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Crystal structure of *catena*-poly[[[*trans*-bis(acetonitrile-κN)diaquacobalt(II)]-μ-pyrazine-$\kappa^2 N{:}N'$] dinitrate]

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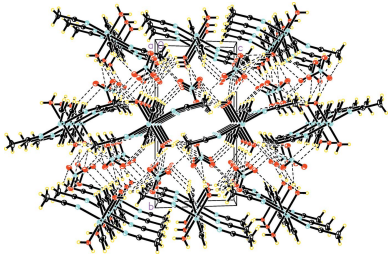
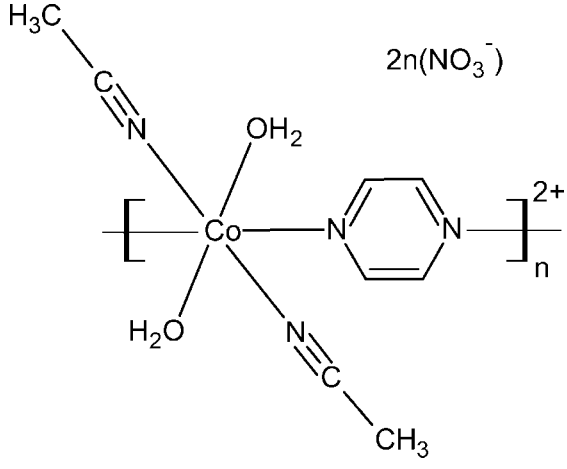
The central structural motif of the title coordination polymer, $[Co(NO_3)_2(C_4H_4N_2)(CH_3CN)_2(H_2O)_2]_n$, is a chain composed of Co^{II} ions linked by bis-monodentate bridging pyrazine ligands through their N atoms. The Co^{II} ion is located on an inversion center and is additionally coordinated by two O atoms of water molecules and two N atoms of acetonitrile molecules. The resultant N_4O_2 coordination sphere is distorted octahedral. The linear cationic chains extend parallel to the *a* axis and are aligned into layers parallel to the *ac* plane. Nitrate anions are situated in the space between the Co^{II} chains and form O—H···O hydrogen bonds with the coordinating water molecules, leading to a three-dimensional network structure. Weak C—H···O hydrogen bonds are also present between pyrazine or acetonitrile molecules and the nitrate anions.

1. Chemical context

In the design of coordination polymers, the choice of bridging ligands between metal atoms plays an important role in the formation of the final structure and the resulting properties. During our investigations of the preparation conditions and magnetic properties of compounds with ladder-like structures, we have used pyrazine as a bis-monodentate bridging ligand to link paramagnetic metal cations. From the point of view of mediating magnetic interactions, the pyrazine molecule offers some advantages compared to other bidentate bridging ligands such as 4,4′-bipyridine. In some of the structures with the latter ligand, the two pyridine rings are not co-planar and therefore can magnetically isolate metal atoms (Losier & Zaworotko, 1996; Ruan *et al.*, 2009; Seidel *et al.*, 2011; Lehleh *et al.*, 2013).





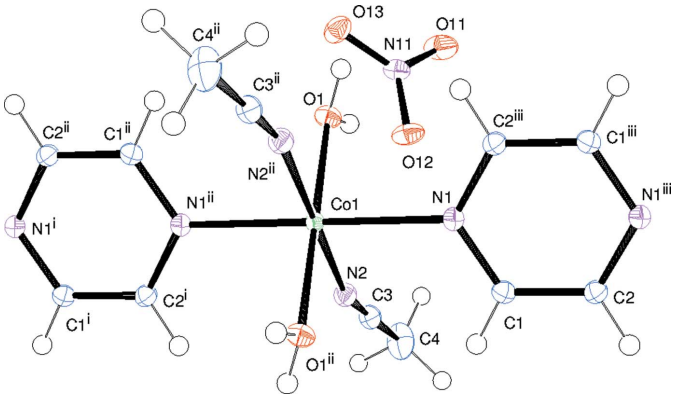


Figure 1
A fragment of the one-dimensional chain structure of the title compound with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $1 + x, y, z$; (ii) $-3 - x, 1 - y, -z$; (iii) $-4 - x, 1 - y, -z$.]

We herein report the preparation and structure of a pyrazine-bridged chain structure obtained by reacting pyrazine and cobalt(II) nitrate hexahydrate using acetonitrile as the solvent.

2. Structural commentary

The asymmetric unit of the title compound, $[Co(C_4H_4N_2)(CH_3CN)_2(H_2O)_2(NO_3)_2]_n$, contains one Co^{II} cation located on an inversion center, one water molecule, one acetonitrile molecule, one nitrate anion, and one half of a pyrazine molecule, the latter being completed by inversion symmetry. The Co^{II} cation exhibits an N_4O_2 coordination set defined by two O atoms [O1, O1^{ii}; symmetry code: (ii) $-3 - x, 1 - y, -z$] of two coordinating water molecules, two N atoms (N2, N2^{ii}) of two coordinating acetonitrile molecules, and two nitrogen atoms (N1, N1^{ii}) of two bridging pyrazine molecules (Fig. 1). The two Co—O_{water} bonds have a length of 2.0315 (8) Å, considerably shorter than the two Co—$N_{acetonitrile}$ bonds of 2.1263 (9) Å, and the two Co—$N_{pyrazine}$ bonds of 2.1493 (10) Å. The resulting coordination sphere is compressed octahedral with all bond lengths in good agreement with similar structures (Choudhury *et al.*, 2002; Holman *et al.*, 2005; Aşkin *et al.*, 2015). In contrast to the N_2O_4

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1Y···O13^{i}	0.83 (2)	1.85 (2)	2.6819 (12)	173.5 (18)
O1—H1X···O12^{ii}	0.80 (2)	1.99 (2)	2.7869 (12)	174.1 (19)
O1—H1X···O13^{ii}	0.80 (2)	2.562 (19)	3.0912 (12)	125.3 (17)
C1—H1A···O11^{iii}	0.95	2.54	3.1572 (14)	123
C2—H2A···O13^{iv}	0.95	2.59	3.4644 (14)	153
C4—H4A···O13^{v}	0.98	2.49	3.2785 (17)	138
C4—H4B···O11^{vi}	0.98	2.49	3.2823 (17)	138

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

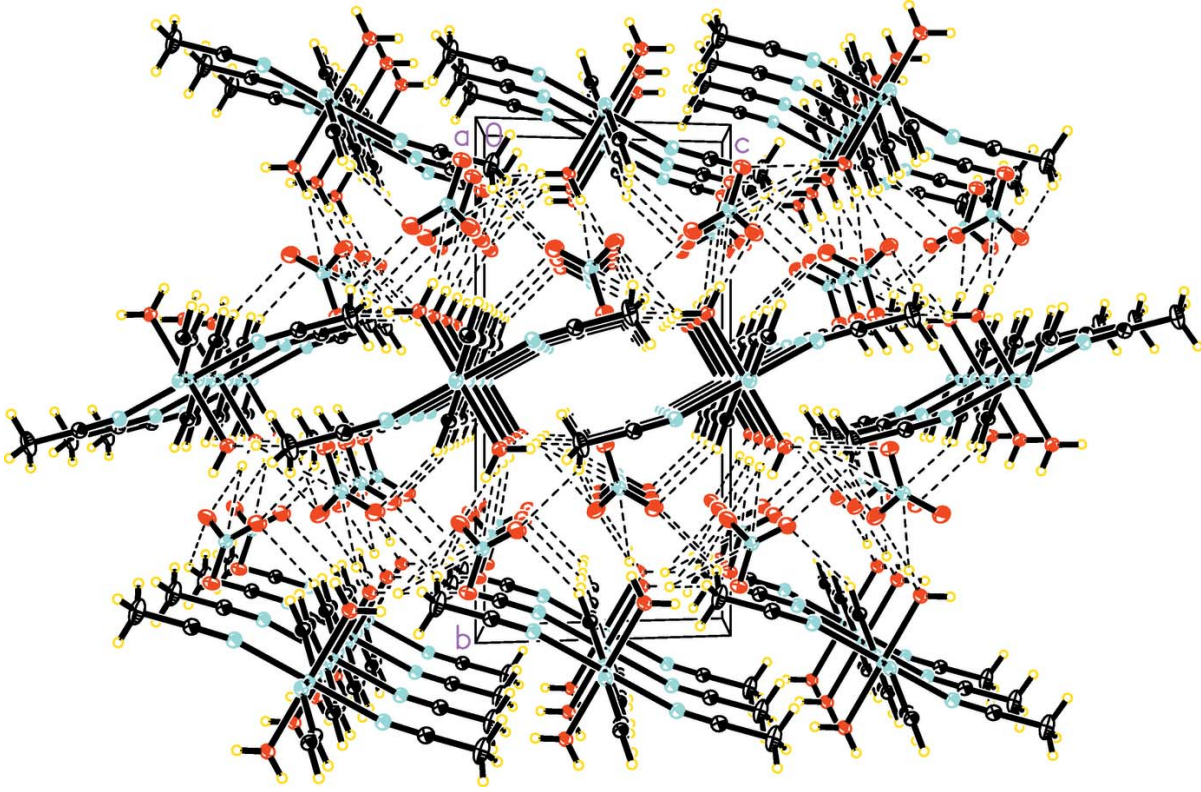


Figure 2
Crystal packing of the title compound, showing hydrogen bonds as dashed lines.

coordination spheres observed more frequently in the structures of other Co-containing compounds (Choudhury *et al.*, 2002; Holman *et al.*, 2005; Hyun *et al.*, 2011; Aşkin *et al.*, 2015), the title structure exhibits an N_4O_2 coordination sphere due to the inclusion of the solvent acetonitrile molecules in the coordination sphere of Co^{II}. The bridging bis-monodentate pyrazine molecules link the Co^{II} ions, forming linear chains extending parallel to the *a* axis. The distance between two symmetry-related Co^{II} ions within a chain (symmetry code: $1 + x, y, z$) is 7.0798 (3) Å, in good agreement with those reported for similar structures (Choudhury *et al.*, 2002; Holman *et al.*, 2005; Aşkin *et al.*, 2015).

3. Supramolecular features

In the crystal, the cationic chains are arranged to form sheets parallel to the *ac* plane, and neighboring sheets are related by a glide plane. Nitrate ions are sandwiched in the space between the sheets and form columns parallel to the *a* axis. Each Co^{II} chain is surrounded by six columns of nitrate ions that are related by the inversion centers located along the cationic chains. Each cationic chain is further surrounded by six other chains. This structural motif with alternating layers has been observed in similar structures (Choudhury *et al.*, 2002; Yang *et al.*, 2003; Holman *et al.*, 2005; Aşkin *et al.*, 2015). Co^{II} chains in neighboring sheets interact through nitrate ions by forming O—H···O hydrogen bonds where the donor O—H groups are provided by the coordinating water molecules and the acceptor oxygen provided by the nitrate ions. One of those hydrogen bonds is bifurcated. For numerical values and symmetry operators, see Table 1. Weak C—H···O hydrogen bonds are also present between the C—H groups of bridging pyrazine and coordinating acetonitrile molecules, and the oxygen atoms of nitrate ions, linking Co^{II} chains both within the same sheet and to adjacent sheets (Table 1, Fig. 2).

4. Synthesis and crystallization

The title compound was obtained by a slow diffusion method in an U-shaped glass tube. The tube was first partially filled with acetonitrile. An acetonitrile solution of 0.333 mmol (97.0 mg) of $Co(NO_3)_2{\cdot}6H_2O$ was then placed in one arm of the tube. Another acetonitrile solution of 0.500 mmol (40.0 mg) of pyrazine was placed in the other arm of the tube. The slow diffusion of the two solutions in the tube produced pink needle–shaped crystals within one day. The crystals were collected by filtration and washed with fresh acetonitrile and kept under inert atmosphere (yield 31.5%). Selected IR bands (KBr, cm^{-1}): 3273 (O—H), 2283 (C≡N), 1633, 1413, 1384 (N=O), 479 (bridging pyrazine).

5. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 2. C-bound H atoms were calculated in geometrically idealized positions and refined riding on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$ (aromatic) and $1.5U_{eq}(C)$ (methyl), and with C—H = 0.95 Å (aromatic) and 0.98 Å (methyl). The methyl H atoms were allowed to rotate around the corresponding C—C bond. H atoms bound to water molecules were found in a difference map and were freely refined.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Co(NO_3)_2(C_4H_4N_2)(C_2H_3N)_2(H_2O)_2]$
M_r	381.18
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, *b*, *c* (Å)	7.0798 (3), 15.0376 (6), 7.9329 (3)
β (°)	110.8803 (6)
V (Å^3)	789.10 (5)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.14
Crystal size (mm)	0.29 × 0.11 × 0.08
Data collection	
Diffractometer	Bruker APEXII DUO CCD
Absorption correction	Analytical based on measured indexed crystal faces using *SHELXTL2014* (Sheldrick, 2015*b*)
T_{min}, T_{max}	0.735, 0.904
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21292, 1811, 1687
R_{int}	0.022
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.019, 0.055, 1.07
No. of reflections	1811
No. of parameters	115
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, −0.31

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXLT* (Sheldrick, 2015*a*), *SHELXL2014*/7 (Sheldrick, 2015*b*), *XP* in *SHELXTL-Plus* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

Acknowledgements

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References

Aşkın, G. Ş., Çelik, F., Dilek, N., Necefoğlu, H. & Hökelek, T. (2015). *Acta Cryst.* E**71**, 339–341.
Bruker (2014). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Choudhury, C. R., Dey, S. K., Sen, S., Bag, B., Mitra, S. & Gramlich, V. (2002). *Z. Naturforsch. Teil B*, **57**, 1191–1194.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Holman, K. T., Hammud, H. H., Isber, S. & Tabbal, M. (2005). *Polyhedron*, **24**, 221–228.

Hyun, M. Y., Kim, P.-G., Kim, C. & Kim, Y. (2011). *Acta Cryst.* E**67**, m390.
Lehleh, A., Boutebdja, M., Beghidja, A., Beghidja, C. & Merazig, H. (2013). *Acta Cryst.* E**69**, m177–m178.
Losier, P. & Zaworotko, M. J. (1996). *Angew. Chem. Int. Ed. Engl.* **35**, 2779–2782.
Ruan, M.-B., Deng, J.-C., Li, Z.-G. & Xu, J.-W. (2009). *Acta Cryst.* E**65**, m743.
Seidel, R. W., Goddard, R., Zibrowius, B. & Oppel, I. M. (2011). *Polymers*, **3**, 1458–1474.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Yang, S.-Y., Long, L.-S., Huang, R.-B., Zheng, L.-S. & Ng, S. W. (2003). *Acta Cryst.* E**59**, m961–m963.

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Crystal structure of *catena*-poly[[[*trans*-bis(acetonitrile-κN)diaquacobalt(II)]-μ-pyrazine-κ^2N:N'] dinitrate]

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Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: *SHELXLT* (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2014*/7 (Sheldrick, 2015*b*); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 2008) and *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

catena-Poly[[[*trans*-bis(acetonitrile-κN)diaquacobalt(II)]-μ-pyrazine-κ^2N:N'] dinitrate]

Crystal data

$[Co(NO_3)_2(C_4H_4N_2)(C_2H_3N)_2(H_2O)_2]$
M_r = 381.18
Monoclinic, $P2_1/c$
a = 7.0798 (3) Å
b = 15.0376 (6) Å
c = 7.9329 (3) Å
β = 110.8803 (6)°
V = 789.10 (5) Å^3
Z = 2
$F(000)$ = 390
D_x = 1.604 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9896 reflections
θ = 2.0–28.0°
μ = 1.14 mm^{-1}
T = 100 K
Needle, pink
0.29 × 0.11 × 0.08 mm

Data collection

Bruker APEXII DUO CCD diffractometer
Radiation source: fine-focus sealed tube
φ– and ω–scans
Absorption correction: analytical based on measured indexed crystal faces using *SHELXTL2014* (Sheldrick, 2015*b*)
T_{min} = 0.735, T_{max} = 0.904
21292 measured reflections
1811 independent reflections
1687 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 27.5°, θ_{min} = 2.7°
h = −9→9
k = −19→19
l = −10→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.055
S = 1.07
1811 reflections
115 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0316P)^2 + 0.2947P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.5000	0.5000	0.0000	0.00977 (8)
O1	0.45432 (12)	0.38331 (6)	−0.13782 (12)	0.01522 (17)
H1Y	0.431 (3)	0.3365 (13)	−0.092 (2)	0.035 (5)*
H1X	0.391 (3)	0.3842 (13)	−0.243 (3)	0.036 (5)*
N1	0.19570 (15)	0.49931 (6)	−0.00181 (13)	0.01163 (19)
N2	0.39794 (14)	0.56807 (6)	−0.25144 (13)	0.01470 (19)
C1	0.07744 (16)	0.57128 (7)	−0.05354 (15)	0.0134 (2)
H1A	0.1283	0.6228	−0.0923	0.016*
C2	−0.11795 (16)	0.57209 (7)	−0.05167 (14)	0.0131 (2)
H2A	−0.1981	0.6242	−0.0889	0.016*
C3	0.31802 (17)	0.58923 (8)	−0.39744 (16)	0.0158 (2)
C4	0.2144 (2)	0.61342 (10)	−0.58544 (17)	0.0278 (3)
H4A	0.3122	0.6380	−0.6346	0.042*
H4B	0.1106	0.6580	−0.5939	0.042*
H4C	0.1508	0.5605	−0.6545	0.042*
N11	0.23020 (15)	0.30295 (7)	0.44860 (13)	0.0172 (2)
O11	0.09637 (15)	0.26787 (6)	0.31960 (13)	0.0295 (2)
O12	0.21017 (14)	0.38082 (6)	0.49826 (12)	0.0228 (2)
O13	0.39023 (13)	0.26094 (6)	0.53329 (12)	0.0230 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.00857 (12)	0.01064 (12)	0.01028 (12)	−0.00011 (7)	0.00357 (8)	0.00023 (7)
O1	0.0187 (4)	0.0130 (4)	0.0136 (4)	−0.0023 (3)	0.0053 (3)	−0.0011 (3)
N1	0.0107 (4)	0.0130 (5)	0.0112 (4)	0.0000 (3)	0.0038 (3)	−0.0005 (3)
N2	0.0142 (4)	0.0151 (5)	0.0151 (5)	0.0002 (4)	0.0056 (4)	0.0010 (4)
C1	0.0135 (5)	0.0125 (5)	0.0144 (5)	−0.0006 (4)	0.0051 (4)	0.0011 (4)
C2	0.0128 (5)	0.0127 (5)	0.0138 (5)	0.0012 (4)	0.0045 (4)	0.0013 (4)
C3	0.0144 (5)	0.0164 (5)	0.0178 (6)	−0.0005 (4)	0.0072 (4)	0.0008 (4)
C4	0.0215 (6)	0.0426 (8)	0.0162 (6)	0.0002 (6)	0.0029 (5)	0.0093 (5)
N11	0.0222 (5)	0.0137 (5)	0.0149 (4)	−0.0015 (4)	0.0057 (4)	0.0004 (4)
O11	0.0319 (5)	0.0190 (5)	0.0236 (5)	−0.0026 (4)	−0.0073 (4)	−0.0018 (4)
O12	0.0315 (5)	0.0134 (4)	0.0213 (4)	0.0030 (4)	0.0067 (4)	−0.0024 (3)
O13	0.0207 (4)	0.0198 (4)	0.0232 (5)	0.0041 (3)	0.0012 (3)	−0.0054 (3)

Geometric parameters (Å, º)

Co1—O1	2.0315 (8)	C1—C2	1.3888 (15)
Co1—O1^{i}	2.0315 (8)	C1—H1A	0.9500
Co1—N2^{i}	2.1263 (9)	C2—N1^{ii}	1.3425 (14)
Co1—N2	2.1263 (9)	C2—H2A	0.9500
Co1—N1^{i}	2.1493 (10)	C3—C4	1.4542 (16)
Co1—N1	2.1493 (10)	C4—H4A	0.9800
O1—H1Y	0.83 (2)	C4—H4B	0.9800
O1—H1X	0.80 (2)	C4—H4C	0.9800
N1—C1	1.3401 (14)	N11—O11	1.2378 (13)
N1—C2^{ii}	1.3425 (14)	N11—O12	1.2595 (13)
N2—C3	1.1383 (15)	N11—O13	1.2616 (13)
O1—Co1—O1^{i}	180.0	C1—N1—Co1	120.89 (7)
O1—Co1—N2^{i}	91.42 (4)	C2^{ii}—N1—Co1	121.65 (7)
O1^{i}—Co1—N2^{i}	88.58 (4)	C3—N2—Co1	165.59 (9)
O1—Co1—N2	88.58 (4)	N1—C1—C2	121.32 (10)
O1^{i}—Co1—N2	91.42 (4)	N1—C1—H1A	119.3
N2^{i}—Co1—N2	180.0	C2—C1—H1A	119.3
O1—Co1—N1^{i}	88.55 (3)	N1^{ii}—C2—C1	121.23 (10)
O1^{i}—Co1—N1^{i}	91.45 (3)	N1^{ii}—C2—H2A	119.4
N2^{i}—Co1—N1^{i}	89.51 (4)	C1—C2—H2A	119.4
N2—Co1—N1^{i}	90.49 (4)	N2—C3—C4	178.24 (13)
O1—Co1—N1	91.45 (3)	C3—C4—H4A	109.5
O1^{i}—Co1—N1	88.55 (3)	C3—C4—H4B	109.5
N2^{i}—Co1—N1	90.49 (4)	H4A—C4—H4B	109.5
N2—Co1—N1	89.51 (4)	C3—C4—H4C	109.5
N1^{i}—Co1—N1	180.0	H4A—C4—H4C	109.5
Co1—O1—H1Y	121.0 (12)	H4B—C4—H4C	109.5
Co1—O1—H1X	118.3 (14)	O11—N11—O12	121.09 (10)
H1Y—O1—H1X	110.2 (18)	O11—N11—O13	120.29 (10)
C1—N1—C2^{ii}	117.45 (10)	O12—N11—O13	118.61 (10)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*; (ii) −*x*, −*y*+1, −*z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*Y*···O13^{iii}	0.83 (2)	1.85 (2)	2.6819 (12)	173.5 (18)
O1—H1*X*···O12^{iv}	0.80 (2)	1.99 (2)	2.7869 (12)	174.1 (19)
O1—H1*X*···O13^{iv}	0.80 (2)	2.562 (19)	3.0912 (12)	125.3 (17)
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C2—H2*A*···O13^{v}	0.95	2.59	3.4644 (14)	153
C4—H4*A*···O13^{i}	0.98	2.49	3.2785 (17)	138
C4—H4*B*···O11^{vi}	0.98	2.49	3.2823 (17)	138

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