

# A chiral three-dimensional network in poly[ $\mu$ -4,4'-bipyridine-di- $\mu$ -formato-cadmium(II)]

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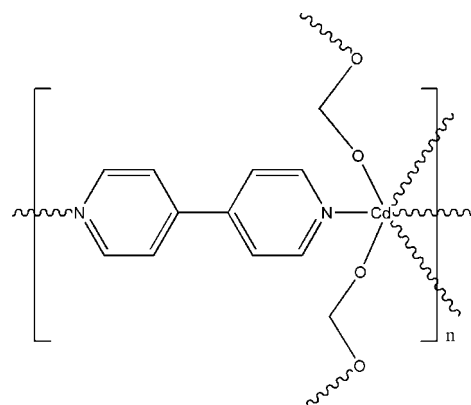
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.018;  $wR$  factor = 0.046; data-to-parameter ratio = 15.5.

In the title compound,  $[\text{Cd}(\text{HCOO})_2(\text{C}_{10}\text{H}_8\text{N}_2)]_n$ , the  $\text{Cd}^{\text{II}}$  ion, located on a position with 2.22 site symmetry, is surrounded by two 4,4'-bipyridine ligands and four formate ligands in a distorted octahedral  $\text{CdN}_2\text{O}_4$  coordination. The 4,4'-bipyridine ligands bridge the metal ions, forming one-dimensional chains along different directions, which are further connected by formate ligands into a topologically  $(10^{10}.12^4.14)(10)_3$  three-dimensional network.

## Related literature

For the design and synthesis of coordination polymer complexes and their potential applications, see: Barbour (2006); Biradha (2003); Brammer (2004); Hosseini (2005); O'Keeffe & Yaghi (2001); Papaefstathiou & MacGillivray (2003); Venkataraman *et al.* (1995). For the 4,4'-bipyridine (4BPY) bridging ligand, see: Hagrman *et al.* (1999); Moulton & Zaworotko (2001); Sharma (2001); Zaworotko (2001). For one-dimensional zigzag networks using 2,2'-bpy as the ancillary ligand, see: Park *et al.* (2001). For the doubly interpenetrated square grid network  $\{[\text{Zn}(\text{bipy})_2(\text{H}_2\text{O})_2][\text{SiF}_6]\}_n$ , see: Subramanian & Zaworotko (1995). For a three-dimensional network with large channels constructed through square grid networks of 4BPY and Zn(II) linked by  $\text{SiF}_6$  anions, see: Gable *et al.* (1990).



## Experimental

### Crystal data

$[\text{Cd}(\text{CHO}_2)_2(\text{C}_{10}\text{H}_8\text{N}_2)]$   
 $M_r = 358.62$   
Tetragonal,  $I4_122$   
 $a = 8.2269$  (12) Å  
 $c = 18.103$  (4) Å  
 $V = 1225.2$  (4) Å<sup>3</sup>

$Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 1.79$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.33 \times 0.33 \times 0.20$  mm

### Data collection

Rigaku R-AXIS RAPID diffractometer  
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)  
 $T_{\text{min}} = 0.554$ ,  $T_{\text{max}} = 0.698$

1106 measured reflections  
711 independent reflections  
681 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.025$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$   
 $wR(F^2) = 0.046$   
 $S = 1.13$   
711 reflections  
46 parameters  
H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.21$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.43$  e Å<sup>-3</sup>  
Absolute structure: Flack (1983), 263 Friedel pairs  
Flack parameter: 0.02 (7)

**Table 1**

Selected geometric parameters (Å, °).

Cd1—N1	2.306 (3)	Cd1—O1 <sup>i</sup>	2.3264 (18)
Cd1—N1 <sup>i</sup>	2.306 (3)	Cd1—O1 <sup>iii</sup>	2.3264 (18)
Cd1—O1 <sup>ii</sup>	2.3264 (18)	Cd1—O1	2.3264 (18)

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXL97*; 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: JH2074).

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**supplementary materials**

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## A chiral three-dimensional network in poly[ $\mu$ -4,4'-bipyridine-di- $\mu$ -formato-cadmium(II)]

L. Zhao, J.-L. Lin, W. Xu and H.-Z. Xie

### Comment

The design and synthesis of coordination polymer complexes, which is an emerging area of research with several potential applications in areas such as catalysis, conductivity, porosity, chirality, luminescence, magnetism, spin-transition and non-linear optics, are of considerable interest from the viewpoint of crystal engineering (Barbour, 2006; Biradha, 2003; Brammer, 2004; Hosseini, 2005; O'Keeffe, 2001; Papaefstathiou, 2003; Venkataraman, 1995). The structures and properties of coordination polymers can be controlled by choosing appropriate bridging ligands and metal ions. Many types of bridging ligand have been reported, of which the most extensively studied bidentate ligands are probably 4,4'-bipyridine (4BPY) (Hagrman, 1999; Moulton, 2001; Sharma, 2001; Zaworotko, 2001). The ligand 4,4'-bipyridine is an ideal connector between the transition metal atoms for the propagation of coordination networks and shown to form a variety of networks ranging from one-dimensional to three-dimensional with several transition metal salts, such as the one-dimensional zigzag networks by using of 2,2'-bpy as the ancillary ligand (Park, 2001), the doubly interpenetrated square grid networks  $\{[\text{Zn}(\text{bipy})_2(\text{H}_2\text{O})_2][\text{SiF}_6]\}_n$  (Gable, 1990) and a three-dimensional network with large channels which is constructed through square grid networks of 4BPY and Zn(II) linked by  $\text{SiF}_6$  anions (Subramanian, 1995). In this contribution, we here report a novel chiral three-dimensional crystal structure built from  $\text{Cd}^{\text{II}}$  ions and mixed-ligand including 4BPY ligands and formic acid ligands.

Compound 1 consists of  $\text{Cd}^{\text{II}}$  ions, 4,4'-bipyridine (4BPY) ligands and formate anions. As illustrated in Figure 1, the  $\text{Cd}^{\text{II}}$  ions are all disposed in a  $\text{N}_2\text{O}_4$  octahedron coordination environment with the equatorial coordination from four formate ligands ( $\text{O1}$ ,  $\text{O1}^{\#2}$ ,  $\text{O1}^{\#5}$ ,  $\text{O1}^{\#12}$ ) [symmetry codes:  $\#2 = 1 - x, -y, z$ ;  $\#5 = -x, 1 - y, z$ ;  $\#12 = 1 - x, -y, z$ ] and the apical sites occupied by two N atoms from two 4BPY ligands ( $\text{N1}$ ,  $\text{N1}^{\#5}$ ) [symmetry code:  $\#5 = -x, 1 - y, z$ ]. The average bond lengths of  $\text{Cd}-\text{O}$  and  $\text{Cd}-\text{N}$  are 2.326 (3) Å and 2.306 (4) Å, respectively. There are two kinds of formate ligands in this structure, one kind of them connect metal ions into right-handed helical chains along  $a$  axis (Figure 2) and the others connect the helical chains along two different orientations  $[011]$  and  $[01\bar{1}]$ , which generate a three-dimensional network. In the resulting structure, 4BPY ligands further link the  $\text{Cd}^{\text{II}}$  ions along  $[110]$  and  $[\bar{1}10]$  directions, respectively, to generate a  $(10^{10}.12^4.14)(10)_3$  topological three-dimensional network (Figure 3). Moreover, the 4BPY ligand displays obvious distortion and the dihedral angle between the two pyridine rings is approximately 46.2°.

### Experimental

4,4'-bpy (0.153 g, 1.0 mmol) and  $\text{CdCO}_3$  (0.177 g, 1.0 mmol) were orderly added in 10 ml  $\text{H}_2\text{O}$ . Under continuous stirring, 5.5 ml  $\text{HCOOH}$  (2 M) solution was subsequently added in the resulting mixture yielding clear solution. After filtration, the filtrate was maintained for slow evaporation at 40°C constant temperature for 3 days. Light yellow granule-like crystals were obtained in a yield of ca 23.7% based on  $\text{CdCO}_3$ .

## Refinement

H atoms bonded to C atoms were placed in geometrically calculated position and were refined using a riding model, with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ . H atoms attached to O atoms were found in a difference Fourier synthesis and were refined using a riding model, with the O—H distances fixed as initially found and with  $U_{\text{iso}}(\text{H})$  values set at  $1.2 U_{\text{eq}}(\text{O})$ .

## Figures

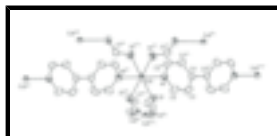


Fig. 1. A view of the complex molecule of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 60% probability level [Symmetry codes: #1 =  $-x + 1/2, -y + 1/2, -z + 3/2$ ; #2 =  $-x + 1, -y, z$ ; #3 =  $x + 1/2, -y + 1, z + 1/4$ ; #4 =  $-x + 1/2, y - 1, z + 1/4$ ; #5 =  $-x, -y + 1, z$ ; #6 =  $x, -y + 2/3, -z + 5/4$ ; #7 =  $x - 1, y + 1, z$ ; #8 =  $x + 1/2, -y, z + 1/4$ ; #9 =  $x, -y + 1/2, z - 1/4$ ; #10 =  $x + 1, y - 1, z$ ; #11 =  $x + 1, -y + 1/2, z - 1/4$ ; #12 =  $1 - x, -y, z$ ].

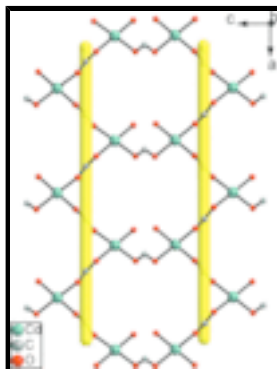


Fig. 2. Right-handed one-dimensional helical chains along  $a$  axis.

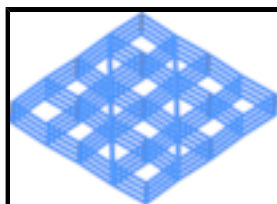


Fig. 3. Topological representation of the three-dimensional structure.

## poly[ $\mu$ -4,4'-bipyridine-di- $\mu$ -formato-cadmium(II)]

### Crystal data

[Cd(CHO<sub>2</sub>)<sub>2</sub>(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)]

$M_r = 358.62$

Tetragonal,  $I4_122$

Hall symbol: I 4bw 2bw

$a = 8.2269 (12) \text{ \AA}$

$b = 8.2269 (12) \text{ \AA}$

$c = 18.103 (4) \text{ \AA}$

$\alpha = 90^\circ$

$\beta = 90^\circ$

$Z = 4$

$F_{000} = 704$

$D_x = 1.944 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1106 reflections

$\theta = 3.2\text{--}27.5^\circ$

$\mu = 1.79 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Granule, yellow

$\gamma = 90^\circ$   $0.33 \times 0.33 \times 0.20$  mm  
 $V = 1225.2$  (4)  $\text{\AA}^3$

*Data collection*

Rigaku R-AXIS RAPID diffractometer	711 independent reflections
Radiation source: fine-focus sealed tube	681 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.025$
Detector resolution: 0 pixels $\text{mm}^{-1}$	$\theta_{\text{max}} = 27.5^\circ$
$T = 293$ K	$\theta_{\text{min}} = 2.7^\circ$
$\omega$ scans	$h = -10 \rightarrow 1$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$k = -10 \rightarrow 1$
$T_{\text{min}} = 0.554$ , $T_{\text{max}} = 0.698$	$l = -23 \rightarrow 1$
1106 measured reflections	

*Refinement*

Refinement on $F^2$	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.018$	$w = 1/[\sigma^2(F_o^2) + (0.018P)^2 + 0.9631P]$
$wR(F^2) = 0.046$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.13$	$(\Delta/\sigma)_{\text{max}} < 0.001$
711 reflections	$\Delta\rho_{\text{max}} = 0.21 \text{ e \AA}^{-3}$
46 parameters	$\Delta\rho_{\text{min}} = -0.43 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none
Secondary atom site location: difference Fourier map	Absolute structure: Flack (1983), 263 Friedel pairs
	Flack parameter: 0.02 (7)

*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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Cd1	0.0000	0.5000	0.7500	0.02047 (10)

## supplementary materials

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O1	0.1521 (3)	0.6479 (3)	0.66505 (10)	0.0380 (4)
N1	0.1982 (2)	0.3018 (2)	0.7500	0.0284 (6)
C1	0.0885 (5)	0.7500	0.6250	0.0354 (9)
H1A	-0.0282	0.7500	0.6250	0.042*
C2	0.3461 (3)	0.3320 (3)	0.72483 (18)	0.0431 (7)
H2	0.3680	0.4350	0.7062	0.052*
C3	0.4696 (3)	0.2183 (3)	0.7249 (2)	0.0432 (8)
H3	0.5731	0.2454	0.7083	0.052*
C4	0.4359 (3)	0.0641 (3)	0.7500	0.0269 (7)

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cd1	0.01803 (12)	0.01803 (12)	0.02535 (16)	0.00289 (14)	0.000	0.000
O1	0.0320 (11)	0.0393 (12)	0.0428 (10)	0.0038 (8)	0.0064 (10)	0.0191 (10)
N1	0.0214 (8)	0.0214 (8)	0.0425 (15)	0.0042 (10)	0.0017 (10)	0.0017 (10)
C1	0.0238 (19)	0.047 (2)	0.0354 (19)	0.000	0.000	0.0116 (18)
C2	0.0256 (13)	0.0257 (13)	0.078 (2)	0.0063 (9)	0.0064 (14)	0.0173 (14)
C3	0.0197 (14)	0.0333 (14)	0.077 (2)	0.0050 (11)	0.0072 (12)	0.0180 (14)
C4	0.0228 (9)	0.0228 (9)	0.0352 (16)	0.0083 (13)	-0.0012 (12)	-0.0012 (12)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

Cd1—N1	2.306 (3)	C1—O1 <sup>iv</sup>	1.227 (3)
Cd1—N1 <sup>i</sup>	2.306 (3)	C1—H1A	0.9600
Cd1—O1 <sup>ii</sup>	2.3264 (18)	C2—C3	1.381 (4)
Cd1—O1 <sup>i</sup>	2.3264 (18)	C2—H2	0.9300
Cd1—O1 <sup>iii</sup>	2.3264 (18)	C3—C4	1.376 (3)
Cd1—O1	2.3264 (18)	C3—H3	0.9300
O1—C1	1.227 (3)	C4—C3 <sup>iii</sup>	1.376 (3)
N1—C2	1.323 (3)	C4—C4 <sup>v</sup>	1.492 (7)
N1—C2 <sup>iii</sup>	1.323 (3)		
N1—Cd1—N1 <sup>i</sup>	180.0	C2—N1—C2 <sup>iii</sup>	117.6 (3)
N1—Cd1—O1 <sup>ii</sup>	90.61 (6)	C2—N1—Cd1	121.20 (16)
N1 <sup>i</sup> —Cd1—O1 <sup>ii</sup>	89.39 (6)	C2 <sup>iii</sup> —N1—Cd1	121.20 (16)
N1—Cd1—O1 <sup>i</sup>	90.61 (6)	O1—C1—O1 <sup>iv</sup>	129.5 (4)
N1 <sup>i</sup> —Cd1—O1 <sup>i</sup>	89.39 (6)	O1—C1—H1A	115.3
O1 <sup>ii</sup> —Cd1—O1 <sup>i</sup>	178.78 (12)	O1 <sup>iv</sup> —C1—H1A	115.3
N1—Cd1—O1 <sup>iii</sup>	89.39 (6)	N1—C2—C3	123.4 (3)
N1 <sup>i</sup> —Cd1—O1 <sup>iii</sup>	90.61 (6)	N1—C2—H2	118.3
O1 <sup>ii</sup> —Cd1—O1 <sup>iii</sup>	97.24 (10)	C3—C2—H2	118.3
O1 <sup>i</sup> —Cd1—O1 <sup>iii</sup>	82.77 (10)	C4—C3—C2	118.4 (3)
N1—Cd1—O1	89.39 (6)	C4—C3—H3	120.8
N1 <sup>i</sup> —Cd1—O1	90.61 (6)	C2—C3—H3	120.8
O1 <sup>ii</sup> —Cd1—O1	82.77 (10)	C3 <sup>iii</sup> —C4—C3	118.7 (3)

O1 <sup>i</sup> —Cd1—O1	97.24 (10)	C3 <sup>iii</sup> —C4—C4 <sup>v</sup>	120.63 (16)
O1 <sup>iii</sup> —Cd1—O1	178.78 (12)	C3—C4—C4 <sup>v</sup>	120.63 (16)
C1—O1—Cd1	121.3 (2)		

Symmetry codes: (i)  $-x, -y+1, z$ ; (ii)  $y-1/2, x+1/2, -z+3/2$ ; (iii)  $-y+1/2, -x+1/2, -z+3/2$ ; (iv)  $x, -y+3/2, -z+5/4$ ; (v)  $-x+1, -y, z$ .

Fig. 1

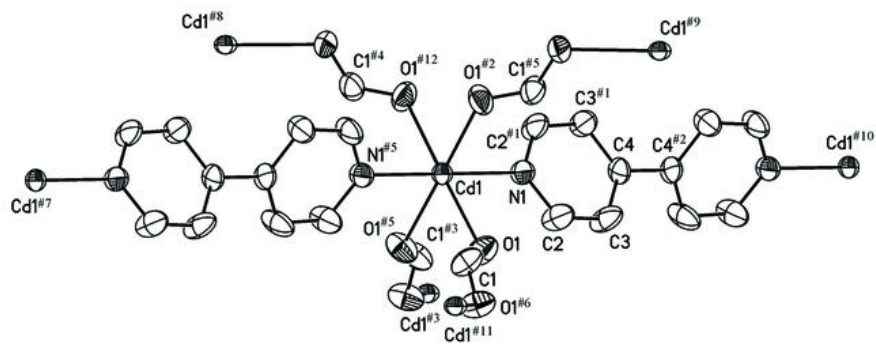


Fig. 2

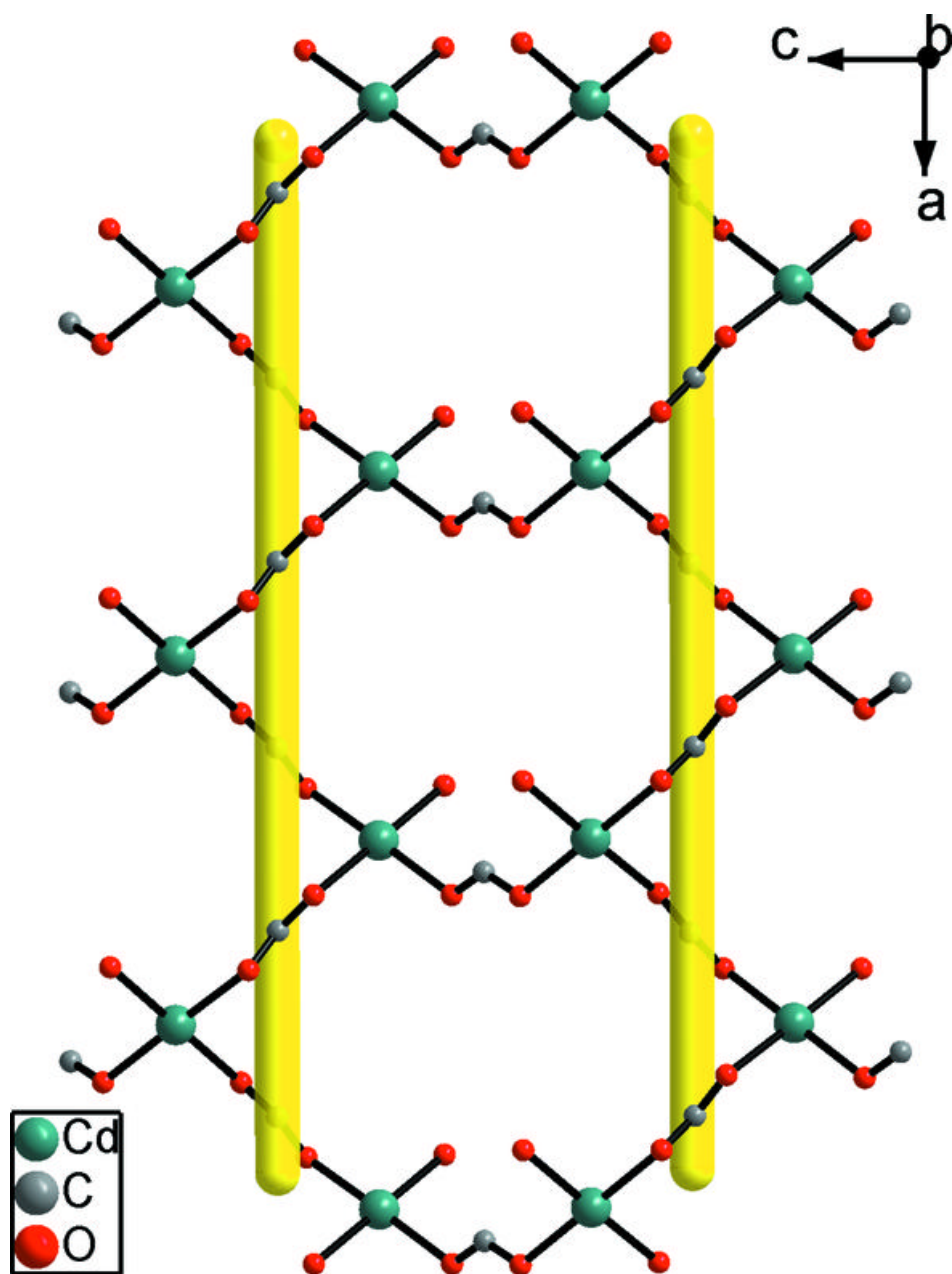


Fig. 3

