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The first dinuclear cobalt complex bridged by acetylamidate ligands: di-μ-acetylamido-κ^2O:N;κ^2N:O-di-μ-hydroxido-κ^4O:O-bis[bis(pyridine-κN)cobalt(III)] bis(perchlorate) acetonitrile disolvate

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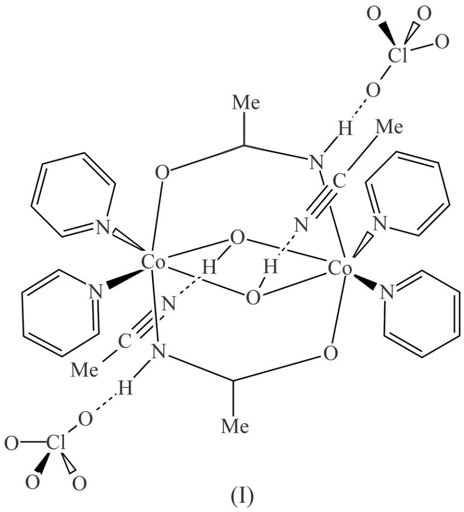
The title compound, $[Co_2(C_2H_4NO)_2(OH)_2(C_5H_5N)_4](ClO_4)_2\cdot 2C_2H_3N$, consists of two octahedral Co^{III} centers arranged around an inversion point in which two *cis* hydroxide and two *trans* acetylamidate ligands link the two centers together, forming a dimeric cationic complex. Each Co^{III} center has two *cis* pyridine ligands which coordinate in the same plane as the *cis* hydroxide ligands. Two acetonitrile solvent molecules and two perchlorate anions are hydrogen bonded to the H atoms on the bridging hydroxide and acetylamidate (N atom) ligands, respectively.

Comment

In the process of studying cobalt phosphinate compounds, we isolated and crystallized di-μ-acetylamido-di-μ-hydroxido-bis[dipyridinecobalt(III)] bis(perchlorate) acetonitrile disolvate, (I). Related dihydroxide- and acetate-bridged cobalt(III) dimers were first produced by Werner (1910) and later characterized crystallographically by Mandel *et al.* (1977). These types of compounds have been studied as model metal centers for different enzymes. Lee *et al.* (2002) stabilized the dimeric core using sterically hindered carbocyclic acid derivatives to study the active site in metallohydrolases. Williams *et al.* (1999) used 1,4,7-triazacyclononane to stabilize a related cobalt dimer in order to study the hydrolyses of phosphate esters in metallophosphatase enzymes. The fact that (I) has bridging acetylamidate ligands is significant since relatively few transition metal compounds containing this ligand have been structurally characterized. Fedotova *et al.* (2008) synthesized a platinum(II) dimer with acetylamidate ligands, Chavan *et al.* (1986) used acetamide to make rhodium(II) dimers, Mironov (1999) stabilized rhenium chalcogen clusters with acetylamidate ligands and Fuma & Ebihara (2006) used acetamide to make dirhodium paddle-wheel units that were bridged by perrhenate.



(I)

Two formula units of (I) constitute the unit cell, with the asymmetric unit consisting of half a complex cation lying about an inversion center, one perchlorate anion and one acetonitrile solvent molecule, both linked to the half cation by hydrogen bonds. The two Co^{III} centers are bridged by two *trans* acetylamidate ligands, through one O atom from one acetylamidate ligand and one N atom from the other, and two *cis* hydroxide ligands (Fig. 1). The Co1—O2 bond length is 1.9374 (12) Å, whereas that for Co1—N1 is 1.9059 (14) Å. The O2—Co—N1 angle is bent towards the adjacent Co^{III} center

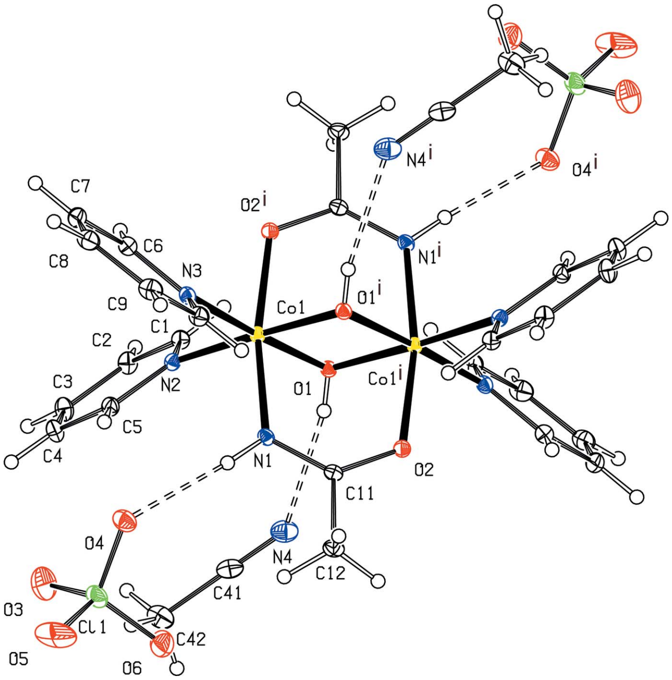


Figure 1
The molecular structure of (I), with hydrogen bonds illustrated as dashed lines. H atoms are represented by spheres of arbitrary radii and displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $-x+1, -y+1, -z+1$.]

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away from linearity to 169.26 (6)°. The C—O bond length [C11—O2 = 1.2973 (19) Å] is shorter than N—C [C11—N1 = 1.313 (2) Å] in the acetylamidate ligands. There are two pyridine molecules coordinated *cis* to each Co^{III} center in the same plane as the hydroxide ligands, with pyridine torsion angles of 47.0 (1) and 45.8 (1)° for the N2 and N3 pyridine (py) ligands, respectively, with respect to the metal–hydroxide plane. The two N_{py}—Co bond lengths are 1.9418 (14) and 1.9374 (14) Å for Co1—N2 and Co1—N3, respectively, and the N2—Co1—N3 angle is slightly larger than 90° at 94.08 (6)°. The Co1—O1 and Co1—O1$^{\text{i}}$ bond lengths are 1.8777 (12) Å and the O1—Co—O1$^{\text{i}}$ angle is 88.73 (5)° [symmetry code: (i) $-x + 1, -y + 1, -z + 1$]; thus, this bridging arrangement constitutes a crystallographically imposed planar but slightly distorted square geometry.

The Co···Co distance in the dimer is 2.6847 (4) Å and is longer than the equivalent Co···Co distance in three other complexes containing the $[\text{Co}_2(\text{OH})_2(\text{O}_2\text{CC}R)_2]^{4+}$ core obtained from a search of the Cambridge Structural Database (CSD, Version 5.33; Allen, 2002): (i) 2.655 (2) Å in a tetrahydrofuran solvate of $[\text{Co}_2(\text{OH})_2(\text{O}_2\text{C}R)_2L_4]^{2+}$ (R = ^{t}Bu and L = 3,5-dimethylpyrazole) (Denisova *et al.*, 2003), (ii) 2.669 (2) Å in the analogous benzene solvate (Denisova *et al.*, 2006) and (iii) 2.6802 (5) Å in $[\text{Co}_2(\text{OH})_2(\text{O}_2\text{C}R)_2L_2L'_2]^{2+}$ (κ^2-$\text{O}_2\text{C}R$ = κ^1-L = 2,6-di-*p*-tolylbenzoate and L' = pyridine; Lee *et al.*, 2002).

The unique perchlorate anion is hydrogen bonded to the H atom of the acetylamidate ligand and the unique acetonitrile ligand is hydrogen bonded to the bridging hydroxide H atoms (Fig. 1 and Table 1).

Experimental

$\text{Co(ClO}_4)_2\cdot6\text{H}_2\text{O}$ (0.203 g) and pyridine (0.5 ml) were dissolved in acetonitrile (15 ml) and heated to 333 K. To this solution was added dropwise 30% by weight H_2O_2 (0.6 ml) which resulted in a change in color of the solution from pink to dark red. This solution was heated under reflux for 1 h, allowed to cool to room temperature and diethyl ether added until the solution became cloudy. After 1 d, large red needle-shaped crystals were obtained (yield 0.073 g, 33.6%).

Crystal data

$[\text{Co}_2(\text{C}_2\text{H}_4\text{NO})_2(\text{OH})_2(\text{C}_5\text{H}_5\text{N})_4]$-$(\text{ClO}_4)_2\cdot2\text{C}_2\text{H}_3\text{N}$
M_r = 865.41
Monoclinic, $P2_1/n$
a = 10.6198 (7) Å
b = 10.2440 (7) Å
c = 16.503 (1) Å
β = 92.167 (1)°
V = 1794.1 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.15 mm^{-1}
T = 100 K
0.46 × 0.22 × 0.17 mm

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···N4	0.72 (2)	2.25 (2)	2.952 (2)	165 (3)
N1—H1B···O4	0.85 (2)	2.14 (2)	2.993 (2)	176 (2)

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{\min}$ = 0.652, $T_{\max}$ = 0.746
21140 measured reflections
5809 independent reflections
4796 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.085
S = 1.04
5809 reflections
245 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ = 0.73 e Å^{-3}
$\Delta\rho_{\min}$ = −0.45 e Å^{-3}

Two H atoms involved in hydrogen bonding were refined freely. The other H atoms were placed at calculated positions, with C—H = 0.95 (aromatic) or 0.98 Å (methyl) and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl groups and $1.2U_{\text{eq}}(\text{C})$ otherwise.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3263). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bruker (2008). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2009). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chavan, M. Y., Lin, X. Q., Ahsan, M. Q., Bernal, I., Bear, J. L. & Kadish, K. M. (1986). *Inorg. Chem.* **25**, 1281–1288.
Denisova, T. O., Dobrokhotova, Zh. V., Ikorskii, V. N. & Nefedov, S. E. (2006). *Russ. J. Inorg. Chem.* **51**, 1454–1495.
Denisova, T. O., Fialkovsky, O. P. & Nefedov, S. E. (2003). *Russ. Chem. Bull.* **52**, 1637–1640.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Fedotova, T. N., Aleksandrov, G. G. & Kuznetsova, G. N. (2008). *Russ. J. Inorg. Chem.* **53**, 372–377.
Fuma, Y. & Ebihara, M. (2006). *Chem. Lett.* **35**, 1298–1299.
Lee, D., Hung, P. L., Spingler, B. & Lippard, S. J. (2002). *Inorg. Chem.* **41**, 521–531.
Mandel, G. S., Marsh, R. E., Schaefer, W. P., Mandel, N. S. & Wang, B. C. (1977). *Acta Cryst.* B**33**, 3185–3188.
Mironov, Y. V. (1999). *Eur. J. Inorg. Chem.* pp. 997–999.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Werner, A. (1910). *Liebigs Ann.* **375**, 1–144.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Williams, N. H., Lebuis, A. M. & Chin, J. (1999). *J. Am. Chem. Soc.* **121**, 3341–3348.

supplementary materials

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Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
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c = 16.503 (1) Å
β = 92.167 (1)°
V = 1794.1 (2) Å^3
Z = 2
$F(000)$ = 888
D_x = 1.602 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4635 reflections
θ = 2.3–29.2°
μ = 1.15 mm^{-1}
T = 100 K
Prism, red
0.46 × 0.22 × 0.17 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed x-ray tube
Graphite monochromator
φ or ω oscillation scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.652, T_{max} = 0.746
21140 measured reflections
5809 independent reflections
4796 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 31.9°, θ_{min} = 2.3°
$h = -15\rightarrow 15$
$k = -15\rightarrow 15$
$l = -24\rightarrow 24$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.085
S = 1.04
5809 reflections
245 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
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0329P)^2 + 1.1062P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.73 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

Special details

Experimental. IR (cm^{-1}): 3393.0 (*w*), 3314.4 (*m*), 2251.7 (*w*), 1606.8 (*m*), 1549.7 (*br*), 1476.2 (*m*), 1449.0 (*s*), 1238.1 (*m*), 1214.2 (*s*), 1154.9 (*w*), 1092.7 (*sh*), 1064.7 (*vs*), 941.4 (*m*), 898.0 (*m*), 771.2 (*sh*), 760.8 (*s*), 693.5 (*vs*).

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.46912 (2)	0.55025 (2)	0.426797 (13)	0.01179 (6)
O1	0.38651 (11)	0.45010 (11)	0.50391 (7)	0.0131 (2)
H1A	0.336 (2)	0.488 (3)	0.5203 (16)	0.033 (7)*
N1	0.42416 (13)	0.70022 (13)	0.48763 (8)	0.0135 (3)
H1B	0.399 (2)	0.772 (2)	0.4665 (13)	0.021 (5)*
O2	0.47517 (11)	0.61555 (11)	0.61550 (7)	0.0145 (2)
N2	0.31450 (13)	0.54632 (13)	0.36017 (8)	0.0135 (3)
C1	0.25497 (16)	0.43048 (16)	0.35255 (10)	0.0163 (3)
H1	0.2946	0.3546	0.3746	0.02*
C2	0.13793 (17)	0.41899 (17)	0.31358 (11)	0.0190 (3)
H2	0.0972	0.3366	0.3097	0.023*
C3	0.08103 (17)	0.52900 (18)	0.28036 (11)	0.0217 (4)
H3	0.0004	0.5233	0.2536	0.026*
C4	0.14303 (17)	0.64758 (18)	0.28664 (11)	0.0209 (3)
H4	0.1063	0.7241	0.2634	0.025*
C5	0.25940 (16)	0.65295 (16)	0.32729 (10)	0.0167 (3)
H5	0.3016	0.7345	0.3321	0.02*
N3	0.56135 (13)	0.64926 (14)	0.34850 (8)	0.0147 (3)
C6	0.55776 (16)	0.61638 (17)	0.26919 (10)	0.0186 (3)
H6	0.5088	0.5432	0.2519	0.022*
C7	0.62304 (18)	0.68584 (19)	0.21237 (11)	0.0230 (4)
H7	0.6184	0.661	0.1569	0.028*
C8	0.69538 (18)	0.79237 (19)	0.23758 (12)	0.0249 (4)
H8	0.74	0.8422	0.1995	0.03*
C9	0.70130 (18)	0.82470 (18)	0.31919 (12)	0.0234 (4)
H9	0.7514	0.8961	0.3381	0.028*
C10	0.63306 (16)	0.75143 (17)	0.37290 (11)	0.0189 (3)
H10	0.637	0.774	0.4288	0.023*
C11	0.44008 (14)	0.70913 (16)	0.56673 (10)	0.0140 (3)
C12	0.41864 (17)	0.83912 (16)	0.60668 (11)	0.0187 (3)
H12A	0.4972	0.8895	0.6081	0.028*
H12B	0.3916	0.8251	0.6621	0.028*
H12C	0.3532	0.8873	0.5758	0.028*
N4	0.15243 (16)	0.58853 (18)	0.54242 (11)	0.0284 (4)
C41	0.07223 (18)	0.64581 (19)	0.51135 (12)	0.0243 (4)

C42	−0.0309 (2)	0.7190 (2)	0.47192 (14)	0.0314 (4)
H42A	−0.0668	0.6683	0.4263	0.047*
H42B	0.001	0.8023	0.452	0.047*
H42C	−0.0963	0.7355	0.511	0.047*
Cl1	0.21490 (4)	1.00646 (4)	0.41599 (3)	0.02444 (10)
O3	0.12447 (17)	0.94963 (19)	0.35856 (11)	0.0484 (5)
O4	0.33574 (13)	0.94539 (13)	0.40484 (9)	0.0255 (3)
O5	0.2253 (2)	1.14318 (15)	0.40122 (13)	0.0582 (6)
O6	0.17453 (14)	0.98297 (16)	0.49681 (9)	0.0336 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.01319 (10)	0.01015 (10)	0.01196 (10)	−0.00040 (8)	−0.00044 (7)	0.00032 (8)
O1	0.0135 (5)	0.0121 (5)	0.0137 (5)	0.0004 (4)	0.0006 (4)	0.0008 (4)
N1	0.0147 (6)	0.0103 (6)	0.0154 (6)	0.0006 (5)	−0.0007 (5)	0.0002 (5)
O2	0.0165 (5)	0.0128 (5)	0.0142 (5)	0.0006 (4)	−0.0003 (4)	−0.0007 (4)
N2	0.0149 (6)	0.0128 (6)	0.0127 (6)	−0.0009 (5)	0.0004 (5)	0.0002 (5)
C1	0.0182 (8)	0.0138 (7)	0.0167 (7)	−0.0012 (6)	−0.0006 (6)	−0.0003 (6)
C2	0.0203 (8)	0.0166 (8)	0.0199 (8)	−0.0052 (6)	−0.0028 (6)	−0.0001 (6)
C3	0.0178 (8)	0.0248 (9)	0.0221 (9)	−0.0017 (7)	−0.0055 (7)	0.0030 (7)
C4	0.0219 (8)	0.0189 (8)	0.0215 (8)	0.0020 (7)	−0.0044 (7)	0.0037 (7)
C5	0.0196 (8)	0.0141 (7)	0.0163 (7)	−0.0001 (6)	0.0000 (6)	0.0012 (6)
N3	0.0150 (6)	0.0135 (6)	0.0157 (6)	0.0011 (5)	0.0005 (5)	0.0027 (5)
C6	0.0189 (8)	0.0190 (8)	0.0181 (8)	0.0027 (6)	0.0007 (6)	0.0011 (6)
C7	0.0239 (9)	0.0278 (9)	0.0176 (8)	0.0063 (7)	0.0047 (7)	0.0055 (7)
C8	0.0240 (9)	0.0218 (9)	0.0295 (10)	0.0047 (7)	0.0110 (7)	0.0096 (7)
C9	0.0226 (9)	0.0175 (8)	0.0304 (10)	−0.0016 (7)	0.0064 (7)	0.0033 (7)
C10	0.0193 (8)	0.0162 (8)	0.0212 (8)	−0.0008 (6)	0.0023 (6)	0.0017 (6)
C11	0.0113 (7)	0.0127 (7)	0.0180 (7)	−0.0005 (5)	0.0009 (6)	−0.0008 (6)
C12	0.0207 (8)	0.0138 (7)	0.0216 (8)	0.0014 (6)	0.0000 (6)	−0.0046 (6)
N4	0.0230 (8)	0.0286 (9)	0.0338 (9)	−0.0015 (7)	0.0035 (7)	−0.0061 (7)
C41	0.0233 (9)	0.0211 (9)	0.0290 (10)	−0.0030 (7)	0.0078 (7)	−0.0067 (7)
C42	0.0283 (10)	0.0259 (10)	0.0402 (12)	0.0043 (8)	0.0037 (9)	0.0023 (9)
Cl1	0.0294 (2)	0.01517 (19)	0.0289 (2)	0.00356 (16)	0.00293 (18)	0.00678 (16)
O3	0.0392 (10)	0.0630 (13)	0.0417 (10)	0.0070 (9)	−0.0158 (8)	0.0016 (9)
O4	0.0263 (7)	0.0184 (6)	0.0320 (7)	0.0024 (5)	0.0031 (6)	0.0036 (5)
O5	0.0781 (14)	0.0132 (7)	0.0863 (15)	0.0087 (8)	0.0437 (12)	0.0129 (8)
O6	0.0324 (8)	0.0392 (9)	0.0296 (8)	0.0022 (7)	0.0051 (6)	0.0089 (7)

Geometric parameters (Å, º)

Co1—O1	1.8777 (12)	C6—C7	1.384 (2)
Co1—N1	1.9059 (14)	C6—H6	0.95
Co1—O2^{i}	1.9374 (12)	C7—C8	1.389 (3)
Co1—N3	1.9374 (14)	C7—H7	0.95
Co1—N2	1.9418 (14)	C8—C9	1.386 (3)
Co1—Co1^{i}	2.6847 (4)	C8—H8	0.95
O1—H1A	0.72 (3)	C9—C10	1.387 (2)
N1—C11	1.313 (2)	C9—H9	0.95

N1—H1B	0.85 (2)	C10—H10	0.95
O2—C11	1.2973 (19)	C11—C12	1.507 (2)
N2—C5	1.344 (2)	C12—H12A	0.98
N2—C1	1.348 (2)	C12—H12B	0.98
C1—C2	1.383 (2)	C12—H12C	0.98
C1—H1	0.95	N4—C41	1.140 (3)
C2—C3	1.382 (2)	C41—C42	1.460 (3)
C2—H2	0.95	C42—H42A	0.98
C3—C4	1.384 (3)	C42—H42B	0.98
C3—H3	0.95	C42—H42C	0.98
C4—C5	1.385 (2)	Cl1—O5	1.4265 (16)
C4—H4	0.95	Cl1—O6	1.4367 (16)
C5—H5	0.95	Cl1—O4	1.4456 (14)
N3—C10	1.347 (2)	Cl1—O3	1.4459 (18)
N3—C6	1.351 (2)		

O1—Co1—O1^{i}	88.73 (5)	N2—C5—H5	119
O1—Co1—N1	87.17 (6)	C4—C5—H5	119
O1^{i}—Co1—N1	84.02 (6)	C10—N3—C6	118.58 (15)
O1—Co1—O2^{i}	85.53 (5)	C10—N3—Co1	120.12 (12)
O1^{i}—Co1—O2^{i}	87.96 (5)	C6—N3—Co1	121.28 (12)
N1—Co1—O2^{i}	169.26 (6)	N3—C6—C7	122.13 (17)
O1—Co1—N3	177.39 (6)	N3—C6—H6	118.9
O1^{i}—Co1—N3	89.17 (5)	C7—C6—H6	118.9
N1—Co1—N3	94.15 (6)	C6—C7—C8	119.11 (17)
O2^{i}—Co1—N3	92.85 (5)	C6—C7—H7	120.4
O1—Co1—N2	88.03 (5)	C8—C7—H7	120.4
O1^{i}—Co1—N2	176.71 (5)	C9—C8—C7	118.87 (17)
N1—Co1—N2	95.26 (6)	C9—C8—H8	120.6
O2^{i}—Co1—N2	92.35 (5)	C7—C8—H8	120.6
N3—Co1—N2	94.08 (6)	C8—C9—C10	119.09 (18)
O1—Co1—Co1^{i}	44.37 (4)	C8—C9—H9	120.5
N1—Co1—Co1^{i}	83.83 (4)	C10—C9—H9	120.5
O2^{i}—Co1—Co1^{i}	85.44 (3)	N3—C10—C9	122.19 (17)
N3—Co1—Co1^{i}	133.51 (4)	N3—C10—H10	118.9
N2—Co1—Co1^{i}	132.39 (4)	C9—C10—H10	118.9
Co1—O1—Co1^{i}	91.27 (5)	O2—C11—N1	126.06 (15)
Co1—O1—H1A	109 (2)	O2—C11—C12	115.22 (14)
Co1^{i}—O1—H1A	112 (2)	N1—C11—C12	118.71 (15)
C11—N1—Co1	123.66 (11)	C11—C12—H12A	109.5
C11—N1—H1B	111.9 (14)	C11—C12—H12B	109.5
Co1—N1—H1B	124.1 (14)	H12A—C12—H12B	109.5
C11—O2—Co1^{i}	120.58 (10)	C11—C12—H12C	109.5
C5—N2—C1	118.84 (14)	H12A—C12—H12C	109.5
C5—N2—Co1	123.90 (11)	H12B—C12—H12C	109.5
C1—N2—Co1	117.04 (11)	N4—C41—C42	179.7 (2)
N2—C1—C2	121.90 (16)	C41—C42—H42A	109.5
N2—C1—H1	119.1	C41—C42—H42B	109.5
C2—C1—H1	119.1	H42A—C42—H42B	109.5

C3—C2—C1	119.13 (16)	C41—C42—H42C	109.5
C3—C2—H2	120.4	H42A—C42—H42C	109.5
C1—C2—H2	120.4	H42B—C42—H42C	109.5
C2—C3—C4	119.11 (16)	O5—Cl1—O6	110.53 (11)
C2—C3—H3	120.4	O5—Cl1—O4	109.18 (10)
C4—C3—H3	120.4	O6—Cl1—O4	110.07 (9)
C3—C4—C5	118.98 (16)	O5—Cl1—O3	109.69 (13)
C3—C4—H4	120.5	O6—Cl1—O3	109.08 (11)
C5—C4—H4	120.5	O4—Cl1—O3	108.25 (10)
N2—C5—C4	122.02 (16)		

O1^{i}—Co1—O1—Co1^{i}	0	C1—N2—C5—C4	0.7 (2)
N1—Co1—O1—Co1^{i}	−84.07 (6)	Co1—N2—C5—C4	−173.72 (13)
O2^{i}—Co1—O1—Co1^{i}	88.05 (5)	C3—C4—C5—N2	0.6 (3)
N2—Co1—O1—Co1^{i}	−179.44 (6)	O1^{i}—Co1—N3—C10	−44.90 (13)
O1—Co1—N1—C11	47.42 (13)	N1—Co1—N3—C10	39.04 (13)
O1^{i}—Co1—N1—C11	−41.60 (13)	O2^{i}—Co1—N3—C10	−132.81 (13)
O2^{i}—Co1—N1—C11	0.2 (4)	N2—Co1—N3—C10	134.63 (13)
N3—Co1—N1—C11	−130.33 (13)	Co1^{i}—Co1—N3—C10	−46.39 (15)
N2—Co1—N1—C11	135.18 (13)	O1^{i}—Co1—N3—C6	133.65 (13)
Co1^{i}—Co1—N1—C11	3.03 (13)	N1—Co1—N3—C6	−142.42 (13)
O1—Co1—N2—C5	129.66 (14)	O2^{i}—Co1—N3—C6	45.73 (13)
N1—Co1—N2—C5	42.69 (14)	N2—Co1—N3—C6	−46.83 (13)
O2^{i}—Co1—N2—C5	−144.89 (13)	Co1^{i}—Co1—N3—C6	132.15 (11)
N3—Co1—N2—C5	−51.87 (14)	C10—N3—C6—C7	−1.4 (2)
Co1^{i}—Co1—N2—C5	129.13 (12)	Co1—N3—C6—C7	−179.96 (13)
O1—Co1—N2—C1	−44.81 (12)	N3—C6—C7—C8	0.4 (3)
N1—Co1—N2—C1	−131.79 (12)	C6—C7—C8—C9	0.9 (3)
O2^{i}—Co1—N2—C1	40.63 (12)	C7—C8—C9—C10	−1.2 (3)
N3—Co1—N2—C1	133.66 (12)	C6—N3—C10—C9	1.0 (3)
Co1^{i}—Co1—N2—C1	−45.34 (14)	Co1—N3—C10—C9	179.62 (13)
C5—N2—C1—C2	−1.5 (2)	C8—C9—C10—N3	0.3 (3)
Co1—N2—C1—C2	173.27 (13)	Co1^{i}—O2—C11—N1	8.1 (2)
N2—C1—C2—C3	1.0 (3)	Co1^{i}—O2—C11—C12	−170.77 (11)
C1—C2—C3—C4	0.3 (3)	Co1—N1—C11—O2	−7.7 (2)
C2—C3—C4—C5	−1.1 (3)	Co1—N1—C11—C12	171.23 (12)

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···N4	0.72 (2)	2.25 (2)	2.952 (2)	165 (3)
N1—H1*B*···O4	0.85 (2)	2.14 (2)	2.993 (2)	176 (2)
C1—H1···O5^{ii}	0.95	2.33	3.070 (2)	134
C5—H5···O4	0.95	2.49	3.345 (2)	150
C6—H6···O3^{iii}	0.95	2.46	3.286 (3)	145
C12—H12*A*···O4^{iv}	0.98	2.47	3.428 (2)	167
C12—H12*C*···O6	0.98	2.46	3.439 (2)	173

C42—H42*B*···O3	0.98	2.55	3.470 (3)	155
C42—H42*C*···O5^{v}	0.98	2.38	3.311 (3)	158

Symmetry codes: (ii) *x*, *y*−1, *z*; (iii) −*x*+1/2, *y*−1/2, −*z*+1/2; (iv) −*x*+1, −*y*+2, −*z*+1; (v) −*x*, −*y*+2, −*z*+1.