metal-organic compounds

catena-Poly[[triaquacadmium(II)]-μ-pyridine-2,3-dicarboxylato-$\kappa^3N,O^2:O^3$]

Hossein Aghabozorg,[a]* Elham Motyeian,[a] Ramona Khadivi,[b] Mohammad Ghadermazi[c] and Faranak Manteghi[a]

[a]Faculty of Chemistry, Teacher Training University, 49 Mofateh Ave., 15614 Tehran, Iran, [b]Department of Chemistry, Islamic Azad University, North Tehran Branch, Tehran, Iran, and [c]Department of Chemistry, Faculty of Science, University of Kurdistan, Sanandaj, Iran

Correspondence e-mail: haghabozorg@yahoo.com

The title polymeric compound, $[Cd(C_7H_3NO_4)(H_2O)_3]_n$ or $[Cd(py\text{-}2,3\text{-}dc)(H_2O)_3]_n$, where py-2,3-dcH₂ is pyridine-2,3-dicarboxylic acid, was obtained by the reaction of cadmium(II) nitrate hexahydrate with (pipzH₂)(py-2,3-dc) as a proton-transfer compound in aqueous solution (pipz is piperazine). The molecular structure shows that only the anionic fragment of the starting proton-transfer compound is present in the complex, while the (pipzH₂)²⁺ dication has been lost. Each (py-2,3-dc)²⁻ ligand bridges two Cd^II atoms in two different coordination modes, *i.e.* one end acts as a monodentate and the other end as a bidentate ligand. The three remaining coordination sites on the metal center are occupied by water molecules. The geometric arrangement of the six donor atoms around the Cd^II atom is distorted octahedral. In the crystal structure, O—H···O and C—H···O hydrogen bonds play an important role in stabilizing the supramolecular structure.

Related literature

For related ion pairs or complexes, see: Aghabozorg, Daneshvar, Motyeian *et al.* (2007); Aghabozorg *et al.* (2008); Manteghi *et al.* (2007); Aghabozorg, Sadr-khanlou *et al.* (2007); Li *et al.* (2004).
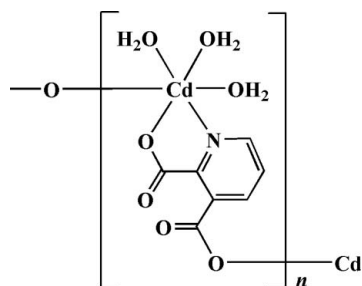
Experimental

Crystal data

$[Cd(C_7H_3NO_4)(H_2O)_3]$	$V = 992.3$ (3) Å³
$M_r = 331.55$	$Z = 4$
Orthorhombic, $Pca2_1$	Mo $K\alpha$ radiation
$a = 16.820$ (3) Å	$\mu = 2.22$ mm⁻¹
$b = 6.8076$ (14) Å	$T = 100$ (2) K
$c = 8.6658$ (17) Å	$0.40 \times 0.08 \times 0.05$ mm

Data collection

Bruker APEX 1000 CCD area-detector diffractometer	8990 measured reflections
Absorption correction: multi-scan (*APEX2*; Bruker, 2005)	2255 independent reflections
	1848 reflections with $I > 2\sigma(I)$
$T_{min} = 0.810$, $T_{max} = 0.901$	$R_{int} = 0.060$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.056$	
$S = 1.01$	
2255 reflections	$\Delta\rho_{max} = 0.61$ e Å⁻³
151 parameters	$\Delta\rho_{min} = -0.84$ e Å⁻³
7 restraints	Absolute structure: Flack (1983), 1042 Friedel pairs
	Flack parameter: 0.05 (4)

Table 1
Selected geometric parameters (Å, °).

Cd1—O1W	2.254 (4)	Cd1—O4	2.279 (3)
Cd1—O2^i	2.259 (3)	Cd1—N1^i	2.302 (4)
Cd1—O3W	2.274 (3)	Cd1—O2W	2.385 (3)
O3W—Cd1—O4	156.89 (12)	O2^i—Cd1—O2W	171.30 (12)
O1W—Cd1—N1^i	163.70 (14)		

Symmetry code: (i) $-x + \frac{3}{2}, y, z - \frac{1}{2}$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1···O2W^ii	0.85 (2)	1.99 (2)	2.782 (5)	155.61
O1W—H2···O3^iii	0.87 (2)	1.86 (2)	2.702 (5)	163.55
O2W—H3···O1^iii	0.88 (2)	1.85 (2)	2.731 (5)	177.88
O2W—H4···O3^iv	0.87 (2)	1.84 (2)	2.687 (5)	164.45
O3W—H5···O4^iii	0.86 (2)	1.86 (2)	2.712 (4)	171.29
O3W—H6···O1^v	0.87 (2)	1.89 (2)	2.735 (8)	164.32
C3—H3A···O1W^vi	0.95 (2)	2.49 (2)	3.420 (6)	165

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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supplementary materials

catena-Poly[[triaquacadmium(II)]-*μ*-pyridine-2,3-dicarboxylato-$\kappa^3N,O^2:O^3$]

H. Aghabozorg, E. Motyeian, R. Khadivi, M. Ghadermazi and F. Manteghi

Comment

Recently, ion pairs or complexes related to the title compound have been reported (Aghabozorg, Daneshvar, Motyeian *et al.*, 2007). Proton transfer from pyridine-2,3-dicarboxylic acid (py-2,3-dcH$_2$) to amines, such as piperazine (pipz) and propane-1,3-diamine (pn), resulted in the formation of novel systems (Aghabozorg, Manteghi *et al.*, 2007 submitted; Manteghi *et al.*, 2007). The resulting compounds, with some remaining sites as electron donors, can coordinate to metallic ions (Aghabozorg, Sadr-khanlou *et al.*, 2007). The molecular structure of the title compound shows that only the anionic fragment of starting proton transfer compound is incorporated into the complex and that the (pipzH$_2$)$^{2+}$ dication has been lost. Each cadmium(II) atom is coordinated by five O-atoms and one N-atom. The asymmetric unit consists of one cadmium, one bridging (py-2,3-dc)$^{2-}$ and three coordinated water molecules (Fig. 1). The (py-2,3-dc)$^{2-}$ groups bridge two cadmium ions by adopting two different coordination modes, bidentate and monodentate. The existance of both coordination modes is seldom found in pyridine multicarboxylate coordination polymers (Li *et al.* 2004). The bond lengths and bond angles of the equatorial bonds around the metal center with atoms N1A, O2A, O1W and O2W, and the axial bonds with atoms O4 and O3W, indicate that the geometric arrangement of the six donor atoms around the cadmium(II) atom is distorted octahedral (Table 1). It is noticeable that one of the carboxylate groups is almost coplannar with the pyridine ring and the other is perpendicular to it (Fig. 1). The formation of the polymeric chains along the *c* axis is illustrated in Fig. 2. There are a number of O—H⋯O hydrogen bonds (Table 2) involving the coordinated water molecules and other O-atoms, [D⋯A distances ranging from 2.685 (5) to 2.789 (5) Å], and a C—H⋯O bond [D⋯A distance of 3.430 (6) Å], that give rise to the formation of a three-dimensional network (Fig. 3).

Experimental

The proton transfer ion pair was prepared according to the literature (Aghabozorg *et al.*, 2008, in press). A solution of Cd(NO$_3$)$_2$. 6H$_2$O (158 mg, 0.5 mmol) in water (20 ml) was added to a solution of (pipzH$_2$)(py- 2,3-dc) (253 mg, 1.0 mmol) in water (20 ml), in a 1:2 molar ratio. Colorless crystals of the title compound suitable for X-ray characterization were obtained after a few days at room temperature.

Refinement

All the hydrogen atoms could be located from the difference Fourier syntheses. The water H-atoms were refined isotropically with U_{iso}(H) = 0.022. The C-bond H-atoms were included in calculated positions and treated as riding atoms: C—H = 0.95 Å with U_{iso}(H) = 1.2 U_{eq}(C).
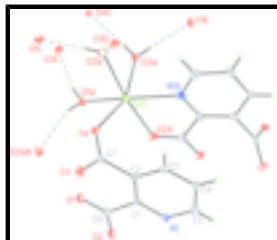
Figures

Fig. 1. Molecular structure of the title compound, showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level. Hydrogen bonds are shown as dashed lines. Atoms marked with suffixes A—E are related by the symmetry codes (A) $-x + 3/2, y, z - 1/2$; (B) $-x + 1, -y + 1, z + 1/2$; (C) $-x + 1, -y + 1, z - 1/2$; (D) $-x + 1, -y + 2, z - 1/2$; (E) $x, y, z - 1$).
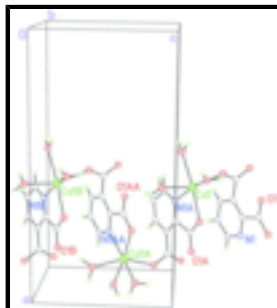

Fig. 2. A view of the polymeric chain of the title compound extending along the c axis.
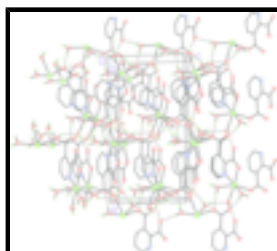

Fig. 3. A view along the b axis of the crystal packing of the title compound [the hydrogen bonds are shown as dashed lines and the hydrogen atoms of the pyridine-2,3-dicarboxylates ligands are omitted for clarity].

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Crystal data

[Cd(C$_7$H$_3$NO$_4$)(H$_2$O)$_3$]	$F_{000} = 648$
$M_r = 331.55$	$D_x = 2.219$ Mg m^{-3}
Orthorhombic, $Pca2_1$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: P 2c -2ac	Cell parameters from 1136 reflections
$a = 16.820$ (3) Å	$\theta = 3.0–24.6°$
$b = 6.8076$ (14) Å	$\mu = 2.22$ mm^{-1}
$c = 8.6658$ (17) Å	$T = 100$ (2) K
$V = 992.3$ (3) Å^3	Needle, colourless
$Z = 4$	$0.40 \times 0.08 \times 0.05$ mm

Data collection

Bruker APEX 1000 CCD area-detector diffractometer	2255 independent reflections
Radiation source: fine-focus sealed tube	1848 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.060$

$T = 100(2)$ K	$\theta_{max} = 27.5°$
ω scans	$\theta_{min} = 2.4°$
Absorption correction: multi-scan (APEX2; Bruker, 2005)	$h = -21 \rightarrow 21$
$T_{min} = 0.810$, $T_{max} = 0.901$	$k = -8 \rightarrow 8$
8990 measured reflections	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Hydrogen site location: difference Fourier map
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.029$	$w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.056$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.01$	$\Delta\rho_{max} = 0.61$ e Å^{-3}
2255 reflections	$\Delta\rho_{min} = -0.84$ e Å^{-3}
151 parameters	Extinction correction: none
7 restraints	Absolute structure: Flack (1983), 1042 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.05 (4)
Secondary atom site location: difference Fourier map	

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 $F^2 > \sigma(F^2)$ 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	0.602315 (16)	0.57263 (4)	1.12348 (5)	0.01148 (8)
O1	0.64375 (15)	0.5438 (4)	1.6269 (10)	0.0146 (4)
O2	0.77114 (19)	0.4893 (5)	1.6812 (4)	0.0146 (4)
O3	0.55536 (18)	0.9159 (5)	1.5507 (4)	0.0139 (7)
O4	0.56140 (18)	0.7169 (5)	1.3472 (4)	0.0131 (8)
C1	0.7384 (3)	0.7512 (7)	1.5083 (6)	0.0114 (10)
C2	0.6813 (3)	0.8656 (7)	1.4333 (6)	0.0120 (11)
C3	0.7065 (3)	1.0220 (8)	1.3431 (7)	0.0110 (11)
H3A	0.6685	1.1023	1.2920	0.013*
C4	0.7868 (3)	1.0616 (8)	1.3272 (7)	0.0149 (11)

H4A	0.8050	1.1660	1.2636	0.018*
C5	0.8403 (3)	0.9424 (8)	1.4080 (6)	0.0168 (11)
H5A	0.8956	0.9694	1.4001	0.020*
C6	0.7166 (2)	0.5813 (6)	1.6146 (9)	0.0146 (4)
C7	0.5934 (3)	0.8271 (7)	1.4475 (5)	0.0113 (10)
N1	0.8168 (2)	0.7919 (6)	1.4961 (5)	0.0125 (9)
O1W	0.5482 (2)	0.2964 (6)	1.2211 (4)	0.0145 (8)
H1	0.526 (3)	0.302 (9)	1.309 (4)	0.022*
H2	0.509 (2)	0.227 (7)	1.183 (5)	0.022*
O2W	0.47743 (19)	0.6981 (5)	1.0383 (4)	0.0134 (7)
H3	0.439 (2)	0.618 (6)	1.065 (6)	0.020*
H4	0.464 (3)	0.818 (4)	1.060 (6)	0.020*
O3W	0.59058 (19)	0.3963 (5)	0.9018 (4)	0.0147 (8)
H5	0.5445 (19)	0.350 (8)	0.879 (7)	0.022*
H6	0.609 (3)	0.420 (8)	0.811 (3)	0.022*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.00902 (12)	0.01505 (14)	0.01036 (13)	−0.00047 (13)	0.0004 (3)	0.0018 (3)
O1	0.0109 (8)	0.0186 (11)	0.0144 (10)	0.0005 (8)	0.0029 (11)	0.0048 (12)
O2	0.0109 (8)	0.0186 (11)	0.0144 (10)	0.0005 (8)	0.0029 (11)	0.0048 (12)
O3	0.0112 (16)	0.0158 (18)	0.0146 (16)	−0.0006 (14)	0.0041 (13)	−0.0032 (16)
O4	0.0077 (16)	0.023 (2)	0.0084 (17)	−0.0019 (14)	0.0004 (14)	−0.0031 (16)
C1	0.011 (2)	0.012 (3)	0.011 (2)	−0.0042 (19)	−0.0063 (19)	−0.001 (2)
C2	0.010 (2)	0.014 (3)	0.012 (3)	−0.0018 (19)	0.000 (2)	−0.005 (2)
C3	0.009 (3)	0.013 (3)	0.011 (3)	0.004 (2)	0.000 (2)	−0.002 (2)
C4	0.014 (3)	0.016 (3)	0.014 (3)	−0.002 (2)	−0.001 (2)	0.005 (3)
C5	0.012 (3)	0.020 (3)	0.017 (3)	−0.004 (2)	0.000 (2)	−0.004 (3)
C6	0.0109 (8)	0.0186 (11)	0.0144 (10)	0.0005 (8)	0.0029 (11)	0.0048 (12)
C7	0.013 (2)	0.011 (3)	0.010 (2)	−0.001 (2)	−0.003 (2)	0.0057 (19)
N1	0.011 (2)	0.016 (2)	0.010 (2)	−0.0057 (17)	0.0018 (16)	−0.0007 (18)
O1W	0.0142 (18)	0.022 (2)	0.0070 (17)	−0.0081 (15)	0.0020 (14)	−0.0012 (16)
O2W	0.0127 (17)	0.0119 (19)	0.0156 (19)	0.0014 (14)	−0.0030 (14)	−0.0008 (17)
O3W	0.0113 (18)	0.023 (2)	0.0093 (16)	−0.0033 (15)	0.0003 (14)	−0.0040 (16)

Geometric parameters (Å, °)

Cd1—O1W	2.254 (4)	C2—C7	1.506 (6)
Cd1—O2^i	2.259 (3)	C3—C4	1.385 (6)
Cd1—O3W	2.274 (3)	C3—H3A	0.9500
Cd1—O4	2.279 (3)	C4—C5	1.400 (7)
Cd1—N1^i	2.302 (4)	C4—H4A	0.9500
Cd1—O2W	2.385 (3)	C5—N1	1.338 (7)
O1—C6	1.256 (4)	C5—H5A	0.9500
O2—C6	1.252 (6)	N1—Cd1^{ii}	2.302 (4)
O2—Cd1^{ii}	2.259 (3)	O1W—H1	0.850 (19)
O3—C7	1.255 (6)	O1W—H2	0.869 (19)

O4—C7	1.268 (6)	O2W—H3	0.88 (2)
C1—N1	1.351 (6)	O2W—H4	0.866 (19)
C1—C2	1.397 (7)	O3W—H5	0.858 (19)
C1—C6	1.523 (7)	O3W—H6	0.87 (2)
C2—C3	1.387 (7)		
O1W—Cd1—O2^{i}	95.06 (13)	C2—C3—H3A	119.9
O1W—Cd1—O3W	80.89 (13)	C3—C4—C5	117.7 (5)
O2^{i}—Cd1—O3W	97.84 (12)	C3—C4—H4A	121.1
O1W—Cd1—O4	85.31 (13)	C5—C4—H4A	121.1
O2^{i}—Cd1—O4	101.79 (12)	N1—C5—C4	122.6 (5)
O3W—Cd1—O4	156.89 (12)	N1—C5—H5A	118.7
O1W—Cd1—N1^{i}	163.70 (14)	C4—C5—H5A	118.7
O2^{i}—Cd1—N1^{i}	73.25 (13)	O2—C6—O1	125.0 (6)
O3W—Cd1—N1^{i}	89.34 (14)	O2—C6—C1	118.8 (4)
O4—Cd1—N1^{i}	107.87 (14)	O1—C6—C1	116.2 (5)
O1W—Cd1—O2W	93.38 (13)	O3—C7—O4	123.9 (4)
O2^{i}—Cd1—O2W	171.30 (12)	O3—C7—C2	118.3 (4)
O3W—Cd1—O2W	81.44 (12)	O4—C7—C2	117.6 (4)
O4—Cd1—O2W	80.96 (12)	C5—N1—C1	119.4 (4)
N1^{i}—Cd1—O2W	98.06 (13)	C5—N1—Cd1^{ii}	126.5 (3)
C6—O2—Cd1^{ii}	117.6 (3)	C1—N1—Cd1^{ii}	114.0 (3)
C7—O4—Cd1	135.2 (3)	Cd1—O1W—H1	118 (4)
N1—C1—C2	121.3 (5)	Cd1—O1W—H2	128 (3)
N1—C1—C6	116.0 (4)	H1—O1W—H2	92 (5)
C2—C1—C6	122.6 (4)	Cd1—O2W—H3	110 (3)
C3—C2—C1	118.7 (4)	Cd1—O2W—H4	120 (4)
C3—C2—C7	118.6 (4)	H3—O2W—H4	110 (5)
C1—C2—C7	122.7 (4)	Cd1—O3W—H5	118 (4)
C4—C3—C2	120.2 (5)	Cd1—O3W—H6	130 (4)
C4—C3—H3A	119.9	H5—O3W—H6	101 (5)
O1W—Cd1—O4—C7	131.6 (5)	C2—C1—C6—O2	−177.9 (5)
O2^{i}—Cd1—O4—C7	37.4 (5)	N1—C1—C6—O1	179.6 (6)
O3W—Cd1—O4—C7	−175.1 (4)	C2—C1—C6—O1	2.7 (9)
N1^{i}—Cd1—O4—C7	−38.6 (5)	Cd1—O4—C7—O3	168.0 (3)
O2W—Cd1—O4—C7	−134.3 (5)	Cd1—O4—C7—C2	−7.0 (7)
N1—C1—C2—C3	0.9 (7)	C3—C2—C7—O3	−87.1 (6)
C6—C1—C2—C3	177.6 (5)	C1—C2—C7—O3	92.4 (6)
N1—C1—C2—C7	−178.5 (4)	C3—C2—C7—O4	88.2 (6)
C6—C1—C2—C7	−1.8 (8)	C1—C2—C7—O4	−92.3 (6)
C1—C2—C3—C4	0.6 (9)	C4—C5—N1—C1	0.2 (8)
C7—C2—C3—C4	−179.9 (5)	C4—C5—N1—Cd1^{ii}	176.0 (4)
C2—C3—C4—C5	−1.7 (9)	C2—C1—N1—C5	−1.3 (7)
C3—C4—C5—N1	1.3 (9)	C6—C1—N1—C5	−178.3 (5)
Cd1^{ii}—O2—C6—O1	175.2 (6)	C2—C1—N1—Cd1^{ii}	−177.7 (4)
Cd1^{ii}—O2—C6—C1	−4.1 (7)	C6—C1—N1—Cd1^{ii}	5.4 (6)

N1—C1—C6—O2   −1.0 (8)

Symmetry codes: (i) −x+3/2, y, z−1/2; (ii) −x+3/2, y, z+1/2.

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1W—H1⋯O2W^{iii}	0.85 (2)	1.99 (2)	2.782 (5)	155.61
O1W—H2⋯O3^{iv}	0.87 (2)	1.86 (2)	2.702 (5)	163.55
O2W—H3⋯O1^{iv}	0.88 (2)	1.85 (2)	2.731 (5)	177.88
O2W—H4⋯O3^{v}	0.87 (2)	1.84 (2)	2.687 (5)	164.45
O3W—H5⋯O4^{iv}	0.86 (2)	1.86 (2)	2.712 (4)	171.29
O3W—H6⋯O1^{vi}	0.87 (2)	1.89 (2)	2.735 (8)	164.32
C3—H3A⋯O1W^{vii}	0.95 (2)	2.49 (2)	3.420 (6)	165

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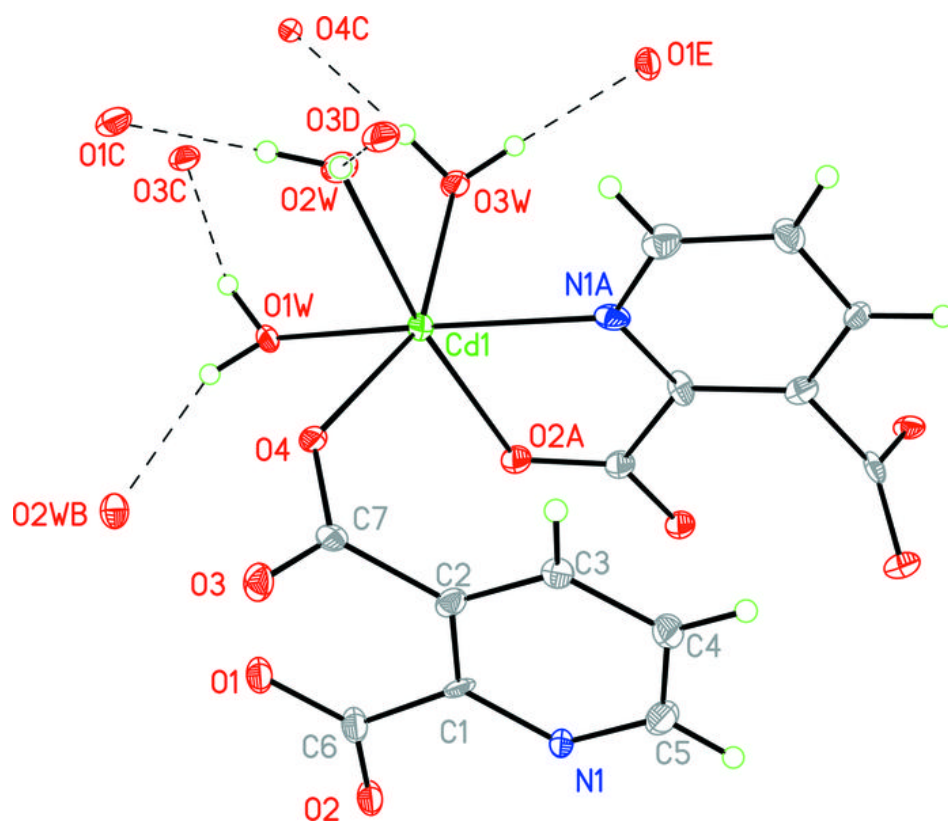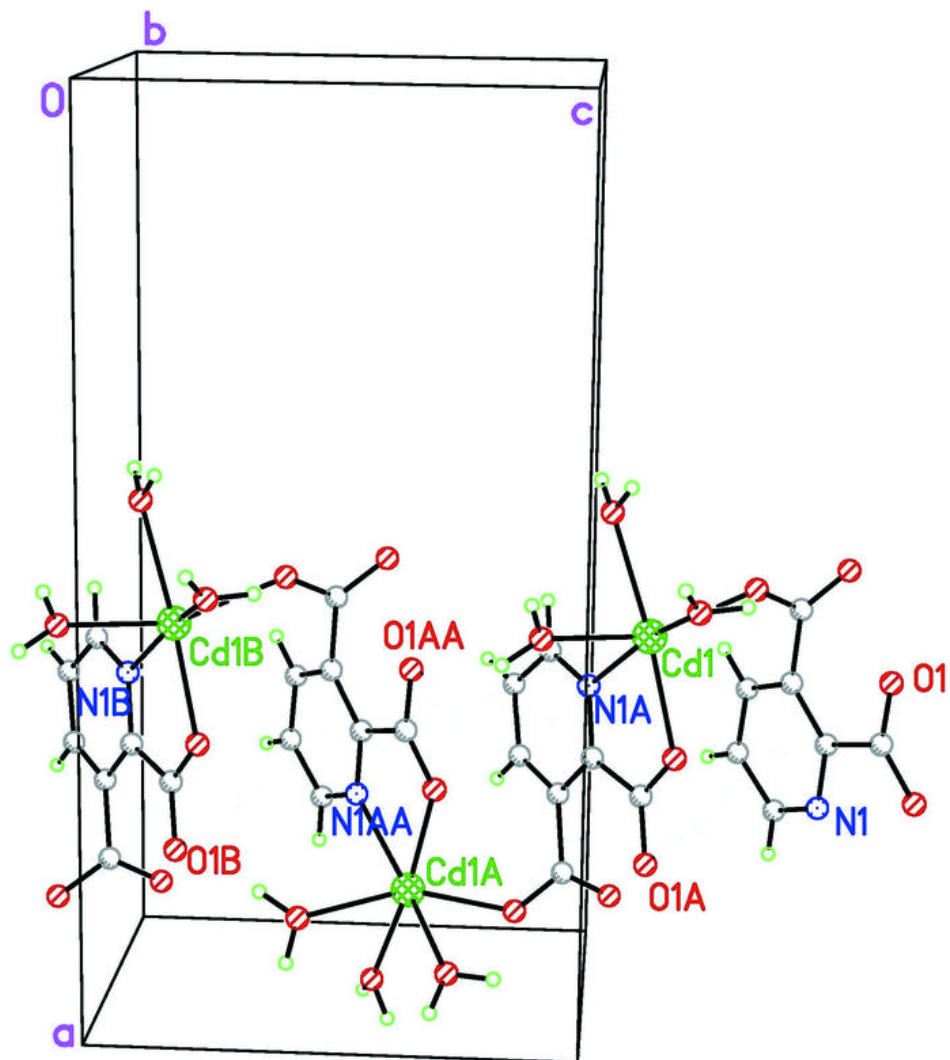
Fig. 1

Fig. 2

Fig. 3