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研究简报

基于三核镉的二维金属有机骨架 $[Cd_3(L)_2(cis\text{-}1,4\text{-chdc})_2(trans\text{-}1,4\text{-chdc})]$的合成、结构和表征

徐占林*,1 马晓媛[1] 刘 洋[2] 孔治国[1]
([1] 吉林师范大学化学学院,四平 136000)
([2] 吉林师范大学物理学院,四平 136000)

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Synthesis, Structure and Characterization of a Two-Dimensional Cd(Ⅱ)-Organic Framework Based on Trinuclear Cd(Ⅱ) Clusters: $[Cd_3(L)_2(cis\text{-}1,4\text{-chdc})_2(trans\text{-}1,4\text{-chdc})]$

XU Zhan-Lin*,1 MA Xiao-Yuan[1] LIU Yang[2] KONG Zhi-Guo[1]
([1]*Department of Chemistry, Jilin Normal University, Siping, Jilin* 136000)
([2]*Department of Physics, Jilin Normal University, Siping, Jilin* 136000)

Abstract: The title metal-organic framework, $[Cd_3(L)_2(cis\text{-}1,4\text{-chdc})_2(trans\text{-}1,4\text{-chdc})]$ (**1**, L=2-(4-fluorophenyl)-1H-imidazo [4,5-f][1,10]phenanthroline, 1,4-H_2chdc=1,4-cyclohexanedicarboxylic acid) has been synthesized under hydrothermal condition and characterized by elemental analysis, IR and single-crystal X-ray diffraction. It crystallizes in triclinic, space group $P\bar{1}$ with a=0.851 71(17) nm, b=1.199 9(2) nm, c=1.521 4(3) nm, α=68.13(3)°, β=79.48(3)°, γ=82.32(3)°, V=1.415 0(5) nm^3, Z=1, $C_{62}H_{52}Cd_3F_2N_8O_{12}$, M_r=1 476.32, D_c=1.732 g·cm^{-3}, F(000)=738, μ(Mo $K\alpha$)=1.197 mm^{-1}, R=0.067 6 and wR=0.135 4. The *cis*-1,4-chdc^{2-} ligands bridge the Cd(Ⅱ) cations to form a trinuclear Cd(Ⅱ) based double chain along the a axis. Further, the *trans*-chdc^{2-} ligands link the adjacent double chains to yield an interesting two-dimensional network. The L ligands are attached on both sides of the layers. CCDC: 792221.

Key words: metal-organic framework; crystal structure; trinuclear Cd(Ⅱ); 1,4-cyclohexanedicarboxylic acid

0 Introduction

Metal-organic frameworks (MOFs) based on polynuclear metal clusters are an attractive area of research in recent years due to their interesting molecular topologies and potential applications as functional materials[1-5]. The polynuclear metal clusters can be very versatile in terms of coordination properties and rigidity as well as displaying intriguing physical properties in comparison with mononuclear species[6-8]. In order to fabricate desired polynuclear metal cluster, the choice of organic ligands has gradually become established as a useful strategy[9-11]. In this regard, the multi-carboxylate building blocks with special configurations are

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*通讯联系人。E-mail：xuzljl@yahoo.com.cn
第一作者：徐占林，男，46 岁，教授；研究方向：功能配位化学、材料化学。

widely selected in design of the polynuclear metal cluster. Following this idea, a variety of MOFs based on polynuclear metal clusters have been obtained using the multi-carboxylate building blocks[12]. Typically, 1,3-benzenedicarboxylic acid and 1,4-benzenedicarboxylic acid have been widely used for the design and synthesis of the MOFs with polynuclear metal cluster [13]. However, so far, less effort has been made on the 1,4-cyclohexanedicarboxylic acid (1,4-H_2chdc). Here, we selected 1,4-H_2chdc as an organic linker and L (L=2-(4-fluorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline) as a N-donor chelating ligand, generating a new two-dimensional MOF, [$Cd_3(L)_2$(*cis*-1,4-chdc)$_2$(*trans*-1,4-chdc)] (**1**).

1 Experimental

1.1 Generals

The L ligand was synthesized according to the reported method[14] and all other materials were analytical reagent grade and used as received without further purification. Elemental analysis was carried out with a Perkin-Elmer 240C analyzer; IR spectra were obtained on a Perkin-Elmer 2400LSII spectrometer.

1.2 Synthesis and crystal growth

$CdCl_2\cdot 2.5H_2O$ (1 mmol), 1,4-H_2chdc (1 mmol) and L (0.5 mmol) were placed in water (12 mL), and triethylamine was added until the pH value of the solution was about 5.6. The resultant solution was heated at 456 K in a Teflon-lined stainless steel autoclave for five days. The reaction system was then slowly cooled to room temperature. Pale yellow crystals of 1 suitable for single crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with distilled water and dried in air at ambient temperature. Yield: 39% based on Cd(Ⅱ). IR (KBr, cm^{-1}): 1 615m, 1 612w, 1 580m, 1 542 m, 1 465w, 1 342m, 732w, 628w. Anal. Calcd. For $C_{62}H_{52}Cd_3F_2N_8O_{12}$(%): C, 50.40; H, 3.52; N, 7.59. Found(%): C, 50.62; H, 3.65; N, 7.22.

1.3 X-ray structure determination

A single crystal with dimensions of 0.28 mm×0.21 mm×0.18 mm was selected and mounted on a Rigaku RAXIS-RAPID single crystal diffractometer equipped with a narrow-focus, 5.4 kW sealed tube X-ray source (graphite-monochromated Mo $K\alpha$ radiation, λ=0.071 073 nm) at a temperature of (20±2) ℃. The data processing was accomplished with the PROCESS-AUTO processing program. Out of the total 13 838 reflections collected in the 3.02° $\leqslant\theta\leqslant$27.48° range, 6 394 were independent with R_{int}=0.08, of which 4 088 were considered to be observed ($I>2\sigma(I)$) and used in the succeeding refinement. The structure was solved by Direct Method with SHELXS-97 program[15] and refined with SHELXL 97[16] by full-matrix least-squares techni ques on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. The final R=0.067 6 and wR=0.135 4 ($w=1/[\sigma^2(F_o^2)+(0.042\,6P)^2+1.974\,0P]$, where $P=(F_o^2+2F_c^2)/3$). S=1.113, $(\Delta\rho)_{max}$=1 134 e·nm^{-3}, $(\Delta\rho)_{min}$=−1 614 e·nm^{-3} and $(\Delta/\sigma)_{max}$=0.000.

CCDC: 792221.

2 Results and discussion

2.1 Description of crystal structure

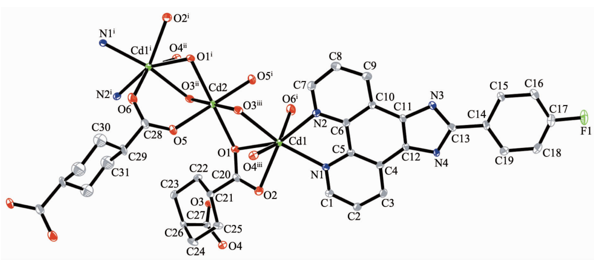
The selected bond distances and angles are listed in Table 1. The single-crystal analysis of the structure reveals that compound **1** is a two-dimensional network built up by L, *cis*- and *trans*-1,4-chdc^{2-} ligands with Cd(Ⅱ) cations. The *trans*-chdc^{2-} ligand lies about an inversion centre. As shown in Fig.1, the Cd1 shows a distorted monocapped trigonal prism coordination geometry, coordinated by five oxygen atoms from two different *cis*-1,4-chdc^{2-} and one *trans*-1,4-chdc^{2-} ligands, and two nitrogen atoms from one L ligand. The Cd2 cation, however, is six-coordinated by six carboxylate oxygen atoms from four distinct *cis*-1,4-chdc^{2-} and two different *trans*-1,4-chdc^{2-} ligands in a distorted octahedral coordination environment. The Cd-O bond lengths vary from 0.221 4(5) to 0.255 9(5) nm, and the Cd-N distances are 0.232 2(6) and 0.241 3(6) nm. The Cd-O and Cd-N distances are comparable with the reported ones[17]. The *cis*-1,4-chdc^{2-} ligands bridge the Cd(Ⅱ) cations to form a trinuclear Cd(Ⅱ) based double chain along the a axis (Fig.2). Further, the trans-chdc^{2-} ligands link the adjacent double chains to yield an interesting two-dimensional network. The L ligands are attached on both sides of the layers (Fig.2). A better insight into the structure of **1** can be achieved by the

Table 1　Selected bond distances (nm) and angles (°)

Cd(1)-O(1)	0.234 1(4)	Cd(1)-O(2)	0.246 6(5)	Cd(1)-O(6)^{i}	0.222 9(6)
Cd(1)-O(3)^{iii}	0.255 9(5)	Cd(1)-O(4)^{iii}	0.233 3(5)	Cd(1)-N(1)	0.232 2(6)
Cd(1)-N(2)	0.241 3(6)	Cd(2)-O(1)	0.228 2(5)	Cd(2)-O(5)^{i}	0.221 4(5)
Cd(2)-O(1)^{i}	0.228 2(5)	Cd(2)-O(3)^{iii}	0.233 6(4)	Cd(2)-O(3)^{ii}	0.233 6(4)
O(3)^{iii}-Cd(2)-O(3)^{ii}	180	O(6)i-Cd(1)-N(1)	95.4(2)	O(6)i-Cd(1)-O(4)^{iii}	150.0(2)
N(1)-Cd(1)-O(4)^{iii}	107.90(19)	O(6)i-Cd(1)-O(1)	85.4(2)	N(1)-Cd(1)-O(1)	132.98(18)
O(4)^{iii}-Cd(1)-O(1)	91.97(18)	O(6)i-Cd(1)-N(2)	81.7(2)	N(1)-Cd(1)-N(2)	70.2(2)
O(4)^{iii}-Cd(1)-N(2)	88.6(2)	O(1)-Cd(1)-N(2)	154.67(19)	O(6)i-Cd(1)-O(2)	116.1(2)
N(1)-Cd(1)-O(2)	85.14(18)	O(4)^{iii}-Cd(1)-O(2)	85.20(19)	O(1)-Cd(1)-O(2	53.78(17)
N(2)-Cd(1)-O(2)	151.28(19)	O(6)i-Cd(1)-O(3)^{iii}	97.9(2)	N(1)-Cd(1)-O(3)^{iii}	149.87(16)
O(4)^{iii}-Cd(1)-O(3)^{iii}	52.90(16)	O(1)-Cd(1)-O(3)^{iii}	75.21(16)	N(2)-Cd(1)-O(3)^{iii}	85.09(18)
O(2)-Cd(1)-O(3)^{iii}	112.58(17)	O(5)-Cd(2)-O(5)^{i}	180	O(5)-Cd(2)-O(1)	86.9(2)
O(5)i-Cd(2)-O(1)	93.1(2)	O(5)-Cd(2)-O(1)^{i}	93.1(2)	O(5)^{i}-Cd(2)-O(1)^{i}	86.9(2)
O(1)-Cd(2)-O(1)^{i}	180	O(5)-Cd(2)-O(3)^{iii}	89.50(19)	O(5)^{iv}-Cd(2)-O(3)^{iii}	89.50(19)
O(1)-Cd(2)-O(3)^{iii}	80.86(17)	O(1)-Cd(2)-O(3)^{ii}	99.14(17)		

Symmetry codes: ^{i} $-x, -y+1, -z+1$; ^{ii} $-x+1, -y+1, -z+1$; ^{iii} $x-1, y, z$; ^{iv} $-x, -y+2, -z+1$.

application of topological approach, that is, reducing multidimensional structures to simple node-and-linker nets. As discussed above, each trinuclear Cd(Ⅱ) cluster is surrounded by eight organic ligands: six bridging 1,4-chdc and two chelating L. Although each Cd(Ⅱ) cluster is connected by eight bridging ligands, it is virtually linked to four nearest neighbors, because two pairs of *cis*-1,4-chdc^{2-} ligands form two "double-bridges" (Fig. 2). From the topological point of view, this cluster can be defined as a four-connected node. Thus, the overall topology of the two-dimensional framework is best described as a four-connected (4,4) network (Fig.3).



Symmetric codes: ^{i} $x, 1-y, 1-z$; ^{ii} $1-x, 1-y, 1-z$; ^{iii} $x-1, y, z$;
Displacement ellipsoids at the 20% probability level

Fig.1 View of the trinuclear Cd(Ⅱ) cluster of complex **1**

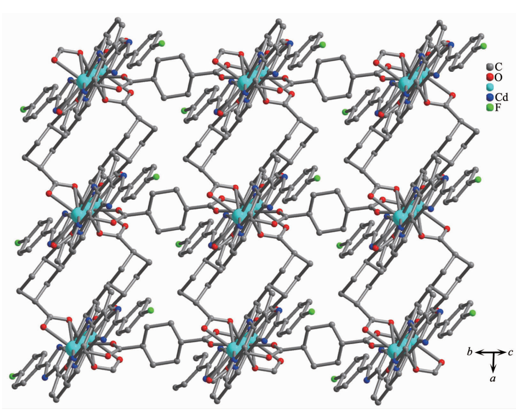


Fig.2　View of the layer structure of complex **1**

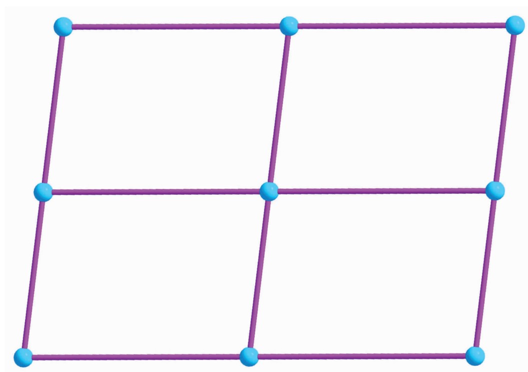


Fig.3　View of the (4,4) network structure of complex **1**

2.2　IR analysis

IR spectrum of complex **1** shows the characteristic bands of the carboxylate group at 1 615 cm^{-1} for the anti-symmetric stretching and 1 542 cm^{-1} for the symmetric stretching. Peaks at 1 612, 1 580 and 1 465 cm^{-1} could be attributed to ν(C=C) vibration of aromatic ring. The peak at 1 342 cm^{-1} is ascribed to the ν(C=N) vibration of L.

References:

[1] Rosi N L, Kim J, Eddaoudi M, et al. *J. Am. Chem. Soc.*, **2005**, **127**:1504-1518

[2] Batten S R. *CrystEngCommun*, **2001**,**3**:67-73

[3] Abrahams B F, Batten S R, Grannas M J, et al. *Angew. Chem. Int. Ed.*, **1999**,**38**:1475-1477

[4] Chen B, Eddaoudi M, Reineke T M, et al. *J. Am. Chem. Soc.*, **2000**,**122**:11559-11560

[5] Hagrman P J, Hagrman D, Zubieta J. *Angew. Chem. Int. Ed.*, **1999**,**38**:2638-2684

[6] Ferey G. *Chem. Mater.*, **2001**,**13**:3084-3098

[7] Kim J, Chen B, Reineke T M. et al. *J. Am. Chem. Soc.*, **2001**, **123**:8239-8247

[8] Batten S R, Robson R. *Angew. Chem. Int. Ed.*, **1998**,**37**:1460-1494

[9] HU Bin(胡 斌), QU Zhi-Rong(瞿志荣). *Chinese J. Inorg. Chem.*(*Wuji Huaxue Xuebao*), **2007**,**23**(2):283-285

[10]Zhang X M, Tong M L, Gong M L, et al. *Eur. J. Inorg. Chem.*, **2003**,**1**:138-142

[11]Wang S N, Bai J F, Li Y Z, et al. *CrystEngComm*, **2001**,**9**:228-235

[12]Hong X L, Li Y Z, Hu H M, et al. *Cryst. Growth Des.*, **2006**,**6**:1211-1226

[13]Fan J, Sun W Y, Okamura T, et al. *New J. Chem.*, **2002**,**2**:199-201

[14]Yang J, Ma J F, Liu Y Y, et al. *Cryst. Growth Des.*, **2009**,**9**:1894-1911

[15]Sheldrick G M. *SHELXS* 97, *Program for the Solution of Crystal Structure*, University of Göttingen, Germany, **1997**.

[16]Sheldrick G M. *SHELXS* 97, *Program for the Refinement of Crystal Structure*, University of Göttingen, Germany, **1997**.

[17]GENG Xiao-Hong(耿晓红), FENG Yun-Long(冯云龙). *Chinese J. Inorg. Chem.*(*Wuji Huaxue Xuebao*), **2010**,**26**(2):360-364