

# Crystal structure of *catena*-poly[[diaquadiimidazolecobalt(II)]- $\mu_2$ -2,3,5,6-tetrabromobenzene-1,4-dicarboxylato]

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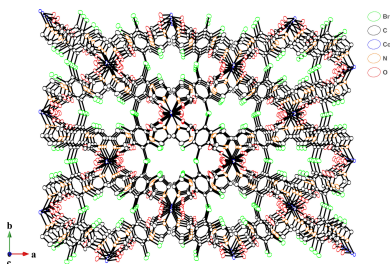
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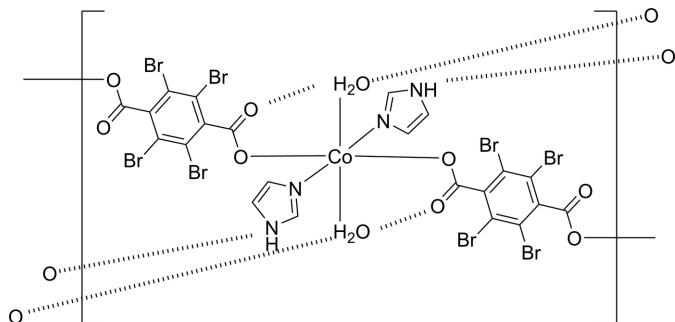
The asymmetric unit of the title compound,  $[\text{Co}(\text{C}_8\text{Br}_4\text{O}_4)(\text{C}_3\text{H}_4\text{N}_2)_2(\text{H}_2\text{O})_2]_n$  or  $[\text{Co}(\text{Br}_4\text{bdc})(\text{im})_2(\text{H}_2\text{O})_2]_n$ , comprises half of  $\text{Co}^{\text{II}}$  ion, tetrabromobenzene-dicarboxylate ( $\text{Br}_4\text{bdc}^{2-}$ ), imidazole (im) and a water molecule. The  $\text{Co}^{\text{II}}$  ion exhibits a six-coordinated octahedral geometry with two oxygen atoms of the  $\text{Br}_4\text{bdc}^{2-}$  ligand, two oxygen atoms of the water molecules, and two nitrogen atoms of the im ligands. The carboxylate group is nearly perpendicular to the benzene ring and shows monodentate coordination to the  $\text{Co}^{\text{II}}$  ion. The  $\text{Co}^{\text{II}}$  ions are bridged by the  $\text{Br}_4\text{bdc}^{2-}$  ligand, forming a one-dimensional chain. The carboxylate group acts as an intermolecular hydrogen-bond acceptor toward the im ligand and a coordinated water molecule. The chains are connected by interchain  $\text{N}-\text{H}\cdots\text{O}(\text{carboxylate})$  and  $\text{O}-\text{H}(\text{water})\cdots\text{O}(\text{carboxylate})$  hydrogen-bonding interactions and are not arranged in parallel but cross each other *via* interchain hydrogen bonding and  $\pi$ - $\pi$  interactions, yielding a three-dimensional network.

## 1. Chemical context

Infinite assemblies of metal ions bridged by organic linkers, so-called metal-organic frameworks (MOFs) or coordination polymers (CPs), are being actively investigated (Cheetham *et al.*, 1999; Férey, 2008; Kitagawa *et al.*, 2004; Rao *et al.*, 2008; Yaghi, *et al.*, 2019). Benzenedicarboxylate ( $\text{bdc}^{2-}$  dianion), also known as terephthalate dianion, is a well-known linker that gives functional MOFs or CPs (Eddaoudi *et al.*, 2002; Kurmoo 2009). We have not only been preparing electrode materials using terephthalate dianion and its analogues (Ogihara *et al.*, 2014, 2017, 2023; Yasuda *et al.*, 2014; Mikita *et al.*, 2020) but also fine tuning the crystal structures and properties of MOFs and CPs using  $R_4\text{bdc}^{2-}$  dianions ( $R = \text{H}, \text{F}, \text{Cl}, \text{Br}$ ) in which halogen atoms and metal ions are systematically varied (Kumagai *et al.*, 2012, 2021). We have used 4,4'-bipyridine (4,4'-bpy) or pyrazine (pyz) as co-ligands and have reported on the structure, thermal stability, and water adsorption/desorption properties of the resultant materials. In this contribution, we focused on using the  $\text{Br}_4\text{bdc}^{2-}$  dianion and imidazole (im) as a co-ligand instead of a pyz ligand in the synthesis of a  $\text{Co}^{\text{II}}-\text{Br}_4\text{bdc}^{2-}$  dianion system to observe the structural change resulting from the substitution of im for pyz. Although the pyz ligand coordinates two metal centers linearly, one of the two nitrogen atoms of the im ligand is protonated and undergoes hydrogen-bonding interactions. Here, we report on the single-crystal structure and properties of  $[\text{Co}(\text{Br}_4\text{bdc})(\text{im})_2(\text{H}_2\text{O})_2]$ . This is the first

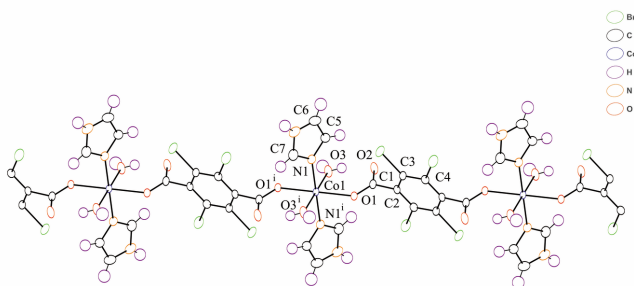


structural characterization of a metal complex having the  $\text{Br}_4\text{bdc}^{2-}$  dianion and im as a co-ligand.



## 2. Structural commentary

The title compound,  $[\text{Co}(\text{Br}_4\text{bdc})(\text{im})_2(\text{H}_2\text{O})_2]$ , consists of a  $\text{Co}^{\text{II}}$  ion, a tetrabromobenzenedicarboxylate dianion ( $\text{Br}_4\text{bdc}^{2-}$ ), two imidazole (im) molecules, and two water molecules. Its asymmetric unit consists of half of a  $\text{Co}^{\text{II}}$  ion, half of a  $\text{Br}_4\text{bdc}^{2-}$  dianion, an im molecule, and a water molecule. The key feature of the structure is a three-dimensional (3D) hydrogen-bonding network that consists of one-dimensional (1D) coordination chains built up by  $\text{CoO}_4\text{N}_2$  octahedra bridged by  $\text{Br}_4\text{bdc}^{2-}$  ligands and interchain  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{O}$  hydrogen-bonding interactions. Fig. 1 shows the chain structure of  $[\text{Co}(\text{Br}_4\text{bdc})(\text{im})_2(\text{H}_2\text{O})_2]$ . The  $\text{Co}^{\text{II}}$  ion occupies a crystallographically special position, and each pair of  $\text{Br}_4\text{bdc}^{2-}$  ligands, water molecules, and im ligands coordinates *trans* to each other; the coordination environment is similar to that of a two-dimensional (2D) material synthesized from  $\text{Br}_4\text{bdc}^{2-}$  and pyz ligands,  $[\text{Co}(\text{Br}_4\text{bdc})(\text{pyz})_2(\text{H}_2\text{O})_2]$  (Kumagai *et al.*, 2021). The carboxylate group exhibits a monodentate coordination, and the benzene ring and the carboxylate group are nearly perpendicular dihedral angle =  $90.5(3)^\circ$ . The im ligand coordinates to the  $\text{Co}^{\text{II}}$  ion *via* nitrogen atom N1 as a neutral imidazole ligand rather than as an imidazolate anion, and a hydrogen atom is attached to the remaining nitrogen atom N2. The  $\text{Co}-\text{O}3$  ( $\text{H}_2\text{O}$ ) and  $\text{Co}-\text{O}1$  (carboxylate) bond lengths



**Figure 1**  
One-dimensional chain structure of title compound, along with labeling scheme and 50% probability displacement ellipsoids. [Symmetry code: (i)  $-x + 1, -y + 2, -z + 2$ .]

**Table 1**  
Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

$\text{Co}1-\text{N}1^i$	2.0850 (18)	$\text{Co}1-\text{O}3$	2.1007 (16)
$\text{Co}1-\text{N}1$	2.0850 (18)	$\text{Co}1-\text{O}1^i$	2.1678 (13)
$\text{Co}1-\text{O}3^i$	2.1006 (16)	$\text{Co}1-\text{O}1$	2.1678 (13)
$\text{N}1^i-\text{Co}1-\text{N}1$	180.00 (11)	$\text{O}3^i-\text{Co}1-\text{O}1^i$	89.81 (6)
$\text{N}1^i-\text{Co}1-\text{O}3^i$	89.06 (7)	$\text{O}3-\text{Co}1-\text{O}1^i$	90.19 (6)
$\text{N}1-\text{Co}1-\text{O}3^i$	90.94 (7)	$\text{N}1^i-\text{Co}1-\text{O}1$	91.69 (6)
$\text{N}1^i-\text{Co}1-\text{O}3$	90.94 (7)	$\text{N}1-\text{Co}1-\text{O}1$	88.31 (6)
$\text{N}1-\text{Co}1-\text{O}3$	89.06 (7)	$\text{O}3^i-\text{Co}1-\text{O}1$	90.19 (6)
$\text{O}3^i-\text{Co}1-\text{O}3$	180.00 (4)	$\text{O}3-\text{Co}1-\text{O}1$	89.81 (6)
$\text{N}1^i-\text{Co}1-\text{O}1^i$	88.31 (6)	$\text{O}1^i-\text{Co}1-\text{O}1$	180.0
$\text{N}1-\text{Co}1-\text{O}1^i$	91.69 (6)		

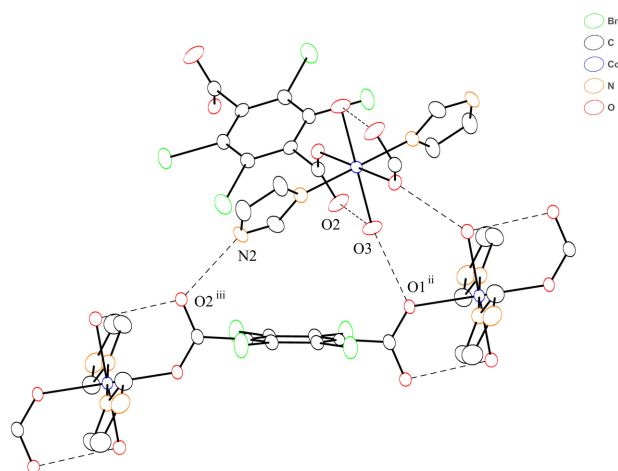
Symmetry code: (i)  $-x + 1, -y + 2, -z + 2$ .

**Table 2**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

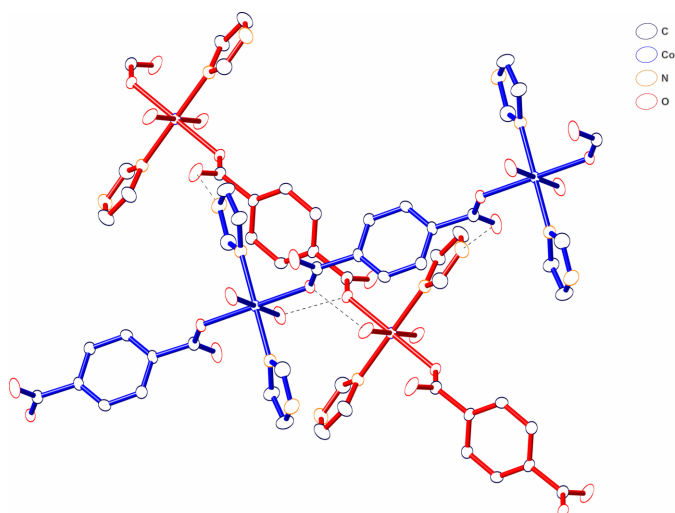
$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N}2-\text{H}1\cdots\text{O}2^{\text{ii}}$	0.80 (3)	2.01 (3)	2.808 (2)	174 (3)
$\text{O}3-\text{H}2\cdots\text{O}2$	0.76 (3)	1.99 (3)	2.700 (2)	155 (3)
$\text{O}3-\text{H}3\cdots\text{O}1^{\text{iii}}$	0.75 (4)	2.06 (4)	2.809 (2)	176 (4)

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

in the title compound are 2.1006 (16) and 2.1678 (13)  $\text{\AA}$  (Table 1), respectively, which are slightly longer than those [2.032 (3)  $\text{\AA}$  and 2.096 (4)  $\text{\AA}$ ] for  $[\text{Co}(\text{Br}_4\text{bdc})(\text{pyz})_2(\text{H}_2\text{O})_2]$  (Kumagai *et al.*, 2021). However, the  $\text{Co}-\text{N}$  bond length of 2.0850 (18)  $\text{\AA}$  is shorter than that of 2.273 (4)  $\text{\AA}$  for  $[\text{Co}(\text{Br}_4\text{bdc})(\text{pyz})_2(\text{H}_2\text{O})_2]$ , in which the  $\text{Co}^{\text{II}}$  ion shows an elongated octahedral environment, indicative of the compressed octahedron of the title compound (Kumagai *et al.*, 2021). The angles around the  $\text{Co}^{\text{II}}$  ion lie in the range  $88.31(6)-180.0^\circ$ . The  $\text{Co}\cdots\text{Co}$  separation defined by the  $\text{Co}-\text{Br}_4\text{bdc}^{2-}-\text{Co}$  connectivity within the chain is 11.69  $\text{\AA}$ , which is slightly longer than that for  $[\text{Co}(\text{Br}_4\text{bdc})(\text{pyz})_2(\text{H}_2\text{O})_2]$  (11.24  $\text{\AA}$ ; Kumagai *et al.*, 2021).



**Figure 2**  
View of inter- and intramolecular hydrogen-bonding interactions. Dashed lines represent hydrogen bonds. Hydrogen atoms are omitted for clarity. [Symmetry code: (ii)  $x, -y + 2, z + \frac{1}{2}$ , (iii)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ .]

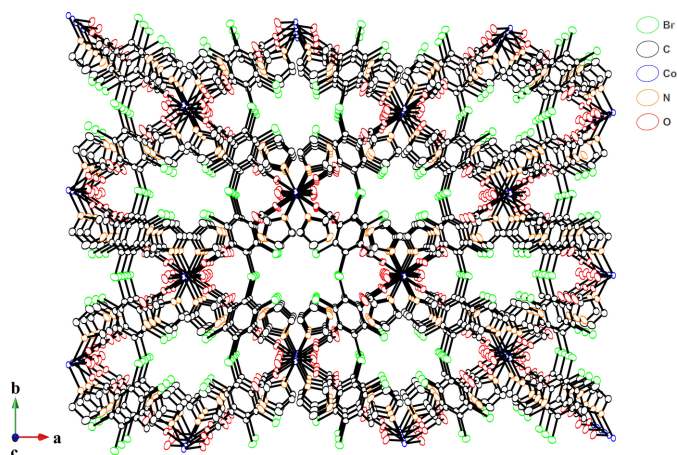


**Figure 3**

Two chains linked by interchain hydrogen-bonding interactions. Dashed lines represent interchain hydrogen bonds. Bromine and hydrogen atoms are omitted for clarity.

### 3. Supramolecular features

In the crystal structure, the im ligands and coordinated water molecules act as hydrogen-bond donors and the oxygen atoms of the carboxylate group of  $\text{Br}_4\text{bdc}^{2-}$  ligand act as hydrogen-bond acceptors (Fig. 2, Table 2). The coordinated water molecule exhibits not only intrachain hydrogen-bonding interactions with oxygen atom O2 of the carboxylate group not bound to a  $\text{Co}^{\text{II}}$  ion but also interchain hydrogen-bonding interactions with the coordinated oxygen atom O1 of carboxylate group in the adjacent chain. Further interchain hydrogen-bonding interactions between the im ligands and coordinated oxygen atoms of the carboxylate groups yield a 3D hydrogen-bonded network. The nearest centroid-centroid distance between the benzene ring and the im ligand, and the shortest  $\text{C}\cdots\text{C}$  distance are 3.95 and 3.63 Å, respectively. These distances are indicative of some degree of  $\pi$ - $\pi$  stacking interactions (Kruszynski & Sierański, 2019). The



**Figure 4**

View of the hydrogen-bonding network along the crystallographic  $c$  axis.

chains are not arranged in parallel but cross each other by hydrogen-bonding and  $\pi$ - $\pi$  stacking interactions (Fig. 3) and appear to have a 1D-channel structure when viewed along the  $c$  axis (Fig. 4).

### 4. Database survey

Although a search of the Sci Finder database for structures with a  $\text{Br}_4\text{bdc}^{2-}$  ion, an im ligand, and a  $\text{Co}^{\text{II}}$  ion resulted in no complete matches, nor were any partially matched structures found. They are metal complexes composed of a  $\text{Br}_4\text{bdc}^{2-}$  ligand and benzimidazole derivatives (Zhang *et al.*, 2016; Hu *et al.*, 2015). A search of the Web of Science database for the keyword tetrabromoterephthalate led to  $\text{Ni}^{\text{II}}$  compounds that also contain a  $\text{Br}_4\text{bdc}^{2-}$  ligand and benzimidazole derivatives (Liu *et al.*, 2015; Hao *et al.*, 2020).

### 5. Synthesis and crystallization

An aqueous solution (5 mL) of cobalt(II) nitrate hexahydrate (0.35 g, 1.25 mmol) was transferred to a glass tube, and an ethanol-water mixture (5 mL) of 2,3,5,6-tetrabromobenzene-dicarboxylic acid (0.60 g, 1.25 mmol), NaOH (0.10 g, 2.50 mmol), and imidazole (0.10 g, 1.25 mmol) was poured into the glass tube without the two solutions being mixed. Pink crystals began to form at ambient temperature in 1 week, one of which was used for the X-ray crystallography study.

### 6. Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 3. The non-hydrogen atoms were refined anisotropically. The hydrogen atom attached to a nitrogen atom of the im ligand and the water molecules were located in difference-Fourier maps. Other hydrogen atoms were placed in idealized positions and were refined using a riding model.

### 7. Additional investigations

To assess the thermal properties of the title compound, we carried out a thermogravimetric analysis (TGA) under a nitrogen atmosphere. The TGA curve is characterized by two weight-loss steps in the range 120–500°C (Fig. S1). The first weight loss of 6% was observed in the temperature range 120–160°C, and the second weight loss of 90% was observed in the range 200–470°C. The first weight loss corresponds to the loss of two coordinated water molecules to give the dehydrated phase,  $[\text{Co}(\text{Br}_4\text{bdc})(\text{im})_2]$ . The second weight loss is due to thermal decomposition of the compound. The DTG curve exhibited a sharp peak at 215°C. This result indicates that the compound is stable up to about 200°C. Electronic diffuse-reflectance spectra were recorded for as-synthesized  $[\text{Co}(\text{Br}_4\text{bdc})(\text{im})_2(\text{H}_2\text{O})_2]$  and the dehydrated phase,  $[\text{Co}(\text{Br}_4\text{bdc})(\text{im})_2]$ , obtained after heat treatment at 140°C. Because the compounds were not soluble in any solvent, we acquired the electronic diffuse-reflectance spectra of solid-

state samples. After the heat treatment, a color change from pink to blue was observed and two strong absorption bands appeared at  $\sim 480$  nm and  $\sim 1000$  nm, indicating that the coordination environment of the six-coordinate  $\text{Co}^{\text{II}}$  center had changed to a four-coordinate  $\text{Co}^{\text{II}}$  environment as a result of the loss of coordinated water molecules (Fig. S2). In the IR spectrum, the characteristic band for the coordinated water molecules was observed as a broad band at  $3340\text{ cm}^{-1}$ ; the band disappeared after the heat treatment (Fig. S3). This result is in good agreement with the TGA and electronic diffuse-reflectance spectra measurement results. Nitrogen adsorption–desorption measurements were conducted; however, almost no nitrogen was adsorbed. This lack of nitrogen adsorption is speculatively attributed to insufficient space for nitrogen molecules because of the large ionic radius of the bromine.

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**Table 3**  
Experimental details.

Crystal data	
Chemical formula	$[\text{Co}(\text{C}_8\text{Br}_4\text{O}_4)(\text{C}_3\text{H}_4\text{N}_2)_2(\text{H}_2\text{O})_2]$
$M_r$	710.85
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	173
$a, b, c$ (Å)	18.8050 (7), 12.2925 (6), 10.8938 (5)
$\beta$ (°)	121.853 (3)
$V$ (Å <sup>3</sup> )	2138.97 (17)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	8.31
Crystal size (mm)	0.60 × 0.60 × 0.60
Data collection	
Diffractometer	Rigaku R-AXIS RAPID
Absorption correction	Multi-scan ( <i>ABSCOR</i> ; Rigaku, 1995)
$T_{\text{min}}, T_{\text{max}}$	0.004, 0.007
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	10419, 2448, 2277
$R_{\text{int}}$	0.046
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.028, 0.067, 1.07
No. of reflections	2448
No. of parameters	145
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.61, -0.60

Computer programs: *RAPID AUTO* (Rigaku, 1995), *SUPERFLIP* (Palatinus & Chapuis, 2007), *SHELXL2018/3* (Sheldrick, 2015) and *CrystalStructure* (Rigaku, 2019).

## supporting information

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## Crystal structure of *catena*-poly[[diaquadiimidazolecobalt(II)]- $\mu_2$ -2,3,5,6-tetrabromobenzene-1,4-dicarboxylato]

Hitoshi Kumagai, Satoshi Kawata and Nobuhiro Ogihara

### Computing details

*catena*-Poly[[diaquadiimidazolecobalt(II)]- $\mu_2$ -2,3,5,6-tetrabromobenzene-1,4-dicarboxylato]

#### Crystal data

[Co(C<sub>8</sub>Br<sub>4</sub>O<sub>4</sub>)(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]

$M_r = 710.85$

Monoclinic, *C2/c*

$a = 18.8050$  (7) Å

$b = 12.2925$  (6) Å

$c = 10.8938$  (5) Å

$\beta = 121.853$  (3)°

$V = 2138.97$  (17) Å<sup>3</sup>

$Z = 4$

$F(000) = 1356$

$D_x = 2.207$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71075$  Å

Cell parameters from 9142 reflections

$\theta = 3.3$ – $27.5$ °

$\mu = 8.31$  mm<sup>-1</sup>

$T = 173$  K

Block, pink

0.60 × 0.60 × 0.60 mm

#### Data collection

Rigaku R-AXIS RAPID  
diffractometer

$\omega$  scans

Absorption correction: multi-scan  
(ABSCOR; Rigaku, 1995)

$T_{\min} = 0.004$ ,  $T_{\max} = 0.007$

10419 measured reflections

2448 independent reflections

2277 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.046$

$\theta_{\max} = 27.5$ °,  $\theta_{\min} = 3.3$ °

$h = -22$ → $24$

$k = -15$ → $15$

$l = -14$ → $14$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.067$

$S = 1.07$

2448 reflections

145 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0356P)^2 + 0.8085P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.61$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.59$  e Å<sup>-3</sup>



*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.40878 (2)	1.36557 (2)	0.78290 (2)	0.02796 (9)
Br2	0.30071 (2)	1.49911 (2)	0.46852 (3)	0.03101 (10)
Co1	0.500000	1.000000	1.000000	0.01141 (10)
O1	0.40770 (8)	1.08127 (12)	0.80246 (14)	0.0157 (3)
O2	0.31711 (10)	1.14631 (14)	0.85848 (17)	0.0282 (4)
O3	0.41853 (11)	1.01046 (14)	1.0767 (2)	0.0236 (4)
N1	0.44446 (11)	0.85236 (14)	0.90200 (19)	0.0179 (3)
N2	0.34569 (13)	0.73172 (17)	0.7762 (2)	0.0275 (4)
C1	0.34466 (12)	1.13493 (16)	0.7774 (2)	0.0159 (4)
C2	0.29633 (12)	1.19335 (16)	0.6314 (2)	0.0153 (4)
C3	0.31735 (12)	1.29953 (17)	0.6185 (2)	0.0159 (4)
C4	0.27151 (13)	1.35524 (16)	0.4882 (2)	0.0167 (4)
C5	0.47955 (14)	0.76163 (19)	0.8814 (3)	0.0254 (5)
H5	0.537318	0.752777	0.915853	0.030*
C6	0.41879 (16)	0.6861 (2)	0.8039 (3)	0.0329 (6)
H6	0.425979	0.616103	0.775114	0.039*
C7	0.36370 (14)	0.8307 (2)	0.8368 (2)	0.0257 (5)
H7	0.323364	0.879232	0.833300	0.031*
H1	0.2999 (19)	0.706 (2)	0.733 (3)	0.036 (8)*
H2	0.383 (2)	1.050 (3)	1.028 (3)	0.032 (8)*
H3	0.418 (2)	0.987 (2)	1.139 (4)	0.040 (9)*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.02444 (15)	0.02595 (15)	0.01768 (14)	-0.00432 (8)	0.00031 (11)	-0.00049 (8)
Br2	0.03257 (17)	0.02081 (15)	0.02504 (16)	-0.00629 (8)	0.00522 (13)	0.00651 (8)
Co1	0.00890 (19)	0.0133 (2)	0.0105 (2)	0.00010 (12)	0.00411 (16)	0.00132 (12)
O1	0.0144 (7)	0.0176 (7)	0.0121 (7)	0.0044 (5)	0.0050 (6)	0.0030 (5)
O2	0.0253 (8)	0.0442 (10)	0.0199 (8)	0.0198 (7)	0.0153 (7)	0.0143 (7)
O3	0.0199 (8)	0.0337 (10)	0.0229 (9)	0.0100 (7)	0.0151 (8)	0.0135 (7)
N1	0.0168 (8)	0.0168 (9)	0.0171 (8)	-0.0012 (7)	0.0069 (7)	0.0008 (6)
N2	0.0229 (10)	0.0309 (11)	0.0267 (11)	-0.0149 (8)	0.0116 (9)	-0.0068 (8)
C1	0.0126 (9)	0.0171 (10)	0.0137 (10)	0.0012 (7)	0.0039 (8)	0.0018 (7)
C2	0.0128 (9)	0.0188 (10)	0.0144 (9)	0.0051 (8)	0.0073 (8)	0.0031 (7)
C3	0.0125 (9)	0.0176 (10)	0.0144 (9)	0.0013 (7)	0.0049 (8)	0.0000 (7)
C4	0.0181 (10)	0.0140 (9)	0.0175 (10)	0.0015 (7)	0.0090 (9)	0.0024 (7)
C5	0.0208 (11)	0.0230 (11)	0.0264 (12)	-0.0008 (9)	0.0084 (10)	-0.0056 (9)
C6	0.0358 (13)	0.0267 (13)	0.0335 (13)	-0.0074 (10)	0.0165 (12)	-0.0107 (10)

C7      0.0192 (11)      0.0282 (12)      0.0279 (12)      -0.0049 (9)      0.0112 (10)      -0.0022 (10)

*Geometric parameters (Å, °)*

Br1—C3	1.890 (2)	N1—C5	1.373 (3)
Br2—C4	1.897 (2)	N2—C7	1.340 (3)
Co1—N1 <sup>i</sup>	2.0850 (18)	N2—C6	1.363 (3)
Co1—N1	2.0850 (18)	N2—H1	0.80 (3)
Co1—O3 <sup>i</sup>	2.1006 (16)	C1—C2	1.531 (3)
Co1—O3	2.1007 (16)	C2—C4 <sup>ii</sup>	1.388 (3)
Co1—O1 <sup>i</sup>	2.1678 (13)	C2—C3	1.392 (3)
Co1—O1	2.1678 (13)	C3—C4	1.392 (3)
O1—C1	1.254 (2)	C5—C6	1.364 (3)
O2—C1	1.246 (2)	C5—H5	0.9500
O3—H2	0.76 (3)	C6—H6	0.9500
O3—H3	0.75 (4)	C7—H7	0.9500
N1—C7	1.320 (3)		
N1 <sup>i</sup> —Co1—N1	180.00 (11)	C7—N2—H1	124 (2)
N1 <sup>i</sup> —Co1—O3 <sup>i</sup>	89.06 (7)	C6—N2—H1	128 (2)
N1—Co1—O3 <sup>i</sup>	90.94 (7)	O2—C1—O1	127.11 (18)
N1 <sup>i</sup> —Co1—O3	90.94 (7)	O2—C1—C2	116.28 (17)
N1—Co1—O3	89.06 (7)	O1—C1—C2	116.61 (16)
O3 <sup>i</sup> —Co1—O3	180.00 (4)	C4 <sup>ii</sup> —C2—C3	118.53 (18)
N1 <sup>i</sup> —Co1—O1 <sup>i</sup>	88.31 (6)	C4 <sup>ii</sup> —C2—C1	121.38 (18)
N1—Co1—O1 <sup>i</sup>	91.69 (6)	C3—C2—C1	120.00 (17)
O3 <sup>i</sup> —Co1—O1 <sup>i</sup>	89.81 (6)	C4—C3—C2	120.56 (18)
O3—Co1—O1 <sup>i</sup>	90.19 (6)	C4—C3—Br1	121.29 (15)
N1 <sup>i</sup> —Co1—O1	91.69 (6)	C2—C3—Br1	118.15 (14)
N1—Co1—O1	88.31 (6)	C2 <sup>ii</sup> —C4—C3	120.90 (18)
O3 <sup>i</sup> —Co1—O1	90.19 (6)	C2 <sup>ii</sup> —C4—Br2	118.19 (15)
O3—Co1—O1	89.81 (6)	C3—C4—Br2	120.90 (15)
O1 <sup>i</sup> —Co1—O1	180.0	C6—C5—N1	109.6 (2)
C1—O1—Co1	128.92 (12)	C6—C5—H5	125.2
Co1—O3—H2	109 (2)	N1—C5—H5	125.2
Co1—O3—H3	135 (3)	N2—C6—C5	106.0 (2)
H2—O3—H3	117 (3)	N2—C6—H6	127.0
C7—N1—C5	105.28 (19)	C5—C6—H6	127.0
C7—N1—Co1	125.05 (15)	N1—C7—N2	111.6 (2)
C5—N1—Co1	129.53 (14)	N1—C7—H7	124.2
C7—N2—C6	107.5 (2)	N2—C7—H7	124.2
Co1—O1—C1—O2	-6.2 (3)	Br1—C3—C4—C2 <sup>ii</sup>	-179.05 (15)
Co1—O1—C1—C2	173.49 (12)	C2—C3—C4—Br2	-178.98 (14)
O2—C1—C2—C4 <sup>ii</sup>	-87.3 (2)	Br1—C3—C4—Br2	1.6 (2)
O1—C1—C2—C4 <sup>ii</sup>	93.0 (2)	C7—N1—C5—C6	-0.2 (3)
O2—C1—C2—C3	89.4 (2)	Co1—N1—C5—C6	-176.08 (16)
O1—C1—C2—C3	-90.4 (2)	C7—N2—C6—C5	-0.4 (3)

C4 <sup>ii</sup> —C2—C3—C4	-0.3 (3)	N1—C5—C6—N2	0.4 (3)
C1—C2—C3—C4	-177.08 (16)	C5—N1—C7—N2	0.0 (3)
C4 <sup>ii</sup> —C2—C3—Br1	179.07 (14)	Co1—N1—C7—N2	176.07 (15)
C1—C2—C3—Br1	2.3 (2)	C6—N2—C7—N1	0.3 (3)
C2—C3—C4—C2 <sup>ii</sup>	0.4 (3)		

Symmetry codes: (i)  $-x+1, -y+2, -z+2$ ; (ii)  $-x+1/2, -y+5/2, -z+1$ .

*Hydrogen-bond geometry (Å, °)*

<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>
C6—H6 $\cdots$ Br1 <sup>iii</sup>	0.95	3.10	3.946 (3)	149
N2—H1 $\cdots$ O2 <sup>iv</sup>	0.80 (3)	2.01 (3)	2.808 (2)	174 (3)
O3—H2 $\cdots$ O2	0.76 (3)	1.99 (3)	2.700 (2)	155 (3)
O3—H3 $\cdots$ O1 <sup>v</sup>	0.75 (4)	2.06 (4)	2.809 (2)	176 (4)

Symmetry codes: (iii)  $x, y-1, z$ ; (iv)  $-x+1/2, y-1/2, -z+3/2$ ; (v)  $x, -y+2, z+1/2$ .