

两个金属-二氰胺-异烟酰胺配位超分子的合成与结构表征

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摘要: 以二氰胺钠[Na(dca)]和异烟酰胺(L)为共配体分别与铜盐和镉盐反应合成了 2 种新的配合物: 一维的[Cu(L)₂(dca)₂] \cdot 2MeOH (**1**)和二维的[Cd(L)₂(dca)₂] (**2**)。通过元素分析和红外光谱进行了表征。X 射线晶体结构分析表明配合物 **1** 属于三斜晶系, $P\bar{1}$ 空间群, $a=0.680\,07(6)$ nm, $b=0.737\,59(6)$ nm, $c=1.154\,05(10)$ nm, $\alpha=99.955\,0(10)^\circ$, $\beta=90.307\,0(10)^\circ$, $\gamma=103.294\,0(10)^\circ$, $V=0.554\,28(8)$ nm³, $Z=2$ 。**2** 属于单斜晶系, $P2_1/c$ 空间群, $a=1.043\,77(7)$ nm, $b=0.956\,30(6)$ nm, $c=1.055\,93(7)$ nm, $\beta=119.333\,0(10)^\circ$, $V=0.9188\,5(10)$ nm³, $Z=4$ 。**1** 是一个中性的配位链, Cu^{II} 之间通过双 $\mu_{1,5}$ -dca 桥而连接, L 是单齿配位的。这些配位链通过链间的 N-H \cdots N 氢键作用扩展为二维的层, 甲醇分子位于层间, 甲醇分子与酰胺基团之间的 N-H \cdots O, O-H \cdots O 氢键作用进一步将二维的层拓展为三维的网络。在 **2** 中, 每个镉离子通过 $\mu_{1,5}$ -dca 连接相邻的 4 个镉离子, 从而形成了二维的(4,4)网, 层与层之间通过酰胺基团之间的氢键作用扩展为三维的网络。

关键词: 异烟酰胺; 二氰胺; 铜(II); 镉(II)

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Synthesis and Crystal Structures of Two M^{II}-dicyanamide-isonicotinamide Supramolecular Complexes

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Abstract: Reaction of sodium dicyanamide (Na(dca)) and isonicotinamide (L) with Cu(NO₃)₂ \cdot 3H₂O or Cd(NO₃)₂ \cdot 6H₂O, generating two complexes, 1D [Cu(L)₂(dca)₂] \cdot 2MeOH (**1**) and 2D [Cd(L)₂(dca)₂] (**2**), which were characterized by elemental analysis and IR. X-ray crystal structure analysis displays that **1** crystallizes in the triclinic system, space group $P\bar{1}$ with $a=0.680\,07(6)$ nm, $b=0.737\,59(6)$ nm, $c=1.154\,05(10)$ nm, $\alpha=99.955\,0(10)^\circ$, $\beta=90.307\,0(10)^\circ$, $\gamma=103.294\,0(10)^\circ$, $V=0.554\,28(8)$ nm³, $Z=2$. **2** is in the monoclinic system, space group $P2_1/c$ with $a=1.043\,77(7)$ nm, $b=0.956\,30(6)$ nm, $c=1.055\,93(7)$ nm, $\beta=119.333\,0(10)^\circ$, $V=0.9188\,5(10)$ nm³, $Z=4$. **1** is a neutral 1D coordination chain, in which the Cu^{II} centers are interlinked through double $\mu_{1,5}$ -dca bridges and L acts as monodentate terminal ligand. These coordination chains are further expanded into a 2D layer through N-H \cdots N hydrogen bonds. The N-H \cdots O, O-H \cdots O interactions from CH₃OH molecules and L generate a 3D supramolecular architecture. While in **2**, each cadmium ion coordinates to four dca anions in a $\mu_{1,5}$ mode to link neighboring four metal ions to generate a 2D (4,4) sheet. The N-H \cdots O and N-H \cdots N hydrogen-bonding interactions between L expand these layers into a 3D supramolecular network. CCDC: 742680, **1**; 742679, **2**.

Key words: isonicotinamide; dicyanamide; copper(II); cadmium(II)

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In the last two decades, crystal engineering is growing interest, and great efforts have been devoted to the assembly of supramolecular systems of organic molecular solids and coordination polymers through hydrogen bonds and or coordination bonds, for the resultant crystalline materials having a great potential applications in optical, electronic, magnetic, absorbent, catalytic materials and so on^[1-4]. The coordination polymers of dicyanamide (dca) have been attracting a lot of attention, for transferring various magnetic exchanging interactions^[5]. Moreover, from the structural point, dca is also a remarkable building block to construct various polyfunctional coordination architectures, such as discrete mononuclear and dinuclear compounds, as well as 1D chain, 2D sheet and 3D supramolecular frameworks^[6], when coligands (L) are introduced to the M-dca-L system, more compounds with novel structure can be synthesized^[7]. Moreover, interesting in situ nucleophilic addition reactions were observed between dca and the auxiliary ligands^[8-9]. In our early work, 4-(1Himidazol-1-yl)aniline was chosen as coligand, and two supramolecular architectures were constructed through coordination and hydrogen-bonding interactions^[10]. To continue this work, and discuss the effect of various coligands on the ultimately supramolecular architecture, isonicotinamide was employed as coligand to construct supramolecular architectures in this work, and 1D chain $[\text{Cu}(\text{dca})_2(\text{L})_2] \cdot 2\text{MeOH}$ (**1**), 2D coordination layer $[\text{Cd}(\text{dca})_2(\text{L})_2]$ (**2**) were obtained and characterized by IR, EA and X-ray crystal diffraction.

1 Experimental

1.1 Materials and physical measurements

All the reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The FTIR spectra were recorded from KBr pellets in the range 4 000~400 cm^{-1} on a Bruker TENSOR27 spectrometer.

1.2 Synthesis

1.2.1 Synthesis of $[\text{Cu}(\text{dca})_2(\text{L})_2] \cdot 2\text{MeOH}$ (**1**)

A CH_3OH solution (20 mL) containing L (0.122 g,

1.0 mmol) was added to the methanol solution (10 mL) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.122 g, 0.50 mmol), then the water solution of dca (0.089 g, 1.0 mmol) was added to the above solution. The mixture solution was stirred about 30 min, then filtered and evaporated solvent at room temperature. Blue block crystals were obtained within 1 week (yield 32%, based on Cu^{II}). Elemental anal. (%) calcd for $\text{C}_9\text{H}_{10}\text{Cu}_0.5\text{N}_5\text{O}_2$: C, 42.90; H, 4.00; N, 27.79. Found(%): C, 42.80; H, 4.06; N, 27.63. IR(KBr, cm^{-1}): 3 571w, 3 481s, 3 412vw, 3 351s, 3 180m, 3 109vw, 3 077vw, 2 280w, 2 249s, 2 194s, 1 945vw, 1 690vs, 1 638vw, 1 599s, 1 556s, 1 414s, 1 378s, 1 329s, 1 231w, 1 142w, 1 061m, 1 023w, 948w, 853m, 761m, 702m, 626s, 530m, 509w, 467w, 428m.

1.2.2 Synthesis of $[\text{Cd}(\text{L})_2(\text{dca})_2]$ (**2**)

L (0.122 g, 1.0 mmol) and dca (0.089 g, 1.0 mmol) were dissolved in a CH_3OH mixture (25 mL). To the above solution was added a dilute aqueous solution (5 mL) of $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.172 g, 0.5 mmol) under stirring. The resultant solution was filtered and left to stand at room temperature. Colorless block crystals were collected within 6 days in 38% yield based on Cd^{II} . Elemental anal. (%) calcd for $\text{C}_8\text{H}_6\text{Cd}_{0.5}\text{N}_5\text{O}$: C, 39.32; H, 2.47; N, 28.66. Found(%): C, 39.69; H, 2.58; N, 28.51. IR(KBr, cm^{-1}): 3 566m, 3 529w, 3 396m, 3 317m, 3 260w, 3 204m, 3 064s, 2 761w, 2 458vw, 2 261s, 2 229s, 2 143s, 1 860w, 1 603m, 1 553s, 1 347m, 1 224s, 1 143m, 1 014s, 970w, 937w, 854m, 763s, 717s, 672w, 621s, 554s, 507s, 451w.

1.3 Crystal structure determination

Data collection of **1** and **2** was performed on a Bruker Smart Apex CCD diffractometer with Mo $K\alpha$ radiation ($\lambda=0.071\,073\,\text{nm}$) at 293(2) K. The raw data frames were integrated with SAINT⁺^[11], and the corrections were applied for Lorentz and polarization effects. Absorption correction was applied by using the multiscan program SADABS^[12]. The structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXL program^[13]. Hydrogen atoms on organic ligands were generated by the riding mode ($\text{C-H}=0.093\,\text{nm}$). Crystal data as well as details of data collection and refinements for complexes **1** and **2** are summarized in

Table 1. Selected bond distances and bond angles

Table 3.

are listed in Table 2. Hydrogen bonds are listed in

CCDC: 742680, **1**; 742679, **2**.**Table 1 Crystal data and structure parameters for complexes **1** and **2****

Complex	1	2
Formula	C ₉ H ₁₀ Cu _{0.5} N ₅ O ₂	C ₈ H ₆ Cd _{0.5} N ₅ O
Formula weight	251.99	244.38
Temperature	293(2)	293(2)
Wavelength	0.710 73	0.710 73
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a / nm	0.680 07(6)	1.043 77(7)
b / nm	0.737 59(6)	0.956 30(6)
c / nm	1.154 05(10)	1.055 93(7)
$\alpha / (^\circ)$	99.955 0(10)	90.00
$\beta / (^\circ)$	90.3070(10)	119.333 0(10)
$\gamma / (^\circ)$	103.294 0(10)	90.00
V / nm^3	0.554 28(8)	0.918 85(10)
Z	2	4
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.510	1.767
Absorption coefficient / mm^{-1}	1.033	1.226
$F(000)$	259	484
Crystal size / mm	0.28×0.24×0.19	0.25×0.23×0.17
θ range for data collection / $(^\circ)$	1.79~26.00	2.24~26.00
Limiting indices	$-8 \leq h \leq 7, -9 \leq k \leq 9, -14 \leq l \leq 12$	$-12 \leq h \leq 12, -11 \leq k \leq 11, -13 \leq l \leq 11$
Reflections collected	4 360	4 870
Independent reflections (R_{int})	2 158 (0.016 6)	1 805 (0.015 7)
Reflections [$I > 2\sigma(I)$]	2 080	1 643
Completeness / %	98.8	99.7
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2 158 / 3 / 164	1 805 / 0 / 142
Goodness-of-fit on F^2	1.086	1.073
Final R indices [$I > 2\sigma(I)$]	$R_1^a=0.036\ 0, wR_2^b=0.095\ 6$	$R_1^a=0.018\ 7, wR_2^b=0.050\ 1$
R indices (all data)	$R_1^a=0.036\ 9, wR_2^b=0.095\ 6$	$R_1^a=0.020\ 7, wR_2^b=0.051\ 6$
Largest diff. peak and hole / $(\text{e} \cdot \text{nm}^{-3})$	496, -252	315, -206

$$^a R_1 = \sum \|F_o| - |F_c|\| / \sum |F_o|, ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

Table 2 Bond lengths (nm) and angles ($^\circ$) for **1 and **2****

1					
Cu(1)-N(1)	0.198 1(2)	Cu(1)-N(1a)	0.198 1(2)	Cu(1)-N(4)	0.202 44(18)
Cu(1)-N(4a)	0.202 44(18)	Cu(1)-N(3)	0.253 2(7)	Cu(1)-N(3a)	0.253 2(7)
N(1)-Cu(1)-N(1a)	180.00(14)	N(1)-Cu(1)-N(4)	89.29(8)	N(1a)-Cu(1)-N(4)	90.71(8)
N(1)-Cu(1)-N(4a)	90.71(8)	N(1a)-Cu(1)-N(4a)	89.29(8)	N(4)-Cu(1)-N(4a)	180.00(11)
2					
Cd(1)-N(1a)	0.229 37(18)	Cd(1)-N(1)	0.229 37(18)	Cd(1)-N(4)	0.235 84(14)
Cd(1)-N(4a)	0.235 84(14)	Cd(1)-N(3b)	0.238 9(2)	Cd(1)-N(3c)	0.238 9(2)

Continued Table 2

N(1a)-Cd(1)-N(1)	180.00(11)	N(1a)-Cd(1)-N(4)	88.81(6)	N(1)-Cd(1)-N(4)	91.19(6)
N(1a)-Cd(1)-N(4a)	91.19(6)	N(1)-Cd(1)-N(4a)	88.81(6)	N(4)-Cd(1)-N(4a)	180.000(1)
N(1a)-Cd(1)-N(3b)	91.89(6)	N(1)-Cd(1)-N(3b)	88.11(6)	N(4)-Cd(1)-N(3b)	93.17(6)
N(4a)-Cd(1)-N(3b)	86.83(6)	N(1a)-Cd(1)-N(3c)	88.11(6)	N(1)-Cd(1)-N(3c)	91.89(6)
N(4)-Cd(1)-N(3c)	86.83(6)	N(4a)-Cd(1)-N(3c)	93.17(6)	N(3b)-Cd(1)-N(3c)	180.0

Symmetry codes for **1**: a: $-x, -y, -z$; for **2**: a: $-x-1, -y-1, -z-2$; b: $x, -y-3/2, z-1/2$; c: $-x-1, y+1/2, -z-3/2$.

Table 3 Hydrogen bonds for **1** and **2**

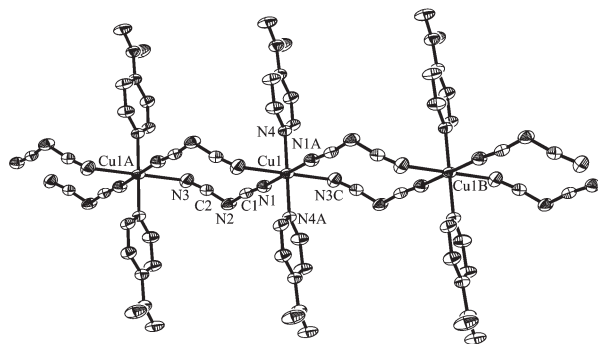
D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle(\text{DHA}) / (^\circ)$
1				
N5-H5A...O2a	0.084 6(10)	0.203 4(15)	0.285 3(4)	163(3)
N5-H5B...N2b	0.084 6(10)	0.233 6(19)	0.309 8(3)	150(3)
O2-H2...O1	0.084 1(10)	0.187 0(13)	0.270 3(3)	171(5)
C6-H6...O2	0.093 0(1)	0.243 8(1)	0.334 5(1)	165(1)
2				
N5-H5A...N3a	0.084 7	0.230 2	0.308 2	153.16
N5-H5B...O1b	0.088 7	0.204 0	0.290 6	164.96

Symmetry codes for **1**: a: $x-1, y, z$; b: $x, y, z-1$; for **2**: a: $-x, y+1/2, -z-1/2$; b: $-x, y-1/2, -z-1/2$.

2 Results and discussion

2.1 Structure of $[\text{Cu}(\text{L})_2(\text{dca})_2] \cdot 2\text{MeOH}$ (**1**)

Single-crystal structure reveals that compound **1** crystallizes in triclinic space group $P\bar{1}$ and is made up of $[\text{Cu}(\text{L})_2]$ units bridged by doubly $\mu_{1,5}$ -dca ligands to form a 1D chain running along a -axis with metals separated by 0.737 6(2) nm. The ORTEP drawing of a part of the chain with the atom labeling scheme is shown in Fig.1. The Cu(II) ion locates on a center of symmetry and coordinates to two L via pyridyl nitrogen atoms in trans position ($\text{Cu-N}=0.202\ 4(2)$ nm) and four nitrile nitrogen atoms ($\text{Cu-N}=0.198\ 1(2), 0.253\ 2(1)$ nm) of dca. The coordination geometry of Cu^{II} center (CuN_6)



Symmetry codes: A: $-x, -y, -z$; B: $-x, -1-y, -z$; C: $x, 1+y, z$

Fig.1 ORTEP drawing of 1D polymeric chain of $[\text{Cu}(\text{L})_2(\text{dca})_2]$ in **1**

can be described as a pseudo Jahn-Teller elongated octahedron, and the axial positions are occupied by N3 atoms. These values are comparable to those found in pyridine derivatives^[14].

Analysis of the crystal packing of complex **1** reveals that the 1D coordination chains are cross-linked by N-H...N ($\text{N5}\cdots\text{N2}=0.309\ 8(3)$ nm, $\angle\text{NHN}=150(3)^\circ$) hydrogen bonding interactions between free amide nitrogen atoms of the dca ligands and hydrogen atoms of CONH_2 group from adjoining chains to generate a 2D supramolecular structure (Fig.2a). It is different from the coplanar disposed chains found in pyridine and analogue complexes, which neighboring chains are interlinked by π - π stacking interactions between pyridyl rings^[15]. The MeOH molecules locate between adjoining chains (Fig.2b) and the existences of MeOH molecules provide rich interlayer hydrogen-bonding interactions. The hydrogen atom of CONH_2 and oxygen atom of MeOH form N-H...O hydrogen bond ($\text{N5}\cdots\text{O2}=0.285\ 3(4)$ nm, $\angle\text{NHO}=163(3)^\circ$); moreover, the hydrogen atom of hydroxyl group and carbonyl oxygen atom form strong O-H...O ($\text{O2}\cdots\text{O1}=0.270\ 3(3)$ nm, $\angle\text{OHO}=171(5)^\circ$); weak C-H...O hydrogen bond ($\text{C6}\cdots\text{O2}=0.334\ 5(1)$ nm, $\angle\text{CHO}=165^\circ$) have also been observed, which is shown in Fig.3. These hydrogen

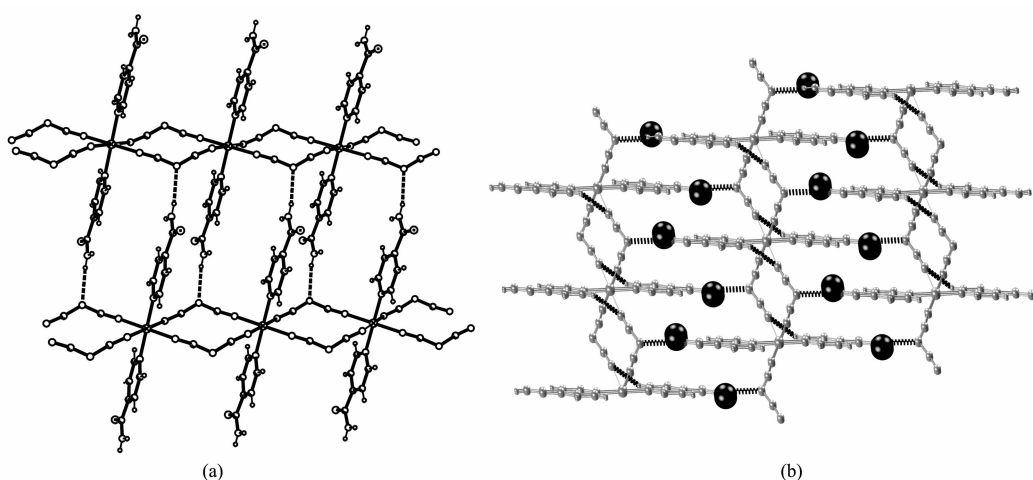
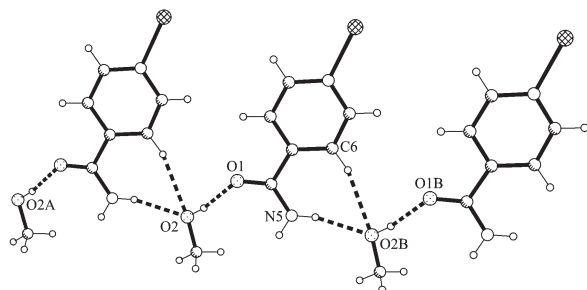


Fig.2 Perspective views of hydrogen-bonded 2D layer (a) and 3D supramolecular architecture (b) in **1**

bonding interactions link neighboring chains along *b* axis, expanding 2D layers into a 3D supramolecular architecture.



Symmetry codes: A: $x, y+1, z$; B: $x-1, y, z$

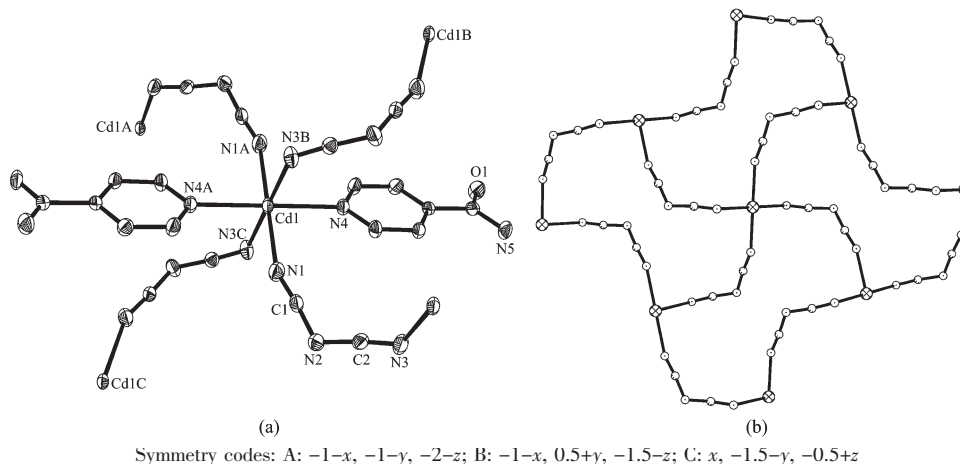
Fig.3 View of the hydrogen-bonding interactions of MeOH molecules and L in **1**

2.2 Structure of $[\text{Cd}(\text{L})_2(\text{dca})_2]$ (**2**)

The crystal structure analysis displays **2** crystallizing in $P2_1/c$ space group and consists of a 2D layer. The asymmetric unit of **2** consists of half formula unit. The

cadmium ions are coordinated to two L ligand via pyridyl nitrogen atoms in trans position ($\text{Cd-N}=0.235\ 8(2)$ nm) and four nitrile nitrogen atoms ($\text{Cd-N}=0.224(2), 0.238\ 9(2)$ nm) from four $\mu_{1,5}$ -dca anions (Fig.4a), featuring a distorted CdN_6 octahedron environment. Different to **1**, Each cadmium ion is connected to other four cadmium ions by means of four single $\mu_{1,5}$ -dca bridges ($\text{Cd}\cdots\text{Cd}=0.712\ 3(1)$ nm), leading to a 2D (4,4) coordination layer (Fig.4b).

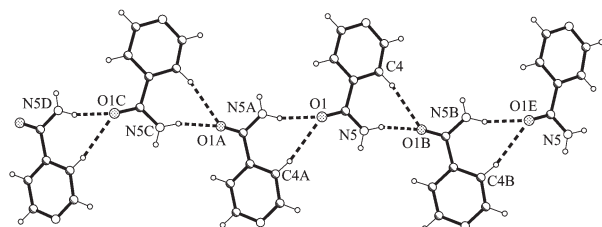
The packing view of **2** shows interdigitation of adjacent layers through hydrogen-bonding interaction of CONH_2 groups. The carbonyl oxygen atom forms $\text{N5-H5b}\cdots\text{O1}$ ($\text{N5}\cdots\text{O1}=0.290\ 6(2)$ nm, $\angle\text{NHO}=165(2)^\circ$) hydrogen bond with hydrogen atom of CONH_2 group from adjacent layers (Fig.5). Meanwhile, another hydrogen atom of CONH_2 group forms $\text{N5-H5a}\cdots\text{N3}$ ($\text{N5}\cdots\text{N3}=0.308\ 2(3)$ nm, $\angle\text{NHO}=153(2)^\circ$) with the



Symmetry codes: A: $-1-x, -1-y, -2-z$; B: $-1-x, 0.5+y, -1.5-z$; C: $x, -1.5-y, -0.5+z$

Fig.4 Coordination environment of cadmium atoms (a) and 2D (4, 4) layer (b) in **2**

nitrile nitrogen atom of dca from the neighboring layer. These hydrogen-bonding interactions expand the 2D layers into a 3D supramolecular architecture, as shown in Fig.6.



Symmetry codes: A: $-x, 0.5+y, -0.5-z$; B: $-x, -0.5+y, -0.5-z$;

C: $x, y+1, z$; D: $-x, 1.5+y, -0.5-z$; E: $x, y-1, z$

Fig.5 View of the hydrogen-bonding interaction of L groups in **2**

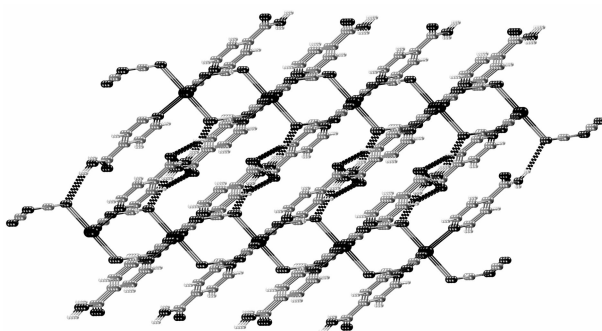


Fig.6 View of the hydrogen-bonding 3D supramolecular network in **2**

References:

- [1] Holman K T, Pivovar A M, Swift J A, et al. *Acc. Chem. Res.*, **2001**,**34**:107-116
- [2] (a)Blake A J, Champness N R, Hubberstey P, et al. *Coord. Chem. Rev.*, **1999**,**183**:117-138
(b)Carlucci L, Ciani G D, Proserpio M. *Coord. Chem. Rev.*, **2003**,**246**:247-289
- [3] Rao C N R, Natarajan S, Vaidhyanathan R. *Angew. Chem., Int. Ed.*, **2004**,**43**:1466-1496
- [4] Eddaoudi M D, Moler B, Yaghi O M. *Acc. Chem. Res.*, **2001**, **34**:319-330
- [5] (a)Batten S R, Jensen P, Murray K S, et al. *J. Chem. Soc., Dalton Trans.*, **1999**:2987-2997
(b)Batten S R, Murray K S, Robson R. *Chem. Commun.*, **1998**: 439-440
- [6] (a)Kuang S M, Fanwick P E, Walton R A. *Inorg. Chem.*, **2001**,**40**:5682-5690
(b)Zhang L Y, Shi L X, Chen Z N. *Inorg. Chem.*, **2003**,**42**:633-640
- [7] Batten S R, Murray K S. *Coord. Chem. Rev.*, **2003**,**246**:103-130
- [8] (a)Tong M L, Wu Y M, Kitagawa S, et al. *Eur. J. Inorg. Chem.*, **2003**:2385-2388
(b)Zheng L L, Zhang W X, Tong M L, et al. *Inorg. Chem.*, **2007**,**46**:9548-9557
(c)Zheng L L, Li H X, Tong M L, et al. *Eur. J. Inorg. Chem.*, **2008**:213-217
(d)Zheng L L, Leng, J D, Tong M L, et al. *Eur. J. Inorg. Chem.*, **2008**:4616-4624
- [9] Igashira-Kamiyama A, Kajiwarra T, Ito T, et al. *Inorg. Chem.*, **2006**,**45**:6460-6466
- [10]Zheng L L, Tan C K, Tong M L. *Chinese J. Inorg. Chem.*, **2006**,**22**:1426-1430
- [11]*Software Packages SMART and SAINT*, Siemens Analytical X-ray Instrument Inc., Madison, WI, **1996**.
- [12]Sheldrick G M. *SADABS 2.05*, University of Göttingen, Germany, **1996**.
- [13]Sheldrick G M. *SHELXTL-97, Program for Crystal Structure Refinement*, Göttingen University, Germany, **1997**.
- [14]Du M, Zhao X J, Batten S. R, et al. *Cryst. Growth. Des.*, **2005**,**5**:901-909
- [15]Ghoshal D, Ghosh A K, Chauduri N R, et al. *Cryst. Growth Des.*, **2005**,**5**:941-947