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## Structure Reports

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Tris[(2*E*)-1,3-bis(4-chlorophenyl)triaz-2-en-1-ido- $\kappa^2N^1,N^3$ ]cobalt(III)Gang Yu,<sup>a</sup> Shu-Zhong Zhan<sup>a</sup> and Seik Weng Ng<sup>b,c,\*</sup>

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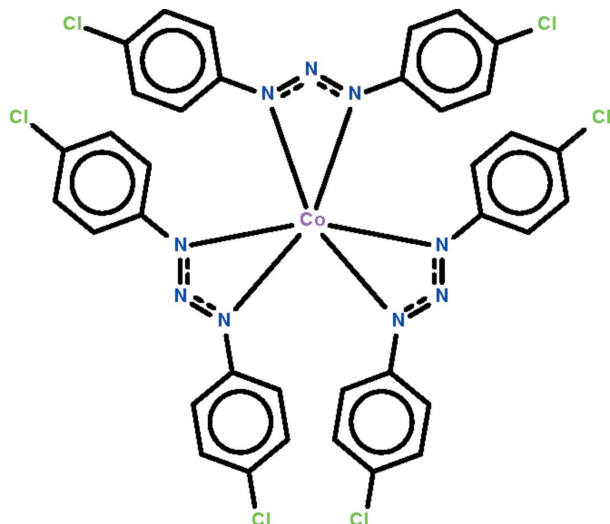
Received 7 May 2012; accepted 7 May 2012

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

Molecules of the title compound,  $[\text{Co}(\text{C}_{12}\text{H}_8\text{Cl}_2\text{N}_3)_3]$ , lie on a threefold rotation axis. The tris- $N,N'$ -chelated  $\text{Co}^{\text{III}}$  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

$[\text{Co}(\text{C}_{12}\text{H}_8\text{Cl}_2\text{N}_3)_3]$   
 $M_r = 854.27$   
Trigonal,  $R\bar{3}$   
 $a = 19.383$  (3) Å  
 $c = 17.546$  (2) Å  
 $V = 5708.5$  (10) Å<sup>3</sup>

$Z = 6$   
Mo  $K\alpha$  radiation  
 $\mu = 0.91$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.30 \times 0.25 \times 0.20$  mm

## Data collection

Bruker SMART APEX  
diffractometer  
Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 1996)  
 $T_{\text{min}} = 0.771$ ,  $T_{\text{max}} = 0.839$

8131 measured reflections  
2891 independent reflections  
1714 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.053$

## 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  
 $\Delta\rho_{\text{max}} = 0.35$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.34$  e Å<sup>-3</sup>

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: *pubCIF* (Westrip, 2010).

We thank South China University of Technology and the Ministry of Higher Education of Malaysia (grant No. UM-C/HIR/MOHE/SC/12) for supporting this study.

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

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## supplementary materials

*Acta Cryst.* (2012). E68, m758 [doi:10.1107/S1600536812020569]

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

Gang Yu, Shu-Zhong Zhan and Seik Weng Ng

**Comment**

The diaryltriazenido anion *N,N'*-chelates to a large number of metal atoms; for Co<sup>III</sup> 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<sub>12</sub>H<sub>8</sub>Cl<sub>2</sub>N<sub>3</sub>)<sub>3</sub> (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<sup>III</sup> atom shows octahedral coordination (Fig. 2). With respect to the delocalized –N=N=N– fragment, one phenylene ring is twisted by 9.5 (3) ° and the other by 21.1 (2) °.

**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<sub>12</sub>H<sub>9</sub>Cl<sub>2</sub>N<sub>3</sub>: C 54.16, H 3.41, N 15.79%. Found: C 54.07, H 3.39, N 15.66.%

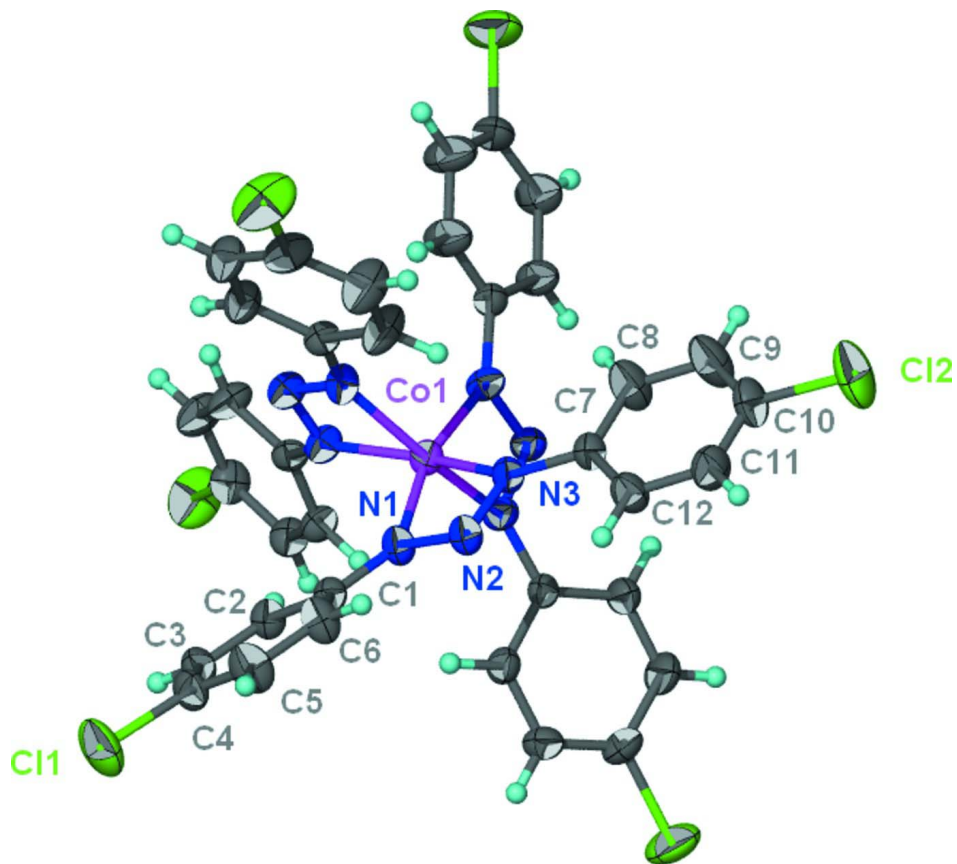
To a solution of the ligand (0.798 g, 3 mmol) and triethylamine (0.300 g, 3 mmol) in dichloromethane/acetonitrile (30 ml, 1:1) was added cobalt(II) chloride hexahydrate (0.238 g, 1 mmol). The solvent was allowed to evaporate over several days. Red crystals were isolated in 50% yield. Calc. for C<sub>36</sub>H<sub>24</sub>CoN<sub>9</sub>Cl<sub>6</sub>: C 50.59, H 2.81, N 14.76%. Found: C 51.19, H 2.68, N 14.81%.

**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).

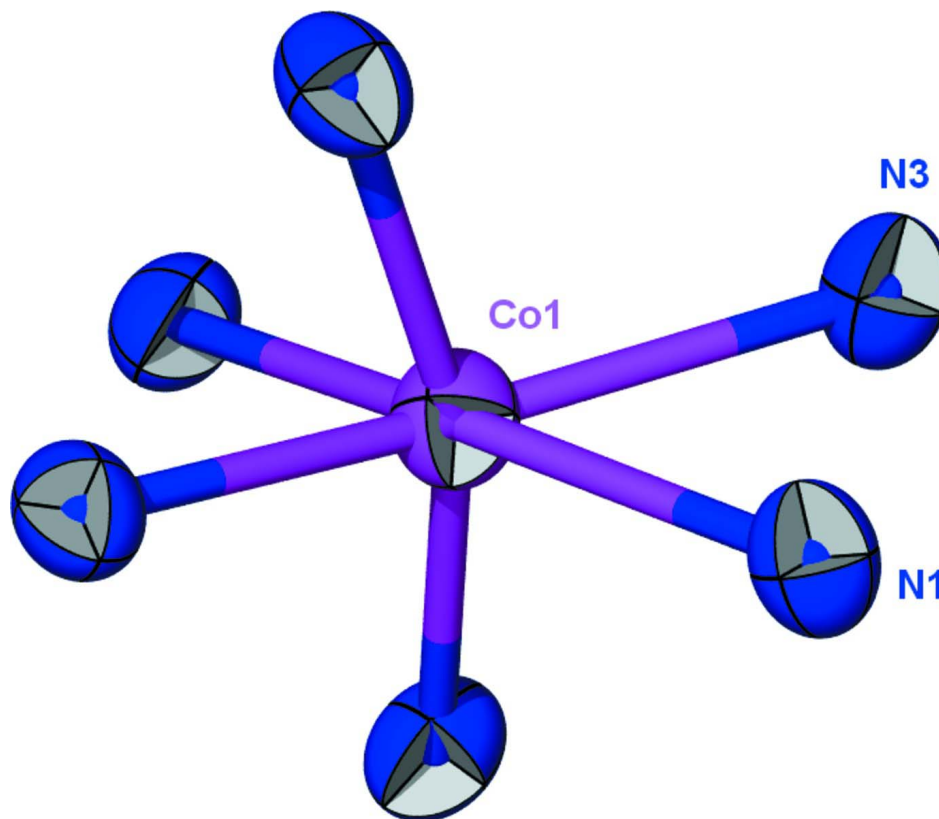
**Computing details**

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINTE* (Bruker, 2005); data reduction: *SAINTE* (Bruker, 2005); 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).



**Figure 1**

Anisotropic displacement ellipsoid plot (Barbour, 2001) of  $\text{Co}(\text{C}_{12}\text{H}_8\text{Cl}_2\text{N}_3)_3$  at the 50% probability level; hydrogen atoms are drawn as spheres of arbitrary radius. Symmetry-related atoms are not labeled.


**Figure 2**

Octahedral coordination geometry of Co<sup>III</sup>.

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

*Crystal data*

[Co(C<sub>12</sub>H<sub>8</sub>Cl<sub>2</sub>N<sub>3</sub>)<sub>3</sub>]

$M_r = 854.27$

Trigonal,  $R\bar{3}$

Hall symbol:  $-\bar{R}3$

$a = 19.383(3) \text{ \AA}$

$c = 17.546(2) \text{ \AA}$

$V = 5708.5(10) \text{ \AA}^3$

$Z = 6$

$F(000) = 2592$

$D_x = 1.491 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1211 reflections

$\theta = 2.6\text{--}22.1^\circ$

$\mu = 0.91 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Prism, red

$0.30 \times 0.25 \times 0.20 \text{ mm}$

*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  $I > 2\sigma(I)$

$R_{\text{int}} = 0.053$

$\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 1.7^\circ$

$h = -24 \rightarrow 20$

$k = -24 \rightarrow 22$

$l = -22 \rightarrow 22$

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  $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.35 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.34 \text{ e } \text{\AA}^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
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, °)*

Co1—N1	1.909 (3)	C4—C5	1.373 (5)
Co1—N1 <sup>i</sup>	1.909 (3)	C5—C6	1.376 (5)
Co1—N1 <sup>ii</sup>	1.909 (3)	C5—H5	0.9300
Co1—N3 <sup>i</sup>	1.927 (3)	C6—H6	0.9300
Co1—N3	1.927 (3)	C7—C8	1.368 (5)
Co1—N3 <sup>ii</sup>	1.927 (3)	C7—C12	1.386 (5)
Co1—N2 <sup>ii</sup>	2.441 (3)	C7—N3	1.406 (4)
Co1—N2 <sup>i</sup>	2.441 (3)	C8—C9	1.381 (6)
C11—C4	1.737 (4)	C8—H8	0.9300
C12—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 <sup>i</sup>	103.22 (10)	C2—C3—H3	120.3
N1—Co1—N1 <sup>ii</sup>	103.22 (10)	C5—C4—C3	121.3 (3)
N1 <sup>i</sup> —Co1—N1 <sup>ii</sup>	103.22 (10)	C5—C4—C11	120.0 (3)
N1—Co1—N3 <sup>i</sup>	163.88 (12)	C3—C4—C11	118.7 (3)
N1 <sup>i</sup> —Co1—N3 <sup>i</sup>	64.54 (12)	C4—C5—C6	119.6 (4)
N1 <sup>ii</sup> —Co1—N3 <sup>i</sup>	90.28 (12)	C4—C5—H5	120.2
N1—Co1—N3	64.54 (12)	C6—C5—H5	120.2
N1 <sup>i</sup> —Co1—N3	90.28 (12)	C5—C6—C1	120.3 (3)
N1 <sup>ii</sup> —Co1—N3	163.88 (12)	C5—C6—H6	119.8
N3 <sup>i</sup> —Co1—N3	103.63 (10)	C1—C6—H6	119.8
N1—Co1—N3 <sup>ii</sup>	90.28 (12)	C8—C7—C12	119.3 (3)
N1 <sup>i</sup> —Co1—N3 <sup>ii</sup>	163.88 (12)	C8—C7—N3	118.7 (3)
N1 <sup>ii</sup> —Co1—N3 <sup>ii</sup>	64.54 (12)	C12—C7—N3	122.0 (3)
N3 <sup>i</sup> —Co1—N3 <sup>ii</sup>	103.63 (10)	C7—C8—C9	120.3 (4)
N3—Co1—N3 <sup>ii</sup>	103.63 (10)	C7—C8—H8	119.8
N1—Co1—N2 <sup>ii</sup>	98.78 (11)	C9—C8—H8	119.8
N1 <sup>i</sup> —Co1—N2 <sup>ii</sup>	134.58 (11)	C10—C9—C8	120.4 (4)

N1 <sup>ii</sup> —Co1—N2 <sup>ii</sup>	32.42 (10)	C10—C9—H9	119.8
N3 <sup>i</sup> —Co1—N2 <sup>ii</sup>	97.33 (11)	C8—C9—H9	119.8
N3—Co1—N2 <sup>ii</sup>	135.13 (11)	C9—C10—C11	120.7 (4)
N3 <sup>ii</sup> —Co1—N2 <sup>ii</sup>	32.14 (10)	C9—C10—C12	120.5 (4)
N1—Co1—N2 <sup>i</sup>	134.58 (11)	C11—C10—C12	118.8 (3)
N1 <sup>i</sup> —Co1—N2 <sup>i</sup>	32.42 (10)	C10—C11—C12	119.7 (4)
N1 <sup>ii</sup> —Co1—N2 <sup>i</sup>	98.78 (11)	C10—C11—H11	120.1
N3 <sup>i</sup> —Co1—N2 <sup>i</sup>	32.14 (10)	C12—C11—H11	120.1
N3—Co1—N2 <sup>i</sup>	97.33 (11)	C11—C12—C7	119.5 (4)
N3 <sup>ii</sup> —Co1—N2 <sup>i</sup>	135.13 (11)	C11—C12—H12	120.3
N2 <sup>ii</sup> —Co1—N2 <sup>i</sup>	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 <sup>i</sup> —Co1—N1—N2	75.96 (18)
N1—C1—C2—C3	-179.0 (3)	N1 <sup>i</sup> —Co1—N1—C1	-113.8 (3)
C1—C2—C3—C4	0.1 (5)	N1 <sup>ii</sup> —Co1—N1—C1	-6.5 (4)
C2—C3—C4—C5	-1.0 (6)	N3 <sup>i</sup> —Co1—N1—C1	-152.7 (4)
C2—C3—C4—C11	178.3 (3)	N3—Co1—N1—C1	162.3 (4)
C3—C4—C5—C6	1.4 (6)	N3 <sup>ii</sup> —Co1—N1—C1	57.4 (4)
C11—C4—C5—C6	-177.8 (3)	N2 <sup>ii</sup> —Co1—N1—C1	26.2 (4)
C4—C5—C6—C1	-1.0 (6)	N2 <sup>i</sup> —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—C12	177.4 (4)	C8—C7—N3—Co1	10.5 (6)
C9—C10—C11—C12	1.6 (7)	C12—C7—N3—Co1	-169.6 (3)
C12—C10—C11—C12	-177.7 (3)	N1—Co1—N3—N2	-1.69 (19)
C10—C11—C12—C7	0.1 (6)	N1 <sup>i</sup> —Co1—N3—N2	-106.2 (2)
C8—C7—C12—C11	-1.4 (6)	N1 <sup>ii</sup> —Co1—N3—N2	41.0 (5)
N3—C7—C12—C11	178.6 (3)	N3 <sup>i</sup> —Co1—N3—N2	-170.04 (19)
C2—C1—N1—N2	-167.4 (3)	N3 <sup>ii</sup> —Co1—N3—N2	82.0 (3)
C6—C1—N1—N2	13.3 (5)	N2 <sup>ii</sup> —Co1—N3—N2	74.52 (18)
C2—C1—N1—Co1	34.7 (5)	N2 <sup>i</sup> —Co1—N3—N2	-138.0 (2)
C6—C1—N1—Co1	-144.5 (3)	N1—Co1—N3—C7	171.9 (4)
N1 <sup>i</sup> —Co1—N1—N2	85.6 (3)	N1 <sup>i</sup> —Co1—N3—C7	67.4 (4)
N1 <sup>ii</sup> —Co1—N1—N2	-167.2 (2)	N1 <sup>ii</sup> —Co1—N3—C7	-145.5 (4)
N3 <sup>i</sup> —Co1—N1—N2	46.6 (5)	N3 <sup>i</sup> —Co1—N3—C7	3.5 (4)
N3—Co1—N1—N2	1.67 (19)	N3 <sup>ii</sup> —Co1—N3—C7	-104.4 (3)

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N3 <sup>ii</sup> —Co1—N1—N2	-103.3 (2)	N2 <sup>ii</sup> —Co1—N3—C7	-111.9 (4)
N2 <sup>ii</sup> —Co1—N1—N2	-134.4 (2)	N2 <sup>i</sup> —Co1—N3—C7	35.6 (4)

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