

The azide-bridged mixed-valent cobalt(II,III) compound $[(\text{CH}_3)_3\text{NH}]_2[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\text{N}_3)_{10}]$

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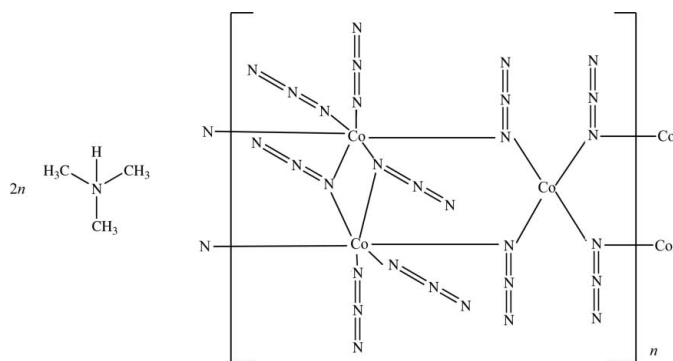
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{N}-\text{C}) = 0.006$ Å; R factor = 0.032; wR factor = 0.061; data-to-parameter ratio = 12.6.

The crystal structure of the title compound, poly[bis(trimethylammonium) hexa- $\mu_{1,1}$ -azido-tetraazidotricobaltate(II,III)], $[(\text{CH}_3)_3\text{NH}]_2[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\text{N}_3)_{10}]$, consists of anionic chains $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}_2(\text{N}_3)_{10}]^{2-}$ extending parallel to the c axis and $[(\text{CH}_3)_3\text{NH}]^+$ counter-cations situated between the chains. In the anionic chain, one tetrahedrally coordinated Co^{II} atom (site symmetry 2) and two octahedrally coordinated Co^{III} atoms are arranged alternately and are linked by $\mu_{1,1}$ -azide bridges. The anionic chains and cations are connected *via* $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonding into a three-dimensional structure.

Related literature

For background to transition-metal azido-complexes templated by counter-cations of various sizes, see: Liu *et al.* (2006, 2008). For related cobalt complexes, see: Zhang *et al.* (2010).



Experimental

Crystal data

$(\text{C}_3\text{H}_{10}\text{N})_2[\text{Co}_3(\text{N}_3)_{10}]$
 $M_r = 717.33$
 Monoclinic, $C2/c$

$a = 21.7200$ (6) Å
 $b = 11.3812$ (4) Å
 $c = 12.1628$ (4) Å

$\beta = 115.524$ (2)°
 $V = 2713.21$ (15) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

$\mu = 1.88$ mm⁻¹
 $T = 293$ K
 $0.10 \times 0.06 \times 0.05$ mm

Data collection

Rigaku Saturn diffractometer
 Absorption correction: multi-scan
 (*REQAB*; Jacobson, 1998)
 $T_{\text{min}} = 0.708$, $T_{\text{max}} = 0.823$

22049 measured reflections
 2389 independent reflections
 1481 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.103$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.061$
 $S = 0.98$
 2389 reflections
 190 parameters

24 restraints
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.31$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.35$ e Å⁻³

Table 1
 Selected bond lengths (Å).

Co1—N7	1.944 (3)	Co1—N13	2.008 (3)
Co1—N4	1.948 (3)	Co2—N1 ⁱⁱ	1.968 (3)
Co1—N10	1.964 (3)	Co2—N1	1.968 (3)
Co1—N1	1.979 (3)	Co2—N10 ⁱ	2.014 (3)
Co1—N13 ⁱ	2.008 (3)	Co2—N10 ⁱⁱⁱ	2.014 (3)

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

Table 2
 Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N16}-\text{H16}\cdots\text{N7}$	0.91	2.02	2.890	159

Data collection: *CrystalClear* (Rigaku/MSC, 2006); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2430).

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supporting information

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The azide-bridged mixed-valent cobalt(II,III) compound



Yan-Ju Liu, Yu-Xian Li, Min Xu and Xia Wang

S1. Comment

Azido-bridged complexes have attracted a lot of attention in recent times because of their importance in diverse fields, encompassing condensed matter physics, materials chemistry, biological chemistry, *etc.* Having diverse coordination modes and being an efficient magnetic coupler, the azide anion is a versatile ligand in bridging different transition metals, generating rich and fascinating architectures ranging from discrete polynuclears to extended three-dimensional networks with interesting magnetic properties (antiferromagnetic, ferromagnetic, ferrimagnetic, canted and alternating systems). In fact, remarkable structural variations of azido-bridged complexes have been reported by using various ancillary ligands, with different number of coordination sites and steric hindrance, to control over the dimensions of complexes and bridging modes of the azide anions, thus leading to the control over their magnetic properties. However, only a few metal-azido systems devoid of ancillary ligands have been obtained by varying the size of the counterions (Liu *et al.*, 2006, 2008). A small counterion such as $(\text{CH}_3)_4\text{N}^+$ produced the one-dimensional ferromagnetic complex $[(\text{CH}_3)_4\text{N}][\text{Cu}(\text{N}_3)_3]$, in which the Cu(II) ions are connected by a triple azido-bridge, including two $\mu_{1,3}\text{-N}_3$ and one $\mu_{1,1}\text{-N}_3$ anions. When more bulky counterions were employed, the mononuclear paramagnetic complex $[(\text{CH}_3\text{CH}_2)_4\text{N}][\text{Cu}(\text{N}_3)_4]$, the dinuclear antiferromagnetic complex $[(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}]_2[\text{Cu}_2(\text{N}_3)_6]$ and the one-dimensional ferromagnetic complex $[(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{N}]_2[\text{Cu}_3(\text{N}_3)_8]$ were obtained separately. For manganese(II)-azido complexes, use of small counterions like $(\text{CH}_3)_4\text{N}^+$ and Cs^+ produced compounds with interesting three-dimensional structures $[(\text{CH}_3)_4\text{N}][\text{Mn}(\text{N}_3)_3]$ and $\text{Cs}[\text{Mn}(\text{N}_3)_3]$, where the cations are situated in the voids of the anionic Mn^{II}-azido network. When using the more bulky cation $(\text{CH}_3\text{CH}_2)_4\text{N}^+$, the one-dimensional ferromagnetic complex $[(\text{CH}_3\text{CH}_2)_4\text{N}][\text{Mn}(\text{N}_3)_3]$ was obtained. Despite the results obtained above, azido-bridged complexes with mixed-valent metal ions have not been reported. In this work, we report on a mixed-valence cobalt(II,III) complex, $[(\text{CH}_3)_3\text{NH}]_2[\text{Co}^{\text{II}}\text{Co}^{\text{III}}_2(\text{N}_3)_{10}]$, (I).

The structure of (I) consists of anionic chains $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}_2(\text{N}_3)_{10}]^{2-}$ extending parallel to the *c*-axis. The $[(\text{CH}_3)_3\text{NH}]^+$ counterions are situated between the chains (Fig. 1). In the $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}_2(\text{N}_3)_{10}]^{2-}$ anionic chain, the Co^{II} atom (Co2, site symmetry 2) is tetrahedrally coordinated by N atoms, whereas the Co^{III} atom (Co1) is octahedrally coordinated. Co^{II} and Co^{III} atoms are linked by $\mu_{1,1}$ -azido ligands and are alternatively arranged along the chain direction. The Co1—N distances range between 1.944 (3)–2.008 (3) Å, slightly longer than those expected for Co^{III}. The Co2—N distances range between 1.968 (3)–2.014 (3) Å, slightly shorter than those expected for Co^{II} (Zhang *et al.*, 2010). The anionic chain and the cations are connected *via* N—H⋯N hydrogen bonding between the donating N—H function of the cation and non-bridging azido groups of the anion (Fig 2).

S2. Experimental

In a test tube a 5 ml methanol solution of 0.10M $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was layered carefully with 3 ml methanol and then with 10 ml methanol solution of 0.20M HCl, 0.20M NaN_3 , and 0.10M trimethylamine. The tube was sealed and kept undisturbed. Tiny red columnar crystals appeared overnight. Crystallization time of one week produced crystals in a yield of 25% based on the metal salt.

S3. Refinement

Hydrogen atoms were added geometrically and were refined using a riding model, with $\text{C}-\text{H} = 0.98 \text{ \AA}$ (CH_3) and $\text{N}-\text{H} = 0.89 \text{ \AA}$.

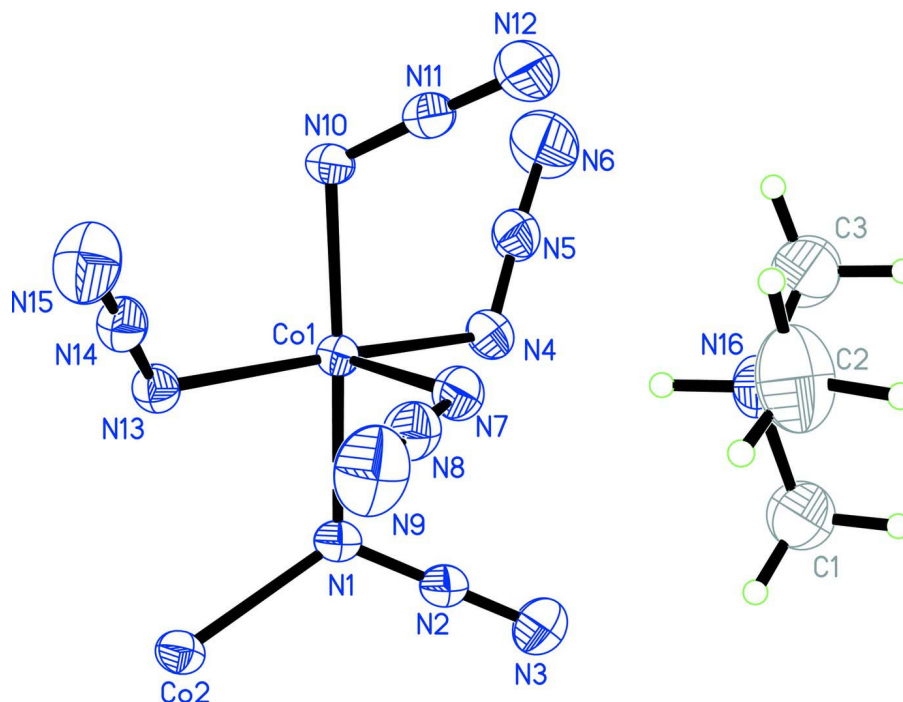


Figure 1

The asymmetric unit of the title structure. All non-H atoms are labelled and are shown with displacement ellipsoids at the 30% probability level. H atoms have been omitted.

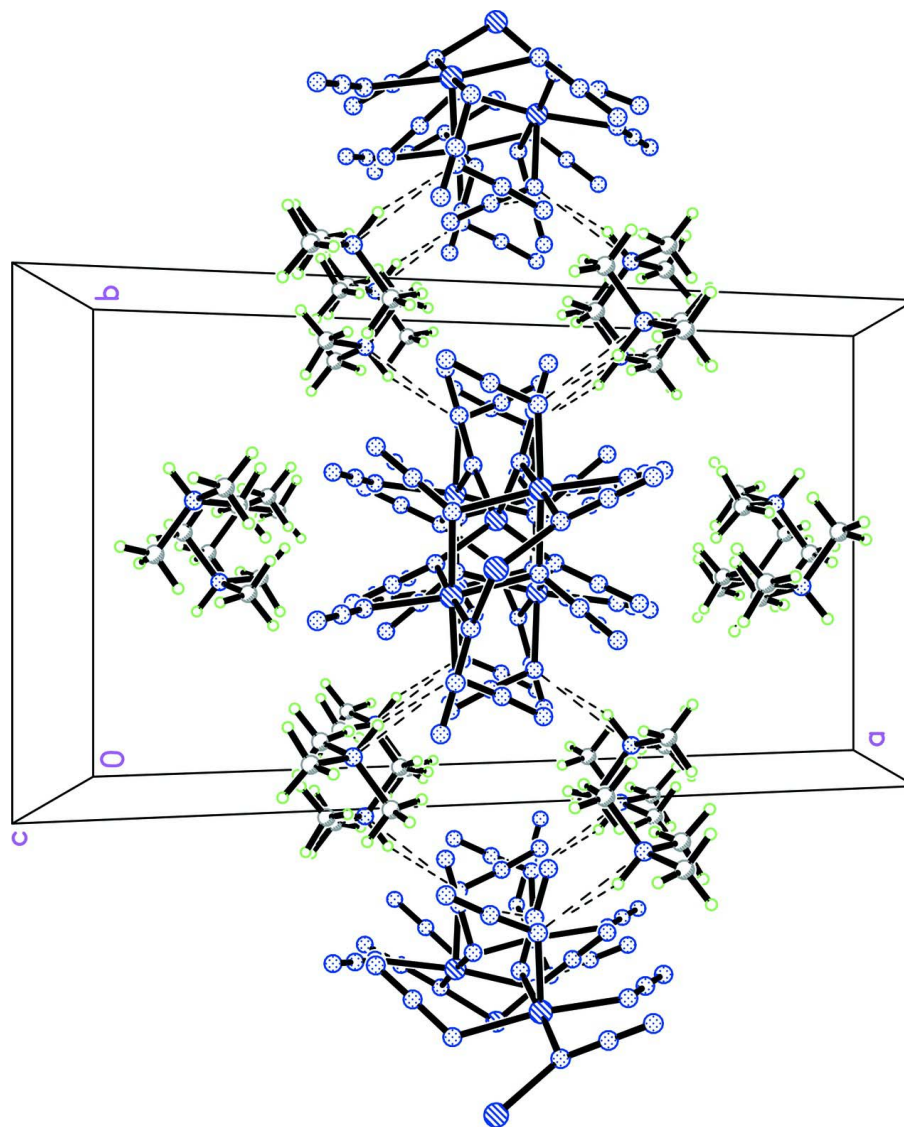


Figure 2

A view of the crystal packing along the *c* axis.

poly[bis(trimethylammonium) [hexa- $\mu_{1,1}$ -azido-tetraazidotricobaltate(II,III)]]

Crystal data

$(C_3H_{10}N)_2[Co_3(N_3)_{10}]$

$M_r = 717.33$

Monoclinic, *C2/c*

Hall symbol: -C 2yc

$a = 21.7200$ (6) Å

$b = 11.3812$ (4) Å

$c = 12.1628$ (4) Å

$\beta = 115.524$ (2)°

$V = 2713.21$ (15) Å³

$Z = 4$

$F(000) = 1444$

$D_x = 1.756$ Mg m⁻³

Mo *K* α radiation, $\lambda = 0.71073$ Å

Cell parameters from 14377 reflections

$\theta = 3.4$ – 25.0°

$\mu = 1.88$ mm⁻¹

$T = 293$ K

Pillar, red

$0.10 \times 0.06 \times 0.05$ mm

Data collection

Rigaku Saturn
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 0.76 pixels mm⁻¹
dtprofit.ref scans
Absorption correction: multi-scan
(*REQAB*; Jacobson, 1998)
 $T_{\min} = 0.708$, $T_{\max} = 0.823$

22049 measured reflections
2389 independent reflections
1481 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.103$
 $\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 3.6^\circ$
 $h = -25 \rightarrow 25$
 $k = -13 \rightarrow 13$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.061$
 $S = 0.98$
2389 reflections
190 parameters
24 restraints
Primary atom site location: structure-invariant
direct methods
Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0204P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.31 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.35 \text{ e } \text{\AA}^{-3}$
Extinction correction: *SHELXL97* (Sheldrick,
2008), $F_c^* = kFc[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00084 (18)

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.04965 (2)	0.10300 (4)	0.05706 (4)	0.03529 (17)
Co2	0.0000	-0.04737 (5)	0.2500	0.0402 (2)
N1	0.06948 (14)	0.0409 (2)	0.2209 (3)	0.0428 (6)
N2	0.12002 (17)	0.0827 (3)	0.3042 (3)	0.0448 (6)
N3	0.16669 (18)	0.1210 (3)	0.3810 (3)	0.0740 (10)
N4	0.14720 (14)	0.1256 (2)	0.1097 (3)	0.0523 (7)
N5	0.16894 (15)	0.1348 (3)	0.0363 (3)	0.0540 (7)
N6	0.1925 (2)	0.1442 (4)	-0.0308 (4)	0.1069 (15)
N7	0.04578 (16)	0.2621 (2)	0.1120 (3)	0.0489 (8)
N8	-0.00656 (18)	0.3009 (3)	0.1097 (3)	0.0504 (8)
N9	-0.05415 (18)	0.3426 (3)	0.1100 (3)	0.0806 (12)
N10	0.02748 (13)	0.1593 (3)	-0.1084 (2)	0.0434 (6)
N11	0.04393 (15)	0.2609 (3)	-0.1156 (2)	0.0492 (6)
N12	0.0599 (2)	0.3555 (3)	-0.1195 (3)	0.0930 (13)

N13	-0.04827 (13)	0.0595 (2)	0.0083 (2)	0.0384 (6)
N14	-0.09288 (16)	0.1253 (3)	-0.0627 (3)	0.0425 (6)
N15	-0.13450 (17)	0.1858 (3)	-0.1255 (3)	0.0715 (10)
N16	0.16193 (14)	0.4179 (3)	0.2144 (3)	0.0539 (8)
H16	0.1336	0.3554	0.1828	0.065*
C1	0.2022 (2)	0.3949 (5)	0.3459 (4)	0.1044 (17)
H1A	0.2292	0.4628	0.3840	0.157*
H1B	0.2316	0.3287	0.3565	0.157*
H1C	0.1719	0.3783	0.3826	0.157*
C2	0.1190 (3)	0.5217 (4)	0.1950 (5)	0.1125 (19)
H2A	0.0852	0.5067	0.2242	0.169*
H2B	0.0970	0.5396	0.1096	0.169*
H2C	0.1468	0.5871	0.2384	0.169*
C3	0.2062 (2)	0.4251 (5)	0.1509 (4)	0.1121 (19)
H3A	0.1787	0.4379	0.0655	0.168*
H3B	0.2311	0.3529	0.1621	0.168*
H3C	0.2377	0.4891	0.1837	0.168*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0382 (3)	0.0364 (3)	0.0331 (3)	-0.0041 (2)	0.0171 (2)	-0.0013 (2)
Co2	0.0487 (4)	0.0370 (4)	0.0412 (5)	0.000	0.0253 (4)	0.000
N1	0.0456 (15)	0.0502 (15)	0.0338 (16)	-0.0052 (12)	0.0181 (13)	0.0022 (12)
N2	0.0475 (15)	0.0518 (15)	0.0353 (16)	-0.0042 (13)	0.0180 (13)	0.0033 (13)
N3	0.065 (2)	0.095 (3)	0.052 (2)	-0.019 (2)	0.015 (2)	-0.006 (2)
N4	0.0449 (15)	0.0647 (16)	0.0528 (17)	-0.0104 (12)	0.0264 (12)	-0.0027 (13)
N5	0.0453 (15)	0.0637 (16)	0.0561 (18)	-0.0079 (12)	0.0249 (13)	-0.0055 (13)
N6	0.097 (3)	0.148 (4)	0.112 (4)	-0.027 (3)	0.079 (3)	-0.026 (3)
N7	0.061 (2)	0.0407 (19)	0.051 (2)	-0.0085 (16)	0.0293 (18)	-0.0088 (15)
N8	0.062 (2)	0.040 (2)	0.050 (2)	-0.0019 (17)	0.025 (2)	-0.0050 (15)
N9	0.071 (3)	0.068 (3)	0.103 (3)	0.009 (2)	0.037 (3)	-0.020 (2)
N10	0.0570 (15)	0.0435 (16)	0.0329 (14)	-0.0095 (13)	0.0222 (12)	0.0004 (13)
N11	0.0626 (15)	0.0478 (16)	0.0348 (15)	-0.0086 (14)	0.0186 (12)	0.0007 (13)
N12	0.150 (4)	0.054 (2)	0.064 (3)	-0.036 (2)	0.036 (3)	0.004 (2)
N13	0.0378 (15)	0.0388 (15)	0.0414 (17)	-0.0002 (10)	0.0197 (13)	-0.0025 (11)
N14	0.0408 (15)	0.0412 (16)	0.0447 (17)	-0.0017 (11)	0.0176 (13)	-0.0036 (11)
N15	0.058 (2)	0.058 (2)	0.081 (3)	0.0085 (19)	0.014 (2)	0.005 (2)
N16	0.0501 (19)	0.050 (2)	0.061 (2)	-0.0163 (15)	0.0234 (19)	-0.0118 (16)
C1	0.083 (3)	0.143 (5)	0.067 (4)	-0.039 (3)	0.013 (3)	0.007 (3)
C2	0.115 (4)	0.052 (3)	0.165 (6)	0.015 (3)	0.055 (4)	-0.001 (3)
C3	0.093 (4)	0.173 (5)	0.099 (4)	-0.055 (4)	0.069 (3)	-0.045 (4)

Geometric parameters (Å, °)

Co1—N7	1.944 (3)	N11—N12	1.139 (4)
Co1—N4	1.948 (3)	N13—N14	1.234 (4)
Co1—N10	1.964 (3)	N13—Co1 ⁱ	2.008 (3)

Co1—N1	1.979 (3)	N14—N15	1.131 (4)
Co1—N13 ⁱ	2.008 (3)	N16—C2	1.460 (5)
Co1—N13	2.008 (3)	N16—C3	1.473 (4)
Co2—N1 ⁱⁱ	1.968 (3)	N16—C1	1.478 (5)
Co2—N1	1.968 (3)	N16—H16	0.9100
Co2—N10 ⁱ	2.014 (3)	C1—H1A	0.9600
Co2—N10 ⁱⁱⁱ	2.014 (3)	C1—H1B	0.9600
N1—N2	1.224 (4)	C1—H1C	0.9600
N2—N3	1.129 (4)	C2—H2A	0.9600
N4—N5	1.181 (4)	C2—H2B	0.9600
N5—N6	1.140 (4)	C2—H2C	0.9600
N7—N8	1.209 (4)	C3—H3A	0.9600
N8—N9	1.139 (4)	C3—H3B	0.9600
N10—N11	1.225 (4)	C3—H3C	0.9600
N10—Co2 ⁱ	2.014 (3)		
N7—Co1—N4	88.05 (12)	Co1—N10—Co2 ⁱ	121.43 (14)
N7—Co1—N10	91.18 (12)	N12—N11—N10	178.5 (4)
N4—Co1—N10	92.62 (12)	N14—N13—Co1 ⁱ	114.1 (2)
N7—Co1—N1	90.55 (12)	N14—N13—Co1	118.0 (2)
N4—Co1—N1	88.97 (12)	Co1 ⁱ —N13—Co1	100.22 (11)
N10—Co1—N1	177.69 (12)	N15—N14—N13	178.2 (4)
N7—Co1—N13 ⁱ	176.56 (13)	C2—N16—C3	112.7 (4)
N4—Co1—N13 ⁱ	94.61 (11)	C2—N16—C1	110.9 (4)
N10—Co1—N13 ⁱ	86.53 (11)	C3—N16—C1	111.2 (3)
N1—Co1—N13 ⁱ	91.67 (11)	C2—N16—H16	107.3
N7—Co1—N13	97.71 (11)	C3—N16—H16	107.3
N4—Co1—N13	173.16 (12)	C1—N16—H16	107.3
N10—Co1—N13	90.96 (11)	N16—C1—H1A	109.5
N1—Co1—N13	87.29 (11)	N16—C1—H1B	109.5
N13 ⁱ —Co1—N13	79.78 (11)	H1A—C1—H1B	109.5
N1 ⁱⁱ —Co2—N1	118.61 (16)	N16—C1—H1C	109.5
N1 ⁱⁱ —Co2—N10 ⁱ	120.58 (11)	H1A—C1—H1C	109.5
N1—Co2—N10 ⁱ	97.86 (11)	H1B—C1—H1C	109.5
N1 ⁱⁱ —Co2—N10 ⁱⁱⁱ	97.86 (11)	N16—C2—H2A	109.5
N1—Co2—N10 ⁱⁱⁱ	120.58 (11)	N16—C2—H2B	109.5
N10 ⁱ —Co2—N10 ⁱⁱⁱ	101.58 (16)	H2A—C2—H2B	109.5
N2—N1—Co2	122.3 (2)	N16—C2—H2C	109.5
N2—N1—Co1	115.0 (2)	H2A—C2—H2C	109.5
Co2—N1—Co1	120.82 (15)	H2B—C2—H2C	109.5
N3—N2—N1	179.9 (5)	N16—C3—H3A	109.5
N5—N4—Co1	119.7 (3)	N16—C3—H3B	109.5
N6—N5—N4	177.2 (4)	H3A—C3—H3B	109.5
N8—N7—Co1	120.8 (2)	N16—C3—H3C	109.5
N9—N8—N7	176.5 (4)	H3A—C3—H3C	109.5

N11—N10—Co1	115.5 (2)	H3B—C3—H3C	109.5
N11—N10—Co2 ⁱ	121.6 (2)		

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

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

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N16—H16 \cdots N7	0.91	2.02	2.890	159
