Synthesis and crystal structure of poly[[bis(aqua-κO)tetrakis(μ-4,4′-bipyridine-κ2N,N′)hexakis(3-chlorobenzoato)-κ5O;κ2O′-tricobalt(II)] methanol disolvate]

Phakamat Promwit,* Kittipong Chainokb and Nanthawat Wannarita,b*

Received 28 December 2021
Accepted 21 January 2022

A novel ladder-chain cobalt(II) coordination polymer, \([\text{Co}_3(\text{4,4′-bipy})_4(\text{3-Clbenz})_6(\text{H}_2\text{O})_2]_n\cdot 2\text{CH}_3\text{OH}\), was synthesized and characterized. The structure contains two CoII centres with different octahedral environments, \([\text{Co}(1)\text{N}_3\text{O}_3]\) and \([\text{Co}(2)\text{N}_2\text{O}_4]\). The \(\text{O}\)-donating 3-chlorobenzoate anions (3-Clbenz) act as the terminal ligands, while the \(\text{N}\)-donating 4,4′-bipy molecules play the role of linkers. The Co(1) ions are linked by 4,4′-bipy molecules into linear chains. Two such chains are joined by \([\text{Co}(2)(\text{3-Clbenz})_2(\text{H}_2\text{O})_2]\) units via two 4,4′-bipy bridging ligands, thus forming the ladder-chain structure. The crystal packing of the title compound is stabilized by supramolecular interactions, such as hydrogen bonding, \(\pi-\pi\) and halogen···\(\pi\) contacts, giving a three-dimensional framework. The spectroscopic and thermal properties of the title compound have also been investigated.

1. Chemical context

The exploration and synthesis of new one-dimensional coordination polymers based on transition metals and mixed \(\text{N}\)-and \(\text{O}\)-donating ligands such as 4,4′-bipyridine (4,4′-bipy) and benzoate derivatives have been intensively developed (Kaes et al., 2000; Saelim et al., 2020; Topor et al., 2021). The substituent groups at the benzoate ligands play an important role not only for electron densities on the aromatic ring, but also for flexible supramolecular interactions, resulting in various bulk physical properties, such as CO\(_2\) adsorption (Takahashi et al., 2014, 2015), photoluminescence (Lin, 2015) and conductivity (Islam et al., 2019). Among the reported compounds, the majority contain mixed 4,4′-bipy and \(\text{para}\)-substituted benzoate derivatives, but there is a limited number of examples containing \(\text{meta}\)-substituent benzoate ligands (Fang & Nie, 2011; Kar et al., 2011; Xin-Jian et al., 2013; Lin, 2015). We have therefore tried to expand investigations in this area by using various \(\text{meta}\)-substituted benzoate ligands containing hydroxy, nitro and halogen substituents. During this study, we employed 3-chlorobenzoate (3-Clbenz), which is expected to support crystal structures via \(\pi-\pi\) and halogen···\(\pi\) intermolecular interactions, together with the 4,4′-bipy organic linker and have synthesized the new CoII coordination polymer \([\text{Co}_3(4,4′-\text{bipy})_4(3\text{-Clbenz})_6(\text{H}_2\text{O})_2]_n\cdot 2\text{CH}_3\text{OH}\), which has an interesting one-dimensional ladder-chain structure. This report describes the synthesis, crystal structure, spectroscopic and thermal properties of the title compound.
2. Structural commentary

The asymmetric unit of the title compound comprises two Co$^{2+}$ ions, three 3-Clbenz anions, two 4,4'-bipy molecules, one coordinated water molecule and one methanol solvate molecule as shown in Fig. 1. One of the Co$^{2+}$ ions (containing Co2), is situated at an inversion centre. One pyridine ring (C1–C5) and the methanol solvate molecule are disordered over two sets of sites with occupancies of 0.584 (19):0.416 (19) and 0.72 (3):0.28 (3), respectively. Both Co$^{2+}$ ions are six-coordinated and have octahedral environments. The Co1 ion is coordinated by three nitrogen atoms from three 4,4'-bipy bridging ligands and three oxygen atoms from the carboxylate groups of one monodentate and one bidentate 3-Clbenz ligands, providing a distorted octahedral geometry with angles O2—Co1—O1, O2—Co1—O3 and O2—Co1—N1 of 59.88 (6), 119.93 (7) and 148.87 (7)$^\circ$, respectively. The Co2 ion is coordinated by two nitrogen atoms from two 4,4'-bipy bridging ligands and four oxygen atoms from two monodentate 3-Clbenz ligands and two coordinated water molecules. The angles in its environment deviate from ideal values no more than by 3.5$^\circ$. There is an intramolecular hydrogen bond in the coordination environment of Co2 between the aqua and 3-Clbenz ligands (see Table 1). The Co1 ions are connected by the 4,4'-bipy linkers into linear chains along the $a$-axis direction, and adjacent chains are linked via the Co2 ions by the 4,4'-bipy ligands, thus forming the ladder-chain structure shown in Fig. 2.

3. Supramolecular features

The crystal packing is stabilized by intermolecular interactions such as hydrogen bonds (classical O—H⋯O and non-classical C—H⋯O and C—H⋯N), aromatic $\pi$⋯$\pi$ and Cl⋯$\pi$ interactions (see Table 1, Figs. 3 and 4). The solvate methanol molecule forms hydrogen bonds to the non-coordinated O4 atom of the 3-Clbenz ligand at Co1 as an H-atom donor and to the coordinated water molecule at Co2 as an H-atom acceptor (see Figs. S1–S3 in the supporting information). Aromatic $\pi$⋯$\pi$ interactions involving the phenyl rings of two 3-Clbenz ligands have an intercentroid $Cg_6$⋯$Cg_7$ (1 + $x$, −1 + $y$, $z$) separation of 3.917 (2) Å (Fig. 3) ($Cg_6$ and $Cg_7$ are the centroids of the C22–C27 and C29–C34 rings, respectively). There are also halogen⋯$\pi$ interactions between the 3-Clbenz ligands and

| D—H⋯A | D—H | H⋯A | D⋯A | D−H⋯A |
|-------|-----|-----|-----|-------|
| O7—H7A⋯O6$^i$ | 0.85 (2) | 1.84 (2) | 2.648 (3) | 158 (3) |
| O7—H7B⋯O8$^ii$ | 0.85 (2) | 1.93 (2) | 2.777 (10) | 177 (3) |
| O7—H7B⋯O8A$^ii$ | 0.85 (2) | 1.88 (4) | 2.72 (3) | 168 (3) |
| O8—H8A⋯O4 | 0.82 | 1.90 | 2.708 (10) | 169 |
| O8A—H8AA⋯O4 | 0.82 | 2.04 | 2.67 (3) | 133 |
| Cl—H1⋯O3 | 0.93 | 2.59 | 3.102 (7) | 115 |
| Cl—H5⋯O1 | 0.93 | 2.48 | 3.057 (9) | 121 |
| Cl4—H1A⋯O3 | 0.93 | 2.52 | 3.088 (9) | 120 |
| Cl5A—H5A⋯O1 | 0.93 | 2.33 | 2.991 (12) | 128 |
| C9—H9⋯O5 | 0.93 | 2.71 | 3.189 (3) | 113 |
| C11—H11⋯O2 | 0.93 | 2.57 | 3.084 (3) | 115 |
| C15—H15⋯N1 | 0.93 | 2.60 | 3.198 (4) | 123 |
| C26—H26⋯O6$^{ii}$ | 0.93 | 2.60 | 3.524 (4) | 176 |

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

Figure 1
Asymmetric unit of the title compound with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

Figure 2
View of the ladder-chain structure along the $a$-axis direction. The hydrogen atoms located at carbon atoms and methanol solvate molecules are omitted for clarity.
the pyridine rings of 4,4'-bipy ligands with C24—Cl1···Cg5 (x, 
−1 + y, z) = 3.5833 (14) Å and C31—Cl2···Cg4 (−1 + x, 1 + y, 
z) = 3.7558 (15) Å (Fig. 3) (Cg4 and Cg5 are the centroids 
of the N3/C11—C15 and N4/C16—C20 rings, respectively). These 
interactions stabilize the structure, leading to a three-dimen-
sional supramolecular framework (Fig. 4).

4. Spectroscopic characterization
The FT–IR spectrum of the title compound (Fig. S4) has a 
characteristic broad peak centred at 3330 cm\(^{-1}\) assigned to the 
O—H stretching vibrations of coordinated water molecules and 
the methanol solvate. The strong and sharp peaks at about 
1608 and 1382 cm\(^{-1}\) are attributed to the asymmetric and 
symmetric COO\(^{-}\) stretching vibration of the monodentate 
3-Clbenz ligands, and the peaks appearing at about 1557 and 
1488 cm\(^{-1}\) are attributed to the asymmetric and symmetric 
COO\(^{-}\) stretching vibration of the chelating 3-Clbenz ligand

(Xin-Jian et al., 2013). The strong superimposed bands 
appearing at 1557 and 1488 cm\(^{-1}\) could be assigned to the 
C—C(C—N) stretching vibration of the aromatic rings of the 
3-Clbenz and 4,4'-bipy ligands. The medium-strong peaks in 
the region of 760 and 731 cm\(^{-1}\) are assigned to C—Cl vibra-
tion and C—H bending vibration of the 3-Clbenz ligands. In 
addition, the medium-strong peak at 1219 cm\(^{-1}\) is assigned to 
the weak C—N stretching vibration (Xin-Jian et al., 2013) and 
the bands between 1016 and 1145 cm\(^{-1}\) are assignable to the 
pyridine ring-breathing modes (Dey et al., 2011) of the 4,4'- 

bipy ligands. The characteristic C—H out-of-plane and in-
plane deformation bands for pyridine rings are observed at 
808 and 631 cm\(^{-1}\), and are shifted to a higher frequency as 
compared to the values observed for the free ligand (805 and 
607 cm\(^{-1}\)), suggesting coordinated 4,4'-bipy ligands (Seidel 
et al., 2011). The solid-state electronic spectrum (Fig. S5) of the 
title compound shows \(d-d\) transitions with two broad bands at 
489 and 1099 nm, assigned to the \(v_2: ^4T_{1g} \rightarrow ^4T_{1g}(P)\) and 
\(v_1: ^4T_{1g} \rightarrow ^4T_{2g}\) transitions, respectively (Fu et al., 2007; 
Piromchom et al., 2014). The results correspond to the typical 
\(d-d\) transitions for Co\(^{II}\) in a distorted octahedral geometry, as 
confirmed by the X-ray structure.

5. PXRD and thermal analysis
The PXRD patterns (Fig. S6) of the title compound used to 
check the phase purity show good accordance with its simu-
lated PXRD pattern generated from the single-crystal X-ray 
diffraction data, confirming that the title compound has high 
phase purity. The TGA curve (Fig. S7) shows the thermal 
stability of the title compound below 325°C. The first complex 
step with a weight loss of 29.57% (calculated 30.88%) was 
found in the temperature range from 100 to 325°C, which was 
attributed to the loss of methanol molecule of crystallization, 
two coordinated water and three 3-Clbenz molecules. Then, 
the structure starts to collapse with a weight loss of 49.24% 
(calculated 49.44%) in the temperature range from 325–685°C 
that can be attributed to the removal of three remaining 
3-Clbenz and three remaining 4,4'-bipy molecules. After that, 
the residual product is assumed to be CoO.

6. Database survey
To the best of our knowledge, only two transition-metal-based 
coordination polymers structurally related to the title 
compound, namely [Co\((\text{dca})_2(\text{nic})(\text{H}_2\text{O})_2]2\text{H}_2\text{O} \) (CSD 
refcode XOGLOU; Kutasi et al., 2002) and [Cu\((\text{dca})_2-
(\text{nic})(\text{H}_2\text{O})_3]2\text{H}_2\text{O} \) (KAPMEO; Madalan et al., 2005) (dca = 
dicyanamide and nic = 3-pyridinecarboxylate) are reported in 
the literature. These compounds are isosctructural to each 
other and differ only by the kind of transition metal.

7. Synthesis and crystallization
A methanolic solution (5 ml) of 4,4'-bipy (0.4586 g, 3 mmol) 
was added to a solution of Co(NO\(_3\)_2:6H\(_2\)O (0.2910 g, 1 mmol) 
in 10 mL of MeOH/H\(_2\)O (v:v = 8:2) solution. After stirring for
30 min, a methanolic solution (5 mL) of m-chlorobenzoic acid (0.3131 g, 2 mmol) was added slowly, and the mixture was stirred continuously at room temperature for 15 minutes. The resulting clear red solution was allowed to evaporate slowly in air. After 4 days, red rod-shaped crystals suitable for single-crystal X-ray diffraction were obtained. Yield 115.2 mg (32.6% based on CoII salt). Analysis calculated for Co₃(C₇H₄ClO₂)₆(C₁₀H₈N₂)₄·2CH₄O: C, 54.98; H, 3.74; N, 6.11%. Found: C, 53.28; H, 3.60; N, 6.50%. IR (KBr, cm⁻¹): 3330(w), 2348(w), 1608(s), 1557(s), 1488(w), 1415(s), 1382(s), 1263(w), 1219(m), 1145(w), 1068(m), 1031(w), 1010(w), 817(m), 808(m), 760(m), 731(m), 674(w), 657(w), 631(m), 574(w), 499(w), 439(w).

8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All C-bound hydrogen atoms were positioned geometrically and refined as riding, with C—H = 0.96 Å for methyl groups [U(eq)(H) = 1.5 U(eq)(C)], C—H = 0.93 Å for aromatic [U(eq)(H) = 1.2 U(eq)(C)]. The oxygen-bound hydrogen atom of methanol was positioned with O—H = 0.82 Å [U(eq)(H) = 1.5 U(eq)(O)], and the OH group was allowed to rotate (AFX 147). Hydrogen atoms of the coordinated water molecule were located in the differential electron density map and refined with the O—H distance constrained to 0.84 Å.

Acknowledgements

The authors are grateful to Faculty of Science and Technology, Thammasat University for funds to purchase the X-ray diffractometer.

Funding information

Funding for this research was provided by: Financial assistance from the Graduate Development Scholarship 2020, National Research Council of Thailand (contract No. 4/2563 to P. Promwit); Scholarship for talented student to study graduate program in Faculty of Science and Technology Thammasat University (contract No. TB23/2560 to P. Promwit); the Thammasat University Research Unit in Multifunctional Crystalline Materials and Applications Research Unit (TU-MCMA) (grant to K. Chainok, N. Wannarit).

References

Bucker (2016). APEX3, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
Dey, D., Roy, S., Purkayastha, R. N. D., Pallepogu, R., Male, L. & Meek, V. (2011). J. Coord. Chem. 64, 1165–1176.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). J. Appl. Cryst. 42, 339–341.
Fang, Z. & Nie, Q. (2011). J. Coord. Chem. 64, 2573–2582.
Fu, S.-J., Cheng, C.-Y. & Lin, K.-J. (2007). Cryst. Growth Des. 7, 1381–1384.
Islam, S., Datta, J., Maity, S., Dutta, B., Ahmed, F., Ghosh, P., Ray, P. & Mir, M. H. (2019). ChemistrySelect, 4, 3294–3299.
Kaias, C., Katz, A. & Hosseini, M. W. (2000). Chem. Rev. 100, 3553–3590.
Kar, P., Biswas, R., Ida, Y., Ishida, T. & Ghosh, A. (2011). Cryst. Growth Des. 11, 5305–5315.
Kutasi, A. M., Batten, S. R., Harris, A. R., Moubaraki, B. & Murray, K. S. (2002). CrystEngComm, 4, 202–204.
Lin, R.-G. (2015). Inorg. Chim. Acta, 432, 46–49.
Madalan, A. M., Paraschiv, C., Sutter, J.-P., Schmidtmann, M., Müller, A. & Andruh, M. (2005). Cryst. Growth Des. 5, 707–711.
Piromchom, J., Wannarit, N., Boonmak, J., Pakawatchai, C. & Youngme, S. (2014). Inorg. Chem. Commun. 40, 59–61.
Saelim, T., Chainok, K., Kielar, F. & Wannarit, N. (2020). Acta Cryst. E76, 1302–1306.
Seidel, R. W., Goddard, R., Zibrowius, B. & Oppel, I. M. (2011). Polymers, 3, 1458–1474.
Sheldrick, G. M. (2015a). Acta Cryst. A71, 3–8.
Sheldrick, G. M. (2015b). Acta Cryst. C71, 3–8.
Takahashi, K., Hoshino, N., Takeda, T., Noro, S., Nakamura, T., Takeda, S. & Akutagawa, T. (2014). Dalton Trans. 43, 9081–9089.
Takahashi, K., Hoshino, N., Takeda, T., Noro, S., Nakamura, T., Takeda, S. & Akutagawa, T. (2015). Inorg. Chem. 54, 9423–9431.
Topor, A., Avram, D., Dascalu, R., Maxim, C., Tiseanu, C. & Andruh, M. (2021). Dalton Trans. 50, 9881–9890.
Xin-Jian, W., Yi-Ping, C., Ze-Min, X., Su-Zhi, G., Feng, C., Ling-Yan, Z. & Jian-Zhong, C. (2013). J. Mol. Struct. 1035, 318–325.
Synthesis and crystal structure of poly[[bis(aqua-κO)tetrakis(µ-4,4'-bipyridine-κ²N:N’)hexakis(3-chlorobenzoato)-κ⁵O;κ²O:O’-tricobalt(II)] methanol disolvate]

Phakamat Promwit, Kittipong Chainok and Nanthawat Wannarit

Computing details
Data collection: APEX3 (Bruker, 2016); cell refinement: SAINT (Bruker, 2016); data reduction: SAINT (Bruker, 2016); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

poly[[bis(aqua-κO)tetrakis(µ-4,4'-bipyridine-κ²N:N’)hexakis(3-chlorobenzoato)-κ⁵O;κ²O:O’-tricobalt(II)] methanol disolvate]

Crystal data

| Parameter                              | Value                        |
|----------------------------------------|------------------------------|
| [Co₃(C₇H₄ClO₂)₆(C₁₀H₈N₂)₄(H₂O)₂]·2CH₄O |                              |
| Mr                                     | 1834.95                      |
| Triclinic, P.bar                      |                              |
| a = 11.388 (2) Å                      |                              |
| b = 11.868 (2) Å                      |                              |
| c = 18.055 (3) Å                      |                              |
| α = 79.516 (6)°                      |                              |
| β = 79.088 (6)°                      |                              |
| γ = 62.148 (6)°                      |                              |
| V = 2106.3 (7) Å³                    |                              |
| Z = 1                                  |                              |
| F(000)                                 | 939                          |
| Dₐ (1.447 Mg m⁻³)                     |                              |
| Mo Kα radiation, λ = 0.71073 Å        |                              |
| Cell parameters from 9884 reflections  |                              |
| θ = 2.9–25.9°                         |                              |
| μ = 0.84 mm⁻¹                         |                              |
| T = 296 K                             |                              |
| 0.43 × 0.32 × 0.26 mm                  |                              |

Data collection

Bruker D8 QUEST CMOS PHOTON II diffractometer
8352 independent reflections
6158 reflections with I > 2σ(I)
Rsex = 0.077
θmin = 26.2°, θmax = 2.9°
h = −14→14
k = −14→14
l = −22→22
Tmin = 0.684, Tmax = 0.745

Refinement

Refinement on F²
8352 reflections
8352 reflections
598 parameters
43 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

\[ w = \frac{1}{\sigma^2(F_o^2) + (0.0352P)^2 + 1.2109P} \]
where \( P = (F_o^2 + 2F_c^2)/3 \)

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

\[ \Delta \rho_{\text{max}} = 0.39 \text{ e} \text{ Å}^{-3} \]
\[ \Delta \rho_{\text{min}} = -0.36 \text{ e} \text{ Å}^{-3} \]

Extinction correction: SHELXL (Sheldrick, 2015b), \( F_c^* = kF_c[1+0.001xF_c^2\sin(2\theta)]^{-1/4} \)
Extinction coefficient: 0.0034 (6)

**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| 0.50698 (3) | 0.68260 (3) | 0.63422 (2) | 0.03063 (10) |          |
| Co2| 0.500000 | 1.000000 | 0.000000 | 0.03999 (13) |          |
| Cl1| 0.99436 (12) | 0.00343 (9) | 0.59982 (7) | 0.1103 (4) |          |
| Cl2| 0.05072 (9) | 1.34860 (8) | 0.61650 (5) | 0.0794 (3) |          |
| Cl3| 1.09130 (10) | 0.45840 (8) | -0.12014 (5) | 0.0856 (3) |          |
| O1 | 0.63032 (18) | 0.48413 (16) | 0.60490 (10) | 0.0500 (4) |          |
| O2 | 0.56402 (17) | 0.52368 (16) | 0.72324 (10) | 0.0471 (4) |          |
| O3 | 0.39489 (17) | 0.86355 (16) | 0.66137 (10) | 0.0500 (4) |          |
| O4 | 0.3946 (2) | 0.80593 (19) | 0.78514 (12) | 0.0682 (6) |          |
| O5 | 0.70423 (17) | 0.88325 (17) | -0.02018 (9) | 0.0489 (4) |          |
| O6 | 0.79423 (19) | 1.0110 (2) | -0.00999 (12) | 0.0637 (5) |          |
| O7 | 0.4670 (2) | 0.83959 (19) | -0.00306 (11) | 0.0554 (5) |          |
| O8 | 0.3828 (18) | 0.870 (3) | -0.0018 (18) | 0.070 (10)* |          |
| O8A| 0.504 (3) | 0.789 (3) | -0.0370 (14) | 0.074 (11)* |          |
| O9 | 0.5835 (9) | 0.6811 (6) | 0.8812 (6) | 0.070 (2) | 0.72 (3) |
| H8A| 0.534267 | 0.713202 | 0.847635 | 0.105* | 0.72 (3) |
| O8A| 0.552 (4) | 0.669 (3) | 0.893 (2) | 0.118 (10) | 0.28 (3) |
| H8AA| 0.513149 | 0.667322 | 0.860315 | 0.177* | 0.28 (3) |
| N1 | 0.50401 (17) | 0.74863 (17) | 0.51524 (10) | 0.0320 (4) |          |
| N2 | 0.5003 (2) | 0.94739 (19) | 0.12052 (10) | 0.0436 (5) |          |
| N3 | 0.68941 (18) | 0.69508 (18) | 0.63878 (11) | 0.0373 (4) |          |
| N4 | 1.32607 (18) | 0.66423 (18) | 0.63798 (11) | 0.0378 (4) |          |
| C1 | 0.4041 (7) | 0.8562 (8) | 0.4894 (4) | 0.0409 (18) | 0.584 (19) |
| H1 | 0.336133 | 0.906039 | 0.524106 | 0.049* | 0.584 (19) |
| C2 | 0.3979 (7) | 0.8961 (8) | 0.4134 (3) | 0.0422 (17) | 0.584 (19) |
| H2 | 0.324386 | 0.970146 | 0.397732 | 0.051* | 0.584 (19) |
| C4 | 0.6000 (9) | 0.7124 (8) | 0.3873 (5) | 0.0385 (19) | 0.584 (19) |
| H4 | 0.668235 | 0.658787 | 0.354224 | 0.046* | 0.584 (19) |
| C5 | 0.5979 (9) | 0.6781 (9) | 0.4639 (4) | 0.0368 (19) | 0.584 (19) |
| H5 | 0.666182 | 0.600802 | 0.481176 | 0.044* | 0.584 (19) |
| C1A| 0.4507 (18) | 0.8730 (9) | 0.4867 (5) | 0.052 (3) | 0.416 (19) |
| H1A| 0.411651 | 0.934175 | 0.520990 | 0.062* | 0.416 (19) |
| C2A| 0.4498 (19) | 0.9156 (8) | 0.4113 (4) | 0.056 (4) | 0.416 (19) |
| Vertex | X    | Y    | Z    | U  | V  | W  |
|--------|------|------|------|----|----|----|
| H2A    | 0.415636 | 1.002838 | 0.395275 | 0.067* | 0.416 (19) |
| C4A    | 0.5608 (15) | 0.7006 (10) | 0.3868 (6) | 0.038 (3) | 0.416 (19) |
| H4A    | 0.602070 | 0.637977 | 0.353428 | 0.045* | 0.416 (19) |
| C5A    | 0.5608 (15) | 0.6653 (12) | 0.4634 (6) | 0.038 (3) | 0.416 (19) |
| H5A    | 0.602681 | 0.578372 | 0.480289 | 0.046* | 0.416 (19) |
| C3     | 0.5007 (2) | 0.8269 (2) | 0.35885 (12) | 0.0355 (5) |
| C6     | 0.5011 (2) | 0.8683 (2) | 0.27628 (12) | 0.0374 (5) |
| C7     | 0.4220 (3) | 0.9934 (2) | 0.24883 (13) | 0.0470 (6) |
| H7     | 0.367277 | 1.05357 | 0.282340 | 0.056* |
| C8     | 0.4246 (3) | 1.0285 (2) | 0.17172 (14) | 0.0504 (7) |
| H8     | 0.370780 | 1.113144 | 0.154564 | 0.060* |
| C9     | 0.5766 (3) | 0.8273 (3) | 0.14692 (14) | 0.0582 (8) |
| H9     | 0.630829 | 0.769104 | 0.112168 | 0.070* |
| C10    | 0.5794 (3) | 0.7848 (3) | 0.22277 (14) | 0.0563 (7) |
| H10    | 0.634247 | 0.699523 | 0.238210 | 0.068* |
| C11    | 0.7468 (2) | 0.6564 (2) | 0.70265 (13) | 0.0415 (6) |
| H11    | 0.702007 | 0.632002 | 0.746159 | 0.050* |
| C12    | 0.8689 (2) | 0.6506 (2) | 0.70775 (13) | 0.0401 (5) |
| H12    | 0.904054 | 0.623321 | 0.753865 | 0.048* |
| C13    | 0.9389 (2) | 0.6852 (2) | 0.64437 (13) | 0.0350 (5) |
| C14    | 0.8759 (3) | 0.7325 (3) | 0.57973 (15) | 0.0589 (8) |
| H14    | 0.915922 | 0.762362 | 0.536209 | 0.071* |
| C15    | 0.7537 (3) | 0.7356 (3) | 0.57951 (15) | 0.0599 (8) |
| H15    | 0.713650 | 0.768076 | 0.534968 | 0.072* |
| C16    | 1.0742 (2) | 0.6734 (2) | 0.64405 (13) | 0.0341 (5) |
| C17    | 1.1168 (2) | 0.6868 (2) | 0.70762 (13) | 0.0405 (6) |
| H17    | 1.061642 | 0.698869 | 0.753556 | 0.049* |
| C18    | 1.2415 (2) | 0.6820 (2) | 0.70222 (14) | 0.0433 (6) |
| H18    | 1.268121 | 0.691561 | 0.745340 | 0.052* |
| C19    | 1.2866 (2) | 0.6468 (2) | 0.57783 (14) | 0.0433 (6) |
| H19    | 1.344921 | 0.631851 | 0.533042 | 0.052* |
| C20    | 1.1646 (2) | 0.6498 (2) | 0.57855 (14) | 0.0439 (6) |
| H20    | 1.142397 | 0.635907 | 0.535167 | 0.053* |
| C21    | 0.6305 (2) | 0.4468 (2) | 0.67475 (15) | 0.0407 (6) |
| C22    | 0.7160 (2) | 0.3079 (2) | 0.69985 (14) | 0.0425 (6) |
| C23    | 0.8002 (3) | 0.2268 (2) | 0.64613 (16) | 0.0516 (7) |
| H23    | 0.798960 | 0.256315 | 0.594778 | 0.062* |
| C24    | 0.8861 (3) | 0.1018 (3) | 0.66913 (18) | 0.0633 (8) |
| C25    | 0.8881 (4) | 0.0552 (3) | 0.7441 (2) | 0.0755 (10) |
| H25    | 0.946344 | −0.029321 | 0.758825 | 0.091* |
| C26    | 0.8032 (4) | 0.1350 (3) | 0.79735 (18) | 0.0734 (9) |
| H26    | 0.803440 | 0.103845 | 0.848487 | 0.088* |
| C27    | 0.7169 (3) | 0.2615 (3) | 0.77596 (16) | 0.0566 (7) |
| H27    | 0.659947 | 0.314862 | 0.812564 | 0.068* |
| C28    | 0.3553 (2) | 0.8863 (2) | 0.73000 (15) | 0.0433 (6) |
| C29    | 0.2493 (2) | 1.0208 (2) | 0.74272 (14) | 0.0409 (6) |
| C30    | 0.2048 (2) | 1.1118 (2) | 0.68156 (14) | 0.0443 (6) |
| H30    | 0.241121 | 1.091367 | 0.632359 | 0.053* |
| Atomic displacement parameters (Å²) | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|-----------------------------------|----------|----------|----------|----------|----------|----------|
| Co1                               | 0.02389 (15) | 0.03470 (17) | 0.03223 (17) | −0.01262 (13) | −0.00512 (12) | −0.00071 (12) |
| Co2                               | 0.0419 (3) | 0.0426 (3) | 0.0269 (2) | −0.0121 (2) | −0.00361 (19) | −0.00320 (19) |
| C11                               | 0.1260 (9) | 0.0567 (5) | 0.1072 (8) | −0.0018 (5) | −0.0107 (7) | −0.0273 (5) |
| C12                               | 0.0859 (6) | 0.0508 (4) | 0.0776 (6) | −0.0133 (4) | −0.0140 (4) | 0.0039 (4) |
| C13                               | 0.0938 (6) | 0.0531 (5) | 0.0815 (6) | −0.0070 (4) | −0.0091 (5) | −0.0155 (4) |
| O1                                | 0.0551 (11) | 0.0391 (10) | 0.0466 (11) | −0.0144 (8) | −0.0147 (8) | 0.0069 (8) |
| O2                                | 0.0441 (10) | 0.0418 (10) | 0.0529 (11) | −0.0168 (8) | −0.0090 (8) | −0.0025 (8) |
| O3                                | 0.0432 (10) | 0.0454 (10) | 0.0546 (11) | −0.0130 (8) | 0.0027 (8) | −0.0172 (8) |
| O4                                | 0.0709 (14) | 0.0511 (12) | 0.0674 (14) | −0.0140 (10) | −0.0191 (11) | 0.0024 (10) |
| O5                                | 0.0422 (10) | 0.0506 (11) | 0.0456 (10) | −0.0136 (8) | −0.0041 (8) | −0.0071 (8) |
| O6                                | 0.0567 (12) | 0.0623 (13) | 0.0704 (14) | −0.0230 (10) | 0.0014 (10) | −0.0232 (11) |
| O7                                | 0.0581 (14) | 0.0516 (12) | 0.0523 (12) | −0.0193 (10) | −0.0037 (10) | −0.0137 (9) |
| O8                                | 0.081 (4) | 0.064 (3) | 0.051 (3) | −0.018 (2) | −0.011 (2) | −0.0108 (18) |
| O8A                               | 0.136 (14) | 0.118 (12) | 0.091 (15) | −0.030 (9) | −0.047 (12) | −0.031 (9) |
| N1                                | 0.0288 (10) | 0.0362 (10) | 0.0299 (10) | −0.0132 (8) | −0.0064 (8) | −0.0021 (8) |
| N2                                | 0.0467 (12) | 0.0432 (12) | 0.0300 (10) | −0.0117 (10) | −0.0034 (9) | −0.0034 (9) |
| N3                                | 0.0281 (10) | 0.0439 (11) | 0.0415 (11) | −0.0184 (9) | −0.0064 (8) | 0.0002 (9) |
| N4                                | 0.0296 (10) | 0.0452 (11) | 0.0416 (11) | −0.0198 (9) | −0.0066 (8) | −0.0010 (9) |
| Atom | C1  | C2  | C3  | C4  | C5  | C1A | C2A | C4A | C5A | C3  | C6  | C7  | C8  | C9  | C10 | C11 | C12 | C13 | C14 | C15 | C16 | C17 | C18 | C19 | C20 | C21 | C22 | C23 | C24 | C25 | C26 | C27 | C28 | C29 | C30 | C31 | C32 | C33 | C34 | C35 | C36 | C37 | C38 | C39 | C40 | C41 | C42 | C42A |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|      | 0.033 (3) | 0.043 (3) | 0.033 (3) | −0.009 (2) | −0.001 (2) | −0.001 (2) |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |   0.114 (12) | 0.102 (11) | 0.121 (15) | −0.044 (8) | −0.020 (11) | −0.022 (9) |

**supporting information**

*Acta Cryst.* (2022). *E78*, 255-258

sup-5
| Bond            | Length (Å) | Angle (°) | Bond          | Length (Å) | Angle (°) |
|-----------------|------------|----------|---------------|------------|----------|
| Co1—O1          | 2.2096 (18) |          | C9—H9         | 0.9300     |          |
| Co1—O2          | 2.1703 (17) |          | C9—C10        | 1.372 (3)  |          |
| Co1—O3          | 2.0166 (17) |          | C10—H10       | 0.9300     |          |
| Co1—N1          | 2.1494 (18) |          | C11—H11       | 0.9300     |          |
| Co1—N3          | 2.1683 (18) |          | C11—C12       | 1.380 (3)  |          |
| Co1—N4          | 2.1584 (18) |          | C12—H12       | 0.9300     |          |
| Co2—O5          | 2.0770 (17) |          | C12—C13       | 1.380 (3)  |          |
| Co2—O5          | 2.0770 (17) |          | C13—C14       | 1.376 (3)  |          |
| Co2—O7          | 2.117 (2)   |          | C13—C16       | 1.479 (3)  |          |
| Co2—O7          | 2.117 (2)   |          | C14—H14       | 0.9300     |          |
| Co2—N2          | 2.1520 (19) |          | C14—C15       | 1.376 (3)  |          |
| Co2—N2          | 2.1519 (19) |          | C15—H15       | 0.9300     |          |
| Cl1—C24         | 1.747 (3)   |          | C16—C17       | 1.388 (3)  |          |
| Cl2—C31         | 1.751 (3)   |          | C16—C20       | 1.388 (3)  |          |
| Cl3—C38         | 1.749 (3)   |          | C17—H17       | 0.9300     |          |
| O1—C21          | 1.259 (3)   |          | C17—C18       | 1.380 (3)  |          |
| O2—C21          | 1.252 (3)   |          | C18—H18       | 0.9300     |          |
| O3—C28          | 1.268 (3)   |          | C19—H19       | 0.9300     |          |
| O4—C28          | 1.235 (3)   |          | C19—C20       | 1.372 (3)  |          |
| O5—C35          | 1.263 (3)   |          | C20—H20       | 0.9300     |          |
| O6—C35          | 1.247 (3)   |          | C21—C22       | 1.505 (3)  |          |
| O7—H7A          | 0.849 (17)  |          | C22—C23       | 1.383 (4)  |          |
| O7—H7B          | 0.848 (18)  |          | C22—C27       | 1.385 (4)  |          |
| O8—H8A          | 0.8200      |          | C23—H23       | 0.9300     |          |
| O8—C42          | 1.436 (9)   |          | C23—C24       | 1.380 (4)  |          |
| O8A—H8AA        | 0.8200      |          | C24—C25       | 1.366 (4)  |          |
| O8A—C42A        | 1.445 (17)  |          | C25—H25       | 0.9300     |          |
| N1—C1           | 1.330 (7)   |          | C25—C26       | 1.371 (5)  |          |
| N1—C5           | 1.332 (8)   |          | C26—H26       | 0.9300     |          |
| N1—C1A          | 1.348 (9)   |          | C26—C27       | 1.387 (4)  |          |
| N1—C5A          | 1.335 (10)  |          | C27—H27       | 0.9300     |          |
| N2—C8           | 1.331 (3)   |          | C28—C29       | 1.511 (3)  |          |
| N2—C9           | 1.329 (3)   |          | C29—C30       | 1.382 (3)  |          |
| N3—C11          | 1.334 (3)   |          | C29—C34       | 1.384 (3)  |          |
| N3—C15          | 1.325 (3)   |          | C30—H30       | 0.9300     |          |
| N4—C18          | 1.340 (3)   |          | C30—C31       | 1.377 (3)  |          |
| N4—C19          | 1.333 (3)   |          | C31—C32       | 1.375 (4)  |          |
| C1—H1           | 0.9300      |          | C32—H32       | 0.9300     |          |
| C1—C2           | 1.372 (7)   |          | C32—C33       | 1.375 (4)  |          |
| C2—H2           | 0.9300      |          | C33—H33       | 0.9300     |          |
| C2—C3           | 1.405 (6)   |          | C33—C34       | 1.383 (4)  |          |
| C4—H4           | 0.9300      |          | C34—H34       | 0.9300     |          |
| C4—C5           | 1.368 (8)   |          | C35—C36       | 1.518 (4)  |          |
| C4—C3           | 1.386 (8)   |          | C36—C37       | 1.387 (4)  |          |
| C5—H5           | 0.9300      |          | C36—C41       | 1.386 (4)  |          |
| C1A—H1A         | 0.9300      |          | C37—H37       | 0.9300     |          |
C1A—C2A 1.364 (10) C37—C38 1.387 (4)
C2A—H2A 0.9300 C38—C39 1.376 (5)
C2A—C3 1.388 (8) C39—H39 0.9300
C4A—H4A 0.9300 C40—C41 1.384 (4)
C4A—C5A 1.372 (11) C41—H41 0.9300
C4A—C3 1.388 (10) C40—C41 1.384 (4)
C5A—H5A 0.9300 C42—H42A 0.9600
C3—C6 1.482 (3) C42—H42B 0.9600
C6—C7 1.383 (3) C42—H42C 0.9600
C6—C10 1.381 (3) C42—H42D 0.9600
C7—H7 0.9300 C42A—H42E 0.9600
C7—C8 1.377 (3) C42A—H42F 0.9600
C8—H8 0.9300

O2—Co1—O1 59.88 (6) C11—C12—H12 120.0
O3—Co1—O1 179.75 (7) C13—C12—C11 119.9 (2)
O3—Co1—O2 119.93 (7) C13—C12—H12 123.1 (2)
O3—Co1—N1 91.08 (7) C14—C13—C12 116.3 (2)
O3—Co1—N3 91.04 (7) C14—C13—C16 120.6 (2)
N1—Co1—O1 89.24 (7) C15—C14—C13 120.0 (2)
N1—Co1—O2 89.12 (7) C15—C14—H14 120.0
N1—Co1—N4 90.81 (7) C15—C14—H14 120.0
N1—Co1—N3 90.81 (7) N3—C15—C14 124.1 (2)
N3—Co1—O1 88.80 (7) N3—C15—H15 117.9
N3—Co1—O2 89.10 (7) C14—C15—C16 117.9
N4—Co1—O1 90.91 (7) C14—C15—C16 122.6 (2)
N4—Co1—O2 87.24 (7) C14—C15—H15 117.9
N4—Co1—N3 175.93 (7) C14—C15—H15 117.9
O5—Co2—O5ii 180.0 C20—C16—C17 116.7 (2)
O5—Co2—O7ii 88.68 (8) C20—C16—C17 120.2
O5—Co2—O7iii 91.32 (8) C20—C16—C17 120.2
O5—Co2—O7 88.68 (8) C20—C16—C17 123.3 (2)
O5—Co2—O7 91.32 (8) C21—O1—Co1 118.4
O5—Co2—N2 91.93 (7) C19—C20—C16 118.4
O5—Co2—N2 91.93 (7) C19—C20—H20 118.4
O5—Co2—N2 88.07 (7) C19—C20—H20 123.4 (2)
O5—Co2—N2 88.07 (7) C19—C20—H20 118.3
O7—Co2—O7 180.00 (11) C16—C20—C19 118.3
O7—Co2—N2 93.42 (8) C16—C20—C19 120.0
O7—Co2—N2 93.42 (8) C16—C20—C19 120.0
O7—Co2—N2 86.58 (8) C16—C20—C19 120.0
O7—Co2—N2 86.58 (8) C16—C20—C19 120.0
O7—Co2—N2 86.58 (8) C16—C20—C19 119.0 (2)
O7—Co2—N2 93.42 (8) C16—C20—C19 121.1 (2)
N2—Co2—N2 180.0 C21—O1—Co1 119.8 (2)
C21—O1—Co1 88.42 (15) C23—C22—C21 119.3 (2)
C21—O2—Co1 90.38 (14) C23—C22—C21 119.4 (2)
C28—O3—Co1 120.99 (17) C27—C22—C21 121.2 (2)
C35—O5—Co2 129.83 (17) C22—C23—H23 120.2
| Bond or Angle | Value 1 | Value 2 | Value 3 |
|--------------|---------|---------|---------|
| Co2—O7—H7A  | 104 (2) |         |         |
| Co2—O7—H7B  | 125 (2) |         |         |
| H7A—O7—H7B  | 108 (3) |         |         |
| C42—O8—H8A  | 109.5   | 125 (2) | 120.3 (2) |
| C42A—O8A—H8AA | 109.5 |         |         |
| C1—N1—Co1   | 121.7 (3) | 119.0 (3) | 120.5 |
| C1—N1—C5    | 117.2 (5) |         |         |
| C5—N1—Co1   | 120.9 (4) |         |         |
| C1A—N1—Co1  | 124.4 (4) |         |         |
| C5A—N1—Co1  | 120.6 (5) |         |         |
| C5A—N1—C1A  | 115.0 (7) |         |         |
| C8—N2—Co2   | 123.55 (16) |         |         |
| C9—N2—Co2   | 119.64 (16) |         |         |
| C9—N2—C8    | 116.8 (2) | 120.2 |         |
| C11—N3—Co1  | 120.60 (15) | 116.0 (2) |         |
| C15—N3—Co1  | 123.58 (16) |         |         |
| C15—N3—C11  | 115.8 (2) | 119.6 (2) |         |
| C18—N4—Co1* | 119.07 (15) |         |         |
| C19—N4—Co1* | 123.78 (15) |         |         |
| C19—N4—C18  | 116.89 (19) |         |         |
| N1—C1—H1    | 118.9 | 120.3 |         |
| N1—C1—C2    | 122.3 (6) | 119.5 (2) |         |
| C2—C1—H1    | 118.9 |         |         |
| C1—C2—H2    | 119.5 | 119.4 (2) |         |
| C1—C2—C3    | 121.1 (5) | 119.0 (2) |         |
| C3—C2—H2    | 119.5 | 121.7 (3) |         |
| C5—C4—H4    | 120.0 | 120.8 |         |
| C5—C4—C3    | 120.1 (8) | 118.4 (3) |         |
| C3—C4—H4    | 120.0 | 120.8 |         |
| N1—C5—C4    | 124.0 (8) | 119.5 |         |
| N1—C5—H5    | 118.0 | 121.1 (3) |         |
| C4—C5—H5    | 118.0 | 119.5 |         |
| N1—C1A—H1A  | 117.6 | 120.1 |         |
| N1—C1A—C2A  | 124.7 (8) | 119.8 (3) |         |
| C2A—C1A—H1A | 117.6 | 120.1 |         |
| C1A—C2A—H2A | 120.5 | 116.0 (2) |         |
| C1A—C2A—C3  | 119.1 (8) | 126.2 (2) |         |
| C3—C2A—H2A  | 120.5 | 117.8 (2) |         |
| C5A—C4A—H4A | 119.7 | 120.0 (2) |         |
| C3—C4A—H4A  | 119.7 | 120.5 (3) |         |
| C3—C4A—C5A  | 120.7 (10) | 119.5 (3) |         |
| N1—C5A—C4A  | 123.7 (11) | 120.4 |         |
| N1—C5A—H5A  | 118.2 | 119.1 (3) |         |
| C4A—C5A—H5A | 118.2 | 120.4 |         |
| C2—C3—C6    | 123.2 (3) | 118.7 (3) |         |
| C4—C3—C2    | 115.1 (5) | 119.8 (2) |         |
| C4—C3—C6    | 121.6 (4) | 121.4 (3) |         |
| C2A—C3—C6   | 121.2 (4) | 120.4 |         |
| Bond/Angle | Value | Bond/Angle | Value |
|-----------|-------|-----------|-------|
| C4A—C3—C2A | 116.6 (6) | C40—C39—C38 | 119.3 (3) |
| C4A—C3—C6 | 121.9 (5) | C40—C39—H39 | 120.4 |
| C7—C6—C3 | 121.4 (2) | C39—C40—C41 | 120.2 (3) |
| C10—C6—C3 | 122.2 (2) | C39—C40—H40 | 119.9 |
| C10—C6—C7 | 116.5 (2) | C41—C40—H40 | 119.9 |
| C6—C7—H7 | 120.1 | C36—C41—C42 | 119.8 |
| C8—C7—C6 | 119.8 (2) | C40—C41—C42 | 120.5 (3) |
| C8—C7—H7 | 120.1 | C40—C41—H41 | 119.8 |
| N2—C8—C7 | 123.4 (2) | O8—C42—H42A | 109.5 |
| N2—C8—H8 | 118.3 | O8—C42—H42B | 109.5 |
| C7—C8—H8 | 118.3 | O8—C42—H42C | 109.5 |
| N2—C9—C10 | 123.4 (2) | H42A—C42—H42B | 109.5 |
| C10—C9—H9 | 118.3 | H42A—C42—H42C | 109.5 |
| C6—C10—C6 | 120.2 (2) | O8A—C42A—H42D | 109.5 |
| C9—C10—C6 | 119.9 | O8A—C42A—H42E | 109.5 |
| N3—C11—C12 | 123.7 (2) | H42D—C42A—H42E | 109.5 |
| C12—C11—H11 | 118.2 | C12—C13—C14—C15 | 4.2 (4) |
| Co1—O1—C21—O2 | 4.4 (2) | C5A—C4A—C3—C2A | 4.7 (12) |
| Co1—O1—C21—C22 | −173.47 (19) | C5A—C4A—C3—C6 | 178.9 (7) |
| Co1—O2—C21—O1 | −4.5 (2) | C3—C4—C5—N1 | 0.3 (10) |
| Co1—O2—C21—C22 | 173.37 (19) | C3—C4A—C5A—N1 | 0.0 (14) |
| Co1—O3—C28—C29 | −167.67 (15) | C3—C6—C7—C8 | −179.9 (2) |
| Co1—O3—C28—O4 | 10.1 (3) | C3—C6—C10—C9 | −180.0 (3) |
| Co1—N1—C1—C2 | −176.8 (4) | C6—C7—C8—N2 | 0.1 (4) |
| Co1—N1—C5—C4 | 178.0 (5) | C7—C6—C10—C9 | 0.1 (4) |
| Co1—N1—C1A—C2A | 179.2 (7) | C8—N2—C9—C10 | 0.5 (4) |
| Co1—N1—C5A—C4A | 179.0 (7) | C9—N2—C8—C7 | −0.4 (4) |
| Co1—N3—C11—C12 | 173.84 (19) | C10—C6—C7—C8 | 0.0 (4) |
| Co1—N3—C15—C14 | −173.5 (3) | C11—N3—C15—C14 | 3.8 (4) |
| Co1—N4—C10—C11 | 172.36 (19) | C11—C12—C13—C14 | 4.2 (4) |
| Co1—N4—C19—C20 | −172.32 (19) | C11—C12—C13—C16 | −175.8 (2) |
| Co2—O5—C35—O6 | 6.2 (4) | C12—C13—C14—C15 | −4.0 (4) |
| Co2—O5—C35—C36 | −173.12 (14) | C12—C13—C16—C17 | −31.6 (3) |
| Co2—N2—C8—C7 | 177.9 (2) | C12—C13—C16—C20 | 149.3 (2) |
| Co2—N2—C9—C10 | −177.8 (2) | C13—C14—C15—N3 | 0.0 (5) |
| C1—C24—C25—C26 | 179.2 (3) | C13—C16—C17—C18 | −176.3 (2) |
| C1—C21—C22—C23 | −179.1 (3) | C13—C16—C20—C19 | 176.0 (2) |
| C1—C21—C22—C27 | 178.5 (3) | C14—C13—C16—C17 | 148.4 (3) |
| C1—C21—C22—C23 | 5.0 (3) | C14—C13—C16—C20 | −30.7 (4) |
| O1—C21—C22—C23 | −178.3 (2) | C15—N3—C11—C12 | −3.6 (4) |
| O2—C21—C22—C27 | −172.9 (2) | C16—C13—C14—C15 | 176.0 (3) |
| O2—C21—C22—C23 | 3.8 (3) | C16—C17—C18—N4 | −0.3 (4) |
| O3—C28—C29—C30 | −2.4 (3) | C17—C16—C20—C19 | −3.1 (4) |
| O3—C28—C29—C34 | 176.1 (2) | C18—N4—C19—C20 | 1.8 (4) |
| Bond/Dihedral | Angle (deg) | Bond/Dihedral | Angle (deg) |
|--------------|-------------|--------------|-------------|
| O4—C28—C29—C30 | 179.7 (2) | C19—N4—C18—C17 | -2.1 (4) |
| O4—C28—C29—C34 | -1.7 (4) | C20—C16—C17—C18 | 2.9 (4) |
| O5—C35—C36—C37 | 3.5 (3) | C21—C22—C23—C24 | 175.2 (2) |
| O5—C35—C36—C41 | -176.3 (2) | C21—C22—C27—C26 | -175.9 (3) |
| O6—C35—C36—C37 | -175.9 (2) | C22—C23—C24—C11 | -178.1 (2) |
| O6—C35—C36—C41 | 4.3 (4) | C22—C23—C24—C25 | 1.2 (5) |
| N1—C1—C2—C3 | -2.6 (9) | C23—C22—C27—C26 | 0.8 (4) |
| N1—C1A—C2A—C3 | 3.5 (15) | C23—C22—C25—C26 | -0.2 (5) |
| N2—C9—C10—C6 | -0.4 (5) | C24—C25—C26—C27 | -0.6 (5) |
| N3—C11—C12—C13 | -0.4 (4) | C25—C26—C27—C22 | 0.2 (5) |
| N4—C19—C20—C16 | 0.8 (4) | C27—C22—C23—C24 | -1.5 (4) |
| C1—N1—C5—C4 | 2.8 (8) | C28—C29—C30—C31 | 178.6 (2) |
| C1—C2—C3—C4 | 5.3 (7) | C28—C29—C34—C33 | -178.2 (3) |
| C1—C2—C3—C6 | -177.8 (4) | C29—C30—C31—C12 | 179.59 (19) |
| C2—C3—C6—C7 | 18.7 (6) | C29—C30—C31—C32 | -1.1 (4) |
| C2—C3—C6—C10 | -161.2 (6) | C30—C29—C34—C33 | 0.3 (4) |
| C4—C3—C6—C7 | -164.7 (6) | C30—C31—C32—C33 | 1.6 (5) |
| C4—C3—C6—C10 | 15.5 (6) | C31—C32—C33—C34 | -1.1 (5) |
| C5—N1—C1—C2 | -1.6 (8) | C32—C33—C34—C29 | 0.2 (5) |
| C5—C4—C3—C2 | -4.2 (8) | C34—C29—C30—C31 | 0.1 (4) |
| C5—C4—C3—C6 | 178.9 (5) | C35—C36—C37—C38 | -179.6 (2) |
| C1A—N1—C5A—C4A | -3.0 (12) | C35—C36—C41—C40 | 179.6 (3) |
| C1A—C2A—C3—C4A | -6.2 (12) | C36—C37—C38—C13 | -178.55 (19) |
| C1A—C2A—C3—C6 | 179.5 (7) | C36—C37—C38—C39 | 0.0 (4) |
| C1A—C2A—C3—C7 | -16.8 (11) | C37—C36—C41—C40 | -0.2 (4) |
| C2A—C3—C6—C7 | 163.3 (11) | C37—C38—C39—C40 | -0.1 (5) |
| C4A—C3—C6—C7 | 169.2 (8) | C38—C39—C40—C41 | 0.0 (5) |
| C4A—C3—C6—C10 | -10.7 (9) | C39—C40—C41—C36 | 0.2 (5) |
| C5A—N1—C1A—C2A | 1.2 (12) | C41—C36—C37—C38 | 0.1 (4) |

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

Hydrogen-bond geometry (Å, °)

| Bond/Dihedral | D—H···A | D—H | H···A | D···A | D—H···A |
|--------------|---------|------|------|-------|---------|
| O7—H7A···O6ii | 0.85 (2) | 1.84 (2) | 2.648 (3) | 158 (3) |
| O7—H7B···O8iv | 0.85 (2) | 1.93 (2) | 2.777 (10) | 177 (3) |
| O7—H7B···O8Aiv | 0.85 (2) | 1.88 (4) | 2.72 (3) | 168 (3) |
| O8—H8A···O4 | 0.82 | 1.90 | 2.708 (10) | 169 |
| O8A—H8A···O4 | 0.82 | 2.04 | 2.67 (3) | 133 |
| C1—H1···O3 | 0.93 | 2.59 | 3.102 (7) | 115 |
| C5—H5···O1 | 0.93 | 2.48 | 3.057 (9) | 121 |
| C14—H14···O3 | 0.93 | 2.52 | 3.088 (9) | 120 |
| C5A—H5A···O1 | 0.93 | 2.33 | 2.991 (12) | 128 |
| C9—H9···O5 | 0.93 | 2.71 | 3.189 (3) | 113 |
| C11—H11···O2 | 0.93 | 2.57 | 3.084 (3) | 115 |
|          |        |        |        |        |
|----------|--------|--------|--------|--------|
| C15—H15···N1 | 0.93   | 2.60   | 3.198 (4) | 123    |
| C26—H26···O6<sup>v</sup> | 0.93   | 2.60   | 3.524 (4) | 176    |

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