Synthesis, crystal structure and Hirshfeld surface analysis of aqua(3-methoxycinnamato-κO)bis(1,10-phenanthroline-κ²N,N')cobalt(II) nitrate

Asma Lehleh, a,* Mehdi Boutebdja, a,b Chahrazed Beghidja a and Adel Beghidja a

a Unité de Recherche de Chimie de l’Environnement et Moléculaire Structurale (CHEMS), Université Frères Mentouri Constantine 1, 25017, Constantine, Algeria, and b Laboratoire Technologie des Matériaux Avancés, École Nationale Polytechnique de Constantine, Nouvelle Ville Universitaire Ali Mendjeli, 25000, Constantine, Algeria. *Correspondence e-mail: asmalehleh25@gmail.com

The title compound, [Co(C10H9O3)(C12H8N2)2(H2O)]NO3 (I), crystallizes in the triclinic space group P̅1 with a monomeric [Co(3-meo-cin)(phen)2(H2O)]+ cation and a nitrate anion (3-meo-cin = 3-methoxy cinnamic acid) in the asymmetric unit. The CoII ion is coordinated by four N atoms from two 1,10-phenanthroline ligands and two O atoms, the first from a methoxy cinnamate ligand and the second from a coordinated water molecule, forming a distorted octahedral geometry. Discrete entities of the cation and nitrate anion are formed by water–nitrate O—H···C1/C1/C1 hydrogen bonds. The components are further assembled into chains along the c-axis direction. Layers are then formed by slipped π–π stacking interactions parallel to the bc plane. The intermolecular interactions in the crystal structure were quantified and analysed using Hirshfeld surface analysis.

1. Chemical context

Cinnamic acid (3-phenyl-2-propenoic acid), a derivative of phenyl alanine, comprises a relatively large family of organic isomers (Ferenc et al., 2012; Madhurambal et al., 2010). Cinnamic acid and its derivatives exhibit biological activities (Rychlicka et al., 2021) including antibacterial (Sova, 2012), antifungal (Ruwizhi & Aderibigbe, 2020) and antiparasitic properties (Kanaani & Ginsburg, 1992) as well as a variety of pharmacological properties (Adisakwattana et al., 2008) including hepatoprotective (Lee et al., 2002), antimalarial (Wiesner et al., 2001), antioxidant (Natella et al., 1999), antitumoral (Ferenc et al., 2012), antihyperglycemic and antityrosinase activities (Lee, 2002). Cinnamic acid and related compounds have attracted particular attention over the last few decades, not only for their biological activities, but also for their carboxylate group. The popularity of such aromatic carboxylic acids as building blocks for generating metal–organic architectures can be explained by their coordination versatility and ability to act as multiple linkers (Lehleh et al., 2015; Gu et al., 2020), high thermal stability, tuneable deprotonation of –COOH groups, remarkable physicochemical properties, as well as the ability to function as hydrogen-bond donors and acceptors, thus facilitating the formation of intricate hydrogen-bonded networks (Gu et al., 2020; Zhang et al., 2019; Zhou et al., 2019). Furthermore, bipyridyl-like ligands such as 2,2'-bipyridine and 1,10-phenanthroline used as auxiliary ligands, are usually used in the formation of different complexes with a variety of transition metals, because of their
versatile roles such as in analytical chemistry, in catalysis, in electrochemistry, in ring-opening metathesis polymerization and biochemistry (Lehleh et al., 2011). Additionally, the pyridine rings can not only interact with each other via π–π stacking interactions, but also act as hydrogen-bond donors and acceptors (Cao et al., 2014; Hao et al., 2011; Lehleh et al., 2011).

In this context, we report the synthesis, structural characterization and Hirshfeld surface analysis of the title compound [Co(C_{10}H_{9}O_{3})(C_{12}H_{8}N_{2})_2(H_2O)] NO_3.

2. Structural commentary

The asymmetric unit of the title compound, illustrated in Fig. 1, consists of a Co^{II} complex cation and one nitrate anion. The Co^{II} ion is in a distorted octahedral geometry, coordinated by two 1,10-phenanthroline (phen) units through both N atoms in the usual bidentate manner, one water molecule and one 3-methoxy cinnamate in a monodentate fashion. The Co—N_{phen} bond distances range from 2.1356 (16) to 2.1488 (17) Å, while the Co—O_{cin} and Co—O_{water} bond lengths are 2.0525 (13) and 2.1011 (17) Å, respectively. The axial bond angles around the Co^{II} ions are in the range 166.30 (7)–173.94 (6)° (Table 1). The large deviation of the axial bond angles from an ideal octahedral geometry (180°) clearly indicates that the coordination environment around the Co^{II} ion is best described as distorted octahedral. The 3-methoxy cinnamate molecule shows disorder over two positions with occupancies of 0.735 (6) and 0.265 (6).

3. Supramolecular features

The structure presents extensive hydrogen bonding with numerical details given in Table 2. The coordinated water molecule (O1W) forms hydrogen bonds with the non-coordinating O atom of the carboxylate group of the 3-meo cinnam-
mate ligand via the H1W atom, the other water H atom (H2W) being involved in the O1W—H2W···O2w hydrogen bond (nit = nitrate anion) linking the nitrate anion to the cationic complex molecule (Fig. 2). The complex moieties are interconnected via moderate C—H···O hydrogen bonds between the 1,10-phenanthroline unit and the coordinating O atom of the 3-meo cinnamate ligand of a neighbouring complex on one side and between the 1,10-phenanthroline molecules and the O atoms of the nitrate anions on the other side, generating supramolecular hydrogen-bonded chains along the c-axis direction (Fig. 2). The chains are linked through slipped π–π stacking interactions with intercentroid distances ranging from 3.729 (2) to 3.891 (2) Å, the most significant being between the pyridyl rings containing phenanthroline atom N4 of each molecule [Cg4···Cg4(1 − x, −y, 1 − z) = 3.7998 (18) Å], forming layers parallel to the bc plane (Fig. 3, Table 3).

| Cg   | Ring       | Cg···Cg | Distance  |
|------|------------|---------|-----------|
| Cg1  | N1/C11–C14/C21 | Cg1···Cg3  | 3.741 (2) |
| Cg2  | N2/C17–C20/C22 | Cg2···Cg3ii | 3.891 (2) |
| Cg3  | C14–C17/C21/C22 | Cg3···Cg3iii | 3.729 (2) |
| Cg4  | N4/C29–C32/C34 | Cg4···Cg4iii | 3.7998 (18) |

4. (Hirshfeld surface analysis)
To further characterize the intermolecular interactions in the title compound, we carried out a Hirshfeld surface (HS) analysis (Spackman & Jayatilaka, 2009) using Crystal Explorer 21 (Spackman et al., 2021) and generated the associated two-dimensional fingerprint plots (McKinnon et al., 2007). The HS mapped over dnorm in the range 0.5087 to +1.3878 a.u. is illustrated in Fig. 4 using colours to indicate contacts that are shorter (red areas), equal to (white areas), or longer than (blue areas) the sum of the van der Waals radii (Ashfaq et al., 2021). The red spots on the surface mapped over dnorm (Fig. 4a) indicate the involvement of atoms in hydrogen-bonding interactions. The HS mapped over shape-index (Fig. 4b) is used to check for the presence of interactions such as C—H···π and π–π stacking (Ashfaq et al., 2021). The existence of adjacent red and blue triangular regions around the aromatic rings confirms the presence of π–π stacking interactions in the title compound (Fig. 4b), and the curvedness plots (Fig. 4c) show flat surface patches characteristic of planar stacking.

The two-dimensional fingerprint plots provide quantitative information about the non-covalent interactions and the crystal packing in terms of the percentage contribution of the interatomic contacts (Spackman & McKinnon, 2002; Ashfaq et al., 2021). Fig. 5 shows the two-dimensional fingerprint plot for

Figure 2
Crystal packing of the title compound shown in projection down the c axis illustrating chain formation along the c-axis direction by C—H···O hydrogen bonding (shown as dashed cyan lines).

Figure 3
Crystal packing of the title compound showing the layers parallel to the bc plane formed by the π–π stacking interactions between the pyridyl rings of the 1,10-phenanthroline units (blue and cyan). Hydrogen bonds are shown by dashed cyan lines.

Figure 4
A view of the Hirshfeld surface mapped over (a) dnorm in the range −0.5087 to +1.3878 arbitrary units, (b) shape-index and (c) curvedness.
the overall interactions in the title compound with relative contributions to the Hirshfeld surface. The most important interatomic contact is H···H as it makes the highest contribution to the crystal packing (42.1%, Fig. 5b). Other major contributors are C···H (27.7%, Fig. 5c) and O···H (17.7%, Fig. 5d) interactions. Smaller contributions are made by C···C (6.5%, Fig. 5e) and C···O (3.8%, Fig. 5f) interactions. Other contacts make a contribution of 2.3% in total and are not discussed in this work.

5. Database survey
A survey of the Cambridge Structural Database (CSD, version 5.43; update of June 2022; Groom et al., 2016) revealed that crystal structures had been reported for complexes of 3-methoxy cinnamic acid derivatives and a number of metal ions, including copper (Drew et al., 1994), cadmium (Zhang et al., 2013), tin (Su et al., 2022), cerium, neodymium, europium, gadolinium (Khalfaoui et al., 2017, 2021) and dysprosium (Khalfaoui et al., 2018, 2017). Only one complex based on copper and 2,5-dimethoxycinnamic acid with 2,9-dimethyl-1,10-phenanthroline has been reported (Battaglia et al., 1991). However, no complexes containing only the cobalt ion and 3-methoxy cinnamic acid associated with 1,10-phenanthroline have been documented in the CSD.

6. Synthesis and crystallization
A mixture of Co(NO₃)₂·6H₂O (0.240 g, 1 mmol), 3-methoxy cinnamic acid (0.178 g, 1 mmol), NaOH (0.04 g, 1 mmol) and 1,10-phen (0.180 g, 1 mmol) were dissolved in 10 mL of mixed solution (MeOH/H₂O: 2/1) in a 20 mL Teflon-lined stainless steel reactor and heated to 393 K for 24 h. It was then allowed to cool to room temperature in a water bath. Green crystals suitable for X-ray analysis were obtained.

7. Refinement
Crystal data, data collection and structure refinement details are summarized in Table 4. Hydrogen atoms of the water molecule were localized in difference-Fourier maps and refined with O—H = 0.85 ± 0.01 Å, and with Uiso(H) set to 1.5Ueq(O). The C-bound H atoms were placed in calculated positions with C—H = 0.93 or 0.96 Å and refined using a riding model with fixed isotropic displacement parameters [Uiso(H) = 1.2—1.5Ueq(C)]. The 3-methoxy cinnamate molecule shows

Table 4
Experimental details.
| Crystal data | Chemical formula |
|--------------|------------------|
| [Co(C₁₀H₉O₃)(C₁₂H₈N₂)₂(H₂O)]·NO₃ | Mᵣ |
| Crystal system, space group | Triclinic, P T |
| Temperature (K) | 296 |
| a, b, c (Å) | 8.3554 (1), 13.6529 (2), 13.8423 (2) |
| α, β, γ (°) | 101.634 (1), 98.239 (1), 97.819 (1) |
| V (Å³) | 1504.73 (4) |
| Z | 2 |
| Radiation type | Mo Kα |
| μ (mm⁻¹) | 0.63 |
| Crystal size (mm) | 0.2 × 0.15 × 0.12 |
| Data collection | Bruker APEXII CCD |
| Diffractometer | Multi-scan (SADABS; Krause et al., 2015) |
| Absorption correction | No. of measured, independent and observed [F > 2σ(F)] reflections |
| Tmin, Tmax | 0.710, 0.746 |
| No. of reflections | 19640, 7385, 5301 |
| No. of parameters | 527 |
| No. of restraints | 205 |
| H-atom treatment | H-atom parameters constrained |
| Δρmax, Δρmin (e Å⁻³) | 0.36, –0.28 |

Computer programs: APEX2 and SAINT (Bruker, 2013), SHELXL2018/3 (Sheldrick, 2015), Mercury (Macrae et al., 2020) and OLEX2 (Dolomanov et al., 2009).
disorder over two positions with final occupancies of 0.735 (6) and 0.265 (6). The disordered atoms were modelled as anisotropic using EXYZ and EADP constraints.

Funding information

The authors acknowledge the Algerian Ministry of Higher Education and Scientific Research and the Algerian Directorate-General for Scientific Research and Technological Development.

References

Adisakwattana, S., Moonsan, P. & Yibchok-anun, S. (2008). *J. Agric. Food Chem.* **56**, 7838–7844.

Ashfaq, M., Tahir, M. N., Muhammad, S., Munawar, K. S., Ali, A., Bogdanov, G. & Alarfaji, S. S. (2021). ACS Omega, 6, 31211–31225.

Battaglia, L. P., Corradi, A. B., Zoroddu, M. A., Manca, G., Basosi, R. & Solinas, C. (1991). *J. Chem. Soc. Dalton Trans.* pp. 2109–2112.

Bruker (2013). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.

Cao, X., Mu, B. & Huang, R. (2014). *CrystEngComm*, **16**, 5093–5102.

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

Drew, M. D. B., Mullins, A. P. & Rice, D. A. (1994). *Polyhedron*, **13**, 1631–1637.

Ferenc, W., Cristóvão, B., Sarzynski, J. & Sadowski, P. (2012). *J. Therm. Anal. Calorim.*, **110**, 739–748.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.

Gu, J.-Z., Wan, S.-M., Kirillova, M. V. & Kirillov, A. M. (2020). *Dalton Trans.* **49**, 7197–7209.

Hao, H.-J., Yin, X.-H., Lin, C.-W., Zhang, F., Luo, Z.-R. & Wu, Q.-L. (2011). *J. Chem. Crystallogr.* **41**, 26–29.

Kanaani, J. & Ginsburg, H. (1992). *Antimicrob. Agents Chemother.* **36**, 1102–1108.

Khalfaoui, O., Beghiddia, A., Beghiddia, C., Guari, Y., Larionova, J. & Long, J. (2021). *Polyhedron*, **207**, 115366.

Khalfaoui, O., Beghiddia, A., Long, J., Beghiddia, C., Guari, Y. & Larionova, J. (2018). *Inorganica*, **6**, 35.

Khalfaoui, O., Beghiddia, A., Long, J., Boussadia, A., Beghiddia, C., Guari, Y. & Larionova, J. (2017). *Dalton Trans.* **46**, 3943–3952.

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

Lee, E. J., Kim, S. R., Kim, J. & Kim, Y. C. (2002). *Planta Med.* **68**, 407–411.

Lee, H.-S. (2002). *J. Agric. Food Chem.* **50**, 1400–1403.

Lehleh, A., Beghiddia, A., Beghiddia, C., Mentré, O. & Welter, R. (2011). *C. R. Chim.* **14**, 462–470.

Lehleh, A., Beghiddia, A., Beghiddia, C., Welter, R. & Kurmoo, M. (2015). *C. R. Chim.* **18**, 530–539.

Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Piccock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.

Madhurambal, G., Ravindran, B., Mariappan, M. & Mojmard, S. C. (2010). *J. Therm. Anal. Calorim.*, **100**, 811–815.

McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.

Nettells, F., Nardini, M., Di Felice, M. & Scaccini, C. (1999). *J. Agric. Food Chem.* **47**, 1453–1459.

Ruwizhi, N. & Aderibigbe, B. A. (2020). *Int. J. Mol. Sci.* **21**, 5712.

Rychlicka, M., Rot, A. & Gliszczynska, A. (2021). *Foods*, **10**, 1417–1420.

Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.

Sova, M. (2012). *Mini Rev. Med. Chem.* **12**, 749–767.

Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.

Spackman, M. A. & McKinnon, J. J. (2002). *CrystEngComm*, **4**, 378–392.

Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Jayatilaka, D. & Spackman, M. A. (2021). *J. Appl. Cryst.* **54**, 1006–1011.

Su, H.-Q., Zhang, R.-F., Guo, Q., Wang, J., Li, Q.-L., Du, X.-M., Ru, J., Zhang, Q.-F. & Ma, C.-L. (2022). *J. Mol. Struct.* **1247**, 131290.

Wiesner, J., Mitsch, A., Wissner, P., Jomaa, H. & Schlitzer, M. (2001). *Bioorg. Med. Chem. Lett.* **11**, 423–424.

Zhang, H.-M., Yang, J., He, Y.-C. & Ma, J.-F. (2013). *Chem. Asian J.* **8**, 2787–2791.

Zhang, Y., Yang, J., Zhao, D., Liu, Z., Li, D., Fan, L. & Hu, T. (2019). *CrystEngComm*, **21**, 6130–6135.

Zhou, X., Guo, X., Liu, L., Shi, Z., Pang, Y. & Tai, X. (2019). *Crystals*, **9**, 166.
Acta Cryst. (2022). E78, 1113-1117  [https://doi.org/10.1107/S2056989022009781]

Synthesis, crystal structure and Hirshfeld surface analysis of aqua(3-methoxy-cinnamato-κO)bis(1,10-phenanthroline-κ²N,N'cobalt(II) nitrate

Asma Lehleh, Mehdi Boutebdja, Chahrazed Beghidja and Adel Beghidja

Computing details

Data collection: APEX2 (Bruker, 2013); cell refinement: SAINT (Bruker, 2013); data reduction: SAINT (Bruker, 2013); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015); molecular graphics: Mercury (Macrae et al., 2020); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

Aqua[3-(3-methoxyphenyl)prop-2-enoato-κO]bis(1,10-phenanthroline-κ²N,N')cobalt(II) nitrate

Crystal data

\[\text{[Co(C}_{10}\text{H}_{9}\text{O}_{3})(\text{C}_{12}\text{H}_{8}\text{N}_{2})(\text{H}_{2}\text{O})]\text{NO}_{3}\]

\[M_r = 676.53\]

Triclinic, \(P\bar{1}\)

\(a = 8.3354\) (1) Å

\(b = 13.6529\) (2) Å

\(c = 13.8423\) (2) Å

\(\alpha = 101.634\) (1)°

\(\beta = 98.239\) (1)°

\(\gamma = 97.819\) (1)°

\(V = 1504.73\) (4) Å³

\(Z = 2\)

\(F(000) = 698\)

\(D_a = 1.493\) Mg m⁻³

Mo Kα radiation, \(\lambda = 0.71073\) Å

Cell parameters from 6690 reflections

\(\theta = 2.4–26.7°\)

\(\mu = 0.63\) mm⁻¹

\(T = 296\) K

Block, green

0.2 × 0.15 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer

\(\varphi\) and \(\omega\) scans

Absorption correction: multi-scan

(SADABS; Krause et al., 2015)

\(T_{\text{min}} = 0.710, T_{\text{max}} = 0.746\)

19640 measured reflections

7385 independent reflections

5301 reflections with \(I > 2\sigma(I)\)

\(R_{\text{int}} = 0.028\)

\(\theta_{\text{max}} = 28.3°, \theta_{\text{min}} = 3.6°\)

\(h = -11\rightarrow 11\)

\(k = -18\rightarrow 18\)

\(l = -17\rightarrow 18\)

Refinement

Refinement on \(F^2\)

Least-squares matrix: full

\(R[F^2 > 2\sigma(F^2)] = 0.044\)

\(wR(F^2) = 0.128\)

\(S = 0.99\)

7385 reflections

527 parameters

205 restraints

Primary atom site location: iterative

Hydrogen site location: mixed

H-atom parameters constrained

\(w = 1/[\sigma^2(F_c^2) + (0.077P)^2]\)

where \(P = (F_c^2 + 2F_{e}^2)/3\)

\((\Delta\sigma)_{\text{max}} = 0.001\)

\(\Delta p_{\text{max}} = 0.36\) e Å⁻³

\(\Delta p_{\text{min}} = -0.28\) 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      | Uiso* / Ueq | Occ. (<1) |
|--------|--------|--------|-------------|------------|
| Co1    | 0.65552 (3) | 0.31049 (2) | 0.71066 (2) | 0.03697 (11) |
| O3     | 1.2849 (2)    | 0.03641 (16) | 1.14993 (16) | 0.0728 (5)   |
| O1W    | 0.7725 (2)    | 0.30532 (13) | 0.58544 (12) | 0.0592 (4)   |
| H1WA   | 0.835428      | 0.260837     | 0.583927     | 0.089*       |
| H1WB   | 0.701199      | 0.283337     | 0.531887     | 0.089*       |
| N1     | 0.5861 (2)    | 0.34285 (13) | 0.85588 (13) | 0.0395 (4)   |
| N2     | 0.7868 (2)    | 0.46154 (12) | 0.77585 (13) | 0.0404 (4)   |
| N3     | 0.4433 (2)    | 0.34579 (13) | 0.62737 (14) | 0.0441 (4)   |
| N4     | 0.5046 (2)    | 0.16423 (12) | 0.65426 (13) | 0.0399 (4)   |
| C11    | 0.4906 (3)    | 0.28302 (19) | 0.8960 (2)   | 0.0548 (6)   |
| H11    | 0.424469      | 0.225251     | 0.854461     | 0.066*       |
| C12    | 0.4848 (4)    | 0.3029 (2)   | 0.9986 (2)   | 0.0668 (8)   |
| H12    | 0.416559      | 0.258239     | 1.023817     | 0.080*       |
| C13    | 0.5762 (4)    | 0.3854 (2)   | 1.0603 (2)   | 0.0676 (8)   |
| H13    | 0.572265      | 0.398436     | 1.128404     | 0.081*       |
| C14    | 0.6786 (3)    | 0.45249 (18) | 1.02188 (17) | 0.0513 (6)   |
| C15    | 0.7823 (4)    | 0.5427 (2)   | 1.0813 (2)   | 0.0690 (8)   |
| H15    | 0.783674      | 0.559246     | 1.149995     | 0.083*       |
| C16    | 0.8774 (4)    | 0.6039 (2)   | 1.0403 (2)   | 0.0707 (9)   |
| H16    | 0.942880      | 0.662327     | 1.081130     | 0.085*       |
| C17    | 0.8811 (3)    | 0.58178 (16) | 0.9352 (2)   | 0.0531 (6)   |
| C18    | 0.9789 (3)    | 0.64185 (18) | 0.8874 (3)   | 0.0686 (8)   |
| H18    | 1.042558      | 0.702893     | 0.923961     | 0.082*       |
| C19    | 0.9811 (3)    | 0.6117 (2)   | 0.7893 (3)   | 0.0716 (8)   |
| H19    | 1.046366      | 0.651427     | 0.757723     | 0.086*       |
| C20    | 0.8851 (3)    | 0.52090 (18) | 0.7354 (2)   | 0.0579 (6)   |
| H20    | 0.889607      | 0.500365     | 0.667730     | 0.070*       |
| C21    | 0.6792 (2)    | 0.42749 (15) | 0.91820 (15) | 0.0392 (5)   |
| C22    | 0.7835 (2)    | 0.49190 (14) | 0.87450 (16) | 0.0395 (5)   |
| C23    | 0.4103 (3)    | 0.43484 (18) | 0.6157 (2)   | 0.0609 (7)   |
| H23    | 0.481135      | 0.492909     | 0.653155     | 0.073*       |
| C24    | 0.2740 (4)    | 0.4463 (2)   | 0.5498 (2)   | 0.0742 (9)   |
| H24    | 0.254763      | 0.510758     | 0.544739     | 0.089*       |
| C25    | 0.1699 (3)    | 0.3628 (2)   | 0.4932 (2)   | 0.0656 (7)   |
| H25    | 0.078529      | 0.369687     | 0.449515     | 0.079*       |
| C26    | 0.2012 (3)    | 0.26581 (17) | 0.50107 (17) | 0.0474 (5)   |
| C27    | 0.1015 (3)    | 0.1734 (2)   | 0.44251 (18) | 0.0555 (6)   |
| H27    | 0.012285      | 0.176044     | 0.394954     | 0.067*       |
| C28    | 0.1349 (3)    | 0.08284 (19) | 0.45521 (18) | 0.0540 (6)   |
|   |    x      |    y      |    z      |    x      |    y      |    z      |
|---|-----------|-----------|-----------|-----------|-----------|-----------|
| H28 | 0.069041  | 0.023818  | 0.415812  | 0.065*    |           |           |
| C29 | 0.2701 (3) | 0.07560 (16)| 0.52828 (16)| 0.0423 (5)|           |           |
| C30 | 0.3060 (3) | 0.07560 (16)| 0.54857 (19)| 0.0506 (6)|           |           |
| H30 | 0.241610  |           | 0.512748  | 0.061*    |           |           |
| C31 | 0.4351 (3) | 0.07560 (16)| 0.62063 (19)| 0.0523 (6)|           |           |
| H31 | 0.457670  |           | 0.635824  | 0.063*    |           |           |
| C32 | 0.5336 (3) | 0.07560 (15)| 0.67175 (17)| 0.0479 (5)|           |           |
| H32 | 0.623143  |           | 0.719928  | 0.058*    |           |           |
| C33 | 0.3384 (2) | 0.26158 (15)| 0.57085 (16)| 0.0399 (5)|           |           |
| C34 | 0.3733 (2) | 0.16419 (15)| 0.58484 (15)| 0.0380 (4)|           |           |
| O4  | 0.7744 (3) | 0.2759 (2) | 0.3583 (2) | 0.1228 (10)|           |           |
| O5  | 0.5477 (3) | 0.2821 (2) | 0.40039 (18)| 0.1124 (9)|           |           |
| O6  | 0.5855 (4) | 0.3196 (2) | 0.26417 (18)| 0.1145 (9)|           |           |
| N5  | 0.6339 (3) | 0.29278 (15)| 0.33897 (16)| 0.0600 (5)|           |           |
| O1_1| 0.84054 (18)| 0.24890 (11)| 0.77807 (11)| 0.0478 (4)| 0.735 (6) |           |
| O2_1| 0.9654 (7) | 0.1792 (3) | 0.6607 (3) | 0.0608 (10)| 0.735 (6) |           |
| C1  | 0.9379 (13)| 0.1928 (9) | 0.7468 (6) | 0.0434 (12)| 0.735 (6) |           |
| C2  | 1.0126 (5) | 0.1398 (3) | 0.8211 (3) | 0.0390 (9) | 0.735 (6) |           |
| H2  | 0.981835  | 0.150243  | 0.883821  | 0.047*    | 0.735 (6) |           |
| C3  | 1.1205 (4) | 0.0787 (2) | 0.8031 (2) | 0.0407 (9) | 0.735 (6) |           |
| H3  | 1.153482  | 0.069490  | 0.740960  | 0.049*    | 0.735 (6) |           |
| C4  | 1.1908 (5) | 0.0247 (3) | 0.8757 (3) | 0.0398 (9) | 0.735 (6) |           |
| C5  | 1.2001 (8) | 0.0580 (4) | 0.9773 (4) | 0.0428 (11)| 0.735 (6) |           |
| H5  | 1.163475  | 0.118108  | 1.001304  | 0.051*    | 0.735 (6) |           |
| C6  | 1.2628 (19)| 0.0042 (8) | 1.0448 (5) | 0.0481 (15)| 0.735 (6) |           |
| C7  | 1.3155 (14)| 0.0869 (6) | 1.0095 (5) | 0.0598 (15)| 0.735 (6) |           |
| H7  | 1.356693  | 0.088283  | 1.054065  | 0.072*    | 0.735 (6) |           |
| C8  | 1.3060 (6) | 0.1216 (4) | 0.9082 (4) | 0.0587 (11)| 0.735 (6) |           |
| H8  | 1.339090  | 0.182963  | 0.884323  | 0.070*    | 0.735 (6) |           |
| C9  | 1.2473 (5) | 0.0659 (3) | 0.8403 (3) | 0.0489 (9) | 0.735 (6) |           |
| H9  | 1.245626  | 0.088822  | 0.772145  | 0.059*    | 0.735 (6) |           |
| C10 | 1.2348 (14)| 0.1263 (8) | 1.1877 (8) | 0.076 (2) | 0.735 (6) |           |
| H10A| 1.301732  | 0.181360  | 1.171057  | 0.114*    | 0.735 (6) |           |
| H10B| 1.259195  | 0.136916  | 1.259195  | 0.114*    | 0.735 (6) |           |
| H10C| 1.121772  | 0.123351  | 1.159119  | 0.114*    | 0.735 (6) |           |
| O1  | 0.84054 (18)| 0.24890 (11)| 0.77807 (11)| 0.0478 (4)| 0.265 (6) |           |
| O2  | 0.966 (2)  | 0.2091 (11)| 0.6365 (10)| 0.078 (3) | 0.265 (6) |           |
| C1  | 0.944 (4)  | 0.205 (2)  | 0.7236 (14)| 0.054 (5) | 0.265 (6) |           |
| C2  | 1.0527 (12)| 0.1394 (7) | 0.7673 (8) | 0.052 (3) | 0.265 (6) |           |
| H2  | 1.127208  | 0.112505  | 0.729946  | 0.062*    | 0.265 (6) |           |
| C3  | 1.0476 (15)| 0.1187 (10)| 0.8532 (8) | 0.056 (3) | 0.265 (6) |           |
| H3  | 0.971590  | 0.147523  | 0.887806  | 0.067*    | 0.265 (6) |           |
| C4  | 1.1423 (15)| 0.0572 (9) | 0.9042 (9) | 0.051 (3) | 0.265 (6) |           |
| C5  | 1.170 (2)  | 0.0793 (12)| 1.0051 (9) | 0.046 (3) | 0.265 (6) |           |
| H5  | 1.125983  | 0.132319  | 1.038905  | 0.055*    | 0.265 (6) |           |
| C6  | 1.263 (5)  | 0.026 (2)  | 1.0604 (14)| 0.056 (5) | 0.265 (6) |           |
| C7  | 1.317 (4)  | 0.0586 (17)| 1.0098 (14)| 0.070 (6) | 0.265 (6) |           |
| H7  | 1.372393  | 0.098231  | 1.045814  | 0.084*    | 0.265 (6) |           |
### Atomic Displacement Parameters (Å²)

| Atom  | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|-------|------|------|------|------|------|------|
| Co1   | 0.04017 (18) | 0.03443 (16) | 0.03103 (17) | 0.00215 (11) | −0.00248 (12) | 0.00417 (11) |
| O3    | 0.0776 (13) | 0.0878 (14) | 0.0628 (13) | 0.0218 (11) | 0.0124 (10) | 0.0340 (11) |
| O1W   | 0.0683 (11) | 0.0677 (11) | 0.0377 (9) | 0.0075 (9) | 0.0080 (8) | 0.0066 (8) |
| N1    | 0.0388 (9) | 0.0400 (9) | 0.0390 (10) | 0.0053 (7) | 0.0055 (8) | 0.0092 (8) |
| N2    | 0.0434 (10) | 0.0363 (9) | 0.0377 (10) | 0.0007 (7) | 0.0015 (8) | 0.0077 (7) |
| N3    | 0.0465 (10) | 0.0401 (9) | 0.0403 (10) | 0.0037 (8) | −0.0035 (8) | 0.0068 (8) |
| N4    | 0.0428 (9) | 0.0359 (9) | 0.0367 (10) | 0.0026 (7) | 0.0006 (8) | 0.0052 (7) |
| C11   | 0.0518 (14) | 0.0562 (14) | 0.0625 (16) | 0.0088 (11) | 0.0172 (12) | 0.0230 (12) |
| C12   | 0.0686 (17) | 0.0821 (19) | 0.072 (2) | 0.0291 (15) | 0.0356 (16) | 0.0423 (17) |
| C13   | 0.086 (2) | 0.094 (2) | 0.0412 (14) | 0.0505 (18) | 0.0217 (14) | 0.0274 (15) |
| C14   | 0.0595 (14) | 0.0637 (14) | 0.0337 (12) | 0.0328 (12) | 0.0026 (11) | 0.0065 (11) |
| C15   | 0.088 (2) | 0.0739 (18) | 0.0364 (14) | 0.0410 (16) | −0.0112 (14) | −0.0089 (13) |
| C16   | 0.0776 (19) | 0.0534 (15) | 0.0586 (18) | 0.0238 (14) | −0.0264 (15) | −0.0208 (13) |
| C17   | 0.0455 (13) | 0.0368 (11) | 0.0630 (16) | 0.0093 (9) | −0.0126 (11) | −0.0069 (10) |
| C18   | 0.0519 (15) | 0.0341 (12) | 0.103 (3) | −0.0050 (10) | −0.0111 (15) | 0.0021 (14) |
| C19   | 0.0602 (16) | 0.0489 (15) | 0.102 (3) | −0.0084 (12) | 0.0070 (16) | 0.0266 (16) |
| C20   | 0.0619 (15) | 0.0507 (13) | 0.0598 (16) | −0.0041 (11) | 0.0105 (13) | 0.0187 (12) |
| C21   | 0.0412 (11) | 0.0419 (11) | 0.0328 (11) | 0.0153 (9) | −0.0005 (9) | 0.0041 (9) |
| C22   | 0.0379 (11) | 0.0328 (10) | 0.0407 (12) | 0.0075 (8) | −0.0055 (9) | −0.0006 (8) |
| C23   | 0.0665 (16) | 0.0387 (12) | 0.0687 (18) | 0.0071 (11) | −0.0112 (13) | 0.0095 (11) |
| C24   | 0.0768 (19) | 0.0530 (15) | 0.088 (2) | 0.0171 (14) | −0.0153 (16) | 0.0214 (15) |
| C25   | 0.0567 (15) | 0.0666 (16) | 0.0705 (18) | 0.0125 (13) | −0.0138 (13) | 0.0245 (14) |
| C26   | 0.0411 (12) | 0.0569 (13) | 0.0409 (13) | 0.0045 (10) | 0.0007 (10) | 0.0104 (10) |
| C27   | 0.0436 (13) | 0.0727 (16) | 0.0409 (13) | −0.0014 (11) | −0.0075 (10) | 0.0093 (12) |
| C28   | 0.0444 (13) | 0.0595 (14) | 0.0432 (14) | −0.0092 (10) | −0.0008 (10) | −0.0043 (11) |
| C29   | 0.0393 (11) | 0.0441 (11) | 0.0349 (11) | −0.0053 (9) | 0.0077 (9) | −0.0036 (9) |
| C30   | 0.0529 (14) | 0.0351 (11) | 0.0568 (15) | −0.0061 (9) | 0.0169 (12) | −0.0021 (10) |
| C31   | 0.0589 (15) | 0.0341 (11) | 0.0625 (16) | 0.0037 (10) | 0.0137 (12) | 0.0088 (10) |
| C32   | 0.0534 (13) | 0.0405 (11) | 0.0479 (14) | 0.0053 (10) | 0.0029 (11) | 0.0114 (10) |
| C33   | 0.0399 (11) | 0.0413 (11) | 0.0346 (11) | 0.0022 (9) | 0.0024 (9) | 0.0055 (9) |
| C34   | 0.0366 (10) | 0.0393 (10) | 0.0341 (11) | 0.0001 (8) | 0.0050 (8) | 0.0043 (8) |
| O4    | 0.0810 (17) | 0.161 (3) | 0.128 (2) | 0.0368 (17) | 0.0016 (16) | 0.037 (2) |
| O5    | 0.1084 (19) | 0.156 (3) | 0.0656 (15) | −0.0122 (17) | 0.0345 (15) | 0.0190 (16) |
| O6    | 0.165 (2) | 0.1119 (19) | 0.0640 (15) | 0.0105 (17) | −0.0126 (15) | 0.0454 (14) |
| O7    | 0.0821 (16) | 0.0535 (12) | 0.0391 (12) | −0.0011 (11) | 0.0024 (11) | 0.0121 (9) |
| O1_1  | 0.0471 (8) | 0.0486 (8) | 0.0418 (9) | 0.0106 (7) | −0.0074 (7) | 0.0054 (7) |

**supporting information**

*Acta Cryst. (2022). E78, 1113-1117*
|    |   |   |   |   |   |   |
|----|---|---|---|---|---|---|
| C1 | 0.041 (2) | 0.039 (3) | 0.041 (3) | 0.0009 (16) | −0.008 (2) | 0.004 (2) |
| C2 | 0.042 (2) | 0.0394 (17) | 0.033 (2) | 0.0064 (13) | 0.0040 (17) | 0.0039 (16) |
| C3 | 0.0410 (16) | 0.0412 (16) | 0.0366 (17) | 0.0061 (12) | 0.0021 (13) | 0.0051 (13) |
| C4 | 0.036 (2) | 0.037 (2) | 0.045 (2) | 0.0068 (17) | 0.0044 (17) | 0.0073 (19) |
| C5 | 0.040 (2) | 0.038 (2) | 0.048 (3) | 0.0077 (16) | 0.003 (2) | 0.006 (2) |
| C6 | 0.048 (3) | 0.050 (4) | 0.048 (2) | 0.004 (3) | 0.004 (2) | 0.020 (2) |
| C7 | 0.061 (3) | 0.060 (4) | 0.072 (3) | 0.023 (3) | 0.016 (2) | 0.035 (2) |
| C8 | 0.058 (2) | 0.045 (3) | 0.079 (3) | 0.020 (2) | 0.012 (2) | 0.020 (2) |
| C9 | 0.046 (2) | 0.044 (2) | 0.057 (2) | 0.0150 (15) | 0.0096 (17) | 0.0080 (18) |
| C10 | 0.093 (6) | 0.080 (4) | 0.047 (4) | −0.002 (3) | 0.009 (3) | 0.011 (3) |
| O1 | 0.0471 (8) | 0.0486 (8) | 0.0418 (9) | 0.0106 (7) | −0.0074 (7) | 0.0054 (7) |
| O2 | 0.084 (6) | 0.096 (9) | 0.076 (7) | 0.051 (6) | 0.033 (6) | 0.030 (6) |
| C1 | 0.053 (10) | 0.037 (9) | 0.052 (10) | 0.013 (8) | −0.028 (7) | −0.010 (8) |
| C2 | 0.047 (5) | 0.053 (5) | 0.045 (6) | 0.009 (4) | −0.004 (5) | −0.007 (4) |
| C3 | 0.047 (6) | 0.061 (7) | 0.050 (7) | 0.008 (5) | −0.006 (5) | 0.000 (5) |
| C4 | 0.048 (6) | 0.046 (6) | 0.054 (6) | 0.011 (4) | 0.007 (5) | 0.004 (4) |
| C5 | 0.053 (8) | 0.038 (7) | 0.042 (6) | 0.005 (5) | 0.001 (6) | 0.002 (5) |
| C6 | 0.035 (8) | 0.061 (12) | 0.076 (9) | 0.009 (9) | 0.008 (8) | 0.023 (7) |
| C7 | 0.067 (9) | 0.065 (12) | 0.092 (8) | 0.032 (10) | 0.002 (7) | 0.047 (8) |
| C8 | 0.076 (8) | 0.048 (8) | 0.106 (8) | 0.034 (6) | 0.025 (7) | 0.018 (8) |
| C9 | 0.055 (7) | 0.059 (9) | 0.047 (6) | 0.023 (7) | 0.016 (5) | 0.011 (6) |
| C10 | 0.046 (9) | 0.117 (16) | 0.081 (19) | 0.026 (9) | 0.001 (9) | −0.013 (11) |

**Geometric parameters (Å, °)**

| Bond | Length (Å) | Angle (°) |
|------|-----------|-----------|
| Co1—O1W | 2.1011 (17) | C28—C29 | 1.430 (3) |
| Co1—N1 | 2.1484 (18) | C29—C30 | 1.411 (3) |
| Co1—N2 | 2.1488 (17) | C29—C34 | 1.399 (3) |
| Co1—N3 | 2.1356 (16) | C30—H30 | 0.9300 |
| Co1—N4 | 2.1416 (17) | C30—C31 | 1.356 (3) |
| Co1—O1' | 2.0525 (13) | C31—H31 | 0.9300 |
| Co1—O1_2 | 2.0525 (13) | C31—C32 | 1.392 (3) |
| O3—C6_1 | 1.409 (6) | C32—H32 | 0.9300 |
| O3—C10_1 | 1.378 (10) | C33—C34 | 1.443 (3) |
| O3—C6_2 | 1.202 (19) | O4—N5 | 1.227 (3) |
| O3—C10_2 | 1.56 (3) | O5—N5 | 1.207 (3) |
| O1W—H1WA | 0.8536 | O6—N5 | 1.201 (3) |
| O1W—H1WB | 0.8535 | O1_1—C1_1 | 1.252 (5) |
| N1—C11 | 1.320 (3) | O2_1—C1_1 | 1.229 (6) |
| N1—C21 | 1.358 (3) | C1_1—C2_1 | 1.485 (6) |
| N2—C20 | 1.333 (3) | C2_1—H2_1 | 0.9300 |
| N2—C22 | 1.350 (3) | C2_1—C3_1 | 1.324 (4) |
| N3—C23 | 1.318 (3) | C3_1—H3_1 | 0.9300 |
| N3—C33 | 1.366 (3) | C3_1—C4_1 | 1.465 (4) |
| N4—C32 | 1.334 (2) | C4_1—C5_1 | 1.374 (6) |
| N4—C34 | 1.349 (2) | C4_1—C9_1 | 1.404 (5) |
| C11—H11 | 0.9300 | C5_1—H5_1 | 0.9300 |

*Acta Cryst. (2022), E78, 1113-1117*
C11—C12 1.400 (4)  C5_1—C6_1 1.389 (6)
C12—H12 0.9300  C6_1—C7_1 1.395 (6)
C12—C13 1.330 (4)  C7_1—H7_1 0.9300
C13—H13 0.9300  C7_1—C8_1 1.374 (6)
C13—C14 1.401 (4)  C8_1—H8_1 0.9300
C14—C15 1.427 (4)  C8_1—C9_1 1.398 (5)
C14—C21 1.407 (3)  C9_1—H9_1 0.9300
C15—H15 0.9300  C10_1—H10A_1 0.9600
C15—C16 1.338 (4)  C10_1—H10B_1 0.9600
C16—H16 0.9300  C10_1—H10C_1 0.9600
C16—C17 1.430 (4)  O1_2—C1_2 1.344 (13)
C17—H17 0.9300  O1_2—C2_2 1.281 (13)
C17—C18 1.402 (4)  O1_2—C3_2 1.445 (12)
C18—H18 0.9300  C1_2—H2_2 0.9300
C18—C19 1.341 (4)  C1_2—C2_2 1.379 (12)
C19—H19 0.9300  C2_2—C3_2 1.346 (13)
C19—C20 1.385 (4)  C2_2—H2_2 0.9300
C20—H20 0.9300  C3_2—C4_2 1.390 (14)
C21—C22 1.433 (3)  C3_2—H3_2 0.9300
C21—C22 1.433 (3)  C4_2—C5_2 1.386 (15)
C22—C23 0.9300  C4_2—H4_2 0.9300
C23—C24 1.432 (3)  C5_2—C6_2 0.9300
C23—C24 1.432 (3)  C5_2—H5_2 0.9300
C24—C25 1.357 (4)  C5_2—C6_2 0.9300
C24—C25 1.357 (4)  C6_2—C7_2 0.9300
C25—C26 1.343 (3)  C6_2—H6_2 0.9300
C26—C27 1.406 (3)  C7_2—C8_2 0.9300
C26—C27 1.406 (3)  C7_2—H7_2 0.9300
C27—C28 0.9300  C7_2—C8_2 0.9300
C28—H28 0.9300  C7_2—H7_2 0.9300

O1W—Co1—N1 166.30 (7)  C29—C28—H28 119.4
O1W—Co1—N2 90.34 (7)  C30—C29—C28 123.7 (2)
O1W—Co1—N3 95.59 (7)  C30—C29—C28 119.5 (2)
O1W—Co1—N4 93.57 (7)  C30—C29—C28 120.5 (2)
N1—Co1—N2 77.08 (7)  C31—C30—C29 119.6 (2)
N3—Co1—N1 97.72 (7)  C31—C30—C29 119.6 (2)
N3—Co1—N2 99.48 (6)  C31—C30—H30 120.2
N3—Co1—N4 77.74 (6)  C31—C30—H30 120.2
N4—Co1—N1 97.85 (7)  C32—C31—C30 120.1
N4—Co1—N2 173.94 (6)  C32—C31—C30 120.1
O1_1—Co1—O1W 89.41 (7)  N4—C32—C31 119.7 (2)
O1_1—Co1—N1 85.52 (6)  N4—C32—H32 120.1
O1_1—Co1—N2 91.21 (6)  C31—C32—C33 118.7
O1_1—Co1—N3 169.27 (6)  C31—C32—C33 118.7
O1_1—Co1—N4 91.71 (6)  C31—C32—C33 123.34 (18)
O1_1—Co1—O1W 89.41 (7)  C31—C32—C33 117.24 (17)
O1_1—Co1—N1 85.52 (6)  C31—C32—C33 119.42 (19)
O1_1—Co1—N2 173.94 (6)  C31—C32—C33 123.39 (18)
| Bond                  | Length (Å) | Error (Å) |
|-----------------------|------------|-----------|
| O1_2—Co1—N2          | 91.21      | 6         |
| O1_2—Co1—N3          | 169.27     | 6         |
| O1_2—Co1—N4          | 91.71      | 6         |
| C10_1—O3—C6_1        | 117.1      | 5         |
| C6_2—O3—Co1_2        | 117.8      | 15        |
| Co1—O1W—H1WA         | 109.4      |           |
| Co1—O1W—H1WB         | 109.6      |           |
| H1WA—O1W—H1WB        | 104.3      |           |
| C11—N1—Co1           | 128.29     | 17        |
| C11—N1—C21           | 117.3      | 2         |
| C21—N1—Co1           | 113.07     | 13        |
| C20—N2—Co1           | 128.43     | 17        |
| C20—N2—C22           | 117.6      | 2         |
| C22—N2—Co1           | 113.33     | 13        |
| C23—N3—Co1           | 129.26     | 16        |
| C23—N3—C33           | 117.30     | 18        |
| C33—N3—Co1           | 113.02     | 12        |
| C32—N4—Co1           | 128.27     | 14        |
| C32—N4—C34           | 117.93     | 18        |
| C34—N4—Co1           | 113.42     | 12        |
| N1—C11—H11           | 118.6      |           |
| N1—C11—C12           | 122.7      | 3         |
| C12—C11—H11          | 118.6      |           |
| C11—C12—H12          | 119.8      |           |
| C13—C12—C11          | 120.4      | 3         |
| C13—C12—H12          | 119.8      |           |
| C12—C13—H13          | 120.2      |           |
| C12—C13—C14          | 119.6      | 2         |
| C14—C13—H13          | 119.3      |           |
| C14—C13—C15          | 124.1      | 2         |
| C13—C14—C21          | 117.1      | 2         |
| C21—C14—C15          | 118.8      | 3         |
| C14—C15—H15          | 119.9      |           |
| C16—C15—C14          | 121.4      | 3         |
| C16—C15—H15          | 119.3      |           |
| C15—C16—C14          | 121.7      | 2         |
| C17—C16—H16          | 119.2      |           |
| C18—C17—C16          | 124.7      | 3         |
| C18—C17—C22          | 116.8      | 2         |
| C22—C17—C16          | 118.5      | 3         |
| C17—C18—H18          | 119.8      |           |
| C19—C18—C17          | 120.3      | 2         |
| C19—C18—H18          | 119.8      |           |
| C18—C19—H19          | 120.3      |           |
| C18—C19—C20          | 119.4      | 3         |
| C20—C19—H19          | 120.3      |           |
| N2—C20—C19           | 123.2      | 3         |
| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|----------------------|--------------|----------------------|--------------|
| N2—C20—H20          | 118.4        | C4_2—C3_2—H3_2      | 115.2        |
| C19—C20—H20         | 118.4        | C5_2—C4_2—C3_2     | 118.3 (11)   |
| N1—C21—C14          | 123.0 (2)    | C5_2—C4_2—C9_2     | 118.4 (10)   |
| N1—C21—C22          | 117.13 (18)  | C9_2—C4_2—C3_2     | 123.3 (11)   |
| C14—C21—C22         | 119.9 (2)    | C4_2—C5_2—H5_2     | 118.9        |
| N2—C22—C17          | 122.2 (2)    | C4_2—C5_2—C6_2     | 122.2 (12)   |
| N2—C22—C21          | 117.57 (18)  | C6_2—C5_2—H5_2     | 118.9        |
| C17—C22—C21         | 119.7 (2)    | O3—C6_2—C5_2       | 126.2 (16)   |
| N3—C23—H23          | 118.4        | O3—C6_2—C7_2       | 114.4 (15)   |
| N3—C23—C24          | 123.2 (2)    | C7_2—C6_2—C5_2     | 118.6 (15)   |
| C24—C23—H23         | 118.4        | C6_2—C7_2—H7_2     | 119.8        |
| C23—C24—H24         | 120.2        | C6_2—C7_2—C8_2     | 120.4 (13)   |
| C25—C24—C23         | 119.6 (2)    | C8_2—C7_2—H7_2     | 119.8        |
| C25—C24—H24         | 120.2        | C7_2—C8_2—H8_2     | 121.0        |
| C24—C25—H25         | 120.2        | C7_2—C8_2—C9_2     | 118.1 (11)   |
| C24—C25—C26         | 119.5 (2)    | C9_2—C8_2—H8_2     | 121.0        |
| C26—C25—H25         | 120.2        | C9_2—C8_2—C9_2     | 121.8 (11)   |
| C25—C26—C27         | 123.7 (2)    | C4_2—C9_2—C8_2     | 121.0        |
| C33—C26—C25         | 116.9 (2)    | C4_2—C9_2—H9_2     | 119.1        |
| C33—C26—C27         | 119.4 (2)    | O3—C10_2—H10A_2    | 109.5        |
| C26—C27—H27         | 119.5        | O3—C10_2—H10B_2    | 109.5        |
| C28—C27—C26         | 121.0 (2)    | O3—C10_2—H10C_2    | 109.5        |
| C28—C27—H27         | 119.5        | H10A_2—C10_2—H10B_2| 109.5        |
| C27—C28—H28         | 119.4        | H10A_2—C10_2—H10C_2| 109.5        |
| C27—C28—C29         | 121.2 (2)    | H10B_2—C10_2—H10C_2| 109.5        |
| Co1—N1—C11—C12      | 164.56 (16)  | C24—C25—C26—C33    | 2.0 (4)      |
| Co1—N1—C21—C14      | −167.13 (14) | C25—C26—C27—C28    | −178.2 (3)   |
| Co1—N1—C21—C22      | 11.8 (2)     | C25—C26—C33—N3     | −2.4 (3)     |
| Co1—N2—C20—C19      | −170.90 (18) | C25—C26—C33—C34    | 177.8 (2)    |
| Co1—N2—C22—C17      | 170.42 (14)  | C26—C27—C28—C29    | 0.6 (4)      |
| Co1—N2—C22—C21      | −7.8 (2)     | C26—C33—C34—N4     | −178.66 (19) |
| Co1—N3—C23—C24      | 172.6 (2)    | C26—C33—C34—C29    | 0.3 (3)      |
| Co1—N3—C33—C26      | −172.22 (17) | C27—C26—C33—N3     | 177.7 (2)    |
| Co1—N3—C33—C34      | 7.6 (2)      | C27—C26—C33—C34    | −2.1 (3)     |
| Co1—N4—C32—C31      | −171.81 (17) | C27—C28—C29—C30    | 176.6 (2)    |
| Co1—N4—C34—C29      | 171.32 (16)  | C27—C28—C29—C34    | −2.5 (4)     |
| Co1—N4—C34—C33      | −9.8 (2)     | C28—C29—C30—C31    | −178.7 (2)   |
| Co1—O1_1—C1_1—O2_1  | 17.0 (18)    | C28—C29—C34—N4     | −179.1 (2)   |
| Co1—O1_1—C1_1—C2_1  | −160.3 (4)   | C28—C29—C34—C33    | 2.0 (3)      |
| Co1—O1_2—C1_2—O2_2  | 13 (5)       | C29—C30—C31—C32    | −1.9 (4)     |
| Co1—O1_2—C1_2—C2_2  | −165.8 (18)  | C30—C29—C34—N4     | 1.7 (3)      |
| O3—C6_1—C7_1—C8_1   | −176.9 (10)  | C30—C29—C34—C33    | −177.16 (19) |
| O3—C6_2—C7_2—C8_2   | 175 (3)      | C30—C31—C32—N4     | 1.4 (4)      |
| N1—C11—C12—C13      | 0.7 (4)      | C32—N4—C34—C29     | −2.2 (3)     |
| N1—C21—C22—N2       | −2.8 (2)     | C32—N4—C34—C33     | 176.65 (19)  |
| N1—C21—C22—C17      | 178.98 (15)  | C33—N3—C23—C24     | 0.6 (4)      |
| N3—C23—C24—C25      | −0.9 (5)     | C33—C26—C27—C28    | 1.7 (4)      |
N3—C33—C34—N4 1.5 (3) C34—N4—C32—C31 0.6 (3)
N3—C33—C34—C29 −179.61 (19) C34—C29—C30—C31 0.4 (3)
C11—N1—C21—C14 0.7 (3) O1_1—C1_1—C2_1—C3_1 −178.8 (7)
C11—N1—C21—C22 179.60 (17) O2_1—C1_1—C2_1—C3_1 3.8 (15)
C11—C12—C13—C14 0.1 (4) C1_1—C2_1—C3_1—C4_1 −178.4 (7)
C12—C13—C14—C15 −179.6 (2) C2_1—C3_1—C4_1—C9_1 154.3 (4)
C12—C13—C14—C21 −0.5 (3) C2_1—C3_1—C4_1—C9_1 154.3 (4)
C13—C14—C15—C16 −180.0 (2) C3_1—C4_1—C5_1—C6_1 178.1 (9)
C13—C14—C15—C33 0.1 (3) C3_1—C4_1—C9_1—C8_1 −176.3 (4)
C14—C15—C16—C17 −179.32 (17) C1_1—C2_1—C3_1—C4_1 −178.4 (7)
C14—C15—C16—C33 176.21 (16) C5_1—C4_1—C9_1—C8_1 2.1 (7)
C14—C21—C22—N2 176.21 (16) C5_1—C4_1—C9_1—C8_1 2.1 (7)
C14—C22—C23—N3 −179.32 (17) C2_1—C3_1—C4_1—C9_1 154.3 (4)
C14—C22—C23—N3 1.1 (3) C2_1—C3_1—C4_1—C9_1 154.3 (4)
C20—N2—C22—C17 −1.1 (3) C9_1—C4_1—C5_1—C6_1 −0.3 (11)
C21—N1—C21—C14 −1.1 (3) C9_1—C4_1—C5_1—C6_1 −0.3 (11)
C21—N1—C21—C22 −179.60 (17) C9_1—C4_1—C5_1—C6_1 −0.3 (11)
C21—C11—C12—C13 0.1 (4) C1_1—C2_1—C3_1—C4_1 −178.4 (7)
C21—C12—C13—C14 −179.6 (2) C1_1—C2_1—C3_1—C4_1 −178.4 (7)
C22—C17—C18—C19 −2.1 (3) C1_1—C2_1—C3_1—C4_1 −178.4 (7)
C22—C17—C18—C19 176.1 (2) C1_1—C2_1—C3_1—C4_1 −178.4 (7)
C23—C24—C25—C26 −0.5 (5) C10_2—O3—C6_2—C5_2 −176.4 (13)
C23—C24—C25—C26 −0.5 (5) C10_2—O3—C6_2—C5_2 −176.4 (13)
C24—C25—C26—C27 −178.1 (3) C10_2—O3—C6_2—C5_2 −176.4 (13)

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| O1W—H1WA···O2_1 | 0.86 | 1.99 | 2.743 (4) | 146 |
| O1W—H1WA···O2_2 | 0.86 | 1.50 | 2.30 (2) | 152 |
| O1W—H1WB···O4_1 | 0.86 | 2.55 | 3.093 (3) | 123 |
| O1W—H1WB···O5_1 | 0.86 | 2.06 | 2.882 (3) | 162 |
| C13—H13···O6_1 | 0.93 | 2.34 | 3.123 (4) | 141 |
| C16—H16···O1_1 | 0.93 | 2.44 | 3.294 (6) | 153 |
| C16—H16···O1_2 | 0.93 | 2.48 | 3.32 (3) | 151 |
| C19—H19···O4_1 | 0.93 | 2.60 | 3.508 (5) | 167 |

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