Acta Crystallographica Section C
Crystal Structure
Communications
ISSN 0108-2701

Poly[[(μ_2-4,4′-bipyridine)(μ_3-5-isonicotinamidoisophthalato)cobalt(II)] trihydrate]

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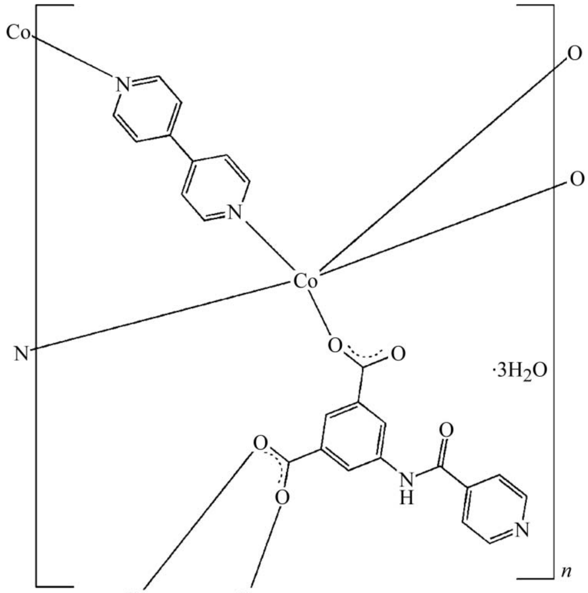
Received 25 June 2012
Accepted 4 July 2012
Online 19 July 2012

In the title compound, $\{[Co(C_{14}H_8N_2O_5)(C_{10}H_8N_2)]\cdot3H_2O\}_n$, the Co^{II} cation is five-coordinated with a slightly distorted trigonal–bipyramidal geometry, and the 5-isonicotinamidoisophthalate ligands link Co^{II} atoms into a layered structure. These two-dimensional arrays are further pillared by rod-like 4,4′-bipyridine ligands to give a three-dimensional framework with pcu (primitive cubic) topology. The magnetic and adsorption properties of the title compound are also discussed.

Comment

In recent years, metal–organic frameworks (MOFs) with carboxylate-containing ligands have been extensively studied because the carboxylate groups can have varied coordination modes resulting in the formation of different structures. MOFs show intriguing architectures and topologies, and have potential applications in catalysis, luminescence, ion exchange, magnetic materials and gas absorption (Férey *et al.*, 2005; Banerjee *et al.*, 2008; Chen *et al.*, 2007). Furthermore, mixed ligands with N-donor groups acting as ancillary connectors are another group of effective building units for constructing novel coordination polymers, because they have strong coordination affinity and can satisfy the geometric need of metal centres. Therefore, many reports show a boom in the exploratory synthesis and construction of porous frameworks to establish systems for selective gas sorption by long spacer ligands (Li *et al.*, 2010; Zang *et al.*, 2011). In the present case, in order to further investigate the influence of organic ligands on the coordination architectures and related properties, reactions with 5-isonicotinamidoisophthalic acid (H_2INAIP) and 4,4′-bipyridine (4,4′-bipy) N-donor bridging ligands were carried out. We report on the crystal structure and properties of a new coordination polymer obtained through solvothermal reaction, namely $\{[Co(INAIP)(4,4'\text{-bipy})]\cdot3H_2O\}_n$, (I).

The results of the structure analysis revealed that (I) exhibits a novel three-dimensional non-interpenetrated pillared framework. It is entirely different from the two-dimensional bilayer complex $[Co(INAIP)(4,4'\text{-bipy})_{0.5}]_n$, (II) (Chen *et al.*, 2010), which was obtained by hydrothermal synthesis from a similar source; therefore, the different structures of (I) and (II) show that the reaction conditions play a crucial role in the formation. The asymmetric unit of (I) contains one unique Co^{II} atom, one $INAIP^{2-}$ ligand, one 4,4′-bipy ligand and three free water molecules (Fig. 1); however, there is only half a 4,4′-bipy molecule in the asymmetric unit of complex (II). In (I), the Co1 atom has an N_2O_3 coordination environment and a distorted trigonal–bipyramidal coordination geometry. The Co—N and Co—O bond lengths are given in Table 1. Each $INAIP^{2-}$ ligand connects three Co^{II} atoms *via* its two carboxylate groups [a weak Co1···O2 interaction of 2.571 (2) Å has been omitted] and the pyridine ring of the ligand is noncoordinating; however, in (II), the pyridine is coordinated to the central Co^{II} atom. It is noteworthy that the two carboxylate groups of the $INAIP^{2-}$ ligand have different



(I)

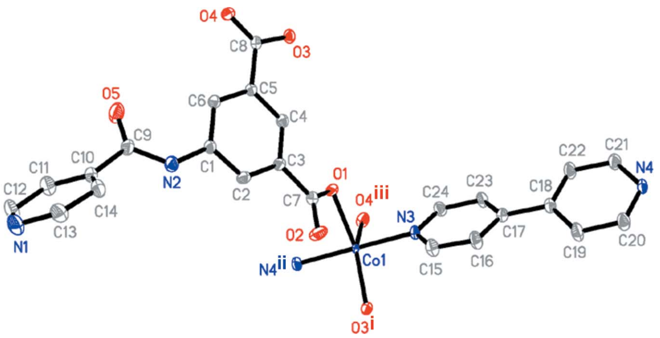


Figure 1
The structure of (I), with displacement ellipsoids drawn at the 30% probability level. [Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x+1, y, z$; (iii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$.]

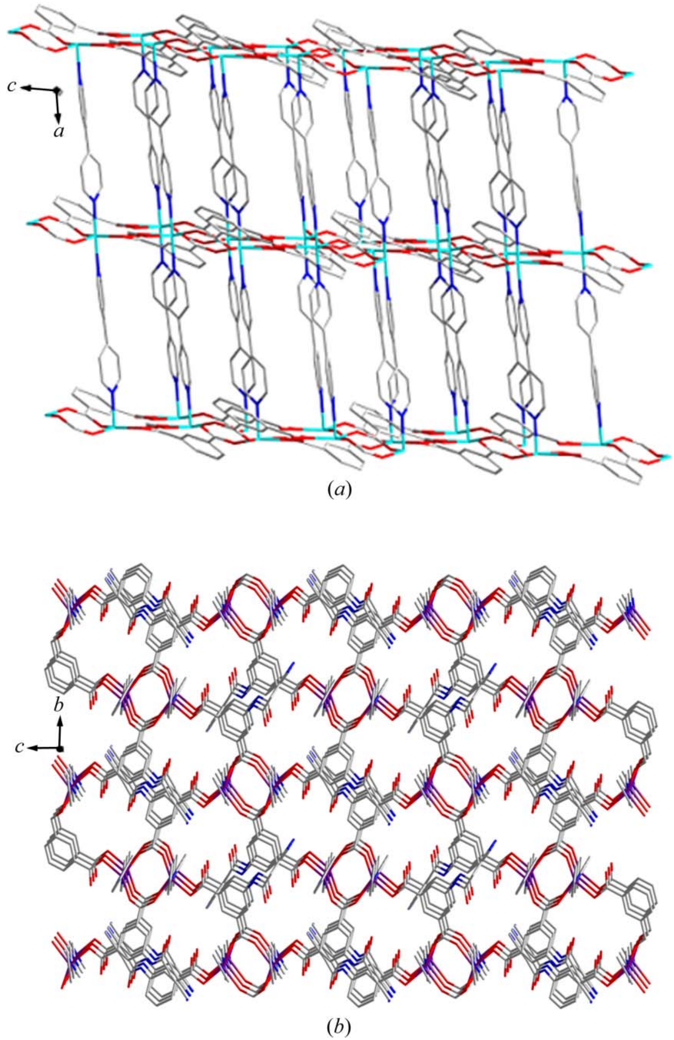


Figure 2
View of the porous framework of (I) along (*a*) the *b* and (*b*) the *a* axis.

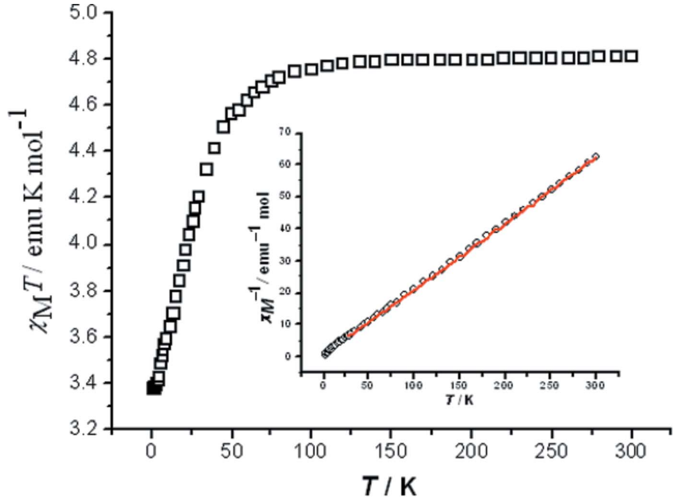


Figure 3
The temperature dependence of the magnetic susceptibility of (I).

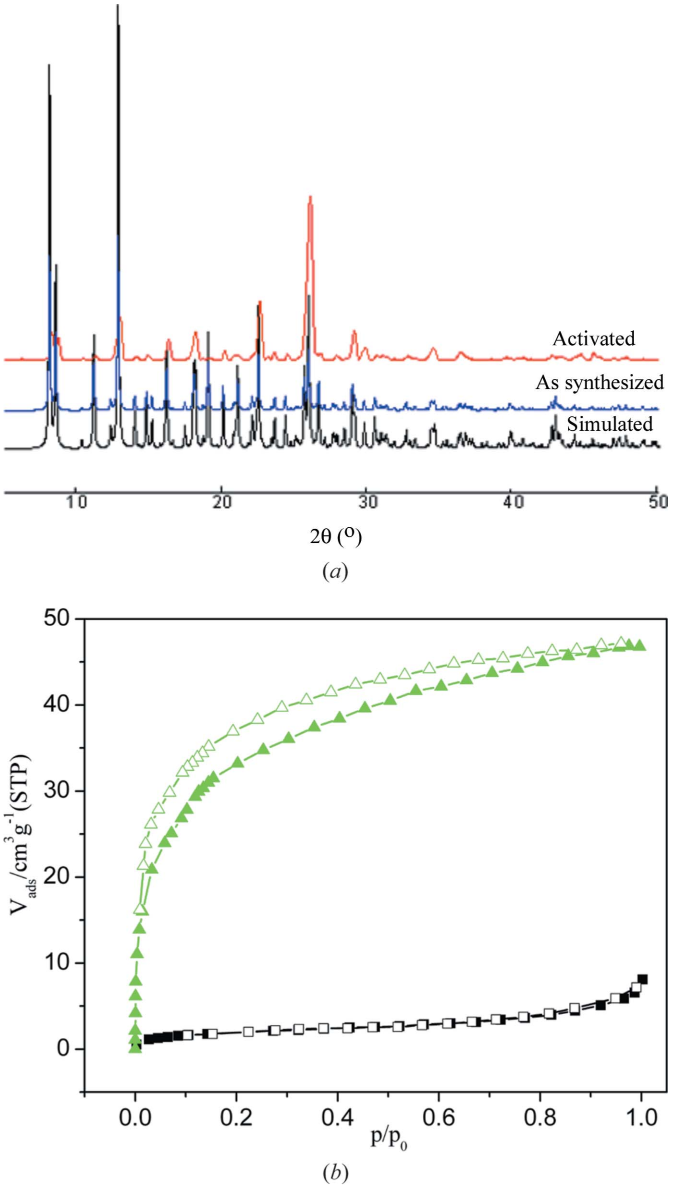


Figure 4
(*a*) The powder X-ray diffraction patterns of complex (I) and (*b*) the N_2 and CO_2 adsorption isotherm (273 K) of (I). Key: square and triangle curves represent N_2 and CO_2 adsorption respectively, filled shapes represent adsorption and open shapes represent desorption. In (*a*), 'activated' is the pattern from the crystal sample by heating under a vacuum pretreatment at an optimized temperature of 413 K for 20 h, 'simulated' is the pattern from the CIF produced by *Mercury* (Macrae *et al.*, 2008) and 'as synthesized' is the pattern from the synthesized crystal.

coordination modes in (I), *viz.* μ_1-η^1:η^0-monodentate and μ_2-η^1:η^1-bridging. The bridging carboxylate group links two metal atoms to give a $\{Co(OCO)\}_2$ unit, and the dimeric $\{Co(OCO)\}_2$ units are linked together by the monodentate carboxylate groups to form a two-dimensional layered structure. The two-dimensional networks are further pillared by rod-like 4,4′-bipy ligands to form a three-dimensional architecture (Fig. 2*a*). The resultant three-dimensional framework contains channels along the *a* axis (Fig. 2*b*). The cavities of the framework are occupied by water molecules. After omitting the solvent molecules, a *PLATON* (Spek, 2009) analysis revealed that the three-dimensional porous structure has large voids of 453.0 Å^3 which represent 18.5% of the unit-cell volume. To further understand this three-dimensional structure of (I), the dimeric

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$\{Co(OCO)\}_2$ units are considered as the nodes, and the topology of (I), calculated by *TOPOS* (Blatov, 2006; available at http://www.topos.ssu.samara.ru), is a uniform 6-connected three-dimensional pcu (primitive cubic) net.

The magnetic susceptibilities were measured on a crystalline sample of (I) in the temperature range 1.8–300 K under 2 kOe using a SQUID magnetometer. At room temperature, the observed $\chi_M T$ value is 4.81 emu K mol^{-1}, which is larger than the expected value of 3.75 emu K mol^{-1} corresponding to the binuclear Co^{II} ($S = 3/2$) ion (Fig. 3). Upon cooling from 300 to 100 K, the values of $\chi_M T$ decrease slowly and then rapidly reach a value of 3.37 emu K mol^{-1} at 1.8 K. The χ_M *versus* T plot follows the Curie–Weiss law, with C = 5.01 emu K mol^{-1} and $\Theta = -5.12$ K. The negative Θ value suggests that there is a weak antiferromagnetic interaction among the Co^{II} atoms transferred through the INAIP^{2-} ligands.

To verify whether the framework of (I) can be sustained after removal of the solvent molecules, powder X-ray diffraction (PXRD) patterns were measured. The framework of (I) still has good crystallinity without solvent molecules (Fig. 4*a*). The results show that (I) has permanent porosity in the absence of free water molecules and thus gas sorption was investigated. The N_2 and CO_2 adsorption isotherms for (I) are shown in Fig. 4(*b*). The results indicate that no N_2 uptake was observed at 273 K and the hysteresis behaviour is characteristic for type H3 (Liu *et al.*, 2008; Cheon & Suh, 2008). In contrast, it was found that significant amounts of CO_2 (273 K) were adsorbed and the isotherms present typical type-I curves, which is characteristic of a microporous material. The CO_2 uptake increases abruptly at the beginning and reaches 46.8 cm^3 (STP)/g (STP is standard temperature and pressure); approximately 0.45 CO_2 molecules per formula unit were adsorbed, indicating a uniform microporous structure. The gas sorption isotherms show a small hysteresis between the adsorption–desorption curves. Therefore, the selective sorption of CO_2 rather than N_2 gas can also be attributed to the significant quadrupole moment of CO_2 (-1.4×10^{-39} C m^2). Also the small difference of the kinetic diameters (3.64 Å of N_2 and 3.3 Å of CO_2) may induce specific interactions with the host framework to open up the channels, because of the favourable interactions between adsorbed CO_2 molecules and the Lewis basic amide functionalities decorating the pores (Chen *et al.*, 2011; Vogiatzis *et al.*, 2009).

Experimental

All reagents and solvents were used as obtained commercially without further purification. A mixture of H_2INAIP (0.029 g, 0.1 mmol), $CoCl_2\cdot6H_2O$ (0.024 g, 0.1 mmol), 4,4′-bipy (0.008 g, 0.05 mmol), *N*,*N*′-dimethylformamide (DMF, 6 ml) and EtOH (6 ml) was placed in a Teflon-lined stainless steel vessel, heated to 403 K for 3 d and then cooled to room temperature over a period of 24 h. Red block-shaped crystals of (I) were obtained (yield of 31%). IR (KBr pellet, cm^{-1}): 3422 (*s*), 2841 (*w*), 1627 (*w*), 1607 (*s*), 1518 (*m*), 1417 (*m*), 1386 (*s*), 1364 (*m*), 1288 (*w*), 789 (*w*), 742 (*w*), 721 (*m*), 585 (*w*).

Crystal data

$[Co(C_{14}H_8N_2O_5)(C_{10}H_8N_2)]\cdot3H_2O$
$M_r = 553.39$
Monoclinic, $P2_1/c$
$a = 11.1247$ (11) Å
$b = 13.8704$ (14) Å
$c = 16.0515$ (19) Å
$\beta = 98.621$ (2)°
$V = 2448.8$ (5) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.76$ mm^{-1}
$T = 293$ K
0.18 × 0.14 × 0.10 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
$T_{min} = 0.876$, $T_{max} = 0.928$
12940 measured reflections
4790 independent reflections
3743 reflections with $I > 2\sigma(I)$
$R_{int} = 0.068$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.111$
$S = 1.01$
4790 reflections
334 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.54$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Co1—O3^i	1.9450 (18)	Co1—N4^{ii}	2.027 (2)
Co1—N3	2.010 (2)	Co1—O4^{iii}	2.2546 (19)
Co1—O1	2.0250 (18)		

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x+1, y, z$; (iii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$.

H atoms bonded to C or N atoms were placed geometrically and treated as riding, with C—H = 0.93 Å or N—H = 0.86 Å, and with $U_{iso}(H) = 1.2U_{eq}$(C,N). The H atoms of the water molecules were placed so as to form a reasonable hydrogen-bond network, with O—H distances of 0.85 Å, and were refined as riding, with $U_{iso}(H) = 1.2U_{eq}(O)$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was funded by the Open Fund Project of Key Laboratories in Hunan Universities (grant No. 11 K009) and the Natural Science Foundation of Hunan Province of China (grant No. 10 J J3024).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3154). Services for accessing these data are described at the back of the journal.

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supplementary materials

Acta Cryst. (2012). C**68**, m219–m222 [doi:10.1107/S0108270112030582]

Poly[[(μ_2-4,4′-bipyridine)(μ_3-5-isonicotinamidoisophthalato)cobalt(II)] trihydrate]

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$a = 11.1247$ (11) Å
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$c = 16.0515$ (19) Å
$\beta = 98.621$ (2)°
$V = 2448.8$ (5) Å^3
$Z = 4$

$F(000) = 1140$
$D_x = 1.501$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3735 reflections
$\theta = 2.1$–24.7°
$\mu = 0.76$ mm^{-1}
$T = 293$ K
Block, red
0.18 × 0.14 × 0.10 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
$T_{min} = 0.876$, $T_{max} = 0.928$

12940 measured reflections
4790 independent reflections
3743 reflections with $I > 2\sigma(I)$
$R_{int} = 0.068$
$\theta_{max} = 26.0°$, $\theta_{min} = 2.0°$
$h = -13 \rightarrow 13$
$k = -17 \rightarrow 16$
$l = -9 \rightarrow 19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.111$
$S = 1.01$
4790 reflections
334 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0489P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.54$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C18	−0.0439 (3)	0.4998 (2)	0.8764 (2)	0.0320 (7)
C1	0.6545 (3)	0.57619 (19)	0.51747 (18)	0.0270 (6)
C2	0.6187 (3)	0.5353 (2)	0.58839 (18)	0.0301 (7)
H2	0.6350	0.4706	0.6004	0.036*
C3	0.5589 (2)	0.59009 (19)	0.64180 (17)	0.0256 (6)
C4	0.5326 (2)	0.68525 (19)	0.62320 (17)	0.0262 (6)
H4	0.4943	0.7226	0.6595	0.031*
C5	0.5635 (2)	0.72545 (18)	0.55029 (17)	0.0238 (6)
C6	0.6251 (2)	0.67154 (19)	0.49713 (18)	0.0269 (6)
H6	0.6463	0.6990	0.4485	0.032*
C7	0.5268 (3)	0.5436 (2)	0.72019 (19)	0.0288 (7)
C8	0.5301 (2)	0.82925 (19)	0.52935 (18)	0.0239 (6)
C9	0.7999 (3)	0.5436 (2)	0.4188 (2)	0.0356 (7)
C10	0.8589 (3)	0.4634 (2)	0.37781 (19)	0.0316 (7)
C11	0.9835 (3)	0.4634 (2)	0.3780 (2)	0.0416 (8)
H11	1.0323	0.5114	0.4058	0.050*
C12	1.0333 (3)	0.3899 (3)	0.3358 (2)	0.0496 (9)
H12	1.1172	0.3892	0.3372	0.060*
C13	0.8486 (3)	0.3218 (2)	0.2930 (2)	0.0413 (8)
H13	0.8014	0.2745	0.2629	0.050*
C14	0.7906 (3)	0.3908 (2)	0.3353 (2)	0.0377 (8)
H14	0.7070	0.3881	0.3350	0.045*
C15	0.2714 (3)	0.4336 (2)	0.8364 (2)	0.0370 (8)
H15	0.3089	0.3847	0.8100	0.044*
C16	0.1477 (3)	0.4281 (2)	0.8363 (2)	0.0373 (8)
H16	0.1037	0.3760	0.8111	0.045*
C17	0.0888 (3)	0.5013 (2)	0.8741 (2)	0.0308 (7)
C19	−0.1115 (3)	0.4156 (2)	0.8683 (2)	0.0442 (9)
H19	−0.0739	0.3571	0.8604	0.053*
C20	−0.2351 (3)	0.4184 (2)	0.8719 (2)	0.0405 (8)
H20	−0.2784	0.3608	0.8671	0.049*
C21	−0.2299 (3)	0.5814 (2)	0.8892 (2)	0.0430 (9)
H21	−0.2699	0.6391	0.8960	0.052*
C22	−0.1066 (3)	0.5839 (2)	0.8871 (2)	0.0445 (9)
H22	−0.0653	0.6423	0.8930	0.053*
C23	0.1603 (2)	0.5768 (2)	0.90939 (19)	0.0324 (7)
H23	0.1249	0.6278	0.9344	0.039*

C24	0.2838 (2)	0.5764 (2)	0.90759 (19)	0.0318 (7)
H24	0.3296	0.6280	0.9320	0.038*
Co1	0.52257 (3)	0.50479 (2)	0.87893 (2)	0.01609 (12)
N1	0.9683 (3)	0.31979 (19)	0.29307 (18)	0.0452 (7)
N2	0.7194 (2)	0.51615 (16)	0.46842 (16)	0.0336 (6)
H2A	0.7055	0.4553	0.4707	0.040*
N3	0.3408 (2)	0.50620 (16)	0.87285 (15)	0.0280 (6)
N4	−0.2948 (2)	0.49992 (16)	0.88181 (16)	0.0294 (6)
O1	0.51457 (17)	0.59900 (13)	0.78187 (12)	0.0279 (5)
O2	0.5158 (2)	0.45483 (15)	0.72408 (13)	0.0440 (6)
O3	0.47330 (16)	0.87209 (13)	0.58160 (12)	0.0276 (5)
O4	0.55740 (18)	0.86566 (14)	0.46395 (12)	0.0325 (5)
O5	0.8257 (2)	0.62762 (16)	0.40703 (17)	0.0615 (8)
O1W	0.7424 (2)	0.32033 (16)	0.54060 (17)	0.0674 (8)
H1X	0.8144	0.3159	0.5668	0.081*
H1Y	0.6934	0.3095	0.5754	0.081*
O2W	0.0317 (2)	0.69965 (18)	0.35282 (18)	0.0727 (8)
H2X	−0.0372	0.6815	0.3637	0.087*
H2Y	0.0209	0.7345	0.3088	0.087*
O3W	0.6047 (2)	0.28045 (16)	0.67452 (16)	0.0585 (7)
H3X	0.5667	0.2317	0.6892	0.070*
H3Y	0.5731	0.3311	0.6918	0.070*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C18	0.0225 (16)	0.0339 (17)	0.0411 (19)	0.0001 (13)	0.0091 (13)	0.0013 (14)
C1	0.0279 (16)	0.0249 (15)	0.0304 (17)	0.0026 (12)	0.0115 (13)	−0.0007 (13)
C2	0.0377 (18)	0.0226 (14)	0.0319 (17)	0.0023 (13)	0.0115 (14)	0.0048 (13)
C3	0.0275 (15)	0.0252 (15)	0.0255 (16)	0.0005 (12)	0.0079 (13)	0.0017 (12)
C4	0.0279 (16)	0.0270 (15)	0.0255 (16)	0.0026 (12)	0.0096 (13)	−0.0025 (12)
C5	0.0229 (15)	0.0233 (14)	0.0258 (16)	0.0013 (11)	0.0059 (12)	0.0004 (12)
C6	0.0305 (16)	0.0271 (15)	0.0248 (16)	0.0044 (12)	0.0097 (13)	0.0023 (12)
C7	0.0264 (16)	0.0309 (16)	0.0305 (18)	0.0023 (13)	0.0088 (13)	0.0033 (14)
C8	0.0207 (14)	0.0261 (15)	0.0259 (15)	−0.0009 (11)	0.0062 (12)	−0.0014 (13)
C9	0.0400 (19)	0.0315 (17)	0.039 (2)	0.0022 (14)	0.0192 (16)	0.0014 (15)
C10	0.0343 (17)	0.0312 (16)	0.0321 (18)	0.0048 (13)	0.0145 (14)	0.0019 (14)
C11	0.0341 (18)	0.0429 (18)	0.049 (2)	0.0012 (15)	0.0107 (16)	−0.0062 (17)
C12	0.0309 (19)	0.056 (2)	0.064 (2)	0.0089 (16)	0.0160 (17)	−0.011 (2)
C13	0.040 (2)	0.0381 (18)	0.046 (2)	0.0045 (15)	0.0082 (16)	−0.0044 (16)
C14	0.0303 (17)	0.0410 (18)	0.044 (2)	0.0059 (14)	0.0132 (15)	−0.0015 (16)
C15	0.0264 (17)	0.0402 (18)	0.045 (2)	−0.0013 (14)	0.0064 (15)	−0.0109 (16)
C16	0.0219 (16)	0.0363 (18)	0.054 (2)	−0.0035 (13)	0.0066 (15)	−0.0148 (16)
C17	0.0220 (15)	0.0339 (17)	0.0373 (18)	−0.0004 (13)	0.0073 (13)	0.0047 (14)
C19	0.0245 (17)	0.0316 (17)	0.080 (3)	−0.0007 (13)	0.0176 (17)	−0.0140 (18)
C20	0.0269 (17)	0.0283 (17)	0.068 (2)	−0.0040 (13)	0.0137 (16)	−0.0114 (16)
C21	0.0288 (17)	0.0275 (17)	0.075 (3)	−0.0011 (13)	0.0166 (17)	0.0009 (17)
C22	0.0239 (17)	0.0296 (17)	0.082 (3)	−0.0050 (13)	0.0151 (17)	−0.0022 (18)
C23	0.0226 (15)	0.0322 (16)	0.0439 (19)	0.0013 (12)	0.0098 (14)	−0.0070 (15)
C24	0.0224 (15)	0.0303 (16)	0.0423 (19)	0.0003 (12)	0.0033 (14)	−0.0028 (15)

Co1	0.01091 (18)	0.01686 (19)	0.0217 (2)	−0.00063 (14)	0.00622 (14)	0.00475 (15)
N1	0.0419 (17)	0.0437 (16)	0.0524 (19)	0.0075 (13)	0.0155 (14)	−0.0113 (15)
N2	0.0407 (15)	0.0241 (13)	0.0401 (15)	0.0019 (11)	0.0197 (13)	−0.0038 (11)
N3	0.0166 (12)	0.0339 (14)	0.0345 (14)	0.0001 (10)	0.0076 (10)	0.0046 (12)
N4	0.0166 (11)	0.0302 (13)	0.0430 (15)	−0.0003 (10)	0.0099 (11)	0.0026 (11)
O1	0.0335 (11)	0.0290 (10)	0.0237 (11)	0.0031 (9)	0.0120 (9)	0.0068 (9)
O2	0.0687 (17)	0.0254 (11)	0.0424 (14)	−0.0013 (11)	0.0232 (12)	0.0062 (10)
O3	0.0267 (11)	0.0235 (10)	0.0352 (12)	0.0013 (8)	0.0132 (9)	−0.0023 (9)
O4	0.0389 (12)	0.0289 (11)	0.0328 (12)	0.0079 (9)	0.0151 (10)	0.0088 (10)
O5	0.0731 (18)	0.0319 (13)	0.093 (2)	−0.0012 (12)	0.0570 (16)	0.0013 (14)
O1W	0.0663 (18)	0.0476 (15)	0.092 (2)	0.0089 (13)	0.0239 (16)	0.0166 (15)
O2W	0.0582 (18)	0.0686 (18)	0.095 (2)	−0.0068 (14)	0.0243 (16)	0.0322 (17)
O3W	0.0556 (16)	0.0348 (13)	0.089 (2)	−0.0014 (11)	0.0226 (15)	−0.0042 (13)

Geometric parameters (Å, º)

C18—C22	1.382 (4)	C15—C16	1.378 (4)
C18—C19	1.385 (4)	C15—H15	0.9300
C18—C17	1.483 (4)	C16—C17	1.395 (4)
C1—C2	1.382 (4)	C16—H16	0.9300
C1—C6	1.389 (4)	C17—C23	1.383 (4)
C1—N2	1.416 (3)	C19—C20	1.385 (4)
C2—C3	1.388 (4)	C19—H19	0.9300
C2—H2	0.9300	C20—N4	1.333 (3)
C3—C4	1.375 (4)	C20—H20	0.9300
C3—C7	1.503 (4)	C21—N4	1.337 (3)
C4—C5	1.385 (4)	C21—C22	1.377 (4)
C4—H4	0.9300	C21—H21	0.9300
C5—C6	1.390 (4)	C22—H22	0.9300
C5—C8	1.512 (4)	C23—C24	1.378 (4)
C6—H6	0.9300	C23—H23	0.9300
C7—O2	1.241 (4)	C24—N3	1.329 (3)
C7—O1	1.276 (3)	C24—H24	0.9300
C8—O4	1.243 (3)	Co1—O3^{i}	1.9450 (18)
C8—O3	1.271 (3)	Co1—N3	2.010 (2)
C9—O5	1.221 (4)	Co1—O1	2.0250 (18)
C9—N2	1.340 (4)	Co1—N4^{ii}	2.027 (2)
C9—C10	1.495 (4)	Co1—O4^{iii}	2.2546 (19)
C10—C14	1.379 (4)	N2—H2A	0.8600
C10—C11	1.385 (4)	N4—Co1^{iv}	2.027 (2)
C11—C12	1.386 (4)	O3—Co1^{v}	1.9450 (18)
C11—H11	0.9300	O4—Co1^{vi}	2.2546 (19)
C12—N1	1.337 (4)	O1W—H1X	0.8501
C12—H12	0.9300	O1W—H1Y	0.8499
C13—N1	1.332 (4)	O2W—H2X	0.8500
C13—C14	1.387 (4)	O2W—H2Y	0.8501
C13—H13	0.9300	O3W—H3X	0.8500
C14—H14	0.9300	O3W—H3Y	0.8500
C15—N3	1.348 (3)		

C22—C18—C19	116.5 (3)
C22—C18—C17	121.0 (3)
C19—C18—C17	122.5 (3)
C2—C1—C6	119.8 (3)
C2—C1—N2	116.8 (2)
C6—C1—N2	123.4 (3)
C1—C2—C3	120.5 (3)
C1—C2—H2	119.7
C3—C2—H2	119.7
C4—C3—C2	119.8 (3)
C4—C3—C7	121.6 (3)
C2—C3—C7	118.6 (2)
C3—C4—C5	119.9 (3)
C3—C4—H4	120.0
C5—C4—H4	120.0
C4—C5—C6	120.6 (2)
C4—C5—C8	119.2 (2)
C6—C5—C8	120.2 (2)
C1—C6—C5	119.2 (3)
C1—C6—H6	120.4
C5—C6—H6	120.4
O2—C7—O1	122.4 (3)
O2—C7—C3	120.3 (3)
O1—C7—C3	117.2 (2)
O4—C8—O3	125.2 (3)
O4—C8—C5	119.4 (2)
O3—C8—C5	115.4 (2)
O5—C9—N2	123.8 (3)
O5—C9—C10	120.9 (3)
N2—C9—C10	115.3 (3)
C14—C10—C11	118.6 (3)
C14—C10—C9	121.1 (3)
C11—C10—C9	120.3 (3)
C10—C11—C12	118.2 (3)
C10—C11—H11	120.9
C12—C11—H11	120.9
N1—C12—C11	124.1 (3)
N1—C12—H12	118.0
C11—C12—H12	118.0
N1—C13—C14	123.5 (3)
N1—C13—H13	118.2
C14—C13—H13	118.2
C10—C14—C13	118.9 (3)
C10—C14—H14	120.5
C13—C14—H14	120.5
N3—C15—C16	123.2 (3)
N3—C15—H15	118.4
C16—C15—H15	118.4
C15—C16—C17	119.5 (3)
C15—C16—H16	120.2
C17—C16—H16	120.2
C23—C17—C16	116.8 (3)
C23—C17—C18	120.9 (3)
C16—C17—C18	122.3 (3)
C18—C19—C20	120.0 (3)
C18—C19—H19	120.0
C20—C19—H19	120.0
N4—C20—C19	123.0 (3)
N4—C20—H20	118.5
C19—C20—H20	118.5
N4—C21—C22	123.0 (3)
N4—C21—H21	118.5
C22—C21—H21	118.5
C21—C22—C18	120.4 (3)
C21—C22—H22	119.8
C18—C22—H22	119.8
C24—C23—C17	120.1 (3)
C24—C23—H23	119.9
C17—C23—H23	119.9
N3—C24—C23	123.5 (3)
N3—C24—H24	118.3
C23—C24—H24	118.3
O3$^{\text{i}}$—Co1—N3	89.97 (8)
O3$^{\text{i}}$—Co1—O1	149.03 (8)
N3—Co1—O1	91.64 (8)
O3$^{\text{i}}$—Co1—N4$^{\text{ii}}$	89.22 (8)
N3—Co1—N4$^{\text{ii}}$	178.01 (10)
O1—Co1—N4$^{\text{ii}}$	88.13 (9)
O3$^{\text{i}}$—Co1—O4$^{\text{iii}}$	124.30 (8)
N3—Co1—O4$^{\text{iii}}$	95.85 (8)
O1—Co1—O4$^{\text{iii}}$	86.28 (8)
N4$^{\text{ii}}$—Co1—O4$^{\text{iii}}$	86.10 (9)
C13—N1—C12	116.7 (3)
C9—N2—C1	127.2 (2)
C9—N2—H2A	116.4
C1—N2—H2A	116.4
C24—N3—C15	116.8 (3)
C24—N3—Co1	121.77 (19)
C15—N3—Co1	121.3 (2)
C20—N4—C21	117.1 (3)
C20—N4—Co1$^{\text{iv}}$	122.77 (19)
C21—N4—Co1$^{\text{iv}}$	120.0 (2)
C7—O1—Co1	102.19 (17)
C8—O3—Co1$^{\text{v}}$	131.90 (18)
C8—O4—Co1$^{\text{vi}}$	142.51 (18)
H1X—O1W—H1Y	108.1
H2X—O2W—H2Y	108.7
H3X—O3W—H3Y	108.6

C6—C1—C2—C3	−3.2 (4)	C17—C18—C19—C20	179.3 (3)
N2—C1—C2—C3	177.5 (3)	C18—C19—C20—N4	1.0 (6)
C1—C2—C3—C4	1.3 (4)	N4—C21—C22—C18	0.5 (6)
C1—C2—C3—C7	−177.3 (3)	C19—C18—C22—C21	−0.1 (5)
C2—C3—C4—C5	1.5 (4)	C17—C18—C22—C21	−180.0 (3)
C7—C3—C4—C5	−179.9 (2)	C16—C17—C23—C24	−1.2 (4)
C3—C4—C5—C6	−2.5 (4)	C18—C17—C23—C24	179.2 (3)
C3—C4—C5—C8	177.9 (2)	C17—C23—C24—N3	0.2 (5)
C2—C1—C6—C5	2.2 (4)	C14—C13—N1—C12	−1.1 (5)
N2—C1—C6—C5	−178.5 (3)	C11—C12—N1—C13	−0.8 (5)
C4—C5—C6—C1	0.7 (4)	O5—C9—N2—C1	−2.6 (6)
C8—C5—C6—C1	−179.8 (2)	C10—C9—N2—C1	177.1 (3)
C4—C3—C7—O2	157.8 (3)	C2—C1—N2—C9	−153.1 (3)
C2—C3—C7—O2	−23.6 (4)	C6—C1—N2—C9	27.6 (5)
C4—C3—C7—O1	−23.9 (4)	C23—C24—N3—C15	1.4 (4)
C2—C3—C7—O1	154.7 (3)	C23—C24—N3—Co1	−175.8 (2)
C4—C5—C8—O4	−179.9 (3)	C16—C15—N3—C24	−2.1 (4)
C6—C5—C8—O4	0.5 (4)	C16—C15—N3—Co1	175.1 (2)
C4—C5—C8—O3	−0.9 (4)	O1—Co1—N3—C24	−81.0 (2)
C6—C5—C8—O3	179.6 (3)	O4^{iii}—Co1—N3—C24	5.5 (2)
O5—C9—C10—C14	−130.7 (4)	O3^{i}—Co1—N3—C15	−47.1 (2)
N2—C9—C10—C14	49.6 (4)	O1—Co1—N3—C15	102.0 (2)
O5—C9—C10—C11	45.8 (5)	O4^{iii}—Co1—N3—C15	−171.6 (2)
N2—C9—C10—C11	−133.9 (3)	C19—C20—N4—C21	−0.6 (5)
C14—C10—C11—C12	−0.4 (5)	C19—C20—N4—Co1^{iv}	175.7 (3)
C9—C10—C11—C12	−177.0 (3)	C22—C21—N4—C20	−0.2 (5)
C10—C11—C12—N1	1.5 (5)	C22—C21—N4—Co1^{iv}	−176.5 (3)
C11—C10—C14—C13	−1.3 (5)	O2—C7—O1—Co1	14.4 (3)
C9—C10—C14—C13	175.2 (3)	C3—C7—O1—Co1	−163.9 (2)
N1—C13—C14—C10	2.2 (5)	O3^{i}—Co1—O1—C7	−8.3 (3)
N3—C15—C16—C17	1.1 (5)	N3—Co1—O1—C7	−100.93 (18)
C15—C16—C17—C23	0.6 (5)	N4^{ii}—Co1—O1—C7	77.09 (18)
C15—C16—C17—C18	−179.8 (3)	O4^{iii}—Co1—O1—C7	163.31 (18)
C22—C18—C17—C23	21.8 (5)	O4—C8—O3—Co1^{v}	−36.2 (4)
C19—C18—C17—C23	−158.1 (3)	C5—C8—O3—Co1^{v}	144.80 (19)
C22—C18—C17—C16	−157.8 (3)	O3—C8—O4—Co1^{vi}	−11.4 (5)
C19—C18—C17—C16	22.3 (5)	C5—C8—O4—Co1^{vi}	167.6 (2)
C22—C18—C19—C20	−0.6 (5)		

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+3/2; (ii) *x*+1, *y*, *z*; (iii) *x*, −*y*+3/2, *z*+1/2; (iv) *x*−1, *y*, *z*; (v) −*x*+1, *y*+1/2, −*z*+3/2; (vi) *x*, −*y*+3/2, *z*−1/2.