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Sesqui(piperazinediium) (5-carboxypyridine-2-carboxylato)bis(pyridine-2,5-dicarboxylato)cadmate(II) trihydrate

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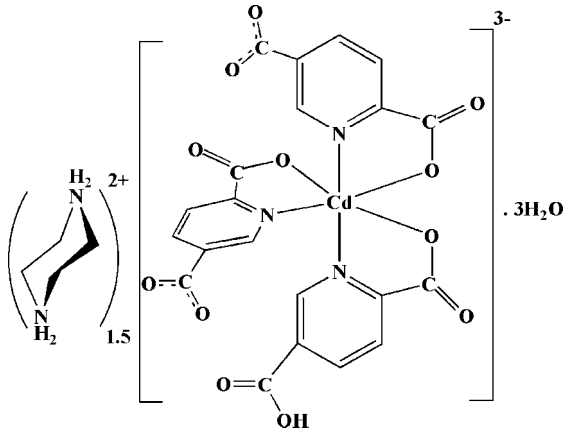
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.028; wR factor = 0.069; data-to-parameter ratio = 20.1.

The reaction of cadmium(II) nitrate tetrahydrate with the proton-transfer compound piperazinium pyridine-2,5-dicarboxylate, or $(pipzH_2)(py\text{-}2,5\text{-}dc)\cdot 2H_2O$ (in which pipz is piperazine and py-2,5-dcH_2 is pyridine-2,5-dicarboxylic acid), in aqueous solution (molar ratio 1:2) leads to the formation of the title compound, $(C_4H_{12}N_2)_{1.5}[Cd(C_7H_3NO_4)_2(C_7H_4NO_4)]\cdot 3H_2O$ or $(pipzH_2)_{1.5}[Cd(py\text{-}2,5\text{-}dc)_2(py\text{-}2,5\text{-}dcH)]\cdot 3H_2O$. The anion is a six-coordinate complex with a distorted octahedral geometry around Cd^{II}. Extensive intermolecular O—H···O, N—H···O and C—H···O hydrogen bonds involving the $(py\text{-}2,5\text{-}dc)^{2-}$ ligand, $(pipzH_2)^{2+}$ as counter-ion and the uncoordinated water molecules connect the various components into a supramolecular structure.

Related literature

For related literature, see: Aghabozorg, Attar Gharamaleki et al. (2007); Aghabozorg, Daneshvar et al. (2007); Aghabozorg, Motyeian *et al.* (2007); Sheshmani *et al.* (2007).



Experimental

Crystal data

$(C_4H_{12}N_2)_{1.5}[Cd(C_7H_3NO_4)_2(C_7H_4NO_4)]\cdot 3(H_2O)$
M_r = 795.00
Monoclinic, $P2_1/n$
a = 13.7672 (12) Å
b = 10.2603 (11) Å
c = 21.6094 (13) Å
β = 94.498 (5)°
V = 3043.3 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.80 mm^{-1}
T = 100 (2) K
0.28 × 0.22 × 0.11 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.806, T_{max} = 0.917
38910 measured reflections
8883 independent reflections
7598 reflections with $I > 2\sigma(I)$
R_{int} = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.070
S = 1.05
8883 reflections
442 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.78 e Å^{-3}
$\Delta\rho_{min}$ = −0.65 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd1—N2	2.2667 (15)	Cd1—N1	2.3159 (15)
Cd1—O9	2.3063 (14)	Cd1—O1	2.3190 (13)
Cd1—N3	2.3074 (16)	Cd1—O5	2.3476 (13)
O9—Cd1—N3	71.01 (5)	N1—Cd1—O1	71.31 (5)
N2—Cd1—N1	133.16 (5)	N2—Cd1—O5	71.86 (5)
N3—Cd1—O1	145.97 (5)	O9—Cd1—O5	152.50 (5)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4A···O6	0.90	1.85	2.714 (2)	159
N4—H4B···O14^{i}	0.90	1.91	2.791 (2)	167
N5—H5B···O3^{i}	0.90	1.93	2.766 (2)	153
N5—H5C···O12	0.90	1.84	2.704 (2)	160
N6—H6A···O15^{ii}	0.90	1.91	2.799 (2)	168
N6—H6B···O1	0.90	1.90	2.780 (2)	164
O11—H11···O8^{iii}	0.89	1.59	2.439 (2)	159
O13—H13A···O10^{iv}	0.82	2.04	2.811 (2)	157
O13—H13B···O4	0.82	1.91	2.727 (2)	173
O14—H14A···O3^{i}	0.82	1.98	2.754 (2)	158
O14—H14B···O13	0.82	1.95	2.771 (2)	175
O15—H15A···O10	0.82	2.07	2.860 (2)	162
O15—H15B···O7^{v}	0.82	1.94	2.761 (2)	177
C9—H9A···O2^{vi}	0.95	2.48	3.161 (2)	129
C19—H19A···O5	0.95	2.41	3.064 (2)	126
C22—H22B···O12	0.99	2.58	3.280 (2)	127
C24—H24A···O15^{vii}	0.99	2.56	3.317 (2)	133
C24—H24B···O4	0.99	2.49	3.251 (2)	133
C26—H26B···O8	0.99	2.38	3.206 (2)	141
C27—H27B···O9	0.99	2.45	3.327 (2)	148

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+2, -y+2, -z+1$; (iii) $x-1, y, z$; (iv) $-x+1, -y+2, -z+1$; (v) $-x+2, -y+1, -z+1$; (vi) $x, y-1, z$; (vii) $x-\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

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SHELXTL (Sheldrick, 1998); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2179).

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supplementary materials

Acta Cryst. (2007). E**63**, m3140-m3141 [**doi:10.1107/S1600536807060606**]

Sesqui(piperazinediium) (5-carboxypyridine-2-carboxylato)bis(pyridine-2,5-dicarboxylato)cadmate(II) trihydrate

H. Aghabozorg, Z. Derikvand, A. Nemati, M. Ghadermazi and J. Attar Gharamaleki

Comment

We have previously reported some proton transfer systems, using pyridine-2,6-dicarboxylic acid ($pydcH_2$), pyridine-2,5-dicarboxylic acid (py-2,5-dcH_2) and piperazine (pipz) which have formed the proton transfer compounds $(pipzH_2)(pydcH)_2{\cdot}3H_2O$ and $(pipzH_2)$(py-2,5-dc)$\cdot 2H_2O$. The crystal structures of some complexes of these systems have been reported (Aghabozorg, Attar Gharamaleki *et al.*, 2007; Aghabozorg, Daneshvar *et al.*, 2007; Aghabozorg, Motyeian *et al.*, 2007). We describe here the crystal structure of the title compound which consists of monomeric units in which the $(pipzH_2)$ units act as counter ions and the $(py\text{-}2,5\text{-}dc)^{2-}$ anions as bidentate ligands. The N3—Cd1—O1 [145.97 (5)°], O5—Cd1—O9 [152.50 (5)°], N2—Cd1—N1 [133.16 (5)°] angles show that the coordination environment around Cd^{II} is distorted octahedral (Table 1 and Fig.1). There are a large number of O—H···O, N—H···O and C—H···O hydrogen bonds with distances ranging from 2.439 (2) Å to 3.327 (2) Å between water molecules, piperazindiium and pyridine-2,5-dicarboxylate fragments (Table 2). These interactions as well as C—H···π interactions between C—H groups and aromatic rings of pyridine-2,5-dicarboxylate with distances of 3.224 and 3.473 Å result in the formation of supramolecular structure (Fig. 2 and Fig. 3).

Experimental

The reaction of $(pipzH_2)$(py-2,5-dc)$\cdot 2H_2O$ (200 mg, 0.797 mmol) (Sheshmani *et al.*, 2007) in water (20 ml) with $Cd(NO_3)_2{\cdot}4H_2O$ (122.2 mg, 0.477 mmol) in water (20 ml) gave yellow crystals of the title compound. Crystals were obtained by slow evaporation of the solvent at room temperature.

Refinement

The hydrogen atoms of NH_2, OH groups and water molecules were found in difference Fourier synthesis. The H(C) atom positions were calculated. All hydrogen atoms were refined in isotropic approximation in riding model with with the U_{iso}(H) parameters equal to 1.2 U_{eq}(Ci), 1.2 U_{eq}(Ni) and 1.2 U_{eq}(Oi) where U(Ci), U(Ni), U(Oi) are respectively the equivalent thermal parameters of the carbon, nitrogen and oxygen atoms to which corresponding H atoms are bonded.

Figures

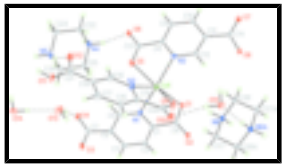

Fig. 1. Molecular structure of the title compound, with displacement ellipsoids drawn at 50% probability level. Hydrogen atoms shown as small spheres.

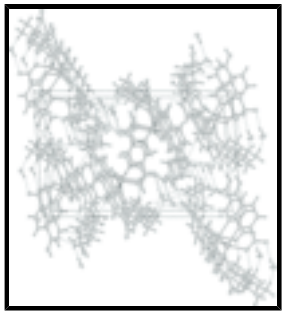

Fig. 2. The crystal packing as viewed down the b direction. Hydrogen bonds are shown as dashed lines.

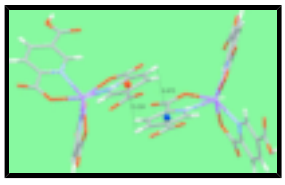

Fig. 3. C—H···π stacking interactions between C—H groups and aromatic rings of (py-2,5-dc)$^{2-}$ units. The C—H···π distances (measured to the centre of phenyl ring) are 3.224 and 3.473 Å, respectively.

Sesqui(piperazinediium) (5-carboxypyridine-2-carboxylato)bis(pyridine-2,5-dicarboxylato)cadmate(II) trihydrate

Crystal data

$(C_4H_{12}N_2)_{1.5}[Cd(C_7H_3N_1O_4)_2(C_7H_4N_1O_4)]\cdot 3(H_2O)$	F_{000} = 1624
M_r = 795.00	D_x = 1.735 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 745 reflections
a = 13.7672 (12) Å	θ = 3–30º
b = 10.2603 (11) Å	μ = 0.80 mm^{-1}
c = 21.6094 (13) Å	T = 100 (2) K
β = 94.498 (5)º	Plate, light-yellow
V = 3043.3 (5) Å^3	0.28 × 0.22 × 0.11 mm
Z = 4	

Data collection

Bruker APEXII CCD area-detector diffractometer	8883 independent reflections
Radiation source: fine-focus sealed tube	7598 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.040
T = 100(2) K	θ_{max} = 30.0º
ω scans	θ_{min} = 1.7º
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	h = −19→19
T_{min} = 0.806, T_{max} = 0.917	k = −14→14
38910 measured reflections	l = −30→30

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.070$

$S = 1.05$

8883 reflections

442 parameters

Primary atom site location: structure-invariant direct methods

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0276P)^2 + 2.5491P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.78$ e Å^{-3}

$\Delta\rho_{min} = -0.64$ e Å^{-3}

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cd1	0.709004 (9)	0.739983 (12)	0.594580 (6)	0.01003 (4)
O1	0.83962 (9)	0.86515 (12)	0.63429 (6)	0.0128 (3)
O2	0.87909 (9)	1.05633 (13)	0.67854 (6)	0.0141 (3)
O3	0.40797 (10)	1.06452 (13)	0.78369 (7)	0.0168 (3)
O4	0.38638 (10)	0.87127 (13)	0.73797 (7)	0.0167 (3)
O5	0.62991 (9)	0.57646 (13)	0.64763 (6)	0.0142 (3)
O6	0.64812 (9)	0.37858 (13)	0.68990 (6)	0.0148 (3)
O7	1.11749 (10)	0.36822 (13)	0.58105 (7)	0.0173 (3)
O8	1.08444 (9)	0.57318 (12)	0.55059 (6)	0.0145 (3)
O9	0.73333 (10)	0.86078 (14)	0.50713 (6)	0.0172 (3)
O10	0.66850 (10)	0.92918 (15)	0.41471 (7)	0.0202 (3)
O11	0.22901 (9)	0.65304 (13)	0.50417 (6)	0.0147 (3)
H11	0.1820	0.6061	0.5189	0.018*
O12	0.32851 (10)	0.53151 (14)	0.56775 (6)	0.0172 (3)
N1	0.65409 (11)	0.88647 (15)	0.66553 (7)	0.0116 (3)
N2	0.80882 (11)	0.56423 (14)	0.60400 (7)	0.0108 (3)
N3	0.56902 (11)	0.73429 (15)	0.52851 (7)	0.0134 (3)
C1	0.71783 (12)	0.97944 (17)	0.68513 (8)	0.0100 (3)
C2	0.69177 (13)	1.08094 (17)	0.72300 (8)	0.0115 (3)
H2A	0.7372	1.1477	0.7350	0.014*
C3	0.59843 (13)	1.08348 (17)	0.74299 (8)	0.0114 (3)
H3A	0.5789	1.1526	0.7685	0.014*
C4	0.53389 (13)	0.98388 (17)	0.72531 (8)	0.0103 (3)

C5	0.56469 (13)	0.88834 (17)	0.68570 (9)	0.0125 (3)
H5A	0.5203	0.8213	0.6723	0.015*
C6	0.82083 (13)	0.96732 (17)	0.66481 (8)	0.0109 (3)
C7	0.43471 (13)	0.97279 (18)	0.75035 (8)	0.0116 (3)
C8	0.77745 (13)	0.46138 (17)	0.63571 (8)	0.0098 (3)
C9	0.83589 (13)	0.35308 (17)	0.64822 (8)	0.0110 (3)
H9A	0.8121	0.2806	0.6698	0.013*
C10	0.92945 (13)	0.35198 (17)	0.62885 (8)	0.0109 (3)
H10A	0.9709	0.2792	0.6377	0.013*
C11	0.96222 (13)	0.45823 (17)	0.59640 (8)	0.0100 (3)
C12	0.89842 (13)	0.56229 (17)	0.58498 (8)	0.0113 (3)
H12A	0.9198	0.6352	0.5626	0.014*
C13	0.67642 (12)	0.47250 (17)	0.65941 (8)	0.0111 (3)
C14	1.06341 (13)	0.46379 (17)	0.57460 (8)	0.0110 (3)
C15	0.56654 (13)	0.81333 (18)	0.47872 (8)	0.0128 (3)
C16	0.48100 (14)	0.83600 (19)	0.44168 (9)	0.0161 (4)
H16A	0.4809	0.8922	0.4067	0.019*
C17	0.39538 (14)	0.77511 (19)	0.45653 (9)	0.0161 (4)
H17A	0.3357	0.7911	0.4326	0.019*
C18	0.39879 (13)	0.69049 (18)	0.50698 (8)	0.0130 (3)
C19	0.48773 (13)	0.67273 (19)	0.54121 (9)	0.0146 (4)
H19A	0.4906	0.6139	0.5752	0.017*
C20	0.66403 (14)	0.87369 (18)	0.46580 (9)	0.0147 (4)
C21	0.31293 (13)	0.61792 (18)	0.52853 (8)	0.0128 (3)
N4	0.46845 (11)	0.42344 (15)	0.72888 (7)	0.0113 (3)
H4A	0.5327	0.4214	0.7238	0.014*
H4B	0.4594	0.3912	0.7667	0.014*
N5	0.27191 (11)	0.48289 (16)	0.68252 (7)	0.0131 (3)
H5B	0.2077	0.4849	0.6878	0.016*
H5C	0.2808	0.5153	0.6447	0.016*
C22	0.41556 (13)	0.34063 (18)	0.68056 (9)	0.0135 (3)
H22A	0.4384	0.2494	0.6852	0.016*
H22B	0.4300	0.3715	0.6389	0.016*
C23	0.30682 (13)	0.34577 (19)	0.68618 (9)	0.0160 (4)
H23A	0.2728	0.2941	0.6524	0.019*
H23B	0.2916	0.3072	0.7263	0.019*
C24	0.32492 (13)	0.56542 (18)	0.73070 (9)	0.0139 (3)
H24A	0.3106	0.5345	0.7724	0.017*
H24B	0.3020	0.6566	0.7261	0.017*
C25	0.43351 (13)	0.56072 (18)	0.72507 (9)	0.0135 (3)
H25A	0.4487	0.5992	0.6849	0.016*
H25B	0.4674	0.6126	0.7588	0.016*
N6	0.98114 (11)	0.96424 (14)	0.56222 (7)	0.0106 (3)
H6A	1.0313	1.0031	0.5841	0.013*
H6B	0.9448	0.9232	0.5891	0.013*
C26	1.01934 (13)	0.86728 (17)	0.51893 (8)	0.0115 (3)
H26A	0.9643	0.8206	0.4966	0.014*
H26B	1.0602	0.8024	0.5428	0.014*
C27	0.92074 (13)	1.06511 (17)	0.52730 (8)	0.0117 (3)

H27A	0.8974	1.1299	0.5567	0.014*
H27B	0.8632	1.0234	0.5052	0.014*
O13	0.27606 (11)	0.82653 (15)	0.62966 (7)	0.0239 (3)
H13A	0.3020	0.8846	0.6108	0.029*
H13B	0.3134	0.8413	0.6603	0.029*
O14	0.08580 (10)	0.80772 (13)	0.66212 (6)	0.0165 (3)
H14A	0.0792	0.7299	0.6693	0.020*
H14B	0.1411	0.8113	0.6507	0.020*
O15	0.86394 (10)	0.88915 (13)	0.38261 (6)	0.0148 (3)
H15A	0.8116	0.8887	0.3982	0.018*
H15B	0.8719	0.8129	0.3931	0.018*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.00777 (6)	0.00968 (6)	0.01284 (6)	0.00003 (4)	0.00212 (4)	0.00010 (5)
O1	0.0094 (6)	0.0130 (6)	0.0164 (6)	−0.0006 (5)	0.0036 (5)	−0.0020 (5)
O2	0.0109 (6)	0.0134 (6)	0.0182 (7)	−0.0029 (5)	0.0024 (5)	−0.0009 (5)
O3	0.0108 (6)	0.0178 (7)	0.0224 (7)	−0.0001 (5)	0.0059 (5)	−0.0067 (5)
O4	0.0126 (6)	0.0156 (6)	0.0226 (7)	−0.0042 (5)	0.0062 (5)	−0.0019 (5)
O5	0.0117 (6)	0.0135 (6)	0.0178 (7)	0.0014 (5)	0.0047 (5)	0.0034 (5)
O6	0.0119 (6)	0.0126 (6)	0.0205 (7)	−0.0004 (5)	0.0060 (5)	0.0034 (5)
O7	0.0120 (6)	0.0122 (6)	0.0285 (8)	0.0026 (5)	0.0059 (6)	0.0036 (5)
O8	0.0113 (6)	0.0113 (6)	0.0219 (7)	−0.0007 (5)	0.0071 (5)	0.0031 (5)
O9	0.0119 (6)	0.0220 (7)	0.0177 (7)	−0.0054 (5)	0.0012 (5)	0.0043 (5)
O10	0.0162 (7)	0.0264 (8)	0.0183 (7)	−0.0048 (6)	0.0037 (5)	0.0093 (6)
O11	0.0089 (6)	0.0208 (7)	0.0144 (6)	−0.0039 (5)	0.0009 (5)	0.0032 (5)
O12	0.0135 (7)	0.0211 (7)	0.0174 (7)	−0.0019 (5)	0.0032 (5)	0.0060 (5)
N1	0.0099 (7)	0.0112 (7)	0.0139 (7)	−0.0008 (5)	0.0027 (6)	−0.0010 (6)
N2	0.0097 (7)	0.0102 (7)	0.0128 (7)	−0.0008 (5)	0.0031 (6)	0.0002 (5)
N3	0.0107 (7)	0.0157 (7)	0.0141 (7)	−0.0024 (6)	0.0019 (6)	0.0019 (6)
C1	0.0089 (8)	0.0118 (8)	0.0095 (8)	0.0000 (6)	0.0015 (6)	0.0024 (6)
C2	0.0115 (8)	0.0106 (8)	0.0124 (8)	−0.0012 (6)	0.0011 (6)	0.0020 (6)
C3	0.0128 (8)	0.0103 (8)	0.0114 (8)	0.0016 (6)	0.0017 (6)	0.0014 (6)
C4	0.0088 (8)	0.0112 (8)	0.0113 (8)	0.0004 (6)	0.0022 (6)	0.0017 (6)
C5	0.0097 (8)	0.0126 (8)	0.0154 (9)	−0.0015 (6)	0.0024 (7)	−0.0018 (7)
C6	0.0092 (8)	0.0124 (8)	0.0112 (8)	0.0007 (6)	0.0013 (6)	0.0031 (6)
C7	0.0083 (8)	0.0154 (8)	0.0113 (8)	0.0008 (6)	0.0010 (6)	0.0027 (6)
C8	0.0098 (8)	0.0101 (7)	0.0098 (8)	−0.0017 (6)	0.0022 (6)	−0.0006 (6)
C9	0.0112 (8)	0.0098 (7)	0.0122 (8)	−0.0016 (6)	0.0023 (6)	0.0005 (6)
C10	0.0107 (8)	0.0086 (7)	0.0133 (8)	0.0006 (6)	0.0003 (6)	−0.0007 (6)
C11	0.0094 (8)	0.0105 (7)	0.0103 (8)	−0.0013 (6)	0.0014 (6)	−0.0009 (6)
C12	0.0101 (8)	0.0109 (8)	0.0135 (8)	−0.0008 (6)	0.0041 (6)	0.0001 (6)
C13	0.0076 (8)	0.0138 (8)	0.0118 (8)	−0.0020 (6)	0.0005 (6)	−0.0026 (6)
C14	0.0092 (8)	0.0118 (8)	0.0120 (8)	−0.0012 (6)	0.0018 (6)	−0.0011 (6)
C15	0.0128 (8)	0.0150 (8)	0.0110 (8)	−0.0030 (6)	0.0025 (6)	0.0002 (6)
C16	0.0154 (9)	0.0203 (9)	0.0127 (8)	−0.0024 (7)	0.0009 (7)	0.0042 (7)
C17	0.0119 (8)	0.0208 (9)	0.0152 (9)	−0.0020 (7)	−0.0004 (7)	0.0021 (7)

C18	0.0103 (8)	0.0168 (8)	0.0119 (8)	−0.0037 (6)	0.0014 (6)	0.0003 (7)
C19	0.0130 (9)	0.0186 (9)	0.0123 (8)	−0.0036 (7)	0.0021 (7)	0.0036 (7)
C20	0.0139 (9)	0.0142 (8)	0.0166 (9)	−0.0019 (7)	0.0051 (7)	0.0009 (7)
C21	0.0109 (8)	0.0172 (8)	0.0106 (8)	−0.0035 (6)	0.0034 (6)	−0.0015 (7)
N4	0.0086 (7)	0.0138 (7)	0.0116 (7)	−0.0001 (5)	0.0006 (5)	0.0021 (6)
N5	0.0081 (7)	0.0200 (8)	0.0115 (7)	0.0007 (6)	0.0026 (5)	0.0006 (6)
C22	0.0126 (8)	0.0141 (8)	0.0140 (8)	0.0007 (6)	0.0019 (7)	−0.0016 (7)
C23	0.0123 (9)	0.0159 (9)	0.0200 (9)	−0.0039 (7)	0.0020 (7)	−0.0033 (7)
C24	0.0127 (8)	0.0130 (8)	0.0162 (9)	0.0010 (6)	0.0026 (7)	−0.0011 (7)
C25	0.0113 (8)	0.0124 (8)	0.0167 (9)	−0.0005 (6)	0.0012 (7)	−0.0008 (7)
N6	0.0121 (7)	0.0106 (7)	0.0094 (7)	−0.0021 (5)	0.0028 (5)	0.0008 (5)
C26	0.0149 (8)	0.0089 (7)	0.0109 (8)	0.0010 (6)	0.0022 (6)	−0.0010 (6)
C27	0.0103 (8)	0.0128 (8)	0.0121 (8)	0.0023 (6)	0.0024 (6)	−0.0002 (6)
O13	0.0258 (8)	0.0231 (8)	0.0226 (8)	−0.0076 (6)	0.0011 (6)	0.0031 (6)
O14	0.0214 (7)	0.0130 (6)	0.0154 (7)	0.0013 (5)	0.0030 (5)	−0.0001 (5)
O15	0.0137 (6)	0.0125 (6)	0.0184 (7)	−0.0028 (5)	0.0024 (5)	0.0011 (5)

Geometric parameters (Å, °)

Cd1—N2	2.2667 (15)	C15—C16	1.391 (3)
Cd1—O9	2.3063 (14)	C15—C20	1.524 (3)
Cd1—N3	2.3074 (16)	C16—C17	1.394 (3)
Cd1—N1	2.3159 (15)	C16—H16A	0.9500
Cd1—O1	2.3190 (13)	C17—C18	1.392 (3)
Cd1—O5	2.3476 (13)	C17—H17A	0.9500
O1—C6	1.276 (2)	C18—C19	1.392 (3)
O2—C6	1.236 (2)	C18—C21	1.502 (2)
O3—C7	1.258 (2)	C19—H19A	0.9500
O4—C7	1.254 (2)	N4—C25	1.489 (2)
O5—C13	1.260 (2)	N4—C22	1.491 (2)
O6—C13	1.247 (2)	N4—H4A	0.9000
O7—C14	1.233 (2)	N4—H4B	0.9000
O8—C14	1.279 (2)	N5—C23	1.487 (2)
O9—C20	1.262 (2)	N5—C24	1.488 (2)
O10—C20	1.248 (2)	N5—H5B	0.8999
O11—C21	1.283 (2)	N5—H5C	0.9001
O11—H11	0.8850	C22—C23	1.512 (3)
O12—C21	1.234 (2)	C22—H22A	0.9900
N1—C5	1.338 (2)	C22—H22B	0.9900
N1—C1	1.342 (2)	C23—H23A	0.9900
N2—C12	1.331 (2)	C23—H23B	0.9900
N2—C8	1.348 (2)	C24—C25	1.510 (2)
N3—C19	1.332 (2)	C24—H24A	0.9900
N3—C15	1.346 (2)	C24—H24B	0.9900
C1—C2	1.389 (2)	C25—H25A	0.9900
C1—C6	1.522 (2)	C25—H25B	0.9900
C2—C3	1.388 (2)	N6—C26	1.489 (2)
C2—H2A	0.9500	N6—C27	1.495 (2)
C3—C4	1.388 (2)	N6—H6A	0.8999

C3—H3A	0.9500	N6—H6B	0.9001
C4—C5	1.389 (2)	C26—C27^{i}	1.513 (2)
C4—C7	1.512 (2)	C26—H26A	0.9900
C5—H5A	0.9500	C26—H26B	0.9900
C8—C9	1.386 (2)	C27—C26^{i}	1.513 (2)
C8—C13	1.524 (2)	C27—H27A	0.9900
C9—C10	1.385 (2)	C27—H27B	0.9900
C9—H9A	0.9500	O13—H13A	0.8196
C10—C11	1.391 (2)	O13—H13B	0.8196
C10—H10A	0.9500	O14—H14A	0.8202
C11—C12	1.392 (2)	O14—H14B	0.8194
C11—C14	1.506 (2)	O15—H15A	0.8194
C12—H12A	0.9500	O15—H15B	0.8198
N2—Cd1—O9	112.04 (5)	C15—C16—H16A	120.5
N2—Cd1—N3	120.43 (6)	C17—C16—H16A	120.5
O9—Cd1—N3	71.01 (5)	C18—C17—C16	118.88 (17)
N2—Cd1—N1	133.16 (5)	C18—C17—H17A	120.6
O9—Cd1—N1	105.64 (5)	C16—C17—H17A	120.6
N3—Cd1—N1	97.23 (5)	C19—C18—C17	118.17 (17)
N2—Cd1—O1	87.73 (5)	C19—C18—C21	116.83 (16)
O9—Cd1—O1	81.22 (5)	C17—C18—C21	124.98 (17)
N3—Cd1—O1	145.97 (5)	N3—C19—C18	123.14 (17)
N1—Cd1—O1	71.31 (5)	N3—C19—H19A	118.4
N2—Cd1—O5	71.86 (5)	C18—C19—H19A	118.4
O9—Cd1—O5	152.50 (5)	O10—C20—O9	125.95 (17)
N3—Cd1—O5	83.52 (5)	O10—C20—C15	116.92 (17)
N1—Cd1—O5	87.28 (5)	O9—C20—C15	117.11 (16)
O1—Cd1—O5	126.24 (5)	O12—C21—O11	125.88 (17)
C6—O1—Cd1	117.62 (11)	O12—C21—C18	118.09 (17)
C13—O5—Cd1	117.13 (11)	O11—C21—C18	116.03 (16)
C20—O9—Cd1	119.09 (12)	C25—N4—C22	111.25 (14)
C21—O11—H11	111.1	C25—N4—H4A	109.4
C5—N1—C1	118.86 (15)	C22—N4—H4A	109.4
C5—N1—Cd1	125.56 (12)	C25—N4—H4B	109.3
C1—N1—Cd1	115.52 (11)	C22—N4—H4B	109.4
C12—N2—C8	119.15 (15)	H4A—N4—H4B	108.1
C12—N2—Cd1	123.67 (12)	C23—N5—C24	111.25 (14)
C8—N2—Cd1	116.90 (11)	C23—N5—H5B	109.4
C19—N3—C15	118.78 (16)	C24—N5—H5B	109.4
C19—N3—Cd1	123.98 (12)	C23—N5—H5C	109.3
C15—N3—Cd1	116.55 (12)	C24—N5—H5C	109.4
N1—C1—C2	121.74 (16)	H5B—N5—H5C	108.1
N1—C1—C6	116.86 (15)	N4—C22—C23	110.86 (15)
C2—C1—C6	121.39 (16)	N4—C22—H22A	109.5
C1—C2—C3	119.07 (16)	C23—C22—H22A	109.5
C1—C2—H2A	120.5	N4—C22—H22B	109.5
C3—C2—H2A	120.5	C23—C22—H22B	109.5
C4—C3—C2	119.26 (16)	H22A—C22—H22B	108.1

C4—C3—H3A	120.4	N5—C23—C22	110.28 (15)
C2—C3—H3A	120.4	N5—C23—H23A	109.6
C3—C4—C5	117.99 (16)	C22—C23—H23A	109.6
C3—C4—C7	122.23 (16)	N5—C23—H23B	109.6
C5—C4—C7	119.69 (16)	C22—C23—H23B	109.6
N1—C5—C4	122.95 (16)	H23A—C23—H23B	108.1
N1—C5—H5A	118.5	N5—C24—C25	111.09 (15)
C4—C5—H5A	118.5	N5—C24—H24A	109.4
O2—C6—O1	125.25 (17)	C25—C24—H24A	109.4
O2—C6—C1	118.17 (16)	N5—C24—H24B	109.4
O1—C6—C1	116.59 (15)	C25—C24—H24B	109.4
O4—C7—O3	124.73 (17)	H24A—C24—H24B	108.0
O4—C7—C4	117.73 (16)	N4—C25—C24	110.09 (15)
O3—C7—C4	117.50 (16)	N4—C25—H25A	109.6
N2—C8—C9	121.51 (16)	C24—C25—H25A	109.6
N2—C8—C13	116.72 (15)	N4—C25—H25B	109.6
C9—C8—C13	121.72 (15)	C24—C25—H25B	109.6
C10—C9—C8	119.14 (16)	H25A—C25—H25B	108.2
C10—C9—H9A	120.4	C26—N6—C27	110.82 (13)
C8—C9—H9A	120.4	C26—N6—H6A	109.4
C9—C10—C11	119.48 (16)	C27—N6—H6A	109.4
C9—C10—H10A	120.3	C26—N6—H6B	109.5
C11—C10—H10A	120.3	C27—N6—H6B	109.5
C10—C11—C12	117.74 (16)	H6A—N6—H6B	108.1
C10—C11—C14	122.14 (16)	N6—C26—C27^{i}	110.25 (14)
C12—C11—C14	120.11 (15)	N6—C26—H26A	109.6
N2—C12—C11	122.96 (16)	C27^{i}—C26—H26A	109.6
N2—C12—H12A	118.5	N6—C26—H26B	109.6
C11—C12—H12A	118.5	C27^{i}—C26—H26B	109.6
O6—C13—O5	125.89 (16)	H26A—C26—H26B	108.1
O6—C13—C8	116.81 (15)	N6—C27—C26^{i}	109.89 (14)
O5—C13—C8	117.29 (15)	N6—C27—H27A	109.7
O7—C14—O8	126.16 (17)	C26^{i}—C27—H27A	109.7
O7—C14—C11	119.99 (16)	N6—C27—H27B	109.7
O8—C14—C11	113.85 (15)	C26^{i}—C27—H27B	109.7
N3—C15—C16	121.89 (17)	H27A—C27—H27B	108.2
N3—C15—C20	115.09 (16)	H13A—O13—H13B	89.8
C16—C15—C20	123.02 (17)	H14A—O14—H14B	102.6
C15—C16—C17	119.07 (17)	H15A—O15—H15B	89.1
N2—Cd1—O1—C6	−150.66 (13)	C2—C1—C6—O2	−6.0 (3)
O9—Cd1—O1—C6	96.63 (13)	N1—C1—C6—O1	−4.5 (2)
N3—Cd1—O1—C6	61.45 (16)	C2—C1—C6—O1	174.48 (16)
N1—Cd1—O1—C6	−13.26 (12)	C3—C4—C7—O4	−171.23 (17)
O5—Cd1—O1—C6	−85.20 (13)	C5—C4—C7—O4	5.4 (3)
N2—Cd1—O5—C13	2.77 (13)	C3—C4—C7—O3	6.7 (3)
O9—Cd1—O5—C13	105.82 (15)	C5—C4—C7—O3	−176.75 (17)
N3—Cd1—O5—C13	127.78 (13)	C12—N2—C8—C9	−0.9 (3)

N1—Cd1—O5—C13	−134.63 (13)	Cd1—N2—C8—C9	−175.03 (13)
O1—Cd1—O5—C13	−70.26 (14)	C12—N2—C8—C13	176.65 (15)
N2—Cd1—O9—C20	118.31 (14)	Cd1—N2—C8—C13	2.5 (2)
N3—Cd1—O9—C20	2.29 (14)	N2—C8—C9—C10	1.5 (3)
N1—Cd1—O9—C20	−90.10 (14)	C13—C8—C9—C10	−175.92 (16)
O1—Cd1—O9—C20	−157.77 (14)	C8—C9—C10—C11	−1.1 (3)
O5—Cd1—O9—C20	25.4 (2)	C9—C10—C11—C12	0.2 (3)
N2—Cd1—N1—C5	−104.76 (15)	C9—C10—C11—C14	179.36 (16)
O9—Cd1—N1—C5	112.44 (15)	C8—N2—C12—C11	−0.1 (3)
N3—Cd1—N1—C5	40.20 (15)	Cd1—N2—C12—C11	173.65 (13)
O1—Cd1—N1—C5	−172.76 (16)	C10—C11—C12—N2	0.4 (3)
O5—Cd1—N1—C5	−42.91 (15)	C14—C11—C12—N2	−178.76 (16)
N2—Cd1—N1—C1	78.22 (14)	Cd1—O5—C13—O6	175.94 (14)
O9—Cd1—N1—C1	−64.59 (13)	Cd1—O5—C13—C8	−2.5 (2)
N3—Cd1—N1—C1	−136.82 (13)	N2—C8—C13—O6	−178.51 (16)
O1—Cd1—N1—C1	10.22 (12)	C9—C8—C13—O6	−1.0 (3)
O5—Cd1—N1—C1	140.07 (13)	N2—C8—C13—O5	0.0 (2)
O9—Cd1—N2—C12	32.49 (15)	C9—C8—C13—O5	177.55 (17)
N3—Cd1—N2—C12	112.73 (14)	C10—C11—C14—O7	5.7 (3)
N1—Cd1—N2—C12	−108.61 (15)	C12—C11—C14—O7	−175.15 (17)
O1—Cd1—N2—C12	−47.09 (14)	C10—C11—C14—O8	−173.93 (16)
O5—Cd1—N2—C12	−176.55 (15)	C12—C11—C14—O8	5.2 (2)
O9—Cd1—N2—C8	−153.64 (12)	C19—N3—C15—C16	2.4 (3)
N3—Cd1—N2—C8	−73.39 (14)	Cd1—N3—C15—C16	−168.50 (14)
N1—Cd1—N2—C8	65.27 (15)	C19—N3—C15—C20	−176.79 (16)
O1—Cd1—N2—C8	126.79 (13)	Cd1—N3—C15—C20	12.3 (2)
O5—Cd1—N2—C8	−2.67 (12)	N3—C15—C16—C17	0.0 (3)
N2—Cd1—N3—C19	76.60 (16)	C20—C15—C16—C17	179.08 (18)
O9—Cd1—N3—C19	−178.45 (16)	C15—C16—C17—C18	−1.8 (3)
N1—Cd1—N3—C19	−74.34 (16)	C16—C17—C18—C19	1.3 (3)
O1—Cd1—N3—C19	−141.42 (14)	C16—C17—C18—C21	−179.94 (18)
O5—Cd1—N3—C19	12.07 (15)	C15—N3—C19—C18	−2.9 (3)
N2—Cd1—N3—C15	−113.05 (13)	Cd1—N3—C19—C18	167.22 (14)
O9—Cd1—N3—C15	−8.10 (13)	C17—C18—C19—N3	1.1 (3)
N1—Cd1—N3—C15	96.01 (14)	C21—C18—C19—N3	−177.75 (17)
O1—Cd1—N3—C15	28.93 (18)	Cd1—O9—C20—O10	−175.32 (15)
O5—Cd1—N3—C15	−177.57 (14)	Cd1—O9—C20—C15	3.2 (2)
C5—N1—C1—C2	−3.5 (3)	N3—C15—C20—O10	168.19 (17)
Cd1—N1—C1—C2	173.75 (13)	C16—C15—C20—O10	−11.0 (3)
C5—N1—C1—C6	175.51 (16)	N3—C15—C20—O9	−10.4 (3)
Cd1—N1—C1—C6	−7.25 (19)	C16—C15—C20—O9	170.40 (18)
N1—C1—C2—C3	2.5 (3)	C19—C18—C21—O12	−12.1 (3)
C6—C1—C2—C3	−176.46 (16)	C17—C18—C21—O12	169.21 (19)
C1—C2—C3—C4	0.8 (3)	C19—C18—C21—O11	167.54 (17)
C2—C3—C4—C5	−2.9 (3)	C17—C18—C21—O11	−11.2 (3)
C2—C3—C4—C7	173.78 (16)	C25—N4—C22—C23	−56.94 (19)
C1—N1—C5—C4	1.2 (3)	C24—N5—C23—C22	−56.4 (2)
Cd1—N1—C5—C4	−175.70 (13)	N4—C22—C23—N5	56.2 (2)
C3—C4—C5—N1	1.9 (3)	C23—N5—C24—C25	56.95 (19)

C7—C4—C5—N1	−174.80 (16)	C22—N4—C25—C24	56.59 (19)
Cd1—O1—C6—O2	−165.38 (14)	N5—C24—C25—N4	−56.4 (2)
Cd1—O1—C6—C1	14.12 (19)	C27—N6—C26—C27^{i}	58.1 (2)
N1—C1—C6—O2	175.01 (16)	C26—N6—C27—C26^{i}	−57.9 (2)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4A···O6	0.90	1.85	2.714 (2)	159
N4—H4B···O14^{ii}	0.90	1.91	2.791 (2)	167
N5—H5B···O3^{ii}	0.90	1.93	2.766 (2)	153
N5—H5C···O12	0.90	1.84	2.704 (2)	160
N6—H6A···O15^{i}	0.90	1.91	2.799 (2)	168
N6—H6B···O1	0.90	1.90	2.780 (2)	164
O11—H11···O8^{iii}	0.89	1.59	2.439 (2)	159
O13—H13A···O10^{iv}	0.82	2.04	2.811 (2)	157
O13—H13B···O4	0.82	1.91	2.727 (2)	173
O14—H14A···O3^{ii}	0.82	1.98	2.754 (2)	158
O14—H14B···O13	0.82	1.95	2.771 (2)	175
O15—H15A···O10	0.82	2.07	2.860 (2)	162
O15—H15B···O7^{v}	0.82	1.94	2.761 (2)	177
C9—H9A···O2^{vi}	0.95	2.48	3.161 (2)	129
C19—H19A···O5	0.95	2.41	3.064 (2)	126
C22—H22B···O12	0.99	2.58	3.280 (2)	127
C24—H24A···O15^{vii}	0.99	2.56	3.317 (2)	133
C24—H24B···O4	0.99	2.49	3.251 (2)	133
C26—H26B···O8	0.99	2.38	3.206 (2)	141
C27—H27B···O9	0.99	2.45	3.327 (2)	148

Symmetry codes: (ii) −*x*+1/2, *y*−1/2, −*z*+3/2; (i) −*x*+2, −*y*+2, −*z*+1; (iii) *x*−1, *y*, *z*; (iv) −*x*+1, −*y*+2, −*z*+1; (v) −*x*+2, −*y*+1, −*z*+1; (vi) *x*, *y*−1, *z*; (vii) *x*−1/2, −*y*+3/2, *z*+1/2.

Fig. 1

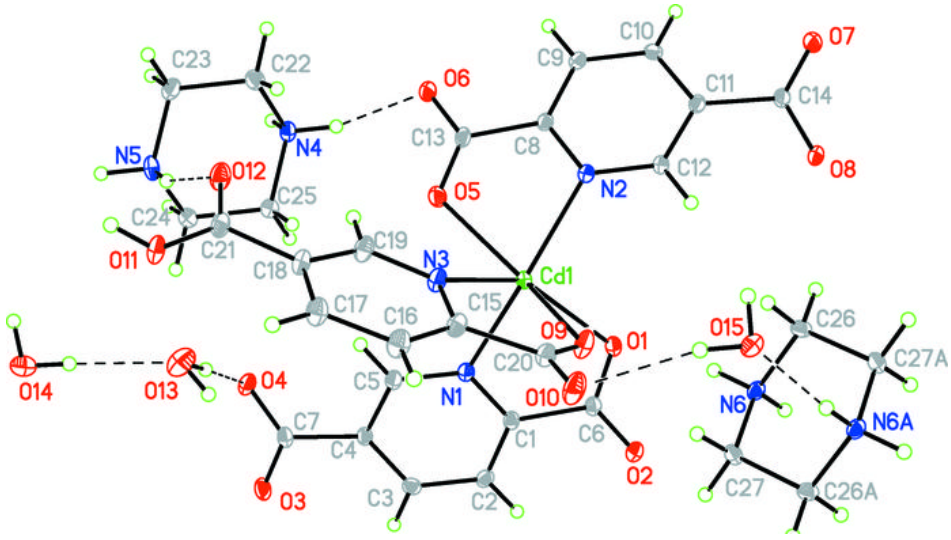
C23
C22
O6
C10
C9
O7
C11
C14
N5
N4
C13
C8
O8
O12
C25
O5
N2
C12
C24
C21
C19
O11
C18
N3
Cd1
C17
C16
C15
O9
O1
O15
C26
C27A
O14
O13
O4
C5
C20
N1
O10
N6
N6A
C7
C4
C1
C6
O2
O3
C3
C2
C27
C26A

Fig. 2

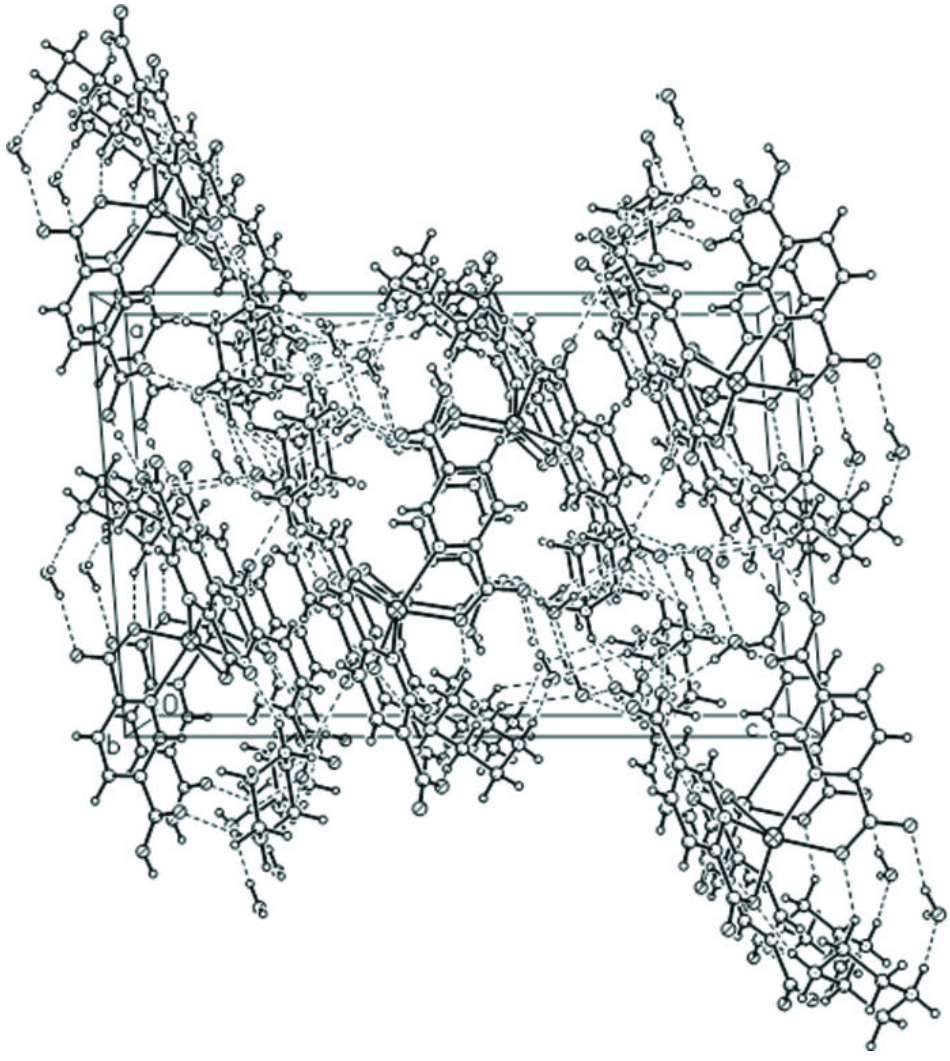
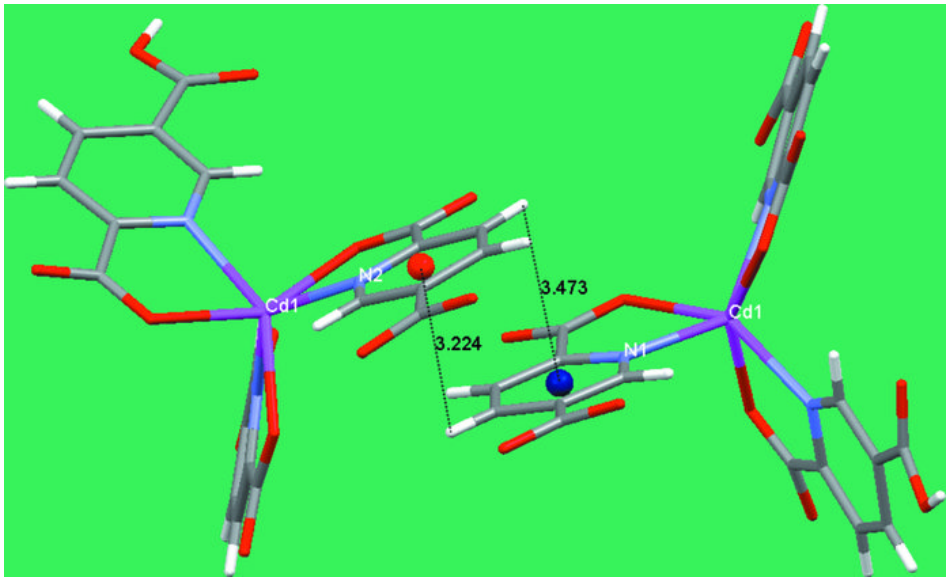
Fig. 3