

Poly[1,4-bis(4-pyridylmethyl)piperazine-dium [[tetraaquacobaltate(II)]- μ -pyromellitate- $\kappa^2 O^1:O^4$] dihydrate]

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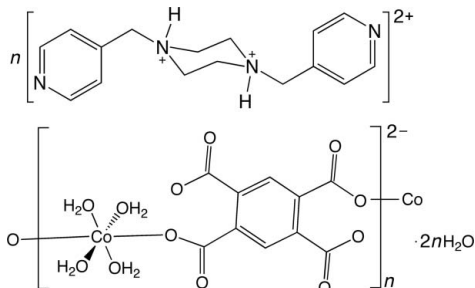
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Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.050; wR factor = 0.153; data-to-parameter ratio = 12.9.

In the title compound, $\{(\text{C}_{16}\text{H}_{22}\text{N}_4)[\text{Co}(\text{C}_{10}\text{H}_2\text{O}_8)(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}\}_n$, the octahedrally coordinated Co^{II} atom is situated on an inversion center and possesses four aqua ligands. The Co atoms are linked into an anionic coordination polymer chain by bis-monodentate pyromellitate ligands. The chain motifs are connected into a supramolecular layer by hydrogen bonding mediated by uncoordinated water molecules. Charge balance is provided by doubly protonated bis(4-pyridylmethyl)piperazine units, which are anchored to the coordination polymer chain motifs by $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonding.

Related literature

For some divalent cobalt pyromellitate coordination polymers containing dipyridyl ligands, see: Majumder *et al.* (2006). For the preparation of bis(4-pyridylmethyl)piperazine, see: Pocić *et al.* (2005).



Experimental

Crystal data

 $(\text{C}_{16}\text{H}_{22}\text{N}_4)[\text{Co}(\text{C}_{10}\text{H}_2\text{O}_8)(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$
 $M_r = 687.52$
Triclinic, $P\bar{1}$
 $a = 7.278$ (2) Å
 $b = 9.752$ (3) Å
 $c = 11.257$ (3) Å
 $\alpha = 66.733$ (3)°
 $\beta = 75.168$ (3)°
 $\gamma = 83.359$ (3)°

 $V = 709.5$ (3) Å³
 $Z = 1$
Mo $K\alpha$ radiation
 $\mu = 0.69$ mm⁻¹
 $T = 173$ K
 $0.24 \times 0.14 \times 0.10$ mm

Data collection

 Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.853$, $T_{\text{max}} = 0.933$

 11370 measured reflections
2908 independent reflections
2511 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.058$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.153$
 $S = 1.05$
2908 reflections
226 parameters
10 restraints

 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 1.23$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.91$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H} \cdots A$ | $D-\text{H}$ | $\text{H} \cdots A$ | $D \cdots A$ | $D-\text{H} \cdots A$ |
|--|--------------|---------------------|--------------|-----------------------|
| $\text{O1W}-\text{H1WA} \cdots \text{O6}^{\text{i}}$ | 0.88 (2) | 2.38 (3) | 2.997 (3) | 128 (3) |
| $\text{O1W}-\text{H1WB} \cdots \text{O1}^{\text{i}}$ | 0.89 (2) | 1.88 (2) | 2.764 (3) | 174 (3) |
| $\text{O5}-\text{H5A} \cdots \text{N1}$ | 0.88 (2) | 1.87 (2) | 2.739 (3) | 177 (3) |
| $\text{O5}-\text{H5B} \cdots \text{O4}$ | 0.85 (2) | 1.87 (2) | 2.697 (3) | 163 (3) |
| $\text{O6}-\text{H6C} \cdots \text{O1W}$ | 0.86 (2) | 1.92 (2) | 2.753 (3) | 165 (3) |
| $\text{O6}-\text{H6D} \cdots \text{O2}^{\text{ii}}$ | 0.86 (2) | 1.81 (2) | 2.624 (3) | 158 (3) |
| $\text{N2}-\text{H2N} \cdots \text{O3}^{\text{iii}}$ | 0.91 (2) | 1.73 (2) | 2.630 (3) | 171 (3) |

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

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: CrystalMaker (Palmer, 2007); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2258).

References

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Acta Cryst. (2009). E65, m1709 [doi:10.1107/S1600536809051101]

Poly[1,4-bis(4-pyridylmethyl)piperazinediium [[tetraaquacobaltate(II)]- μ -pyromellitato- $\kappa^2 O^1:O^4$] dihydrate]

L. K. Sposato and R. L. LaDuca

Comment

The diverse possible binding modes of the pyromellitate ligand (1,2,4,5-benzenetetracarboxylate) has allowed formation of a wide variety of cobalt-containing coordination polymers, especially in the presence of dipyridyl neutral co-ligands (Majumder *et al.*, 2006). This chemistry was further developed by the synthesis of the title compound, which incorporates the long-spanning hydrogen-bonding capable dipyridyl ligand bis(4-pyridylmethyl)piperazine (bpmp).

The asymmetric unit of the title compound consists of a divalent Co^{II} atom on a crystallographic inversion center, one-half of a pyromellitate tetraanion situated across another crystallographic inversion center, one-half of a $(\text{H}_2\text{bpmp})^{2+}$ dication (protonated at each of the two piperazinyl N atoms) sited across another crystallographic inversion center, and one water molecule of crystallization. The local coordination and surrounding supramolecular environment is illustrated in Fig. 1.

Adjacent Co^{II} ions are linked into $[\text{Co}(\text{H}_2\text{O})_4(\text{pyromellitate})]_n^{2n-}$ anionic one-dimensional coordination polymer motifs, *via* symmetrically related monodentate carboxylate termini of the pyromellitate ligands. These chain motifs are oriented parallel to the $[1 \bar{1} 0]$ direction; the $\text{Co}\cdots\text{Co}$ distance along the chain is 11.474 (3) Å. Two of the pyromellitate carboxylate groups do not ligate to Co^{II} ions. Neighboring chain motifs aggregate into supramolecular layers coincident with the *ab* planes (Fig. 2), established by hydrogen-bonding patterns between the co-crystallized water molecules, aqua ligands, and ligated pyromellitate carboxylate O atoms (Table 1). In turn, the supramolecular layers stack in an *AAA* pattern along the *c* axis, with charge-balancing $(\text{H}_2\text{bpmp})^{2+}$ dications situated in the interlamellar regions (Fig. 3), thus forming the three-dimensional crystal structure of the title compound. The closest $\text{Co}\cdots\text{Co}$ contact distance between neighboring layers is 11.257 (3) Å, which defines the *c* lattice parameter.

Experimental

All starting materials were obtained commercially, except for bpmp, which was prepared by a published procedure (Pocic *et al.*, 2005). A mixture of cobalt nitrate hexahydrate (108 mg, 0.37 mmol), pyromellitic acid (94 mg, 0.37 mmol), bpmp (99 mg, 0.37 mmol) and 10.0 g water (550 mmol) was placed into a 23 ml Teflon-lined Parr Acid Digestion bomb, which was then heated under autogenous pressure at 393 K for 48 h. After cooling to 293 K, orange blocks of the title compound were obtained along with a white powder.

Refinement

All H atoms bound to C atoms were placed in calculated positions and refined in riding mode, with C—H = 0.95 and 0.99 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The H atoms bound to the water molecule O atoms and to the piperazinyl N atoms were found in a difference Fourier map and refined with restraints of O—H = 0.89 (1) and N—H = 0.92 (1) Å and with $U_{\text{iso}}(\text{H})$

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= $1.2U_{\text{eq}}(\text{O},\text{N})$. The maximum and minimum residual electron density peaks of 1.234 and $-0.908 \text{ e } \text{\AA}^{-3}$ were located 0.98 and 0.68 \AA from the Co1 and O1W atoms, respectively.

Figures

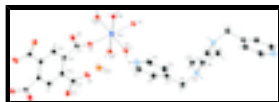


Fig. 1. The coordination environment of the title compound, showing 50% probability ellipsoids. H atom positions are shown as grey sticks. [Color codes: dark blue Co; light blue N; red O; black C; orange O in uncoordinated water molecule. Symmetry code: (i) $-x+2, -y, -z+1$.]

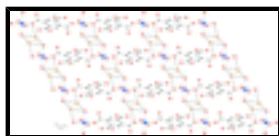


Fig. 2. A view of the supramolecular layer in the title compound. Hydrogen bonding contacts are indicated as dashed bars.

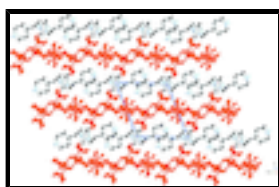


Fig. 3. Stacking diagram for the title compound, viewed down the a axis. Hydrogen bonding contacts are indicated as dashed bars.

Poly[1,4-bis(4-pyridylmethyl)piperazinediium [[tetraaquacobaltate(II)]- μ -pyromellitato- $\kappa^2\text{O}^1:\text{O}^4$] dihydrate]

Crystal data

$(\text{C}_{16}\text{H}_{22}\text{N}_4)[\text{Co}(\text{C}_{10}\text{H}_2\text{O}_8)(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$

$M_r = 687.52$

Triclinic, PT

Hall symbol: $-P 1$

$a = 7.278 (2) \text{ \AA}$

$b = 9.752 (3) \text{ \AA}$

$c = 11.257 (3) \text{ \AA}$

$\alpha = 66.733 (3)^\circ$

$\beta = 75.168 (3)^\circ$

$\gamma = 83.359 (3)^\circ$

$V = 709.5 (3) \text{ \AA}^3$

$Z = 1$

$F(000) = 359$

$D_x = 1.609 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 11370 reflections

$\theta = 2.0\text{--}26.5^\circ$

$\mu = 0.69 \text{ mm}^{-1}$

$T = 173 \text{ K}$

Block, pink

$0.24 \times 0.14 \times 0.10 \text{ mm}$

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube
graphite

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)

$T_{\text{min}} = 0.853, T_{\text{max}} = 0.933$

11370 measured reflections

2908 independent reflections

2511 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.058$

$\theta_{\text{max}} = 26.5^\circ, \theta_{\text{min}} = 2.0^\circ$

$h = -9 \rightarrow 9$

$k = -12 \rightarrow 12$

$l = -14 \rightarrow 14$

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.050$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.153$ | H atoms treated by a mixture of independent and constrained refinement |
| $S = 1.05$ | $w = 1/[\sigma^2(F_o^2) + (0.1134P)^2]$ |
| 2908 reflections | where $P = (F_o^2 + 2F_c^2)/3$ |
| 226 parameters | $(\Delta/\sigma)_{\max} < 0.001$ |
| 10 restraints | $\Delta\rho_{\max} = 1.23 \text{ e } \text{\AA}^{-3}$ |
| | $\Delta\rho_{\min} = -0.91 \text{ e } \text{\AA}^{-3}$ |

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

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|------------|--------------|--------------|----------------------------------|
| Co1 | 1.0000 | 0.0000 | 0.5000 | 0.0155 (2) |
| O1 | 0.8311 (2) | 0.19744 (19) | 0.45730 (18) | 0.0192 (4) |
| O1W | 0.4690 (3) | -0.1576 (2) | 0.6340 (2) | 0.0255 (4) |
| H1WA | 0.437 (4) | -0.070 (3) | 0.639 (3) | 0.031* |
| H1WB | 0.375 (4) | -0.178 (4) | 0.607 (3) | 0.031* |
| O2 | 0.9191 (3) | 0.2866 (2) | 0.58976 (19) | 0.0235 (4) |
| O3 | 0.3143 (3) | 0.2159 (2) | 0.82962 (18) | 0.0236 (4) |
| O4 | 0.5304 (3) | 0.1042 (2) | 0.7189 (2) | 0.0332 (5) |
| O5 | 0.8431 (3) | -0.0690 (2) | 0.69373 (18) | 0.0183 (4) |
| H5A | 0.829 (4) | -0.163 (2) | 0.748 (3) | 0.022* |
| H5B | 0.742 (3) | -0.024 (3) | 0.718 (3) | 0.022* |
| O6 | 0.8063 (3) | -0.0969 (2) | 0.44473 (18) | 0.0193 (4) |
| H6C | 0.705 (3) | -0.132 (3) | 0.504 (3) | 0.023* |
| H6D | 0.876 (4) | -0.166 (3) | 0.425 (3) | 0.023* |
| N1 | 0.7991 (3) | -0.3648 (3) | 0.8552 (2) | 0.0284 (6) |
| N2 | 0.8089 (3) | -0.9425 (2) | 1.0284 (2) | 0.0170 (5) |
| H2N | 0.755 (4) | -1.033 (2) | 1.080 (3) | 0.020* |
| C1 | 0.7611 (4) | -0.4408 (3) | 0.9870 (3) | 0.0258 (6) |
| H1 | 0.7635 | -0.3891 | 1.0426 | 0.031* |
| C2 | 0.7185 (4) | -0.5911 (3) | 1.0460 (3) | 0.0224 (6) |
| H2 | 0.6933 | -0.6409 | 1.1399 | 0.027* |
| C3 | 0.7131 (4) | -0.6683 (3) | 0.9661 (3) | 0.0187 (5) |
| C4 | 0.7549 (4) | -0.5898 (3) | 0.8292 (3) | 0.0242 (6) |
| H4 | 0.7544 | -0.6384 | 0.7709 | 0.029* |
| C5 | 0.7970 (4) | -0.4404 (3) | 0.7793 (3) | 0.0275 (6) |
| H5 | 0.8261 | -0.3883 | 0.6856 | 0.033* |
| C6 | 0.6512 (4) | -0.8286 (3) | 1.0280 (3) | 0.0204 (6) |
| H6A | 0.5805 | -0.8497 | 1.1210 | 0.024* |
| H6B | 0.5619 | -0.8407 | 0.9798 | 0.024* |

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| | | | | |
|-----|------------|-------------|------------|------------|
| C7 | 0.9515 (4) | -0.9366 (3) | 1.1004 (3) | 0.0192 (5) |
| H7A | 0.8864 | -0.9431 | 1.1912 | 0.023* |
| H7B | 1.0192 | -0.8407 | 1.0532 | 0.023* |
| C8 | 0.9075 (4) | -0.9347 (3) | 0.8919 (3) | 0.0196 (5) |
| H8A | 0.9749 | -0.8389 | 0.8415 | 0.024* |
| H8B | 0.8124 | -0.9387 | 0.8443 | 0.024* |
| C11 | 0.8099 (3) | 0.2813 (3) | 0.5227 (2) | 0.0170 (5) |
| C12 | 0.6437 (3) | 0.3901 (3) | 0.5118 (2) | 0.0161 (5) |
| C13 | 0.4741 (4) | 0.3639 (3) | 0.6092 (2) | 0.0172 (5) |
| C14 | 0.6677 (4) | 0.5255 (3) | 0.4034 (3) | 0.0178 (5) |
| H14 | 0.7827 | 0.5429 | 0.3367 | 0.021* |
| C15 | 0.4396 (3) | 0.2173 (3) | 0.7278 (3) | 0.0176 (5) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| Co1 | 0.0153 (3) | 0.0153 (3) | 0.0161 (3) | 0.00250 (18) | -0.0074 (2) | -0.0044 (2) |
| O1 | 0.0192 (9) | 0.0174 (9) | 0.0221 (9) | 0.0051 (7) | -0.0094 (8) | -0.0073 (8) |
| O1W | 0.0222 (10) | 0.0262 (11) | 0.0285 (10) | 0.0026 (8) | -0.0124 (9) | -0.0074 (9) |
| O2 | 0.0238 (10) | 0.0250 (10) | 0.0270 (10) | 0.0084 (8) | -0.0149 (8) | -0.0123 (8) |
| O3 | 0.0281 (10) | 0.0165 (9) | 0.0198 (10) | -0.0002 (8) | -0.0011 (8) | -0.0031 (8) |
| O4 | 0.0277 (11) | 0.0174 (10) | 0.0351 (12) | 0.0074 (8) | 0.0045 (9) | 0.0008 (9) |
| O5 | 0.0186 (9) | 0.0162 (9) | 0.0184 (9) | 0.0007 (7) | -0.0045 (8) | -0.0049 (7) |
| O6 | 0.0165 (9) | 0.0201 (10) | 0.0232 (10) | 0.0033 (7) | -0.0082 (8) | -0.0090 (8) |
| N1 | 0.0265 (13) | 0.0193 (12) | 0.0329 (14) | 0.0013 (9) | -0.0061 (11) | -0.0042 (10) |
| N2 | 0.0187 (11) | 0.0141 (10) | 0.0169 (10) | 0.0003 (8) | -0.0062 (9) | -0.0033 (8) |
| C1 | 0.0251 (14) | 0.0242 (14) | 0.0303 (15) | 0.0026 (11) | -0.0081 (12) | -0.0125 (12) |
| C2 | 0.0236 (14) | 0.0207 (14) | 0.0211 (13) | 0.0019 (11) | -0.0074 (11) | -0.0052 (11) |
| C3 | 0.0156 (12) | 0.0184 (13) | 0.0207 (13) | 0.0023 (9) | -0.0067 (10) | -0.0051 (10) |
| C4 | 0.0260 (14) | 0.0226 (14) | 0.0211 (13) | 0.0030 (11) | -0.0072 (11) | -0.0049 (11) |
| C5 | 0.0297 (15) | 0.0211 (14) | 0.0216 (14) | 0.0035 (11) | -0.0048 (12) | 0.0004 (11) |
| C6 | 0.0181 (13) | 0.0189 (13) | 0.0212 (13) | 0.0013 (10) | -0.0060 (11) | -0.0040 (10) |
| C7 | 0.0216 (13) | 0.0195 (13) | 0.0175 (12) | 0.0017 (10) | -0.0089 (10) | -0.0060 (10) |
| C8 | 0.0204 (13) | 0.0207 (13) | 0.0176 (12) | 0.0027 (10) | -0.0080 (10) | -0.0058 (10) |
| C11 | 0.0149 (12) | 0.0135 (12) | 0.0155 (12) | 0.0013 (9) | -0.0016 (10) | 0.0002 (9) |
| C12 | 0.0167 (12) | 0.0132 (12) | 0.0172 (12) | 0.0022 (9) | -0.0070 (10) | -0.0034 (10) |
| C13 | 0.0178 (12) | 0.0137 (12) | 0.0177 (12) | 0.0020 (9) | -0.0063 (10) | -0.0026 (10) |
| C14 | 0.0163 (12) | 0.0160 (12) | 0.0179 (12) | 0.0013 (9) | -0.0052 (10) | -0.0027 (10) |
| C15 | 0.0142 (12) | 0.0165 (12) | 0.0196 (13) | 0.0008 (9) | -0.0063 (10) | -0.0032 (10) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|----------|-------------|--------|-----------|
| Co1—O5 | 2.0631 (18) | C2—H2 | 0.9500 |
| Co1—O1 | 2.1150 (17) | C3—C4 | 1.392 (4) |
| Co1—O6 | 2.1184 (18) | C3—C6 | 1.507 (4) |
| O1—C11 | 1.274 (3) | C4—C5 | 1.379 (4) |
| O1W—H1WA | 0.881 (18) | C4—H4 | 0.9500 |
| O1W—H1WB | 0.885 (17) | C5—H5 | 0.9500 |
| O2—C11 | 1.246 (3) | C6—H6A | 0.9900 |

| | | | |
|--|-------------|-------------------------|-----------|
| O3—C15 | 1.266 (3) | C6—H6B | 0.9900 |
| O4—C15 | 1.244 (3) | C7—C8 ⁱ | 1.517 (4) |
| O5—H5A | 0.875 (17) | C7—H7A | 0.9900 |
| O5—H5B | 0.852 (17) | C7—H7B | 0.9900 |
| O6—H6C | 0.857 (17) | C8—C7 ⁱ | 1.517 (4) |
| O6—H6D | 0.863 (17) | C8—H8A | 0.9900 |
| N1—C5 | 1.334 (4) | C8—H8B | 0.9900 |
| N1—C1 | 1.340 (4) | C11—C12 | 1.510 (3) |
| N2—C7 | 1.490 (3) | C12—C14 | 1.391 (3) |
| N2—C8 | 1.495 (3) | C12—C13 | 1.397 (3) |
| N2—C6 | 1.502 (3) | C13—C14 ⁱⁱ | 1.395 (3) |
| N2—H2N | 0.906 (18) | C13—C15 | 1.514 (3) |
| C1—C2 | 1.384 (4) | C14—C13 ⁱⁱ | 1.394 (3) |
| C1—H1 | 0.9500 | C14—H14 | 0.9500 |
| C2—C3 | 1.393 (4) | | |
| O5—Co1—O5 ⁱⁱⁱ | 180.0 | C5—C4—C3 | 119.0 (3) |
| O5—Co1—O1 | 88.13 (7) | C5—C4—H4 | 120.5 |
| O5 ⁱⁱⁱ —Co1—O1 | 91.87 (7) | C3—C4—H4 | 120.5 |
| O5—Co1—O1 ⁱⁱⁱ | 91.87 (7) | N1—C5—C4 | 123.7 (3) |
| O5 ⁱⁱⁱ —Co1—O1 ⁱⁱⁱ | 88.13 (7) | N1—C5—H5 | 118.2 |
| O1—Co1—O1 ⁱⁱⁱ | 180.000 (1) | C4—C5—H5 | 118.2 |
| O5—Co1—O6 | 91.72 (7) | N2—C6—C3 | 115.3 (2) |
| O5 ⁱⁱⁱ —Co1—O6 | 88.28 (7) | N2—C6—H6A | 108.4 |
| O1—Co1—O6 | 88.61 (7) | C3—C6—H6A | 108.4 |
| O1 ⁱⁱⁱ —Co1—O6 | 91.39 (7) | N2—C6—H6B | 108.4 |
| O5—Co1—O6 ⁱⁱⁱ | 88.28 (7) | C3—C6—H6B | 108.4 |
| O5 ⁱⁱⁱ —Co1—O6 ⁱⁱⁱ | 91.72 (7) | H6A—C6—H6B | 107.5 |
| O1—Co1—O6 ⁱⁱⁱ | 91.39 (7) | N2—C7—C8 ⁱ | 109.5 (2) |
| O1 ⁱⁱⁱ —Co1—O6 ⁱⁱⁱ | 88.61 (7) | N2—C7—H7A | 109.8 |
| O6—Co1—O6 ⁱⁱⁱ | 180.000 (1) | C8 ⁱ —C7—H7A | 109.8 |
| C11—O1—Co1 | 122.61 (16) | N2—C7—H7B | 109.8 |
| H1WA—O1W—H1WB | 104 (3) | C8 ⁱ —C7—H7B | 109.8 |
| Co1—O5—H5A | 123.9 (19) | H7A—C7—H7B | 108.2 |
| Co1—O5—H5B | 123 (2) | N2—C8—C7 ⁱ | 110.4 (2) |
| H5A—O5—H5B | 105 (2) | N2—C8—H8A | 109.6 |
| Co1—O6—H6C | 116 (2) | C7 ⁱ —C8—H8A | 109.6 |
| Co1—O6—H6D | 102 (2) | N2—C8—H8B | 109.6 |
| H6C—O6—H6D | 112 (3) | C7 ⁱ —C8—H8B | 109.6 |
| C5—N1—C1 | 117.3 (2) | H8A—C8—H8B | 108.1 |
| C7—N2—C8 | 109.8 (2) | O2—C11—O1 | 125.8 (2) |
| C7—N2—C6 | 113.4 (2) | O2—C11—C12 | 117.0 (2) |
| C8—N2—C6 | 112.9 (2) | O1—C11—C12 | 117.1 (2) |
| C7—N2—H2N | 102 (2) | C14—C12—C13 | 119.4 (2) |
| C8—N2—H2N | 111.8 (19) | C14—C12—C11 | 117.6 (2) |
| C6—N2—H2N | 106.2 (19) | C13—C12—C11 | 122.9 (2) |

supplementary materials

| | | | |
|-------------------------------|--------------|-------------------------------|--------------|
| N1—C1—C2 | 123.1 (3) | C14 ⁱⁱ —C13—C12 | 119.4 (2) |
| N1—C1—H1 | 118.5 | C14 ⁱⁱ —C13—C15 | 119.1 (2) |
| C2—C1—H1 | 118.5 | C12—C13—C15 | 121.4 (2) |
| C1—C2—C3 | 119.2 (3) | C12—C14—C13 ⁱⁱ | 121.1 (2) |
| C1—C2—H2 | 120.4 | C12—C14—H14 | 119.4 |
| C3—C2—H2 | 120.4 | C13 ⁱⁱ —C14—H14 | 119.4 |
| C4—C3—C2 | 117.7 (2) | O4—C15—O3 | 123.5 (2) |
| C4—C3—C6 | 121.9 (2) | O4—C15—C13 | 118.8 (2) |
| C2—C3—C6 | 120.3 (2) | O3—C15—C13 | 117.7 (2) |
| O5—Co1—O1—C11 | 54.13 (19) | C7—N2—C8—C7 ⁱ | 59.2 (3) |
| O5 ⁱⁱⁱ —Co1—O1—C11 | -125.86 (19) | C6—N2—C8—C7 ⁱ | -173.3 (2) |
| O6—Co1—O1—C11 | 145.90 (19) | Co1—O1—C11—O2 | 21.7 (3) |
| O6 ⁱⁱⁱ —Co1—O1—C11 | -34.10 (19) | Co1—O1—C11—C12 | -161.93 (16) |
| C5—N1—C1—C2 | -0.8 (4) | O2—C11—C12—C14 | 93.1 (3) |
| N1—C1—C2—C3 | -0.4 (4) | O1—C11—C12—C14 | -83.6 (3) |
| C1—C2—C3—C4 | 1.2 (4) | O2—C11—C12—C13 | -82.8 (3) |
| C1—C2—C3—C6 | -174.9 (2) | O1—C11—C12—C13 | 100.5 (3) |
| C2—C3—C4—C5 | -0.8 (4) | C14—C12—C13—C14 ⁱⁱ | -0.5 (4) |
| C6—C3—C4—C5 | 175.2 (2) | C11—C12—C13—C14 ⁱⁱ | 175.3 (2) |
| C1—N1—C5—C4 | 1.2 (4) | C14—C12—C13—C15 | 178.9 (2) |
| C3—C4—C5—N1 | -0.4 (4) | C11—C12—C13—C15 | -5.3 (4) |
| C7—N2—C6—C3 | 59.1 (3) | C13—C12—C14—C13 ⁱⁱ | 0.5 (4) |
| C8—N2—C6—C3 | -66.5 (3) | C11—C12—C14—C13 ⁱⁱ | -175.6 (2) |
| C4—C3—C6—N2 | 81.0 (3) | C14 ⁱⁱ —C13—C15—O4 | 156.2 (3) |
| C2—C3—C6—N2 | -103.2 (3) | C12—C13—C15—O4 | -23.2 (4) |
| C8—N2—C7—C8 ⁱ | -58.7 (3) | C14 ⁱⁱ —C13—C15—O3 | -21.5 (4) |
| C6—N2—C7—C8 ⁱ | 174.0 (2) | C12—C13—C15—O3 | 159.2 (2) |

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

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------------|----------|-------------|-------------|---------------|
| O1W—H1WA \cdots O6 ^{iv} | 0.88 (2) | 2.38 (3) | 2.997 (3) | 128 (3) |
| O1W—H1WB \cdots O1 ^{iv} | 0.89 (2) | 1.88 (2) | 2.764 (3) | 174 (3) |
| O5—H5A \cdots N1 | 0.88 (2) | 1.87 (2) | 2.739 (3) | 177 (3) |
| O5—H5B \cdots O4 | 0.85 (2) | 1.87 (2) | 2.697 (3) | 163 (3) |
| O6—H6C \cdots O1W | 0.86 (2) | 1.92 (2) | 2.753 (3) | 165 (3) |
| O6—H6D \cdots O2 ⁱⁱⁱ | 0.86 (2) | 1.81 (2) | 2.624 (3) | 158 (3) |
| N2—H2N \cdots O3 ^v | 0.91 (2) | 1.73 (2) | 2.630 (3) | 171 (3) |

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

Fig. 1

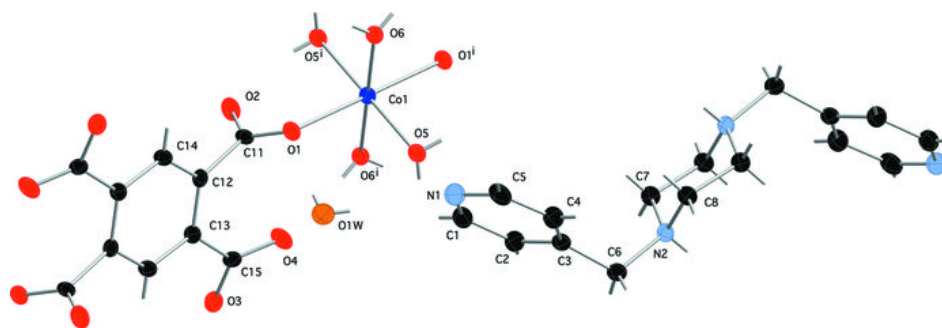


Fig. 2

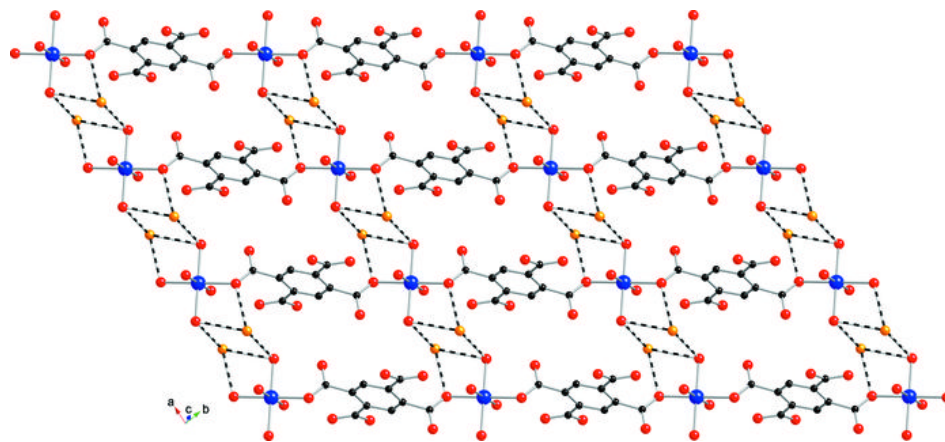


Fig. 3

