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catena-Poly[cobalt(II)-di- μ -chlorido- κ^4 Cl:Cl- μ -1,5-dimethyl-1*H*-tetrazole- κ^2 N³:N⁴]: an X-ray powder investigation

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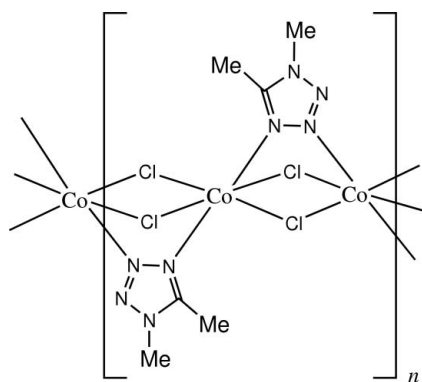
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Key indicators: powder X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.015$ Å; R factor = 0.018; wR factor = 0.024; data-to-parameter ratio = 19.9.

The asymmetric unit of the title compound, $[\text{CoCl}_2(\text{C}_3\text{H}_6\text{N}_4)]_n$, contains two Co atoms, both lying on inversion centres, two Cl atoms and one 1,5-dimethyltetrazole ligand. The coordination polyhedra of both Co atoms adopt flattened octahedral geometry, with two N atoms from two ligands in axial positions and four Cl atoms in equatorial sites. Neighbouring Co atoms are linked together *via* two bridging Cl atoms and one tetrazole ring to form polymeric chains running along the a axis.

Related literature

For the crystal structure of a related Cu complex, see: Ivashkevich *et al.* (2006). For values of radii for ions with octahedral coordination and molecular geometric parameters, see: Shannon (1976) and Allen (2002), respectively. For details of the indexing algorithm, see: Werner *et al.* (1985).



Experimental

Crystal data

$[\text{CoCl}_2(\text{C}_3\text{H}_6\text{N}_4)]$
 $M_r = 227.95$
Triclinic, $P\bar{1}$
 $a = 6.7159$ (4) Å
 $b = 7.5986$ (4) Å
 $c = 8.9231$ (5) Å
 $\alpha = 108.639$ (2)°
 $\beta = 107.259$ (3)°
 $\gamma = 105.769$ (3)°
 $V = 376.72$ (4) Å³

$Z = 2$
Co $K\alpha$ radiation
 $T = 295$ K
Specimen shape: flat sheet
 $30 \times 30 \times 1$ mm
Specimen prepared at 100 kPa
Specimen prepared at 295 K
Particle morphology: finely ground powder, light-violet

Data collection

HZG-4A (Carl Zeiss, Jena)
diffractometer
Specimen mounting: packed powder pellet

Specimen mounted in reflection mode
Scan method: step
 $2\theta_{\min} = 11.0$, $2\theta_{\max} = 130.0$ °
Increment in $2\theta = 0.02$ °

Refinement

$R_p = 0.018$
 $R_{wp} = 0.024$
 $R_{\text{exp}} = 0.025$
 $R_B = 0.023$
 $S = 0.97$
Wavelength of incident radiation:
1.79021 Å
Excluded region(s): none

Profile function: pseudo-Voigt,
 $\eta = 0.664(5)$
896 reflections
45 parameters
7 restraints
H-atom parameters constrained
Preferred orientation correction:
none

Table 1

Selected bond lengths (Å).

Co1—Cl2	2.461 (3)	Co2—Cl1	2.446 (3)
Co1—N4	2.224 (10)	Co2—N3	2.111 (9)
Co1—Cl ⁱ	2.482 (3)	Co2—Cl2 ⁱⁱ	2.479 (3)

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

Data collection: local program; cell refinement: *FULLPROF* (Rodríguez-Carvajal, 2001); data reduction: local program; program(s) used to refine structure: *FULLPROF*; molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *FULLPROF*, *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2491).

References

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supporting information

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catena-Poly[cobalt(II)-di- μ -chlorido- κ^4 Cl:Cl- μ -1,5-dimethyl-1H-tetrazole- κ^2 N³:N⁴]: an X-ray powder investigation

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S1. Comment

In our previous paper (Ivashkevich *et al.*, 2006) we reported the crystal structure of copper(II) chloride complex with 1,5-dimethyltetrazole, CuCl₂L. That was the first experimental findings of bridge coordination of 1,5-disubstituted tetrazoles through the tetrazole ring bridge N3—N4. In the present work, we report another example of such type complexes, namely the title complex of cobalt(II) chloride with 1,5-dimethyltetrazole, (I).

Complex (I) has a 1:1 metal-to-ligand ratio of cobalt(II) with the 1,5-dimethyltetrazole. The asymmetric unit contains two Co atoms, both lying on inversion centres, two Cl atoms and one 1,5-dimethyltetrazole molecule, all in general positions. Co1 is bonded to the tetrazole ring atoms N4, whereas Co2 coordinates the tetrazole ring atoms N3 (Fig. 1). The tetrazole ring geometry is typical of 1- and 1,5-substituted tetrazoles. The complex is a one-dimensional coordination polymer, with polymeric chains running along the *a* axis (Fig.1,2). The chains are formed due to chloride bridges and the tetrazole ring bridges N3—N4 between the neighbouring Co atoms.

Complex (I) is isotypic with the above copper(II) analogue, and it is of interest to compare the structures of the compounds. Whereas Cu coordination octahedra show essential elongation of axial Cu—Cl bonds compared to equatorial Cu—Cl and Cu—N ones, Co octahedra are flattened, with axial Co—N bonds and very similar in lengths equatorial Co—Cl bonds. In Co1 and Co2 octahedra, the difference between the axial and equatorial bond lengths (Table 1), being much less than that in the Cu octahedra, may be related to difference in size of Cl and N atoms. However, essential elongation of the Cu octahedra is probably induced by the Jahn-Teller effect. In complex (I), closely spaced values of all Co—Cl bond lengths are responsible for rather symmetrical chloride bridges between the neighbouring Co atoms in polymeric chains, in contrast to copper(II) analogue with non-symmetrical chloride bridges.

Comparing the cell volumes of the two isotypic compounds [374.15 (4) Å³ for Cu complex and 376.72 (4) Å³ for Co one and taking into account octahedral ionic radii (Shannon, 1976) of Cu^{II} (0.73 Å) and Co^{II} (0.65 Å for low-spin state and 0.75 Å for high-spin state), one may expect that cations Co^{II} in complex(I) are in high-spin state at room temperature. This conclusion is confirmed by EPR investigation of the complex, which does not reveal EPR spectra at room temperature. As known, Co^{II} cations in high-spin state shows EPR signals only at very low temperatures.

S2. Experimental

A solution, containing 1.17 g (0.005 mol) of CoCl₂·6H₂O in 10 ml of a mixture of methanol and triethyl orthoformate (*v/v* = 1:1), was added to a solution of 1,5-dimethyltetrazole (0.5 g, 0.0051 mol) in 10 ml of the same solvent mixture. After stirring the reaction mixture at 323–333 K C for 0.5 h, the obtained light-violet crystals of (I) were filtered off, washed with methanol (2 × 5 ml), and dried in air [0.96 g, yield 84%; m.p. 633 K (decomposition)]. Calc. (%): Co 25.8, Cl 30.6.

Found (%): Co 25.7, Cl 31.1. IR (cm⁻¹): 3044 (*m*), 3025 (*s*), 2962 (*m*), 2938 (*m*), 1535 (*s*), 1480 (*m*), 1454 (*w*), 1409 (*w*), 1396 (*m*), 1383 (*s*), 1332 (*s*), 1265 (*m*), 1235 (*s*), 1144 (*s*), 1090 (*w*), 1060 (*s*), 1031 (*m*), 739 (*s*), 681 (*m*), 607 (*w*), 565 (*w*), 525 (*w*).

S3. Refinement

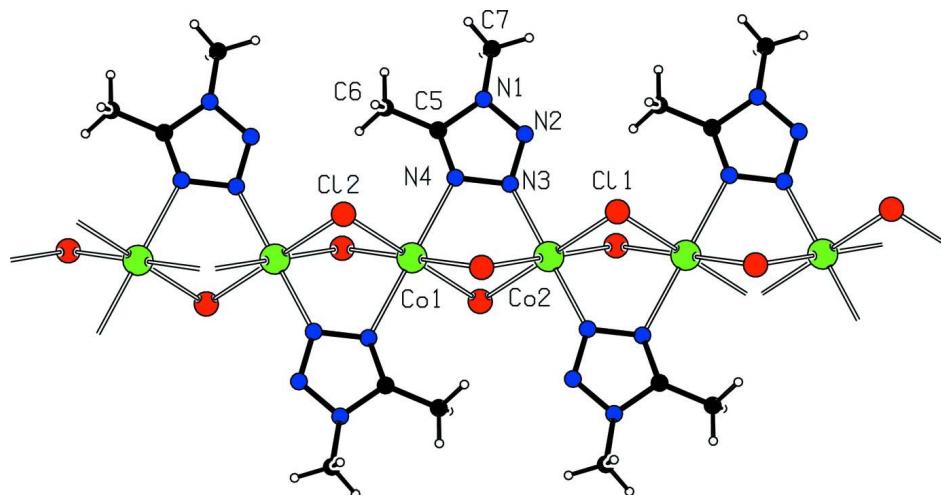
For complex (I), a triclinic unit cell ($a = 6.728$, $b = 7.596$, $c = 8.764$ Å, $\alpha = 109.62$, $\beta = 102.96$, $\gamma = 105.70^\circ$) was determined using the indexing program TREOR90 (Werner *et al.*, 1985). The obtained values as well as observed resemblance of powder patterns indicated isotypism of (I) with investigated earlier coordination polymers CuCl₂L, where $L = 1,5$ -dimethyltetrazole, crystallizing in the space group $P\bar{1}$ (Ivashkevich *et al.*, 2006). This space group and the atomic coordinates of the above copper(II) complex were used as starting parameters for the Rietveld refinement of (I) with the FULLPROF program (Rodríguez-Carvajal, 2001). However, the refinement found difficulty in reaching the agreement of experimental and calculated intensities of reflections. From this fact an assumption was made that the above unit-cell dimensions were inconsistent with the initial atomic coordinates. Search for alternative unit cells resulted in the following cell: $a' = 6.728$, $b' = 7.596$, $c' = 8.997$ Å; $\alpha' = 108.35$, $\beta' = 107.50$, $\gamma' = 105.70^\circ$, which is of the same volume and related to the first one by the vector transformation $a' = -a$, $b' = -b$, $c' = a + b + c$. This cell provided a good agreement of the observed and calculated intensities.

Background intensity was found by Fourier filtering technique as implemented in the FULLPROF program, under visual inspection of the resulting background curve. Correction for profile asymmetry was made for reflections up to $2\theta = 25^\circ$.

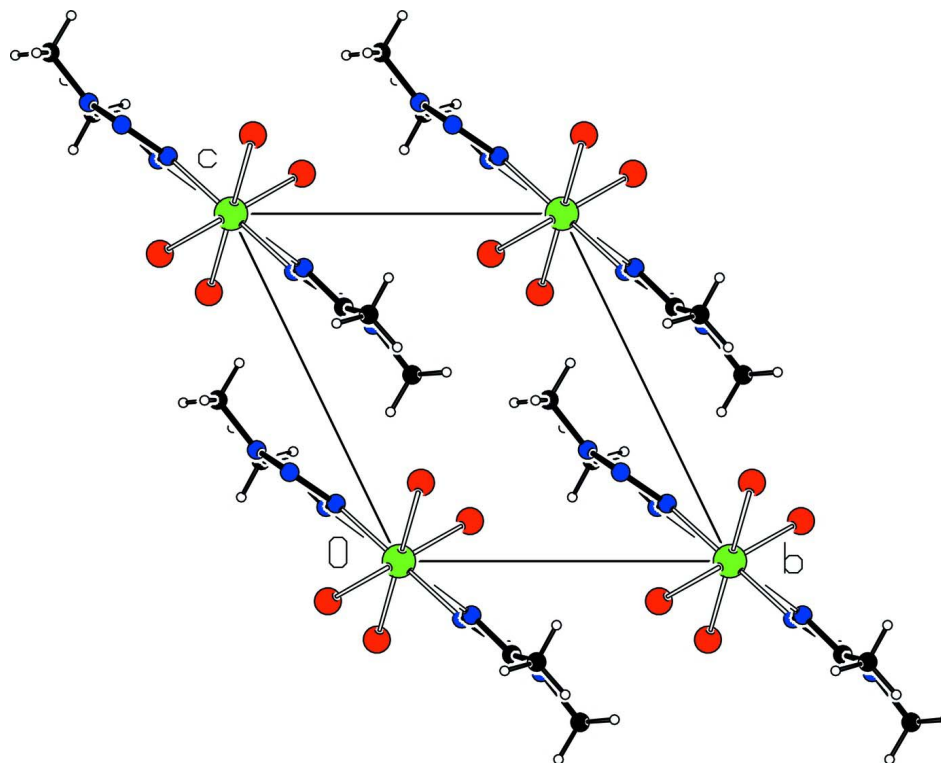
The H atoms of the methyl groups were placed in geometrically calculated positions using the program *SHELXL97* (Sheldrick, 2008), with displacement parameter $B_{\text{iso}}(\text{H}) = 1.5B_{\text{iso}}(\text{C})$. Non-H atoms were refined isotropically. Four independent B_{iso} parameters were employed: one for the two Co, one for the two Cl atoms, one for all N and C atoms of the tetrazole ring, and one for the C atoms of the methyl groups.

For the refinement, suitable restraints were imposed on bond lengths of the ligand molecule, based on a geometry analysis of 1,5-alkyltetrazoles (Cambridge Structural Database, version 5.29 of November 2007; Allen, 2002). The restraints were set as $d(3\sigma)$, where d are mean values of bond distances resulting from a CSD survey, and σ are their s.u. values. For the refined atomic coordinates of (I), the s.u. values are taken from the software and likely to be underestimated.

The observed, calculated and difference diffraction patterns for the refined crystal structure are shown in Fig. 3 (2θ range of $11-90^\circ$ is presented).

**Figure 1**

A portion of the polymeric chain of (I) running along the a axis. The atomic numbering scheme is given for the asymmetric unit.

**Figure 2**

The crystal structure of (I), viewed along the a axis.

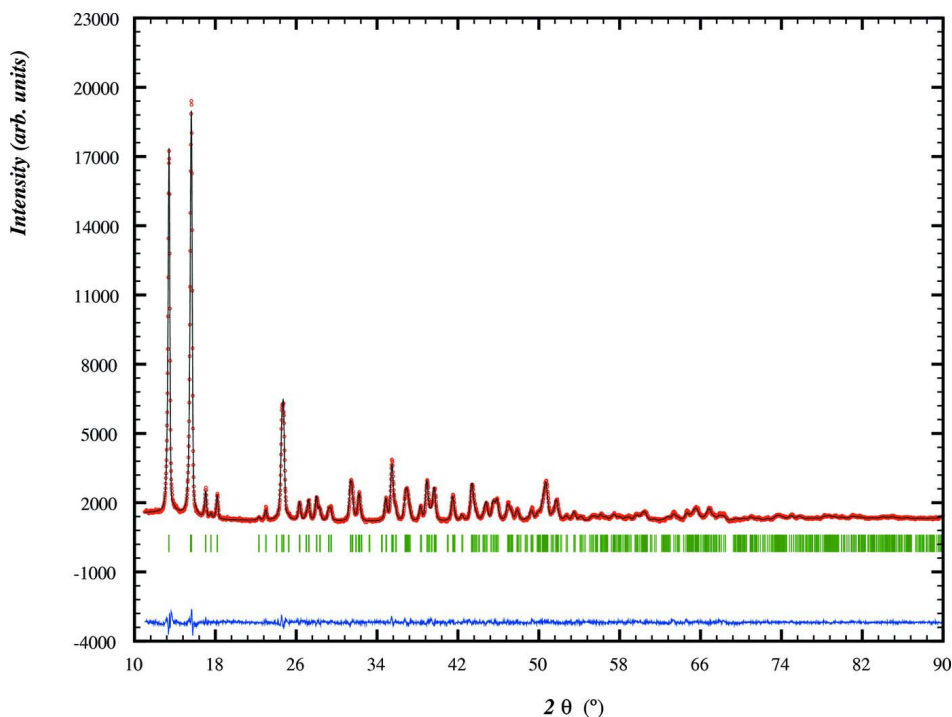


Figure 3

The Rietveld plot for (I), showing the observed (red circles), calculated (black line) and difference (blue line) patterns. The reflection positions are shown as vertical bars above the difference pattern.

catena-Poly[cobalt(II)-di- μ -chlorido- κ^4 Cl:Cl- μ -1,5-dimethyl-1H-tetrazole- κ^2 N³:N⁴]

Crystal data

[CoCl₂(C₃H₆N₄)]
 $M_r = 227.95$
 Triclinic, $P\bar{1}$
 Hall symbol: -P 1
 $a = 6.7159$ (4) Å
 $b = 7.5986$ (4) Å
 $c = 8.9231$ (5) Å
 $\alpha = 108.639$ (2)°
 $\beta = 107.259$ (3)°
 $\gamma = 105.769$ (3)°
 $V = 376.72$ (4) Å³

$Z = 2$
 $F(000) = 226$
 $D_x = 2.010$ Mg m⁻³
 Co $K\alpha$ radiation, $\lambda = 1.79021$ Å
 $T = 295$ K
 Particle morphology: finely ground powder
 light-violet
 flat sheet, 30 × 30 mm
 Specimen preparation: Prepared at 295 K and
 100 kPa

Data collection

HZG-4A (Carl Zeiss, Jena)
 diffractometer
 Radiation source: fine-focus sealed X-ray tube,
 BSV-29
 Fe filtered monochromator

Specimen mounting: packed powder pellet
 Data collection mode: reflection
 Scan method: step
 $2\theta_{\min} = 11.000^\circ$, $2\theta_{\max} = 130.000^\circ$, $2\theta_{\text{step}} = 0.020^\circ$

Refinement

Refinement on I_{net}
 Least-squares matrix: full with fixed elements
 per cycle

$R_p = 0.018$
 $R_{\text{wp}} = 0.024$
 $R_{\text{exp}} = 0.025$

$R_{\text{Bragg}} = 0.023$
 $\chi^2 = 0.941$
 5951 data points
 Excluded region(s): none
 Profile function: pseudo-Voigt, $\eta = 0.664(5)$
 45 parameters
 7 restraints

0 constraints
 H-atom parameters constrained
 Weighting scheme based on measured s.u.'s
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 Background function: Fourier filtering
 Preferred orientation correction: none

Special details

Geometry. Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.00000	1.00000	0.00000	0.0183 (8)*
Co2	0.50000	1.00000	0.00000	0.0183 (8)*
C11	0.6168 (5)	0.7266 (4)	-0.1147 (4)	0.0254 (9)*
C12	-0.1025 (5)	1.1819 (4)	0.2275 (4)	0.0254 (9)*
N1	0.3124 (10)	0.7423 (14)	0.3267 (10)	0.032 (2)*
N2	0.4540 (11)	0.8008 (13)	0.2565 (10)	0.032 (2)*
N3	0.3888 (9)	0.8891 (13)	0.1626 (10)	0.032 (2)*
N4	0.1745 (10)	0.8607 (14)	0.1504 (11)	0.032 (2)*
C5	0.1349 (12)	0.783 (2)	0.2552 (15)	0.032 (2)*
C6	-0.0585 (12)	0.7367 (16)	0.2934 (13)	0.035 (3)*
H6A	-0.03346	0.68164	0.37682	0.053*
H6B	-0.19026	0.63786	0.18797	0.053*
H6C	-0.08251	0.85734	0.33971	0.053*
C7	0.3895 (17)	0.6847 (16)	0.4623 (10)	0.035 (3)*
H7A	0.52906	0.66940	0.46948	0.053*
H7B	0.27627	0.55778	0.43745	0.053*
H7C	0.41569	0.78730	0.57057	0.053*

Geometric parameters (\AA , $^\circ$)

Co1—C12	2.461 (3)	N1—C5	1.341 (14)
Co1—N4	2.224 (10)	N1—C7	1.419 (14)
Co1—C11 ⁱ	2.482 (3)	N2—N3	1.283 (13)
Co1—C12 ⁱⁱ	2.461 (3)	N3—N4	1.361 (11)
Co1—N4 ⁱⁱ	2.224 (10)	N4—C5	1.307 (17)
Co1—C11 ⁱⁱⁱ	2.482 (3)	C5—C6	1.421 (15)
Co2—C11	2.446 (3)	C6—H6A	0.9600
Co2—N3	2.111 (9)	C6—H6B	0.9600
Co2—C12 ^{iv}	2.479 (3)	C6—H6C	0.9600
Co2—C12 ⁱⁱ	2.479 (3)	C7—H7A	0.9600
Co2—C11 ⁱⁱⁱ	2.446 (3)	C7—H7B	0.9600
Co2—N3 ⁱⁱⁱ	2.111 (9)	C7—H7C	0.9600
N1—N2	1.340 (12)		

Cl2—Co1—N4	95.5 (2)	Cl1 ⁱⁱⁱ —Co2—N3 ⁱⁱⁱ	94.9 (3)
Cl1 ⁱ —Co1—Cl2	84.91 (11)	Co1 ^{iv} —Cl1—Co2	85.92 (10)
Cl2—Co1—Cl2 ⁱⁱ	180.00	Co1—Cl2—Co2 ⁱ	85.65 (10)
Cl2—Co1—N4 ⁱⁱ	84.5 (2)	N2—N1—C5	103.6 (9)
Cl1 ⁱⁱⁱ —Co1—Cl2	95.09 (11)	N2—N1—C7	118.7 (8)
Cl1 ⁱ —Co1—N4	93.6 (3)	C5—N1—C7	137.0 (10)
Cl2 ⁱⁱ —Co1—N4	84.5 (2)	N1—N2—N3	113.8 (8)
N4—Co1—N4 ⁱⁱ	180.00	Co2—N3—N2	136.1 (6)
Cl1 ⁱⁱⁱ —Co1—N4	86.4 (3)	Co2—N3—N4	119.0 (7)
Cl1 ⁱ —Co1—Cl2 ⁱⁱ	95.09 (11)	N2—N3—N4	103.5 (8)
Cl1 ⁱ —Co1—N4 ⁱⁱ	86.4 (3)	Co1—N4—N3	115.1 (7)
Cl1 ⁱ —Co1—Cl1 ⁱⁱⁱ	180.00	Co1—N4—C5	134.3 (7)
Cl2 ⁱⁱ —Co1—N4 ⁱⁱ	95.5 (2)	N3—N4—C5	109.6 (9)
Cl1 ⁱⁱⁱ —Co1—Cl2 ⁱⁱ	84.91 (11)	N1—C5—N4	108.8 (9)
Cl1 ⁱⁱⁱ —Co1—N4 ⁱⁱ	93.6 (3)	N1—C5—C6	121.2 (12)
Cl1—Co2—N3	94.9 (3)	N4—C5—C6	130.0 (11)
Cl1—Co2—Cl2 ^{iv}	85.31 (11)	C5—C6—H6A	109.00
Cl1—Co2—Cl2 ⁱⁱ	94.69 (11)	C5—C6—H6B	109.00
Cl1—Co2—Cl1 ⁱⁱⁱ	180.00	C5—C6—H6C	110.00
Cl1—Co2—N3 ⁱⁱⁱ	85.1 (3)	H6A—C6—H6B	109.00
Cl2 ^{iv} —Co2—N3	91.3 (2)	H6A—C6—H6C	110.00
Cl2 ⁱⁱ —Co2—N3	88.7 (2)	H6B—C6—H6C	110.00
Cl1 ⁱⁱⁱ —Co2—N3	85.1 (3)	N1—C7—H7A	109.00
N3—Co2—N3 ⁱⁱⁱ	180.00	N1—C7—H7B	109.00
Cl2 ^{iv} —Co2—Cl2 ⁱⁱ	180.00	N1—C7—H7C	109.00
Cl1 ⁱⁱⁱ —Co2—Cl2 ^{iv}	94.69 (11)	H7A—C7—H7B	109.00
Cl2 ^{iv} —Co2—N3 ⁱⁱⁱ	88.7 (2)	H7A—C7—H7C	110.00
Cl1 ⁱⁱⁱ —Co2—Cl2 ⁱⁱ	85.31 (11)	H7B—C7—H7C	110.00
Cl2 ⁱⁱ —Co2—N3 ⁱⁱⁱ	91.3 (2)		

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