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Crystal structure of *trans*-diaquabis(4-cyano-benzoato- κ O)bis(nicotinamide- κ N¹)cobalt(II)

Gülçin Şefiye Aşkın,^a Hacali Necefoğlu,^{b,c} Gamze Yılmaz Nayir,^b Raziye Çatak Çelik^d and Tuncer Hökelek^{a*}

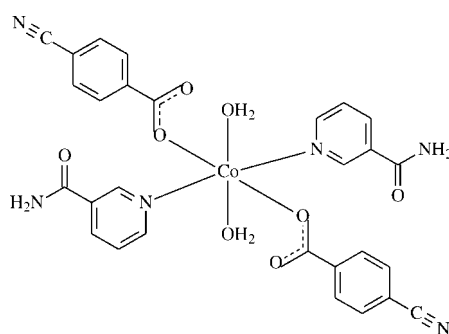
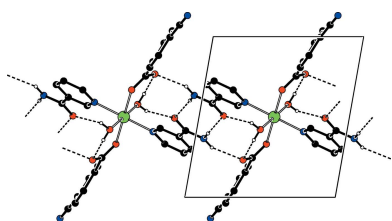
^aDepartment of Physics, Hacettepe University, 06800 Beytepe, Ankara, Turkey, ^bDepartment of Chemistry, Kafkas University, 36100 Kars, Turkey, ^cInternational Scientific Research Centre, Baku State University, 1148 Baku, Azerbaijan, and ^dScientific and Technological Application and Research Center, Aksaray University, 68100 Aksaray, Turkey.

*Correspondence e-mail: merzifon@hacettepe.edu.tr

In the title complex, [Co(C₈H₄NO₂)₂(C₆H₆N₂O)₂(H₂O)₂], the Co^{II} atom is located on an inversion centre and is coordinated by two 4-cyanobenzoate (CNB) anions, two nicotinamide (NA) ligands and two water molecules. The four O atoms in the equatorial plane form a slightly distorted square-planar arrangement, while the slightly distorted octahedral coordination sphere is completed by the two N atoms of the NA ligands in the axial positions. The dihedral angle between the carboxylate group and the adjacent benzene ring is 22.11 (15)°, while the pyridine and benzene rings are oriented at a dihedral angle of 89.98 (5)°. In the crystal, intermolecular N—H...O and O—H...O hydrogen bonds link the molecules, enclosing *R*₂²(8) and *R*₄⁴(8) ring motifs, forming layers parallel to (100). The layers are linked *via* C—H...O and C—H...N hydrogen bonds, resulting in a three-dimensional network. A weak C—H... π interaction is also observed.

1. Chemical context

Nicotinamide (NA) is one form of niacin. A deficiency of this vitamin leads to loss of copper from the body, known as pellagra disease. Victims of pellagra show unusually high serum and urinary copper levels (Krishnamachari, 1974). The nicotinic acid derivative *N,N*-diethylnicotinamide (DENA) is an important respiratory stimulant (Bigoli *et al.*, 1972). Transition metal complexes with biochemical-relevant molecules show interesting physical and/or chemical properties, through which they may find applications in biological systems (Antolini *et al.*, 1982). Some benzoic acid derivatives, such as 4-aminobenzoic acid, have been extensively reported in coordination chemistry, as bifunctional organic ligands, due to the varieties of their coordination modes (Chen & Chen, 2002; Amiraslanov *et al.*, 1979; Hauptmann *et al.*, 2000).



The structure–function–coordination relationships of the arylcarboxylate ion in Zn^{II} complexes of benzoic acid

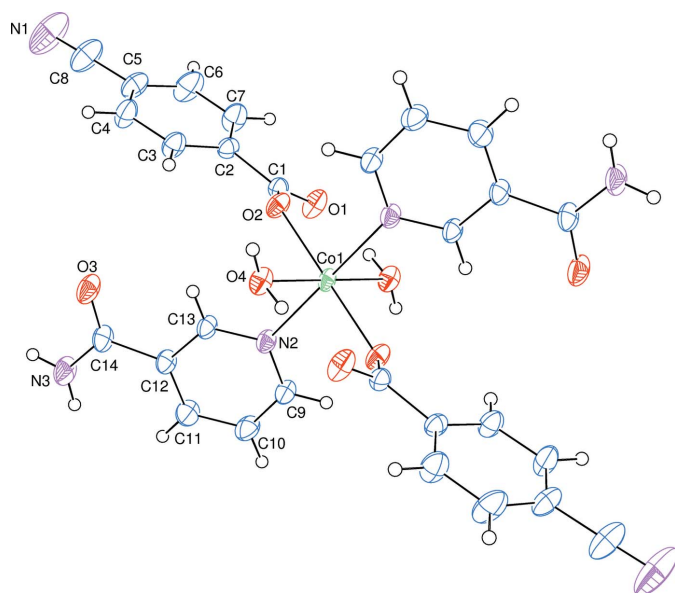


Figure 1
The molecular structure of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Symmetry-related atoms are defined by symmetry code $-x + 1, -y + 1, -z + 1$.

derivatives change depending on the nature and position of the substituted groups on the benzene ring, the nature of the additional ligand molecule or solvent, and the pH and temperature of synthesis (Shnulin *et al.*, 1981; Nadzhafov *et al.*, 1981; Antsyshkina *et al.*, 1980; Adiwidjaja *et al.*, 1978). When pyridine and its derivatives are used instead of water molecules, the structure is completely different (Catterick *et al.*, 1974). In this context, we synthesized the Co^{II} -containing title compound, *trans*-diaquabis(4-cyanobenzoato- κO)bis(nicotinamide- κN^1)cobalt(II), $[\text{Co}(\text{C}_8\text{H}_4\text{O}_2\text{N})_2(\text{C}_6\text{H}_6\text{N}_2\text{O})_2(\text{H}_2\text{O})_2]$, and report herein its crystal structure.

2. Structural commentary

In the mononuclear title complex, the Co^{II} atom is located on an inversion centre and is coordinated by two 4-cyanobenzoate (CNB) anions, two nicotinamide (NA) ligands and two water molecules, with all ligands coordinating in a monodentate manner (Fig. 1).

The two symmetry-related carboxylate O atoms (O2 and O2ⁱ) and the two symmetry-related water O atoms (O4 and O4ⁱ) form a slightly distorted square-planar arrangement, while the slightly distorted octahedral coordination sphere is completed by the two symmetry-related N atoms (N2 and N2ⁱ) of the two NA ligands in the axial positions [symmetry code: (i) $-x + 1, -y + 1, -z + 1$] (Fig. 1).

The very similar C1–O1 [1.254 (2) Å] and C1–O2 [1.256 (2) Å], bond lengths of the carboxylate group indicate delocalized bonding arrangements, rather than localized single and double bonds. The Co–O bond lengths are 2.0835 (12) Å (for benzoate oxygen atoms) and 2.1350 (13) Å (for water oxygen atoms), and the Co–N bond length is 2.1390 (15) Å, close to standard values. The Co1 atom lies 0.3921 (1) Å above

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

Cg2 is the centroid of the C9–C13, N2 ring.

| $D\text{---}H\cdots A$ | $D\text{---}H$ | $H\cdots A$ | $D\cdots A$ | $D\text{---}H\cdots A$ |
|--|----------------|-------------|-------------|------------------------|
| N3–H31 ⁱ ···O3 ⁱ | 0.84 (3) | 2.09 (3) | 2.914 (3) | 166 (3) |
| N3–H32 ⁱ ···O1 ⁱⁱ | 0.87 (3) | 2.13 (3) | 2.910 (3) | 148 (3) |
| O4–H41 ⁱ ···O1 ⁱⁱⁱ | 0.85 (3) | 1.82 (3) | 2.658 (2) | 166 (3) |
| O4–H42 ⁱ ···O3 ^{iv} | 0.80 (3) | 2.11 (3) | 2.877 (2) | 161 (2) |
| C4–H4 ⁱ ···O1 ^v | 0.93 | 2.38 | 3.302 (3) | 173 |
| C9–H9 ⁱ ···N1 ^{vi} | 0.93 | 2.54 | 3.305 (5) | 140 |
| C6–H6 ⁱ ···Cg2 ^{vii} | 0.93 | 2.76 | 3.691 (2) | 176 |

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

the planar (O1/O2/C1) carboxylate group. The O–Co–O and O–Co–N bond angles deviate only slightly from ideal values, with average values of 90 (3)° and 90 (2)°, respectively.

The dihedral angle between the planar carboxylate group (O1/O2/C1) and the adjacent benzene ring [A (C2–C7)] is 22.11 (15)°, while the benzene and pyridine [B (N2/C9–C13)] rings are oriented at a dihedral angle of 89.98 (5)°.

3. Supramolecular features

In the crystal, $\text{N}\text{---}\text{H}\cdots\text{O}_c$ (c = carboxylate), $\text{N}\text{---}\text{H}\cdots\text{O}_n$ (n = nicotinamide), $\text{O}\text{---}\text{H}_w\cdots\text{O}_c$ (w = water) and $\text{O}\text{---}\text{H}_w\cdots\text{O}_n$ hydrogen bonds (Table 1) link the molecules, enclosing $R_2^2(8)$ and $R_4^4(8)$ ring motifs (Bernstein *et al.*, 1995), forming layers parallel to (100) (Fig. 2). The layers are linked *via* $\text{C}\text{---}\text{H}_{\text{cnb}}\cdots\text{O}_c$ (cnb = cyanobenzoate) and $\text{C}\text{---}\text{H}_n\cdots\text{N}_{\text{cnb}}$ hydrogen bonds (Table 1), resulting in a three-dimensional network. A weak $\text{C}\text{---}\text{H}\cdots\pi$ interaction is also observed.

4. Synthesis and crystallization

The title compound was prepared by the reaction of $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ (1.41 g, 5 mmol) in H_2O (50 ml) and nicotinamide (1.22 g, 50 mmol) in H_2O (50 ml) with sodium 4-cyano-

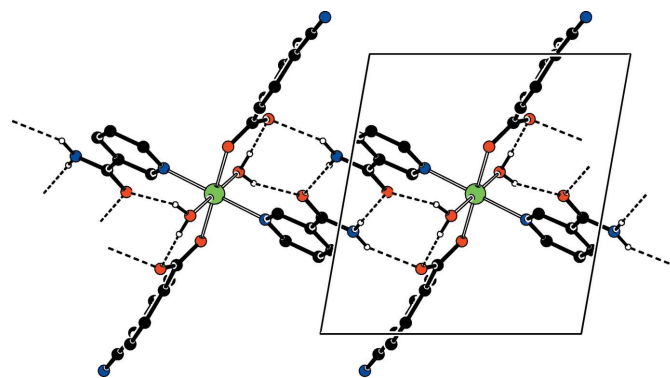


Figure 2
Part of the crystal structure viewed down [100], where the b axis is horizontal and the c axis is vertical. Intermolecular $\text{N}\text{---}\text{H}\cdots\text{O}$ and $\text{O}\text{---}\text{H}\cdots\text{O}$ hydrogen bonds are shown as dashed lines. Non-bonding H atoms have been omitted for clarity.

benzoate (1.69 g, 10 mmol) in H₂O (100 ml). The mixture was filtered and set aside to crystallize at ambient temperature for several days, giving pink-coloured single crystals.

5. Refinement

The experimental details including the crystal data, data collection and refinement are summarized in Table 2. Atoms H31 and H32 (for NH₂) and H41 and H42 (for H₂O) were located in a difference Fourier map and were refined freely. The aromatic C-bound H atoms were positioned geometrically with C–H = 0.93 Å, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The highest electron density and the deepest hole were found 0.80 Å and 0.83 Å, respectively, from Co1.

Acknowledgements

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References

- Adiwidjaja, G., Rossmannith, E. & Küppers, H. (1978). *Acta Cryst.* **B34**, 3079–3083.
- Amiraslanov, I. R., Mamedov, Kh. S., Movsumov, E. M., Musaev, F. N. & Nadzhafov, G. N. (1979). *Zh. Strukt. Khim.* **20**, 1075–1080.
- Antolini, L., Battaglia, L. P., Corradi, A. B., Marcotrigiano, G., Menabue, L., Pellacani, G. C. & Saladini, M. (1982). *Inorg. Chem.* **21**, 1391–1395.
- Antsyshkina, A. S., Chiragov, F. M. & Poray-Koshits, M. A. (1980). *Koord. Khim.* **15**, 1098–1103.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N. L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bigoli, F., Braibanti, A., Pellinghelli, M. A. & Tiripicchio, A. (1972). *Acta Cryst.* **B28**, 962–966.
- Bruker (2012). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc. Madison, Wisconsin, USA.
- Catterick, J., Hursthouse, M. B., New, D. B. & Thornton, P. (1974). *J. Chem. Soc. Chem. Commun.* pp. 843–844.
- Chen, H. J. & Chen, X. M. (2002). *Inorg. Chim. Acta*, **329**, 13–21.

Table 2
Experimental details.

| | |
|--|---|
| Crystal data | |
| Chemical formula | [Co(C ₈ H ₄ NO ₂) ₂ (C ₆ H ₆ N ₂ O) ₂ ·(H ₂ O) ₂] |
| M_r | 631.46 |
| Crystal system, space group | Triclinic, $P\bar{1}$ |
| Temperature (K) | 296 |
| a, b, c (Å) | 7.6474 (3), 9.9266 (4), 10.2782 (4) |
| α, β, γ (°) | 78.680 (2), 84.200 (3), 71.556 (2) |
| V (Å ³) | 725.13 (5) |
| Z | 1 |
| Radiation type | Mo $K\alpha$ |
| μ (mm ⁻¹) | 0.65 |
| Crystal size (mm) | 0.43 × 0.29 × 0.16 |
| Data collection | |
| Diffractometer | Bruker SMART BREEZE CCD |
| Absorption correction | Multi-scan (<i>SADABS</i> ; Bruker, 2012) |
| $T_{\text{min}}, T_{\text{max}}$ | 0.797, 0.901 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 16533, 3639, 3419 |
| R_{int} | 0.036 |
| $(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹) | 0.672 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)], wR(F^2), S$ | 0.044, 0.119, 1.07 |
| No. of reflections | 3639 |
| No. of parameters | 212 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³) | 0.94, -0.49 |

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012) and *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Hauptmann, R., Kondo, M. & Kitagawa, S. (2000). *Z. Kristallogr. New Cryst. Struct.* **215**, 169–172.
- Krishnamachari, K. A. V. R. (1974). *Am. J. Clin. Nutr.* **27**, 108–111.
- Nadzhafov, G. N., Shnulin, A. N. & Mamedov, Kh. S. (1981). *Zh. Strukt. Khim.* **22**, 124–128.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Shnulin, A. N., Nadzhafov, G. N., Amiraslanov, I. R., Usabaliev, B. T. & Mamedov, Kh. S. (1981). *Koord. Khim.* **7**, 1409–1416.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.

supporting information

Acta Cryst. (2015). E71, 561-563 [https://doi.org/10.1107/S2056989015008270]

Crystal structure of *trans*-diaquabis(4-cyanobenzoato- κ O)bis(nicotinamide- κ N¹)cobalt(II)

Gülçin Şefiye Aşkın, Hacali Necefoğlu, Gamze Yılmaz Nayir, Raziye Çatak Çelik and Tuncer Hökelek

Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINTE* (Bruker, 2012); data reduction: *SAINTE* (Bruker, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

trans-Diaquabis(4-cyanobenzoato- κ O)bis(nicotinamide- κ N¹)cobalt(II)

Crystal data

[Co(C₈H₄NO₂)₂(C₆H₆N₂O)₂(H₂O)₂]

$M_r = 631.46$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 7.6474$ (3) Å

$b = 9.9266$ (4) Å

$c = 10.2782$ (4) Å

$\alpha = 78.680$ (2)°

$\beta = 84.200$ (3)°

$\gamma = 71.556$ (2)°

$V = 725.13$ (5) Å³

$Z = 1$

$F(000) = 325$

$D_x = 1.446$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9898 reflections

$\theta = 2.2$ – 28.6 °

$\mu = 0.65$ mm⁻¹

$T = 296$ K

Prism, translucent light pink

$0.43 \times 0.29 \times 0.16$ mm

Data collection

Bruker SMART BREEZE CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2012)

$T_{\min} = 0.797$, $T_{\max} = 0.901$

16533 measured reflections

3639 independent reflections

3419 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 28.6$ °, $\theta_{\min} = 2.0$ °

$h = -10 \rightarrow 10$

$k = -12 \rightarrow 13$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

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

$wR(F^2) = 0.119$

$S = 1.07$

3639 reflections

212 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: inferred from neighbouring sites
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0721P)^2 + 0.2871P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.94 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.49 \text{ e } \text{\AA}^{-3}$

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| Co1 | 0.5000 | 0.5000 | 0.5000 | 0.02573 (12) |
| O1 | 0.6366 (2) | 0.34341 (18) | 0.23257 (16) | 0.0459 (4) |
| O2 | 0.38784 (18) | 0.47948 (14) | 0.33110 (13) | 0.0347 (3) |
| O3 | 0.0668 (2) | 0.16139 (15) | 0.50697 (18) | 0.0476 (4) |
| O4 | 0.22430 (19) | 0.57799 (15) | 0.57811 (16) | 0.0362 (3) |
| H41 | 0.250 (4) | 0.608 (3) | 0.644 (3) | 0.064 (9)* |
| H42 | 0.147 (4) | 0.643 (3) | 0.538 (2) | 0.038 (6)* |
| N1 | -0.0584 (5) | 0.1958 (4) | -0.1318 (4) | 0.1083 (13) |
| N2 | 0.4952 (2) | 0.28815 (16) | 0.59167 (15) | 0.0303 (3) |
| N3 | 0.1614 (3) | -0.0568 (2) | 0.6345 (2) | 0.0473 (5) |
| H31 | 0.080 (4) | -0.079 (3) | 0.602 (3) | 0.063 (9)* |
| H32 | 0.238 (4) | -0.121 (3) | 0.690 (3) | 0.054 (8)* |
| C1 | 0.4662 (2) | 0.40272 (19) | 0.24567 (17) | 0.0300 (3) |
| C2 | 0.3451 (2) | 0.37166 (19) | 0.15590 (17) | 0.0298 (3) |
| C3 | 0.1622 (3) | 0.3852 (2) | 0.19215 (19) | 0.0382 (4) |
| H3 | 0.1098 | 0.4240 | 0.2675 | 0.046* |
| C4 | 0.0562 (3) | 0.3414 (3) | 0.1171 (2) | 0.0457 (5) |
| H4 | -0.0661 | 0.3486 | 0.1430 | 0.055* |
| C5 | 0.1336 (3) | 0.2869 (3) | 0.0037 (2) | 0.0458 (5) |
| C6 | 0.3143 (4) | 0.2788 (3) | -0.0368 (2) | 0.0570 (7) |
| H6 | 0.3641 | 0.2460 | -0.1152 | 0.068* |
| C7 | 0.4203 (3) | 0.3198 (3) | 0.0398 (2) | 0.0470 (5) |
| H7 | 0.5424 | 0.3126 | 0.0137 | 0.056* |
| C8 | 0.0255 (4) | 0.2372 (4) | -0.0727 (3) | 0.0680 (8) |
| C9 | 0.6293 (2) | 0.1956 (2) | 0.66831 (19) | 0.0339 (4) |
| H9 | 0.7280 | 0.2252 | 0.6841 | 0.041* |
| C10 | 0.6261 (3) | 0.0585 (2) | 0.7244 (2) | 0.0428 (5) |
| H10 | 0.7210 | -0.0033 | 0.7772 | 0.051* |
| C11 | 0.4798 (3) | 0.0138 (2) | 0.7013 (2) | 0.0419 (4) |
| H11 | 0.4756 | -0.0786 | 0.7379 | 0.050* |

| | | | | |
|-----|------------|--------------|--------------|------------|
| C12 | 0.3394 (2) | 0.10851 (18) | 0.62286 (18) | 0.0307 (4) |
| C13 | 0.3539 (2) | 0.24444 (18) | 0.57084 (18) | 0.0304 (3) |
| H13 | 0.2601 | 0.3088 | 0.5185 | 0.037* |
| C14 | 0.1776 (3) | 0.07268 (19) | 0.5848 (2) | 0.0352 (4) |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|---------------|---------------|---------------|
| Co1 | 0.02515 (17) | 0.02306 (18) | 0.03406 (19) | -0.01019 (12) | -0.00572 (12) | -0.00978 (12) |
| O1 | 0.0315 (7) | 0.0592 (9) | 0.0516 (8) | -0.0103 (6) | -0.0066 (6) | -0.0234 (7) |
| O2 | 0.0355 (6) | 0.0333 (6) | 0.0400 (7) | -0.0084 (5) | -0.0111 (5) | -0.0157 (5) |
| O3 | 0.0445 (8) | 0.0303 (7) | 0.0743 (11) | -0.0156 (6) | -0.0241 (7) | -0.0061 (7) |
| O4 | 0.0290 (6) | 0.0348 (7) | 0.0464 (8) | -0.0075 (5) | -0.0060 (6) | -0.0120 (6) |
| N1 | 0.104 (2) | 0.126 (3) | 0.121 (3) | -0.030 (2) | -0.052 (2) | -0.065 (2) |
| N2 | 0.0304 (7) | 0.0275 (7) | 0.0370 (7) | -0.0115 (6) | -0.0065 (6) | -0.0082 (6) |
| N3 | 0.0515 (11) | 0.0305 (8) | 0.0691 (13) | -0.0229 (8) | -0.0187 (9) | -0.0046 (8) |
| C1 | 0.0332 (8) | 0.0290 (8) | 0.0312 (8) | -0.0130 (7) | -0.0068 (6) | -0.0040 (6) |
| C2 | 0.0342 (8) | 0.0291 (8) | 0.0288 (8) | -0.0102 (7) | -0.0060 (6) | -0.0078 (6) |
| C3 | 0.0361 (9) | 0.0491 (11) | 0.0349 (9) | -0.0137 (8) | -0.0023 (7) | -0.0184 (8) |
| C4 | 0.0368 (10) | 0.0620 (14) | 0.0475 (11) | -0.0207 (9) | -0.0054 (8) | -0.0196 (10) |
| C5 | 0.0500 (11) | 0.0505 (12) | 0.0437 (11) | -0.0140 (9) | -0.0159 (9) | -0.0190 (9) |
| C7 | 0.0396 (10) | 0.0679 (15) | 0.0403 (10) | -0.0181 (10) | 0.0037 (8) | -0.0253 (10) |
| C6 | 0.0523 (13) | 0.0836 (18) | 0.0428 (11) | -0.0148 (12) | -0.0034 (9) | -0.0377 (12) |
| C8 | 0.0649 (16) | 0.0794 (19) | 0.0706 (17) | -0.0168 (14) | -0.0256 (13) | -0.0357 (15) |
| C9 | 0.0295 (8) | 0.0345 (9) | 0.0404 (9) | -0.0108 (7) | -0.0076 (7) | -0.0083 (7) |
| C10 | 0.0382 (10) | 0.0349 (10) | 0.0529 (12) | -0.0071 (8) | -0.0171 (8) | -0.0012 (8) |
| C11 | 0.0456 (11) | 0.0248 (8) | 0.0561 (12) | -0.0123 (8) | -0.0133 (9) | -0.0006 (8) |
| C12 | 0.0331 (8) | 0.0241 (8) | 0.0395 (9) | -0.0111 (6) | -0.0046 (7) | -0.0106 (7) |
| C13 | 0.0311 (8) | 0.0240 (7) | 0.0399 (9) | -0.0104 (6) | -0.0091 (7) | -0.0069 (7) |
| C14 | 0.0361 (9) | 0.0270 (8) | 0.0490 (10) | -0.0139 (7) | -0.0043 (7) | -0.0133 (7) |

Geometric parameters (Å, °)

| | | | |
|---------------------|-------------|---------|-----------|
| Co1—O2 | 2.0835 (12) | C2—C7 | 1.391 (3) |
| Co1—O2 ⁱ | 2.0835 (12) | C3—C4 | 1.387 (3) |
| Co1—O4 | 2.1350 (13) | C3—H3 | 0.9300 |
| Co1—O4 ⁱ | 2.1350 (13) | C4—C5 | 1.381 (3) |
| Co1—N2 | 2.1390 (15) | C4—H4 | 0.9300 |
| Co1—N2 ⁱ | 2.1390 (15) | C5—C6 | 1.384 (4) |
| O1—C1 | 1.254 (2) | C5—C8 | 1.444 (3) |
| O2—C1 | 1.256 (2) | C6—H6 | 0.9300 |
| O3—C14 | 1.234 (2) | C7—C6 | 1.380 (3) |
| O4—H41 | 0.85 (3) | C7—H7 | 0.9300 |
| O4—H42 | 0.80 (3) | C9—C10 | 1.378 (3) |
| N1—C8 | 1.136 (4) | C9—H9 | 0.9300 |
| N2—C9 | 1.341 (2) | C10—H10 | 0.9300 |
| N2—C13 | 1.335 (2) | C11—C10 | 1.383 (3) |
| N3—C14 | 1.326 (3) | C11—H11 | 0.9300 |

| | | | |
|--------------------------------------|--------------|-------------|--------------|
| N3—H31 | 0.84 (3) | C12—C11 | 1.388 (3) |
| N3—H32 | 0.87 (3) | C12—C13 | 1.385 (2) |
| C1—C2 | 1.506 (2) | C12—C14 | 1.497 (2) |
| C2—C3 | 1.381 (3) | C13—H13 | 0.9300 |
| O2—Co1—O2 ⁱ | 180.0 | C4—C3—H3 | 119.7 |
| O2—Co1—O4 | 87.59 (6) | C3—C4—H4 | 120.3 |
| O2 ⁱ —Co1—O4 | 92.41 (6) | C5—C4—C3 | 119.5 (2) |
| O2—Co1—O4 ⁱ | 92.41 (6) | C5—C4—H4 | 120.3 |
| O2 ⁱ —Co1—O4 ⁱ | 87.59 (6) | C4—C5—C6 | 120.46 (19) |
| O4—Co1—O4 ⁱ | 180.000 (1) | C4—C5—C8 | 119.7 (2) |
| O2—Co1—N2 | 89.99 (6) | C6—C5—C8 | 119.8 (2) |
| O2 ⁱ —Co1—N2 | 90.01 (5) | C5—C6—H6 | 120.1 |
| O2—Co1—N2 ⁱ | 90.01 (5) | C7—C6—C5 | 119.8 (2) |
| O2 ⁱ —Co1—N2 ⁱ | 89.99 (6) | C7—C6—H6 | 120.1 |
| O4—Co1—N2 | 87.40 (6) | C2—C7—H7 | 119.9 |
| O4 ⁱ —Co1—N2 | 92.60 (6) | C6—C7—C2 | 120.3 (2) |
| O4—Co1—N2 ⁱ | 92.60 (6) | C6—C7—H7 | 119.9 |
| O4 ⁱ —Co1—N2 ⁱ | 87.40 (6) | N1—C8—C5 | 178.9 (4) |
| N2 ⁱ —Co1—N2 | 180.00 (4) | N2—C9—C10 | 122.33 (17) |
| C1—O2—Co1 | 127.68 (11) | N2—C9—H9 | 118.8 |
| Co1—O4—H41 | 97 (2) | C10—C9—H9 | 118.8 |
| Co1—O4—H42 | 122.7 (18) | C9—C10—C11 | 119.16 (17) |
| H42—O4—H41 | 107 (3) | C9—C10—H10 | 120.4 |
| C9—N2—Co1 | 123.03 (12) | C11—C10—H10 | 120.4 |
| C13—N2—Co1 | 118.91 (12) | C10—C11—C12 | 119.24 (18) |
| C13—N2—C9 | 118.05 (16) | C10—C11—H11 | 120.4 |
| C14—N3—H31 | 116 (2) | C12—C11—H11 | 120.4 |
| C14—N3—H32 | 123.3 (19) | C11—C12—C14 | 124.94 (17) |
| H32—N3—H31 | 120 (3) | C13—C12—C11 | 117.65 (16) |
| O1—C1—O2 | 125.70 (17) | C13—C12—C14 | 117.35 (16) |
| O1—C1—C2 | 116.72 (16) | N2—C13—C12 | 123.58 (16) |
| O2—C1—C2 | 117.48 (15) | N2—C13—H13 | 118.2 |
| C3—C2—C1 | 120.48 (16) | C12—C13—H13 | 118.2 |
| C3—C2—C7 | 119.43 (17) | O3—C14—N3 | 122.08 (18) |
| C7—C2—C1 | 119.95 (17) | O3—C14—C12 | 119.90 (17) |
| C2—C3—C4 | 120.52 (18) | N3—C14—C12 | 118.00 (18) |
| C2—C3—H3 | 119.7 | | |
| O4—Co1—O2—C1 | -159.74 (16) | O2—C1—C2—C7 | 163.80 (19) |
| O4 ⁱ —Co1—O2—C1 | 20.26 (16) | C1—C2—C3—C4 | -172.77 (19) |
| N2—Co1—O2—C1 | -72.35 (16) | C7—C2—C3—C4 | 2.9 (3) |
| N2 ⁱ —Co1—O2—C1 | 107.65 (16) | C1—C2—C7—C6 | 174.2 (2) |
| O2—Co1—N2—C9 | 141.91 (15) | C3—C2—C7—C6 | -1.6 (4) |
| O2 ⁱ —Co1—N2—C9 | -38.09 (15) | C2—C3—C4—C5 | -1.5 (4) |
| O2—Co1—N2—C13 | -37.22 (14) | C3—C4—C5—C6 | -1.4 (4) |
| O2 ⁱ —Co1—N2—C13 | 142.78 (14) | C3—C4—C5—C8 | 178.2 (2) |
| O4—Co1—N2—C9 | -130.50 (15) | C4—C5—C6—C7 | 2.8 (4) |

| | | | |
|-----------------------------|--------------|-----------------|--------------|
| O4 ⁱ —Co1—N2—C9 | 49.50 (15) | C8—C5—C6—C7 | -176.8 (3) |
| O4—Co1—N2—C13 | 50.36 (14) | C2—C7—C6—C5 | -1.3 (4) |
| O4 ⁱ —Co1—N2—C13 | -129.64 (14) | N2—C9—C10—C11 | 0.0 (3) |
| Co1—O2—C1—O1 | -13.7 (3) | C12—C11—C10—C9 | -0.4 (3) |
| Co1—O2—C1—C2 | 162.49 (12) | C13—C12—C11—C10 | 0.2 (3) |
| Co1—N2—C9—C10 | -178.63 (15) | C14—C12—C11—C10 | 177.2 (2) |
| C13—N2—C9—C10 | 0.5 (3) | C11—C12—C13—N2 | 0.3 (3) |
| Co1—N2—C13—C12 | 178.47 (14) | C14—C12—C13—N2 | -176.86 (17) |
| C9—N2—C13—C12 | -0.7 (3) | C11—C12—C14—O3 | -174.9 (2) |
| O1—C1—C2—C3 | 156.08 (19) | C11—C12—C14—N3 | 3.4 (3) |
| O1—C1—C2—C7 | -19.6 (3) | C13—C12—C14—O3 | 2.1 (3) |
| O2—C1—C2—C3 | -20.5 (3) | C13—C12—C14—N3 | -179.63 (19) |

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

Hydrogen-bond geometry (\AA , $^\circ$)

Cg2 is the centroid of the C9—C13,N2 ring.

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|----------|-------------|-------------|---------------|
| N3—H31 \cdots O3 ⁱⁱ | 0.84 (3) | 2.09 (3) | 2.914 (3) | 166 (3) |
| N3—H32 \cdots O1 ⁱⁱⁱ | 0.87 (3) | 2.13 (3) | 2.910 (3) | 148 (3) |
| O4—H41 \cdots O1 ⁱ | 0.85 (3) | 1.82 (3) | 2.658 (2) | 166 (3) |
| O4—H42 \cdots O3 ^{iv} | 0.80 (3) | 2.11 (3) | 2.877 (2) | 161 (2) |
| C4—H4 \cdots O1 ^v | 0.93 | 2.38 | 3.302 (3) | 173 |
| C9—H9 \cdots N1 ^{vi} | 0.93 | 2.54 | 3.305 (5) | 140 |
| C6—H6 \cdots Cg2 ^{vii} | 0.93 | 2.76 | 3.691 (2) | 176 |

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