# research communications

## Synthesis and structure of hexaaquacobalt bis(2-methyl-1H-imidazol-3-ium) tetraaquabis(benzene-1,3,5-tricarboxylato-κO)cobalt

**Jose de Jesus Velazquez-Garcia[a]\* and Simone Techert[a,b]**

[a]Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, 22607 Hamburg, Germany, and [b]Institut für Röntgenphysik, Georg-August-Universität Göttingen, Friedrich-Hund-Platz 1, Göttingen, 37077, Germany. \*Correspondence e-mail: jose.velazquez@desy.de

The title compound, $(C_4H_7N_2)_2[Co(H_2O)_6][Co(C_9H_3O_6)_2(H_2O)_4]$ (**1**), was synthesized from cobalt(II) chloride, 1,3,5-benzene tricarboxylic acid (Hbtc) and 2-methyl-imidazole (H-2mIm) under ambient conditions. The structure of **1** is here reported and compared with the parent complex hexaaquacobalt bis(1H-imidazol-3-ium) tetraaquabis(benzene-1,3,5-tricarboxylato)cobalt (**2**).

## 1. Chemical context

Effective bifunctional electrocatalysts for oxygen reduction/evolution reactions (ORR/OER) are indispensable for the development of energy storage and conversion systems, such as fuel cells and rechargeable metal–air batteries (Cai *et al.*, 2017; Wang *et al.*, 2014). Currently, platinum-based materials are considered the most effective due to their superior catalytic activity and stability. However, their high cost, caused by the scarcity of the metal, rules them out for scale-up development. Therefore, a great deal of effort has been devoted to the development of cost-effective and earth-abundant replacements for platinum-based catalysts. Among the different substitute materials, a hexaaquacobalt bis(1H-imidazol-3-ium) tetraaquabis(benzene-1,3,5-tricarboxylato)cobalt complex, **2**, has shown excellent bifunctional catalytic activity and durability for both the oxygen-reduction reaction and oxygen-evolution reaction in alkaline media (Wang *et al.*, 2020). Unfortunately, the solvothermal synthesis required to produce the material hinders its implementation on a large scale.
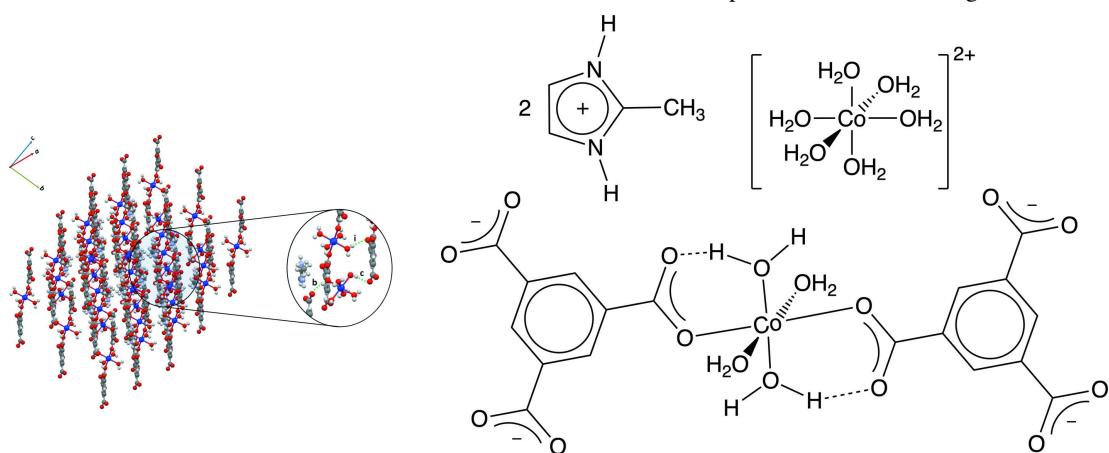


Herein, we present the synthesis and structure of a hexaaquacobalt bis(1H-2-methyl-imidazol-3-ium) tetraaquabis(-

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

| $D—H\cdots A$ | Type | Graph-set | $D—H$ | $H\cdots A$ | $D\cdots A$ | $D—H\cdots A$ |
|---|---|---|---|---|---|---|
| O9—H9A$\cdots$O4 | a | $DC_2^2(20)$ | 0.785 (12) | 1.850 (12) | 2.6339 (12) | 176.4 (19) |
| O9—H9B$\cdots$O7$^{iv}$ | b | $DC_2^2(20)$ | 0.775 (12) | 1.957 (12) | 2.7150 (13) | 165.9 (18) |
| O10—H10A$\cdots$O7$^{ii}$ | c | $DC_2^2(20)$ | 0.791 (12) | 2.085 (12) | 2.8592 (13) | 166.1 (17) |
| O10—H10B$\cdots$O6$^{iii}$ | d | $DC_2^2(20)$ | 0.793 (12) | 1.891 (12) | 2.6835 (12) | 176.3 (18) |
| O11—H11A$\cdots$O8$^{v}$ | e | $DC_2^2(20)$ | 0.778 (12) | 1.919 (13) | 2.6911 (13) | 171.6 (18) |
| O11—H11B$\cdots$O5$^{vi}$ | f | $DC_2^2(20)$ | 0.809 (17) | 1.896 (18) | 2.6989 (13) | 172.0 (17) |
| O1—H1A$\cdots$O7$^{i}$ | g | $C(10)C_2^2(20)R_2^2(20)$ | 0.787 (12) | 2.096 (12) | 2.8789 (13) | 173.5 (19) |
| O1—H1B$\cdots$O4 | h | $S(6)$ | 0.785 (12) | 1.904 (13) | 2.6401 (13) | 155.8 (13) |
| O2—H2A$\cdots$O5$^{ii}$ | i | $C(10)C_2^2(20)R_2^2(20)$ | 0.778 (12) | 2.175 (13) | 2.9371 (13) | 166.5 (19) |
| O2—H2B$\cdots$O6$^{iii}$ | j | $C(10)C_2^2(20)R_2^2(20)$ | 0.783 (12) | 1.965 (12) | 2.7458 (13) | 175 (2) |
| N1—H1$\cdots$O8$^{iv}$ | k | $DD_2^2(17)$ | 0.913 (15) | 1.811 (15) | 2.7214 (13) | 174.6 (16) |
| N2—H2$\cdots$O5$^{vii}$ | l | $DD_2^2(17)$ | 0.890 (15) | 1.931 (15) | 2.8206 (14) | 178.0 (17) |

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

benzene-1,3,5-tricarboxylato)cobalt complex, a related material with the imidazolium cations replaced by 2-methylimidazolium, which can be obtained under ambient conditions. The introduction of the methyl substituent to the $C_2$ position of the imidazolium ring induces only small structural changes, when compared to **2**, and therefore, the title compound could be a promising material for ORR and OER.

## 2. Structural commentary

The complete molecule of **1** (Fig. 1) is generated by a crystallographic centre of symmetry. Both Co-containing ions lie about an inversion centre, and therefore only half of the coordinating ions and molecules are crystallographically independent. One of the two metal centres (Co1) is coordinated by six water molecules to constitute a hexaaquacobalt cation, while the second (Co2) binds with four water molecules and two carboxylate oxygen atoms from two btc$^{3−}$

ligands to form a $[Co(H_2O)_4(btc)_2]^{4−}$ anion. Charge neutrality of the molecule is provided by the presence of two 1-$H$-2-methyl-imidazol-3-ium cations. The observed Co—O$_{carboxylate}$ bond length is 2.0835 (9) Å and the C—O$_{water}$ bond lengths are in the range 2.0576 (9)–2.1196 (9) Å. To estimate the distortion from the ideal octahedral geometry, the parameters $\Sigma$ (Halcrow, 2011) and $\Theta$ (Marchivie *et al.*, 2005) were calculated using the *OctaDist* program (Ketkaew *et al.*, 2021). While $\Sigma$ summarizes the deviation of the *cis* O—Cu—O angles from 90°, $\Theta$ indicates the degree of twist from a perfect octahedron towards a trigonal prism. Both parameters are equal to zero for an ideal octahedron. The calculated values of the distortion parameters $\Sigma/\Theta$ for Co1 and Co2 are equal to 19°/62° and 11°/31°, respectively. Both parameters indicate a slight distortion of the coordination environment of both metal centres.

## 3. Supramolecular features

A packing diagram of the compound as viewed down $[\bar{1}01]$ is shown in Fig. 2. The figure shows layers parallel to the (111)
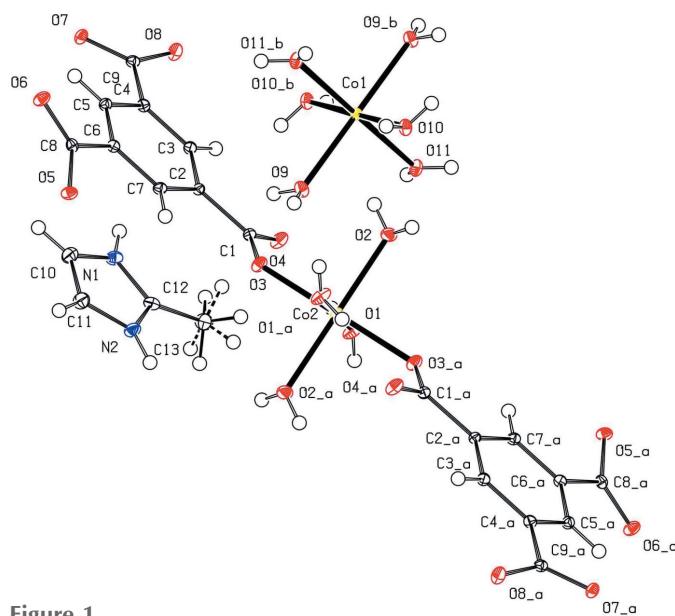


**Figure 1**
The molecular structure of **1** with displacement ellipsoids drawn at the 50% probability level. Symmetry codes: (_a) $2 − x, −y, 2 − z$; (_b) $2 − x, 1 − y, 1 − z$.
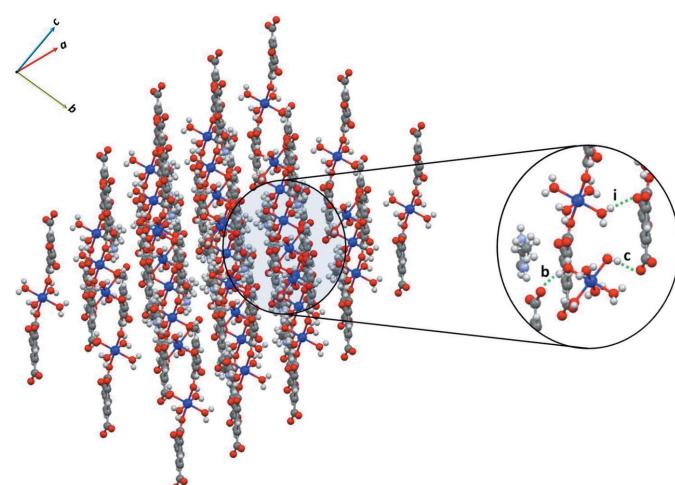


**Figure 2**
Packing diagram of **1** down the $[\bar{1}01]$ direction. O—H$\cdots$O hydrogen bonds of type *b*, *c* and *i* are shown in the magnified region.

plane formed by all ions. Each ion interacts with others *via* hydrogen bonds of the O—H···O or N—H···O type. A summary of the hydrogen-bonding interactions is given in Table 1. The table demonstrates that all possible donor and acceptor groups are involved in moderate hydrogen bonds. The presence of various hydrogen bonds in **1** results in characteristic arrays that may be described by graph-set analysis (Etter *et al.*, 1990; Bernstein *et al.*, 1995). In the structure of **1**, there are 27 possible motifs involved in discrete *D* (types *a–f* and *k–l*) and intermolecular *S* (type *h*) motifs, as well as rings *R* (types *g*, *i* and *j*) and chains *C* (types *a–f*). It is worth noting that while hydrogen bonds *b*, *c* and *i* hold the aforementioned layers together through $C_2^2(20)$ and *D* arrays, other hydrogen bonds, such as type *a* and *e*, form $C_2^2(20)$ arrays, which generates a three-dimensional network with channels along the *a* and *c* axes in which the imidazolium ions are located (Fig. 3).

## 4. Database survey

A search of the Cambridge Structural Database (CSD version 5.41, update of August 2020; Groom *et al.*, 2016) for hexa-aquacobalt and the ditrimesate tetraaquacobalt moiety revealed only one hit, namely refcode: VUHQIA (imidazo-lium)$_2$[Co(H$_2$O)$_6$][Co(H$_2$O)$_4$(btc)$_2$], **2**, (Wang *et al.*, 2020). Compounds **1** and **2** crystallize in the triclinic system, space group $P\bar{1}$. The Co—O$_{carboxylate}$ and C—O$_{water}$ bond lengths are similar in both complexes. The coordination polyhedra of compound **2** are slightly more distorted. The calculated values of Σ/Θ for compound **2** are equal to 21°/63° for Co1 and 10°/39° for Co2 – that is, the trigonal distortion (Θ) in **2** is higher by 1 and 8° for Co1 and Co2, respectively. The slightly different distortion of the metal centres in **2** and the introduction of the imidazolium allow for shorter hydrogen bonds with distances between 1.73 and 2.00 Å. Other complexes with a low degree of similarity to the title compound were also found, for example refcodes DOWFUS (Clegg & Holcroft,

**Table 2**
Experimental details.

| | |
|---|---|
| **Crystal data** | |
| Chemical formula | (C$_4$H$_7$N$_2$)$_2$[Co(H$_2$O)$_6$]-[Co(C$_9$H$_3$O$_6$)$_2$(H$_2$O)$_4$] |
| $M_r$ | 878.48 |
| Crystal system, space group | Triclinic, $P\bar{1}$ |
| Temperature (K) | 296 |
| $a$, $b$, $c$ (Å) | 9.2008 (4), 9.3137 (4), 10.6470 (4) |
| $\alpha$, $\beta$, $\gamma$ (°) | 86.551 (2), 79.378 (2), 72.369 (2) |
| $V$ (Å³) | 854.61 (6) |
| $Z$ | 1 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm⁻¹) | 1.07 |
| Crystal size (mm) | 0.20 × 0.10 × 0.10 |
| | |
| **Data collection** | |
| Diffractometer | Bruker CCD area detector |
| Absorption correction | Multi-scan (*SADABS*; Krause *et al.*, 2015) |
| $T_{min}$, $T_{max}$ | 0.699, 0.746 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 26203, 5250, 4605 |
| $R_{int}$ | 0.026 |
| $(\sin\theta/\lambda)_{max}$ (Å⁻¹) | 0.719 |
| | |
| **Refinement** | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.026, 0.069, 1.04 |
| No. of reflections | 5250 |
| No. of parameters | 285 |
| No. of restraints | 47 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å⁻³) | 0.60, −0.42 |

Computer programs: *APEX2* and *SAINT* (Bruker, 2016), *SHELXT2018/2* (Sheldrick, 2018), *SHELXL2019/2* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

2014), IQOZUK (Li *et al.*, 2011) and SETQOX (Wolodkiewicz *et al.*, 1996). However, these compounds are polymeric and/or incorporate a different organic ligand than btc. Additionally, none of them contain the imidazolium anion. These changes in chemical composition may provide them with totally different properties than those desired for ORR and OER, and therefore, they will not be discussed further.
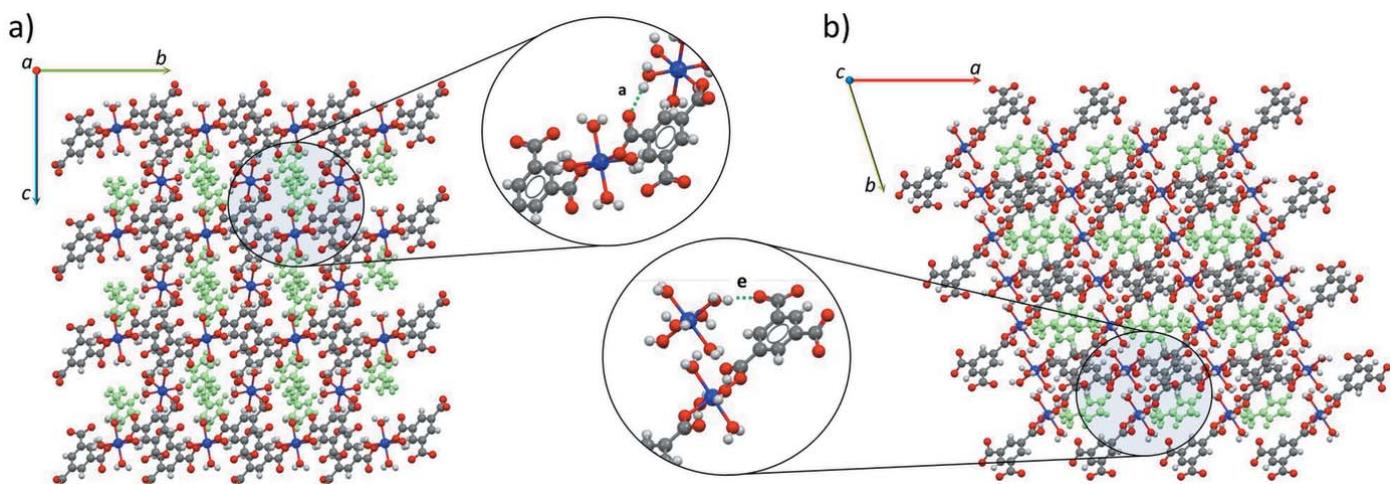


**Figure 3**
The three-dimensional supramolecular network with one-dimensional channels along the (*a*) *a* and (*b*) *c* axes showing O—H···O hydrogen bonds of type *a* and *e* in the magnified area. Imidazolium ions are drawn in green for clarity.

## 5. Synthesis and crystallization

In a typical synthesis, H-2mIm (160 mg, 1.96 mmol), Hbtc (412, 1.96 mmol) and cobalt chloride (127 mg, 0.95mmol) were dissolved in 160 ml of a 1:1:1 mixture of deionized water, ethanol and dimethylformamide by stirring for 10 min at room temperature. After 5 minutes, light-pink crystals of **1** were obtained. The product was collected by filtration and washed three times with ethanol.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Positions of remaining non-H atoms were found from the electron density difference maps. The positions of hydrogen atoms were refined with $U_{iso}(H) = 1.5U_{eq}(C \text{ or } N)$ for CH and NH groups and $U_{iso}(H) = 1.5U_{eq}(C \text{ or } O)$ for others. The O—H and H···H distances in the water molecules as well as the N—H distances were restrained to be approximately equal within each type (*SHELXL* instruction SADI). The protons of the methyl group were refined as disordered over two geometrically idealized positions.

## References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Bruker (2016). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cai, X., Lai, L., Lin, J. & Shen, Z. (2017). *Mater. Horiz.* **4**, 945–976.

Clegg, W. & Holcroft, J. M. (2014). *Cryst. Growth Des.* **14**, 6282–6293.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Halcrow, M. A. (2011). *Chem. Soc. Rev.* **40**, 4119–4142.

Ketkaew, R., Tantirungrotechai, Y., Harding, P., Chastanet, G., Guionneau, P., Marchivie, M. & Harding, D. J. (2021). *Dalton Trans.* **50**, 1086–1096.

Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.

Li, Y., Zou, W.-Q., Wu, M.-F., Lin, J.-D., Zheng, F.-K., Liu, Z.-F., Wang, S.-H., Guo, G.-C. & Huang, J.-S. (2011). *CrystEngComm*, **13**, 3868–3877.

Marchivie, M., Guionneau, P., Létard, J.-F. & Chasseau, D. (2005). *Acta Cryst.* B**61**, 25–28.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Sheldrick, G. M. (2018). *Acta Cryst.* A**74**, a353.

Wang, H., Zhang, X., Yin, F., Chu, W. & Chen, B. (2020). *J. Mater. Chem. A*, **8**, 22111–22123.

Wang, Z.-L., Xu, D., Xu, J.-J. & Zhang, X.-B. (2014). *Chem. Soc. Rev.* **43**, 7746–7786.

Wolodkiewicz, W., Brzyska, W. & Glowiak, T. (1996). *Pol. J. Chem.* **70**, 409–416.

# Synthesis and structure of hexaaquacobalt bis(2-methyl-1*H*-imidazol-3-ium) tetraaquabis(benzene-1,3,5-tricarboxylato-*κO*)cobalt

**Jose de Jesus Velazquez-Garcia and Simone Techert**

**Computing details**

Data collection: *APEX2* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2016); data reduction: *SAINT* (Bruker, 2016); program(s) used to solve structure: *SHELXT2018/2* (Sheldrick, 2018); program(s) used to refine structure: *SHELXL2019/2* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

**Hexaaquacobalt bis(2-methyl-1*H*-imidazol-3-ium) tetraaquabis(benzene-1,3,5-tricarboxylato-*κO*)cobalt**

*Crystal data*

| | |
|---|---|
| $(C_4H_7N_2)_2[Co(H_2O)_6][Co(C_9H_3O_6)_2(H_2O)_4]$ | $Z = 1$ |
| $M_r = 878.48$ | $F(000) = 454$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.707$ Mg m$^{-3}$ |
| $a = 9.2008$ (4) Å | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $b = 9.3137$ (4) Å | Cell parameters from 9913 reflections |
| $c = 10.6470$ (4) Å | $\theta = 2.3$–$30.6°$ |
| $\alpha = 86.551$ (2)° | $\mu = 1.07$ mm$^{-1}$ |
| $\beta = 79.378$ (2)° | $T = 296$ K |
| $\gamma = 72.369$ (2)° | Prism, clear light pink |
| $V = 854.61$ (6) Å$^3$ | $0.20 \times 0.10 \times 0.10$ mm |

*Data collection*

| | |
|---|---|
| Bruker CCD area detector diffractometer | 5250 independent reflections |
| phi and $\omega$ scans | 4605 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015) | $R_{int} = 0.026$ |
| | $\theta_{max} = 30.7°$, $\theta_{min} = 2.0°$ |
| $T_{min} = 0.699$, $T_{max} = 0.746$ | $h = -13 \rightarrow 13$ |
| 26203 measured reflections | $k = -13 \rightarrow 12$ |
| | $l = -15 \rightarrow 14$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: dual |
| Least-squares matrix: full | Hydrogen site location: mixed |
| $R[F^2 > 2\sigma(F^2)] = 0.026$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.069$ | |
| $S = 1.04$ | $w = 1/[\sigma^2(F_o^2) + (0.0331P)^2 + 0.4935P]$ |
| 5250 reflections | where $P = (F_o^2 + 2F_c^2)/3$ |
| 285 parameters | $(\Delta/\sigma)_{max} < 0.001$ |
| 47 restraints | $\Delta\rho_{max} = 0.60$ e Å$^{-3}$ |
| Primary atom site location: difference Fourier map | $\Delta\rho_{min} = -0.42$ 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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Co1 | 1.000000 | 0.500000 | 0.500000 | 0.00661 (6) | |
| Co2 | 1.000000 | 0.000000 | 1.000000 | 0.00734 (6) | |
| O1 | 1.09226 (11) | −0.04186 (11) | 0.80639 (9) | 0.01446 (19) | |
| H1A | 1.128 (2) | −0.1158 (16) | 0.7654 (16) | 0.022* | |
| H1B | 1.0319 (19) | 0.0150 (17) | 0.7699 (17) | 0.022* | |
| O2 | 1.06874 (11) | 0.19677 (11) | 0.98183 (10) | 0.01395 (18) | |
| H2A | 1.107 (2) | 0.215 (2) | 1.0361 (15) | 0.021* | |
| H2B | 1.0153 (19) | 0.2726 (17) | 0.9590 (17) | 0.021* | |
| O3 | 0.78549 (10) | 0.12296 (10) | 0.95554 (8) | 0.01077 (17) | |
| O4 | 0.85774 (10) | 0.18407 (10) | 0.75266 (8) | 0.01246 (18) | |
| O5 | 0.23219 (10) | 0.29950 (10) | 1.15378 (8) | 0.01007 (16) | |
| O6 | 0.10354 (10) | 0.53500 (10) | 1.10793 (8) | 0.01151 (17) | |
| O7 | 0.24698 (10) | 0.69230 (10) | 0.65394 (8) | 0.00982 (16) | |
| O8 | 0.49974 (10) | 0.65513 (10) | 0.58167 (8) | 0.01243 (18) | |
| O9 | 0.91967 (10) | 0.31282 (10) | 0.53041 (9) | 0.01031 (17) | |
| H9A | 0.898 (2) | 0.278 (2) | 0.5975 (12) | 0.015* | |
| H9B | 0.8655 (19) | 0.302 (2) | 0.4862 (14) | 0.015* | |
| O10 | 1.09204 (10) | 0.46619 (10) | 0.67157 (8) | 0.00996 (16) | |
| H10A | 1.1344 (18) | 0.5265 (17) | 0.6797 (16) | 0.015* | |
| H10B | 1.0313 (17) | 0.4689 (19) | 0.7355 (13) | 0.015* | |
| O11 | 1.20606 (10) | 0.36656 (11) | 0.40161 (9) | 0.01061 (17) | |
| H11A | 1.2898 (16) | 0.368 (2) | 0.4028 (16) | 0.016* | |
| H11B | 1.2048 (19) | 0.350 (2) | 0.3281 (17) | 0.016* | |
| N1 | 0.50458 (13) | 0.14060 (12) | 0.61249 (10) | 0.0119 (2) | |
| H1 | 0.510 (2) | 0.2077 (18) | 0.5469 (15) | 0.014* | |
| N2 | 0.57535 (12) | −0.03974 (12) | 0.74458 (10) | 0.0119 (2) | |
| H2 | 0.6351 (19) | −0.1208 (18) | 0.7785 (16) | 0.014* | |
| C1 | 0.76058 (13) | 0.19797 (13) | 0.85484 (11) | 0.0081 (2) | |
| C2 | 0.60272 (13) | 0.31087 (13) | 0.85916 (11) | 0.0074 (2) | |
| C3 | 0.57120 (13) | 0.41453 (13) | 0.76032 (11) | 0.0082 (2) | |
| H3 | 0.647875 | 0.413232 | 0.689599 | 0.010* | |
| C4 | 0.42546 (13) | 0.52015 (13) | 0.76680 (11) | 0.0079 (2) | |
| C5 | 0.31078 (13) | 0.52211 (13) | 0.87313 (11) | 0.0082 (2) | |
| H5 | 0.213899 | 0.593210 | 0.878284 | 0.010* | |
| C6 | 0.34094 (13) | 0.41785 (13) | 0.97165 (11) | 0.0076 (2) | |
| C7 | 0.48664 (13) | 0.31248 (13) | 0.96411 (11) | 0.0081 (2) | |
| H7 | 0.506641 | 0.242605 | 1.029673 | 0.010* | |
| C8 | 0.21698 (13) | 0.41903 (13) | 1.08554 (11) | 0.0078 (2) | |
| C9 | 0.38899 (13) | 0.63054 (13) | 0.65934 (11) | 0.0081 (2) | |

| | | | | | |
|---|---|---|---|---|---|
| C10 | 0.37595 (15) | 0.14698 (15) | 0.70562 (13) | 0.0143 (2) | |
| H10 | 0.277987 | 0.216042 | 0.710213 | 0.017* | |
| C11 | 0.42065 (15) | 0.03308 (15) | 0.78863 (12) | 0.0137 (2) | |
| H11 | 0.359239 | 0.008535 | 0.861228 | 0.016* | |
| C12 | 0.62411 (14) | 0.02705 (14) | 0.63723 (12) | 0.0110 (2) | |
| C13 | 0.78039 (15) | −0.01811 (15) | 0.55720 (13) | 0.0156 (2) | |
| H13A | 0.806962 | −0.121788 | 0.533113 | 0.023* | 0.58 (5) |
| H13B | 0.854729 | −0.005633 | 0.604826 | 0.023* | 0.58 (5) |
| H13C | 0.780728 | 0.043824 | 0.481802 | 0.023* | 0.58 (5) |
| H13D | 0.804580 | 0.069870 | 0.519273 | 0.023* | 0.42 (5) |
| H13E | 0.782325 | −0.084695 | 0.491083 | 0.023* | 0.42 (5) |
| H13F | 0.855513 | −0.068771 | 0.609385 | 0.023* | 0.42 (5) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Co1 | 0.00602 (10) | 0.00746 (11) | 0.00589 (10) | −0.00185 (8) | −0.00054 (7) | 0.00102 (7) |
| Co2 | 0.00718 (10) | 0.00685 (11) | 0.00737 (10) | −0.00111 (8) | −0.00184 (7) | 0.00140 (8) |
| O1 | 0.0144 (4) | 0.0133 (5) | 0.0109 (4) | 0.0036 (4) | −0.0031 (3) | −0.0002 (3) |
| O2 | 0.0155 (4) | 0.0092 (4) | 0.0193 (5) | −0.0037 (3) | −0.0097 (4) | 0.0036 (3) |
| O3 | 0.0100 (4) | 0.0115 (4) | 0.0088 (4) | −0.0005 (3) | −0.0021 (3) | 0.0035 (3) |
| O4 | 0.0111 (4) | 0.0131 (4) | 0.0089 (4) | 0.0006 (3) | 0.0006 (3) | 0.0034 (3) |
| O5 | 0.0123 (4) | 0.0081 (4) | 0.0085 (4) | −0.0021 (3) | −0.0008 (3) | 0.0027 (3) |
| O6 | 0.0101 (4) | 0.0103 (4) | 0.0105 (4) | 0.0001 (3) | 0.0013 (3) | 0.0021 (3) |
| O7 | 0.0078 (4) | 0.0110 (4) | 0.0099 (4) | −0.0013 (3) | −0.0029 (3) | 0.0019 (3) |
| O8 | 0.0091 (4) | 0.0151 (4) | 0.0116 (4) | −0.0030 (3) | −0.0012 (3) | 0.0066 (3) |
| O9 | 0.0123 (4) | 0.0129 (4) | 0.0077 (4) | −0.0067 (3) | −0.0029 (3) | 0.0038 (3) |
| O10 | 0.0089 (4) | 0.0138 (4) | 0.0077 (4) | −0.0047 (3) | −0.0011 (3) | 0.0016 (3) |
| O11 | 0.0077 (4) | 0.0144 (4) | 0.0092 (4) | −0.0028 (3) | −0.0006 (3) | −0.0009 (3) |
| N1 | 0.0147 (5) | 0.0096 (5) | 0.0111 (5) | −0.0029 (4) | −0.0036 (4) | 0.0030 (4) |
| N2 | 0.0116 (5) | 0.0096 (5) | 0.0127 (5) | −0.0012 (4) | −0.0017 (4) | 0.0031 (4) |
| C1 | 0.0081 (5) | 0.0075 (5) | 0.0086 (5) | −0.0020 (4) | −0.0021 (4) | 0.0009 (4) |
| C2 | 0.0073 (5) | 0.0067 (5) | 0.0080 (5) | −0.0016 (4) | −0.0021 (4) | 0.0004 (4) |
| C3 | 0.0082 (5) | 0.0083 (5) | 0.0079 (5) | −0.0026 (4) | −0.0014 (4) | 0.0011 (4) |
| C4 | 0.0089 (5) | 0.0084 (5) | 0.0068 (5) | −0.0033 (4) | −0.0020 (4) | 0.0018 (4) |
| C5 | 0.0081 (5) | 0.0082 (5) | 0.0082 (5) | −0.0022 (4) | −0.0018 (4) | 0.0005 (4) |
| C6 | 0.0084 (5) | 0.0079 (5) | 0.0066 (5) | −0.0028 (4) | −0.0010 (4) | 0.0007 (4) |
| C7 | 0.0095 (5) | 0.0073 (5) | 0.0074 (5) | −0.0022 (4) | −0.0024 (4) | 0.0014 (4) |
| C8 | 0.0086 (5) | 0.0094 (5) | 0.0067 (5) | −0.0039 (4) | −0.0027 (4) | 0.0005 (4) |
| C9 | 0.0099 (5) | 0.0072 (5) | 0.0077 (5) | −0.0025 (4) | −0.0026 (4) | 0.0003 (4) |
| C10 | 0.0121 (5) | 0.0126 (6) | 0.0171 (6) | −0.0020 (4) | −0.0028 (4) | 0.0015 (5) |
| C11 | 0.0123 (5) | 0.0136 (6) | 0.0134 (6) | −0.0030 (5) | 0.0000 (4) | 0.0017 (4) |
| C12 | 0.0140 (5) | 0.0082 (5) | 0.0113 (5) | −0.0042 (4) | −0.0022 (4) | 0.0005 (4) |
| C13 | 0.0148 (6) | 0.0137 (6) | 0.0168 (6) | −0.0046 (5) | 0.0023 (5) | −0.0015 (5) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Co1—O11 | 2.0576 (9) | N1—C12 | 1.3289 (16) |
| Co1—O11<sup>i</sup> | 2.0576 (9) | N1—C10 | 1.3854 (16) |
| Co1—O9<sup>i</sup> | 2.0772 (9) | N1—H1 | 0.913 (15) |
| Co1—O9 | 2.0772 (9) | N2—C12 | 1.3375 (15) |
| Co1—O10 | 2.1196 (9) | N2—C11 | 1.3832 (16) |
| Co1—O10<sup>i</sup> | 2.1196 (9) | N2—H2 | 0.890 (15) |
| Co2—O3<sup>ii</sup> | 2.0835 (9) | C1—C2 | 1.5078 (16) |
| Co2—O3 | 2.0835 (9) | C2—C7 | 1.3934 (15) |
| Co2—O1<sup>ii</sup> | 2.0912 (9) | C2—C3 | 1.3944 (16) |
| Co2—O1 | 2.0912 (9) | C3—C4 | 1.3948 (16) |
| Co2—O2<sup>ii</sup> | 2.1000 (9) | C3—H3 | 0.9300 |
| Co2—O2 | 2.1000 (9) | C4—C5 | 1.3949 (15) |
| O1—H1A | 0.787 (12) | C4—C9 | 1.5066 (16) |
| O1—H1B | 0.785 (12) | C5—C6 | 1.3934 (15) |
| O2—H2A | 0.778 (12) | C5—H5 | 0.9300 |
| O2—H2B | 0.783 (12) | C6—C7 | 1.3926 (16) |
| O3—C1 | 1.2624 (14) | C6—C8 | 1.5019 (15) |
| O4—C1 | 1.2601 (14) | C7—H7 | 0.9300 |
| O5—C8 | 1.2777 (14) | C10—C11 | 1.3537 (17) |
| O6—C8 | 1.2526 (15) | C10—H10 | 0.9300 |
| O7—C9 | 1.2687 (14) | C11—H11 | 0.9300 |
| O8—C9 | 1.2580 (14) | C12—C13 | 1.4818 (17) |
| O9—H9A | 0.785 (12) | C13—H13A | 0.9600 |
| O9—H9B | 0.775 (12) | C13—H13B | 0.9600 |
| O10—H10A | 0.791 (12) | C13—H13C | 0.9600 |
| O10—H10B | 0.793 (12) | C13—H13D | 0.9600 |
| O11—H11A | 0.778 (12) | C13—H13E | 0.9600 |
| O11—H11B | 0.809 (17) | C13—H13F | 0.9600 |
| | | | |
| O11—Co1—O11<sup>i</sup> | 180.0 | C7—C2—C3 | 119.40 (10) |
| O11—Co1—O9<sup>i</sup> | 90.60 (4) | C7—C2—C1 | 119.49 (10) |
| O11<sup>i</sup>—Co1—O9<sup>i</sup> | 89.40 (4) | C3—C2—C1 | 121.11 (10) |
| O11—Co1—O9 | 89.40 (4) | C2—C3—C4 | 120.45 (10) |
| O11<sup>i</sup>—Co1—O9 | 90.60 (4) | C2—C3—H3 | 119.8 |
| O9<sup>i</sup>—Co1—O9 | 180.0 | C4—C3—H3 | 119.8 |
| O11—Co1—O10 | 90.76 (4) | C3—C4—C5 | 119.66 (10) |
| O11<sup>i</sup>—Co1—O10 | 89.24 (4) | C3—C4—C9 | 120.93 (10) |
| O9<sup>i</sup>—Co1—O10 | 86.64 (3) | C5—C4—C9 | 119.40 (10) |
| O9—Co1—O10 | 93.36 (4) | C6—C5—C4 | 120.20 (11) |
| O11—Co1—O10<sup>i</sup> | 89.24 (4) | C6—C5—H5 | 119.9 |
| O11<sup>i</sup>—Co1—O10<sup>i</sup> | 90.76 (4) | C4—C5—H5 | 119.9 |
| O9<sup>i</sup>—Co1—O10<sup>i</sup> | 93.36 (3) | C7—C6—C5 | 119.71 (10) |
| O9—Co1—O10<sup>i</sup> | 86.64 (4) | C7—C6—C8 | 120.09 (10) |
| O10—Co1—O10<sup>i</sup> | 180.0 | C5—C6—C8 | 120.19 (10) |
| O3<sup>ii</sup>—Co2—O3 | 180.00 (5) | C6—C7—C2 | 120.56 (10) |
| O3<sup>ii</sup>—Co2—O1<sup>ii</sup> | 90.97 (4) | C6—C7—H7 | 119.7 |

| | | | |
|---|---|---|---|
| O3—Co2—O1ⁱⁱ | 89.03 (4) | C2—C7—H7 | 119.7 |
| O3ⁱⁱ—Co2—O1 | 89.03 (4) | O6—C8—O5 | 123.36 (11) |
| O3—Co2—O1 | 90.97 (4) | O6—C8—C6 | 118.94 (10) |
| O1ⁱⁱ—Co2—O1 | 180.0 | O5—C8—C6 | 117.70 (10) |
| O3ⁱⁱ—Co2—O2ⁱⁱ | 89.79 (4) | O8—C9—O7 | 124.60 (11) |
| O3—Co2—O2ⁱⁱ | 90.21 (4) | O8—C9—C4 | 118.45 (10) |
| O1ⁱⁱ—Co2—O2ⁱⁱ | 88.38 (4) | O7—C9—C4 | 116.95 (10) |
| O1—Co2—O2ⁱⁱ | 91.62 (4) | C11—C10—N1 | 106.62 (11) |
| O3ⁱⁱ—Co2—O2 | 90.21 (4) | C11—C10—H10 | 126.7 |
| O3—Co2—O2 | 89.79 (4) | N1—C10—H10 | 126.7 |
| O1ⁱⁱ—Co2—O2 | 91.62 (4) | C10—C11—N2 | 106.72 (11) |
| O1—Co2—O2 | 88.38 (4) | C10—C11—H11 | 126.6 |
| O2ⁱⁱ—Co2—O2 | 180.0 | N2—C11—H11 | 126.6 |
| Co2—O1—H1A | 133.6 (14) | N1—C12—N2 | 107.33 (11) |
| Co2—O1—H1B | 104.8 (13) | N1—C12—C13 | 125.58 (11) |
| H1A—O1—H1B | 107.5 (16) | N2—C12—C13 | 127.07 (11) |
| Co2—O2—H2A | 117.6 (14) | C12—C13—H13A | 109.5 |
| Co2—O2—H2B | 121.0 (13) | C12—C13—H13B | 109.5 |
| H2A—O2—H2B | 108.3 (16) | H13A—C13—H13B | 109.5 |
| C1—O3—Co2 | 126.90 (8) | C12—C13—H13C | 109.5 |
| Co1—O9—H9A | 125.1 (13) | H13A—C13—H13C | 109.5 |
| Co1—O9—H9B | 117.8 (13) | H13B—C13—H13C | 109.5 |
| H9A—O9—H9B | 108.5 (16) | C12—C13—H13D | 109.5 |
| Co1—O10—H10A | 111.8 (12) | H13A—C13—H13D | 135.3 |
| Co1—O10—H10B | 115.7 (13) | H13B—C13—H13D | 76.7 |
| H10A—O10—H10B | 106.0 (15) | H13C—C13—H13D | 35.5 |
| Co1—O11—H11A | 128.6 (13) | C12—C13—H13E | 109.5 |
| Co1—O11—H11B | 114.9 (12) | H13A—C13—H13E | 35.5 |
| H11A—O11—H11B | 105.6 (16) | H13B—C13—H13E | 135.3 |
| C12—N1—C10 | 109.77 (10) | H13C—C13—H13E | 76.7 |
| C12—N1—H1 | 124.4 (11) | H13D—C13—H13E | 109.5 |
| C10—N1—H1 | 125.7 (11) | C12—C13—H13F | 109.5 |
| C12—N2—C11 | 109.55 (11) | H13A—C13—H13F | 76.7 |
| C12—N2—H2 | 123.4 (11) | H13B—C13—H13F | 35.5 |
| C11—N2—H2 | 127.0 (11) | H13C—C13—H13F | 135.3 |
| O4—C1—O3 | 124.51 (11) | H13D—C13—H13F | 109.5 |
| O4—C1—C2 | 118.73 (10) | H13E—C13—H13F | 109.5 |
| O3—C1—C2 | 116.76 (10) | | |
| | | | |
| Co2—O3—C1—O4 | 16.76 (18) | C1—C2—C7—C6 | 178.56 (11) |
| Co2—O3—C1—C2 | −163.49 (8) | C7—C6—C8—O6 | 161.30 (11) |
| O4—C1—C2—C7 | 170.61 (11) | C5—C6—C8—O6 | −18.68 (17) |
| O3—C1—C2—C7 | −9.15 (17) | C7—C6—C8—O5 | −19.76 (17) |
| O4—C1—C2—C3 | −9.89 (17) | C5—C6—C8—O5 | 160.27 (11) |
| O3—C1—C2—C3 | 170.35 (11) | C3—C4—C9—O8 | −19.45 (17) |
| C7—C2—C3—C4 | 0.72 (18) | C5—C4—C9—O8 | 161.70 (11) |
| C1—C2—C3—C4 | −178.78 (11) | C3—C4—C9—O7 | 160.47 (11) |
| C2—C3—C4—C5 | 0.16 (18) | C5—C4—C9—O7 | −18.38 (17) |

| | | | |
|---|---|---|---|
| C2—C3—C4—C9 | −178.68 (11) | C12—N1—C10—C11 | −0.03 (15) |
| C3—C4—C5—C6 | −0.83 (18) | N1—C10—C11—N2 | 0.19 (15) |
| C9—C4—C5—C6 | 178.03 (11) | C12—N2—C11—C10 | −0.29 (15) |
| C4—C5—C6—C7 | 0.61 (18) | C10—N1—C12—N2 | −0.15 (15) |
| C4—C5—C6—C8 | −179.42 (11) | C10—N1—C12—C13 | 178.19 (12) |
| C5—C6—C7—C2 | 0.29 (18) | C11—N2—C12—N1 | 0.27 (15) |
| C8—C6—C7—C2 | −179.69 (11) | C11—N2—C12—C13 | −178.04 (13) |
| C3—C2—C7—C6 | −0.95 (18) | | |

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1; (ii) −*x*+2, −*y*, −*z*+2.

*Hydrogen-bond geometry (Å, º)*

| *D*—H⋯*A* | *D*—H | H⋯*A* | *D*⋯*A* | *D*—H⋯*A* |
|---|---|---|---|---|
| O1—H1*A*⋯O7[iii] | 0.79 (1) | 2.10 (1) | 2.8789 (13) | 174 (2) |
| O1—H1*B*⋯O4 | 0.79 (1) | 1.90 (1) | 2.6401 (13) | 156 (2) |
| O2—H2*A*⋯O5[iv] | 0.78 (1) | 2.17 (1) | 2.9371 (13) | 167 (2) |
| O2—H2*B*⋯O6[v] | 0.78 (1) | 1.97 (1) | 2.7458 (13) | 175 (2) |
| O9—H9*A*⋯O4 | 0.79 (1) | 1.85 (1) | 2.6339 (12) | 176 (2) |
| O9—H9*B*⋯O7[vi] | 0.78 (1) | 1.96 (1) | 2.7150 (13) | 166 (2) |
| O10—H10*A*⋯O7[iv] | 0.79 (1) | 2.09 (1) | 2.8592 (13) | 166 (2) |
| O10—H10*B*⋯O6[v] | 0.79 (1) | 1.89 (1) | 2.6835 (12) | 176 (2) |
| O11—H11*A*⋯O8[i] | 0.78 (1) | 1.92 (1) | 2.6911 (13) | 172 (2) |
| O11—H11*B*⋯O5[vii] | 0.81 (2) | 1.90 (2) | 2.6989 (13) | 172 (2) |
| N1—H1⋯O8[vi] | 0.91 (2) | 1.81 (2) | 2.7214 (13) | 175 (2) |
| N2—H2⋯O5[viii] | 0.89 (2) | 1.93 (2) | 2.8206 (14) | 178 (2) |

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