The diaryltriazenido anion *N*,*N*′-chelates to a large number of metal atoms; for $Co^{III}$ in particular, three diphenyltriazenido anions chelate to the metal atom to render a trigonal prismatic coordination geometry. Such a geometry appears to be a consequence of the small bite of the chelate (Krigbaum & Rubin, 1973). In chlorine-substituted $Co(C_{12}H_8Cl_2N_3)_3$ (Scheme I), the metal atom lies on a threefold rotation axis that relates one di(4-chlorophenyl)triazenido chelate to the others (Fig. 1). The $Co^{III}$ atom shows octahedral coordination (Fig. 2). With respect to the delocalized –N–N═N– fragment, one phenylene ring is twisted by 9.5 (3) ånd the other by 21.1 (2) °.

### S2. Experimental

4-Chloroaniline (10 mmol) in water (5 ml) was suspended in 1 *M* hydrochloric acid (30 ml) at 273 K. An aqueous solution (15%) of sodium nitrite (15 mmol) was added dropwise. When the amine had dissolved, a solution of 4-chloroaniline in ethanol (10 mmol) was added at 273 K. The mixture was stirred for 3 h. The reaction mixture was neutralized with a 15% aqueous of sodium acetate to give an orange precipitate. The product was collected and crystallized at 269 K from 9:1 ethyl acetate/n-hexane to give yellow crystals in (65% yield). Calc. for $C_{12}H_9Cl_2N_3$: C 54.16, H 3.41, N 15.79%. Found: C 54.07, H 3.39, N 15.66.%

To a solution of the ligand (0.798 g, 3 mmol) and triethylamine (0.300 g, 3 mmol) in dichloromethane/acetonitrile (30 ml, 1:1) was added cobalt(II) chloride hexahydrate (0.238 g, 1 mmol). The solvent was allowed to evaporate over several days. Red crystals were isolated in 50% yield. Calc. for $C_{36}H_{24}CoN_9Cl_6$: C 50.59, H 2.81, N 14.76%. Found: C 51.19, H 2.68, N 14.81%.

### S3. Refinement

H-atoms were placed in calculated positions (C—H 0.93 Å) and were included in the refinement in the riding model approximation, with *U*(H) set to 1.2*U*(C).

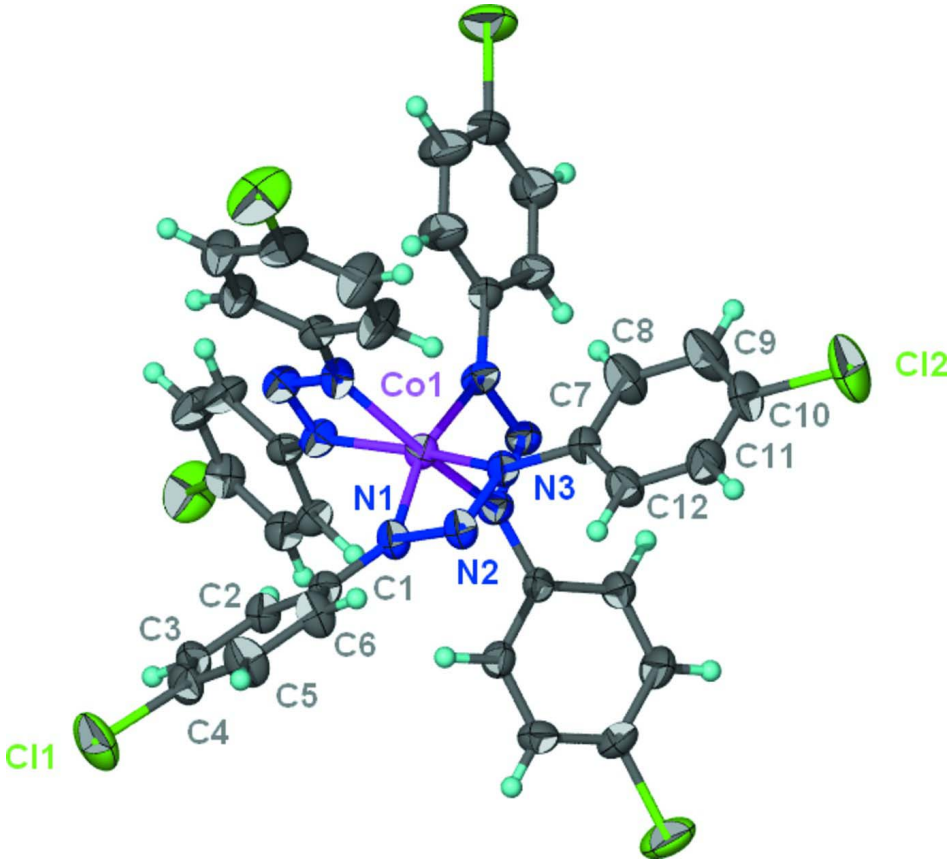


**Figure 1**

Anisotropic displacement ellipsoid plot (Barbour, 2001) of $Co(C_{12}H_8Cl_2N_3)_3$ at the 50% probability level; hydrogen atoms are drawn as spheres of arbitrary radius. Symmetry-related atoms are no labeled.

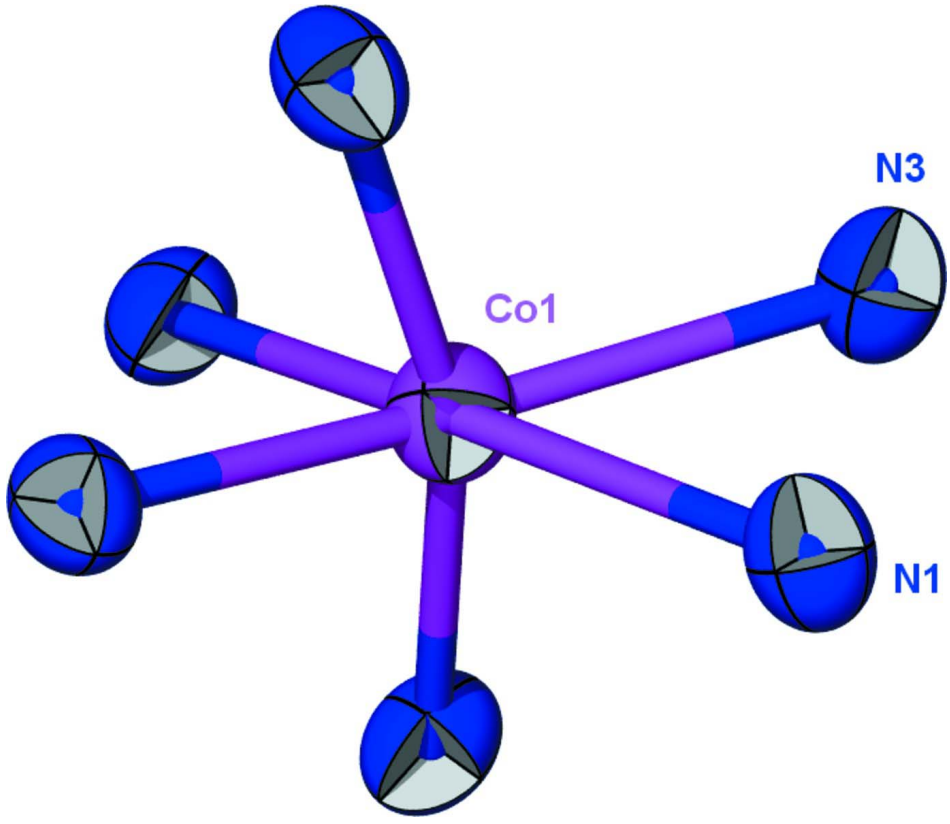


**Figure 2**

Octahedral coordination geometry of $Co^{III}$.

**Tris[(2*E*)-1,3-bis(4-chlorophenyl)triaz-2-en-1-ido- $\kappa^2N^1,N^3$]cobalt(III)**

*Crystal data*

$[Co(C_{12}H_8Cl_2N_3)_3]$
$M_r = 854.27$
Trigonal, $R\overline{3}$
Hall symbol: -R 3
$a = 19.383$ (3) Å
$c = 17.546$ (2) Å
$V = 5708.5$ (10) Å$^3$
$Z = 6$
$F(000) = 2592$
$D_x = 1.491$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1211 reflections
$\theta = 2.6$–$22.1°$
$\mu = 0.91$ mm$^{-1}$
$T = 293$ K
Prism, red
0.30 × 0.25 × 0.20 mm

*Data collection*

Bruker SMART APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.771$, $T_{max} = 0.839$
8131 measured reflections
2891 independent reflections
1714 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 27.5°$, $\theta_{min} = 1.7°$
$h = -24\rightarrow20$
$k = -24\rightarrow22$
$l = -22\rightarrow22$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.159$
$S = 1.04$
2891 reflections
157 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0758P)^2 + 0.3669P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.35$ e Å$^{-3}$
$\Delta\rho_{min} = -0.34$ e Å$^{-3}$

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Co1 | 0.0000 | 0.0000 | 0.25642 (4) | 0.0361 (3) |
| Cl1 | −0.04587 (9) | 0.28231 (8) | 0.51099 (7) | 0.0835 (5) |
| Cl2 | 0.34023 (9) | 0.12548 (9) | −0.01594 (8) | 0.0937 (5) |
| C1 | 0.0269 (2) | 0.1483 (2) | 0.35169 (17) | 0.0349 (8) |
| C2 | −0.0262 (2) | 0.1092 (2) | 0.41122 (18) | 0.0402 (8) |
| H2 | −0.0473 | 0.0547 | 0.4178 | 0.048* |
| C3 | −0.0476 (2) | 0.1507 (2) | 0.46038 (19) | 0.0441 (9) |
| H3 | −0.0830 | 0.1245 | 0.5001 | 0.053* |
| C4 | −0.0162 (2) | 0.2313 (2) | 0.4501 (2) | 0.0477 (10) |
| C5 | 0.0370 (3) | 0.2714 (2) | 0.3925 (2) | 0.0581 (11) |
| H5 | 0.0586 | 0.3261 | 0.3871 | 0.070* |
| C6 | 0.0582 (2) | 0.2301 (2) | 0.3430 (2) | 0.0486 (10) |
| H6 | 0.0935 | 0.2569 | 0.3034 | 0.058* |
| C7 | 0.1553 (2) | 0.0949 (2) | 0.15565 (17) | 0.0368 (8) |
| C8 | 0.1422 (3) | 0.0343 (3) | 0.1071 (2) | 0.0630 (12) |
| H8 | 0.0949 | −0.0142 | 0.1102 | 0.076* |
| C9 | 0.1988 (3) | 0.0447 (3) | 0.0536 (3) | 0.0725 (14) |
| H9 | 0.1893 | 0.0033 | 0.0205 | 0.087* |
| C10 | 0.2671 (3) | 0.1136 (3) | 0.0490 (2) | 0.0547 (11) |
| C11 | 0.2815 (2) | 0.1764 (3) | 0.0959 (2) | 0.0561 (11) |
| H11 | 0.3288 | 0.2247 | 0.0914 | 0.067* |
| C12 | 0.2254 (2) | 0.1673 (2) | 0.1496 (2) | 0.0485 (10) |
| H12 | 0.2347 | 0.2094 | 0.1815 | 0.058* |
| N1 | 0.04549 (18) | 0.10269 (17) | 0.30269 (15) | 0.0398 (7) |
| N2 | 0.10592 (17) | 0.13926 (18) | 0.25527 (15) | 0.0407 (7) |
| N3 | 0.09691 (17) | 0.08162 (18) | 0.21030 (15) | 0.0387 (7) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Co1 | 0.0336 (3) | 0.0336 (3) | 0.0410 (4) | 0.01679 (17) | 0.000 | 0.000 |
| Cl1 | 0.0956 (10) | 0.0685 (9) | 0.0929 (9) | 0.0459 (8) | 0.0247 (7) | −0.0207 (7) |
| Cl2 | 0.0941 (10) | 0.0919 (11) | 0.0959 (9) | 0.0471 (9) | 0.0578 (8) | 0.0140 (8) |
| C1 | 0.037 (2) | 0.036 (2) | 0.0365 (16) | 0.0218 (17) | 0.0013 (15) | 0.0045 (14) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C2 | 0.040 (2) | 0.034 (2) | 0.0469 (19) | 0.0193 (17) | 0.0047 (16) | 0.0030 (15) |
| C3 | 0.042 (2) | 0.048 (2) | 0.0412 (18) | 0.021 (2) | 0.0072 (16) | −0.0016 (17) |
| C4 | 0.051 (2) | 0.045 (2) | 0.054 (2) | 0.029 (2) | 0.0028 (19) | −0.0101 (18) |
| C5 | 0.075 (3) | 0.034 (2) | 0.067 (2) | 0.028 (2) | 0.013 (2) | 0.0024 (19) |
| C6 | 0.059 (3) | 0.036 (2) | 0.052 (2) | 0.024 (2) | 0.0180 (19) | 0.0100 (17) |
| C7 | 0.036 (2) | 0.037 (2) | 0.0390 (17) | 0.0193 (17) | 0.0046 (15) | 0.0031 (15) |
| C8 | 0.060 (3) | 0.041 (2) | 0.070 (3) | 0.012 (2) | 0.025 (2) | −0.004 (2) |
| C9 | 0.078 (3) | 0.053 (3) | 0.074 (3) | 0.023 (3) | 0.027 (3) | −0.013 (2) |
| C10 | 0.057 (3) | 0.059 (3) | 0.054 (2) | 0.033 (2) | 0.023 (2) | 0.012 (2) |
| C11 | 0.040 (2) | 0.052 (3) | 0.064 (2) | 0.014 (2) | 0.0089 (19) | 0.000 (2) |
| C12 | 0.047 (2) | 0.041 (2) | 0.050 (2) | 0.016 (2) | 0.0085 (18) | −0.0059 (17) |
| N1 | 0.0381 (17) | 0.0350 (17) | 0.0450 (15) | 0.0174 (14) | 0.0081 (13) | 0.0005 (13) |
| N2 | 0.0401 (18) | 0.0385 (18) | 0.0438 (15) | 0.0199 (15) | 0.0076 (13) | 0.0020 (13) |
| N3 | 0.0325 (16) | 0.0369 (18) | 0.0445 (14) | 0.0156 (14) | 0.0031 (13) | −0.0061 (13) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Co1—N1 | 1.909 (3) | C4—C5 | 1.373 (5) |
| Co1—N1$^{i}$ | 1.909 (3) | C5—C6 | 1.376 (5) |
| Co1—N1$^{ii}$ | 1.909 (3) | C5—H5 | 0.9300 |
| Co1—N3$^{i}$ | 1.927 (3) | C6—H6 | 0.9300 |
| Co1—N3 | 1.927 (3) | C7—C8 | 1.368 (5) |
| Co1—N3$^{ii}$ | 1.927 (3) | C7—C12 | 1.386 (5) |
| Co1—N2$^{ii}$ | 2.441 (3) | C7—N3 | 1.406 (4) |
| Co1—N2$^{i}$ | 2.441 (3) | C8—C9 | 1.381 (6) |
| Cl1—C4 | 1.737 (4) | C8—H8 | 0.9300 |
| Cl2—C10 | 1.741 (4) | C9—C10 | 1.332 (6) |
| C1—C2 | 1.394 (4) | C9—H9 | 0.9300 |
| C1—C6 | 1.395 (5) | C10—C11 | 1.377 (6) |
| C1—N1 | 1.403 (4) | C11—C12 | 1.382 (5) |
| C2—C3 | 1.378 (5) | C11—H11 | 0.9300 |
| C2—H2 | 0.9300 | C12—H12 | 0.9300 |
| C3—C4 | 1.376 (5) | N1—N2 | 1.318 (4) |
| C3—H3 | 0.9300 | N2—N3 | 1.306 (4) |
| | | | |
| N1—Co1—N1$^{i}$ | 103.22 (10) | C2—C3—H3 | 120.3 |
| N1—Co1—N1$^{ii}$ | 103.22 (10) | C5—C4—C3 | 121.3 (3) |
| N1$^{i}$—Co1—N1$^{ii}$ | 103.22 (10) | C5—C4—Cl1 | 120.0 (3) |
| N1—Co1—N3$^{i}$ | 163.88 (12) | C3—C4—Cl1 | 118.7 (3) |
| N1$^{i}$—Co1—N3$^{i}$ | 64.54 (12) | C4—C5—C6 | 119.6 (4) |
| N1$^{ii}$—Co1—N3$^{i}$ | 90.28 (12) | C4—C5—H5 | 120.2 |
| N1—Co1—N3 | 64.54 (12) | C6—C5—H5 | 120.2 |
| N1$^{i}$—Co1—N3 | 90.28 (12) | C5—C6—C1 | 120.3 (3) |
| N1$^{ii}$—Co1—N3 | 163.88 (12) | C5—C6—H6 | 119.8 |
| N3$^{i}$—Co1—N3 | 103.63 (10) | C1—C6—H6 | 119.8 |
| N1—Co1—N3$^{ii}$ | 90.28 (12) | C8—C7—C12 | 119.3 (3) |
| N1$^{i}$—Co1—N3$^{ii}$ | 163.88 (12) | C8—C7—N3 | 118.7 (3) |
| N1$^{ii}$—Co1—N3$^{ii}$ | 64.54 (12) | C12—C7—N3 | 122.0 (3) |

| | | | |
|---|---|---|---|
| N3$^{i}$—Co1—N3$^{ii}$ | 103.63 (10) | C7—C8—C9 | 120.3 (4) |
| N3—Co1—N3$^{ii}$ | 103.63 (10) | C7—C8—H8 | 119.8 |
| N1—Co1—N2$^{ii}$ | 98.78 (11) | C9—C8—H8 | 119.8 |
| N1$^{i}$—Co1—N2$^{ii}$ | 134.58 (11) | C10—C9—C8 | 120.4 (4) |
| N1$^{ii}$—Co1—N2$^{ii}$ | 32.42 (10) | C10—C9—H9 | 119.8 |
| N3$^{i}$—Co1—N2$^{ii}$ | 97.33 (11) | C8—C9—H9 | 119.8 |
| N3—Co1—N2$^{ii}$ | 135.13 (11) | C9—C10—C11 | 120.7 (4) |
| N3$^{ii}$—Co1—N2$^{ii}$ | 32.14 (10) | C9—C10—Cl2 | 120.5 (4) |
| N1—Co1—N2$^{i}$ | 134.58 (11) | C11—C10—Cl2 | 118.8 (3) |
| N1$^{i}$—Co1—N2$^{i}$ | 32.42 (10) | C10—C11—C12 | 119.7 (4) |
| N1$^{ii}$—Co1—N2$^{i}$ | 98.78 (11) | C10—C11—H11 | 120.1 |
| N3$^{i}$—Co1—N2$^{i}$ | 32.14 (10) | C12—C11—H11 | 120.1 |
| N3—Co1—N2$^{i}$ | 97.33 (11) | C11—C12—C7 | 119.5 (4) |
| N3$^{ii}$—Co1—N2$^{i}$ | 135.13 (11) | C11—C12—H12 | 120.3 |
| N2$^{ii}$—Co1—N2$^{i}$ | 119.993 (4) | C7—C12—H12 | 120.3 |
| C2—C1—C6 | 118.9 (3) | N2—N1—C1 | 119.2 (3) |
| C2—C1—N1 | 118.0 (3) | N2—N1—Co1 | 96.6 (2) |
| C6—C1—N1 | 123.1 (3) | C1—N1—Co1 | 141.9 (2) |
| C3—C2—C1 | 120.5 (3) | N3—N2—N1 | 102.6 (3) |
| C3—C2—H2 | 119.7 | N2—N3—C7 | 120.3 (3) |
| C1—C2—H2 | 119.7 | N2—N3—Co1 | 96.14 (19) |
| C4—C3—C2 | 119.3 (3) | C7—N3—Co1 | 143.3 (3) |
| C4—C3—H3 | 120.3 | | |

| | | | |
|---|---|---|---|
| C6—C1—C2—C3 | 0.3 (5) | N2$^{i}$—Co1—N1—N2 | 75.96 (18) |
| N1—C1—C2—C3 | −179.0 (3) | N1$^{i}$—Co1—N1—C1 | −113.8 (3) |
| C1—C2—C3—C4 | 0.1 (5) | N1$^{ii}$—Co1—N1—C1 | −6.5 (4) |
| C2—C3—C4—C5 | −1.0 (6) | N3$^{i}$—Co1—N1—C1 | −152.7 (4) |
| C2—C3—C4—Cl1 | 178.3 (3) | N3—Co1—N1—C1 | 162.3 (4) |
| C3—C4—C5—C6 | 1.4 (6) | N3$^{ii}$—Co1—N1—C1 | 57.4 (4) |
| Cl1—C4—C5—C6 | −177.8 (3) | N2$^{ii}$—Co1—N1—C1 | 26.2 (4) |
| C4—C5—C6—C1 | −1.0 (6) | N2$^{i}$—Co1—N1—C1 | −123.4 (3) |
| C2—C1—C6—C5 | 0.2 (6) | C1—N1—N2—N3 | −168.8 (3) |
| N1—C1—C6—C5 | 179.4 (4) | Co1—N1—N2—N3 | −2.3 (3) |
| C12—C7—C8—C9 | 1.1 (6) | N1—N2—N3—C7 | −173.3 (3) |
| N3—C7—C8—C9 | −178.9 (4) | N1—N2—N3—Co1 | 2.3 (3) |
| C7—C8—C9—C10 | 0.5 (8) | C8—C7—N3—N2 | −176.9 (3) |
| C8—C9—C10—C11 | −1.9 (8) | C12—C7—N3—N2 | 3.0 (5) |
| C8—C9—C10—Cl2 | 177.4 (4) | C8—C7—N3—Co1 | 10.5 (6) |
| C9—C10—C11—C12 | 1.6 (7) | C12—C7—N3—Co1 | −169.6 (3) |
| Cl2—C10—C11—C12 | −177.7 (3) | N1—Co1—N3—N2 | −1.69 (19) |
| C10—C11—C12—C7 | 0.1 (6) | N1$^{i}$—Co1—N3—N2 | −106.2 (2) |
| C8—C7—C12—C11 | −1.4 (6) | N1$^{ii}$—Co1—N3—N2 | 41.0 (5) |
| N3—C7—C12—C11 | 178.6 (3) | N3$^{i}$—Co1—N3—N2 | −170.04 (19) |
| C2—C1—N1—N2 | −167.4 (3) | N3$^{ii}$—Co1—N3—N2 | 82.0 (3) |
| C6—C1—N1—N2 | 13.3 (5) | N2$^{ii}$—Co1—N3—N2 | 74.52 (18) |
| C2—C1—N1—Co1 | 34.7 (5) | N2$^{i}$—Co1—N3—N2 | −138.0 (2) |
| C6—C1—N1—Co1 | −144.5 (3) | N1—Co1—N3—C7 | 171.9 (4) |

| | | | |
|---|---|---|---|
| N1$^{i}$—Co1—N1—N2 | 85.6 (3) | N1$^{i}$—Co1—N3—C7 | 67.4 (4) |
| N1$^{ii}$—Co1—N1—N2 | −167.2 (2) | N1$^{ii}$—Co1—N3—C7 | −145.5 (4) |
| N3$^{i}$—Co1—N1—N2 | 46.6 (5) | N3$^{i}$—Co1—N3—C7 | 3.5 (4) |
| N3—Co1—N1—N2 | 1.67 (19) | N3$^{ii}$—Co1—N3—C7 | −104.4 (3) |
| N3$^{ii}$—Co1—N1—N2 | −103.3 (2) | N2$^{ii}$—Co1—N3—C7 | −111.9 (4) |
| N2$^{ii}$—Co1—N1—N2 | −134.4 (2) | N2$^{i}$—Co1—N3—C7 | 35.6 (4) |

Symmetry codes: (i) $-x+y, -x, z$; (ii) $-y, x-y, z$.