

## 两个由 1,1'-环己烷二乙酸构筑的镉的配合物的合成、晶体结构和荧光性质

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**摘要:** 通过邻羧苯乙酸、1,10-邻菲罗啉及硝酸镉的溶剂热反应合成了 2 个配合物:  $[\text{Cd}(\text{phen})(\text{chdc})]_n$  (**1**) 和  $[\text{Cd}(\text{phen})(\text{chdc})(\text{H}_2\text{O})]_n$  (**2**)。X-射线单晶衍射显示: **1** 是梯状双链结构; **2** 是单链结构, 单链再通过氢键连接成双链。虽然 **1** 和 **2** 的组分相似, 但它们在固态条件下的荧光发射却大不一样, 可能在光化学方面有潜在的应用。

**关键词:** 柔性配体; 镉配合物; 1,1'-环己烷二乙酸; 溶剂热合成; 荧光

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## Syntheses, Structures and Fluorescence of Two Cd(II) Complexes Constructed from 1,1'-Cyclohexanediactic Acid

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**Abstract:** Two complexes of 1,1'-cyclohexanediactic acid ( $\text{H}_2\text{chdc}$ ),  $[\text{Cd}(\text{phen})(\text{chdc})]_n$  (**1**) and  $[\text{Cd}(\text{phen})(\text{chdc})(\text{H}_2\text{O})]_n$  (**2**), have been synthesized through solvothermal reactions of  $\text{H}_2\text{chdc}$ , 1,10-phenanthroline (phen) and cadmium nitrate. The crystal structures of two complexes reveal that **1** has a ladder-like double-chain structure, while **2** consists of linear single chains, which are further linked to form double-chains through hydrogen bonding. Although consisted of similar components, **1** and **2** exhibit different intense fluorescence emission in solid state, which may have promising application in photophysical chemistry. CCDC: 285079, **1**; 285080, **2**.

**Key words:** flexible ligand; Cd(II) complex; 1,1'-cyclohexanediactic acid; solvothermal synthesis; fluorescence

## 0 Introduction

The current interest in the crystal engineering of coordination polymer frameworks stems not only from their potential application as functional materials, but also from their intriguing variety of architectures and

topologies<sup>[1~4]</sup>. In the past few years, extensive studies have been carried out using rigid ligands such as 1,3,5-benzenetricarboxylic acid, imidazole 4,5-dicarboxylic acid and 1-quinoline carboxylic acid etc.. These rigid polyfunctional ligands are well-known to form grids, rods, bricks, honeycombs, diamondoid

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nets, and other noteworthy species<sup>[5-9]</sup>, while flexible ligands may facilitate the formation of helices and other novel supramolecules<sup>[10-14]</sup>. However, flexible Cyclohexane carboxylic acid ligands have not been extensively exploited, except for some limited cases<sup>[15-19]</sup>. This is probably because the varied conformations and geometries of these ligands make it difficult to forecast and control the final structures<sup>[20]</sup>. Therefore, much more work is required to extend our knowledge of the coordination chemistry of these flexible ligands and establish proper synthetic strategies that lead to the desired species with predictable structures and properties.

In this work, we focus on the controlled assembly of frameworks with interesting topology and special property using flexible 1,1'-cyclohexanediactic acid<sup>[21]</sup>. To our knowledge, there is only one complex constructed from H<sub>2</sub>chdcc reported<sup>[22]</sup>. The complex was synthesized by solution method and composed of 0D discrete dimers. Our study is to explore the solvothermal method, and to construct some new complexes with 1D, 2D and 3D topology. We adopt rigid 1,10-phenanthroline (phen) as auxiliary ligand to adjust the structure, and hope it can bring the complexes with particular luminescence character<sup>[23-26]</sup>. Herein, we report the syntheses, structures and fluorescence of the two complexes [Cd(phen)(chdc)]<sub>n</sub> (**1**) and [Cd(phen)(chdc)(H<sub>2</sub>O)]<sub>n</sub> (**2**).

## 1 Experimental

### 1.1 Materials and physical measurements

All chemicals are used as purchased without further purification. Thermogravimetric analyses were carried out with a NETZSCH STA 449C unit at a heating rate of 15 °C·min<sup>-1</sup> under nitrogen. IR spectra were recorded on a Magna 750 FTIR spectrophotometer as KBr pellets. Elemental analyses were carried out on an Elementar Vario EL III analyzer. Fluorescence spectroscopy was performed on an Edinburgh Analytical instrument FLS920.

### 1.2 Syntheses of complexes **1** and **2**

H<sub>2</sub>chdc (0.080 g, 0.4 mmol), phen (0.080 g, 0.4

mmol), and Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.185 g, 0.6 mmol) were put in a mixed solution of 8 mL distilled H<sub>2</sub>O and 2 mL ethanol, and the pH was adjusted within 5.2~5.8 by diluent NaOH aqueous solution. Then the mixture was sealed in 25 mL Teflon-lined reactor and heated to 160 °C for 3 days, and then slowly cooled to room temperature. Colorless block crystals of **1** (yield: about 31%) and colorless needlelike crystals of **2** (yield: about 17%) were collected. When the pH was adjusted within 5.9~6.3, the pure crystals of **1** were found with yield of about 52%. When the pH was decreased to about 5.0, only crystals of **2** were obtained with yield of about 13%. Anal. Calc. for **1** (%): H, 4.52; C, 53.83; N, 5.71. Found (%): H, 4.57; C, 53.63; N, 5.75. IR(KBr) for **1**: 3 058w, 2 956w, 2 926m, 2 854w, 1 557vs, 1 515s, 1 430s, 1 397vs, 1 318w, 1 261w, 848m, 731m. Anal. Calc. for **2** (%): H, 4.75; C, 51.93; N, 5.51. Found (%): H, 4.89; C, 51.86; N, 5.41. IR(KBr) for **2**: 3 413w, 2 921m, 2 850w, 1 541vs, 1 511s, 1 427s, 1 405s, 845m, 728m.

### 1.3 Diffraction data collection and structure determination

The intensity data of **1** were collected on a SIEMENS SMART CCD diffractometer with graphite-monochromatized Mo K $\alpha$  ( $\lambda$ =0.071 073 nm) radiation at room temperature, and the empirical absorption corrections were performed using the SADABS program<sup>[27]</sup>. The intensity data of **2** were collected on a Rigaku CCD diffractometer with graphite-monochromatized Mo K $\alpha$  ( $\lambda$ =0.071 073 nm) radiation at 173 K, and the empirical absorption corrections were performed using the CrystalClear program<sup>[28]</sup>. The structures were solved by direct methods using the SHELXS-97<sup>[29]</sup> and refined on  $F^2$  by full-matrix least-squares using SHELXL-97<sup>[30]</sup>. All non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically, and the H atoms of water in **2** were located from E-map. The crystallographic data for two complexes are listed in Table 1.

CCDC: 285079, **1**; 285080, **2**.

Table 1 Crystallographic data for complexes **1** and **2**

	<b>1</b>	<b>2</b>
Empirical formula	C <sub>22</sub> H <sub>22</sub> CdN <sub>2</sub> O <sub>4</sub>	C <sub>22</sub> H <sub>24</sub> CdN <sub>2</sub> O <sub>5</sub>
Formula weight	490.80	508.83
<i>T</i> / K	173(2)	293(2)
Wavelength / nm	0.071 073	0.071 073
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> / nm	0.902 23(2)	2.403 2(3)
<i>b</i> / nm	1.792 02(5)	2.153 73(2)
<i>c</i> / nm	1.238 27(2)	0.816 31(8)
$\alpha$ / (°)	90	90
$\beta$ / (°)	94.945(2)	99.285(5)
$\gamma$ / (°)	90	90
<i>V</i> / nm <sup>3</sup>	1.991 29(8)	4.169 8(7)
<i>Z</i>	4	8
<i>D</i> <sub>calc</sub> / (Mg·m <sup>-3</sup> )	1.637	1.621
Absorption coefficient / mm <sup>-1</sup>	1.128	1.084
<i>F</i> (000)	992	2 064
Crystal size / mm	0.46 × 0.32 × 0.28	0.45 × 0.10 × 0.05
$\theta$ range for data collection / (°)	2.54~25.04	3.16~24.71
Index ranges	-10 ≤ <i>h</i> ≤ 9, -18 ≤ <i>k</i> ≤ 21, -14 ≤ <i>l</i> ≤ 10	-28 ≤ <i>h</i> ≤ 28, -25 ≤ <i>k</i> ≤ 21, -9 ≤ <i>l</i> ≤ 9
Reflections collected	5 497	12 818
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data [ <i>I</i> > 2σ( <i>I</i> )] / parameters	3 441 / 262	3 551 / 275
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.080	1.051
<i>R</i> <sub>1</sub> indices [ <i>I</i> > 2σ( <i>I</i> )]	0.033 8	0.050 2
<i>wR</i> <sub>2</sub> indices (all data)	0.107 2	0.142 4
Largest diff. peak and hole / (e·nm <sup>-3</sup> )	334 and -645	651 and -388

## 2 Result and discussion

### 2.1 Syntheses

H<sub>2</sub>chdc ligand contains two carboxylate groups, which can be completely or partially deprotonated with the presence of alkali and consequently exhibit rich coordination modes. Thus, we used diluent NaOH aqueous solution to adjust the pH of the reaction system. It was observed that insoluble precipitates were obtained when the pH was adjusted to above 6.5. It may be attributed to the fact that H<sub>2</sub>chdc deprotonated and the polymerization took place too quickly. To avoid of mass of precipitate, the reactions of cadmium nitrate, H<sub>2</sub>chdc and phen were carried out under lower pH (5.2~5.8), and crystals **1** and **2** were synchronous-

ly obtained. When the parallel reaction was carried out in higher pH (5.9~6.3), only pure crystals of **1** were isolated. When pH value was decreased to about 5.0, the similar reaction yielded crystals of **2** accompanying with some precipitates, and nothing but only precipitates or clear liquid were obtained for lower pH. From the above results, we can conclude the pH value plays a crucial role in synthesizing and separating the complexes, although the exact reaction mechanism has not been determined yet.

### 2.2 Crystal structure of complex **1**

The selected bond lengths and angles of complex **1** are listed in Table 2. The asymmetric unit of **1** consists a unique Cd(II) ion, which is seven-coordinated by two nitrogen atoms from a chelating phen ligand

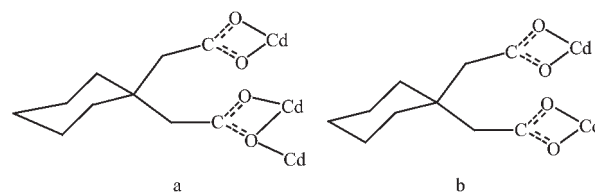
Table 2 Selected bond lengths and angles of complex 1

Cd(1)-O(3)#1	2.268(3)	Cd(1)-O(4)#1	2.487(3)	Cd(1)-O(2)	2.273(3)
Cd(1)-O(2)#2	2.516(3)	Cd(1)-N(1)	2.348(3)	Cd(1)-O(1)	2.534(3)
Cd(1)-N(2)	2.397(3)				
O(3)#1-Cd(1)-N(1)	117.6(2)	O(3)#1-Cd(1)-O(2)#2	84.0(2)	O(2)-Cd(1)-N(1)	106.5(2)
O(2)-Cd(1)-O(2)#2	70.3(2)	O(3)#1-Cd(1)-N(2)	87.5(2)	N(1)-Cd(1)-O(2)#2	82.9(2)
N(1)-Cd(1)-N(2)	70.8(2)	O(4)#1-Cd(1)-O(2)#2	110.9(2)	O(3)#1-Cd(1)-O(4)#1	54.0(2)
O(2)-Cd(1)-O(1)	53.4(9)	O(2)-Cd(1)-O(4)#1	90.8(2)	N(1)-Cd(1)-O(1)	91.8(2)
N(1)-Cd(1)-O(4)#1	161.0(2)	N(2)-Cd(1)-O(1)	85.7(2)	N(2)-Cd(1)-O(4)#1	91.1(2)
O(4)#1-Cd(1)-O(1)	92.4(2)				

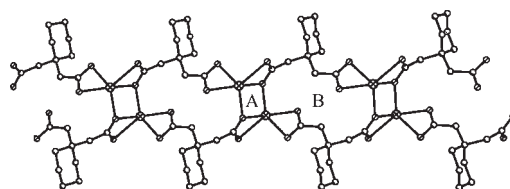
Symmetry transformations used to generate equivalent atoms: #1:  $x-1, y, z$ ; #2:  $-x+1, -y, -z+1$ .

and five oxygen atoms from three  $\text{chdc}^{2-}$  ligands in a highly distorted pentagonal bipyramid coordination geometry, with N1 and O4B in the axial positions, as shown in Fig.1. The Cd-O(N) bond distances are in the range of 0.226 8~0.253 4 nm, with an average value of 0.240 3 nm. The  $\text{chdc}^{2-}$  ligand links three Cd(II) ions, as shown in Scheme 1(a). Through the chelating coordination, the  $\text{chdc}^{2-}$  links Cd(II) ions along the  $a$  axis to form the single chains, with interatomic distance of 0.902 2 nm. Each two of such chains are connected together to form the double chain structure, through the sharing  $\text{chdc}^{2-}$  ligands by the bridging coordination of O2 atoms. Two kinds of macrocyclic rings, one is four-member ring (A) with Cd...Cd distance of 0.391 8 nm and the other is sixteen-member ring (B) with Cd...Cd distance of 0.845 0 nm, are observed in the double chain (Fig.2). The chelating phen

ligands are attached to two sides of the double-chain. The double-chains are further connected by weak  $\pi$ - $\pi$  interaction of phen (about 0.342 8 nm) to form the layer structure along the  $ac$  direction (Fig.3), and the layers are further stacked to form the final structure.

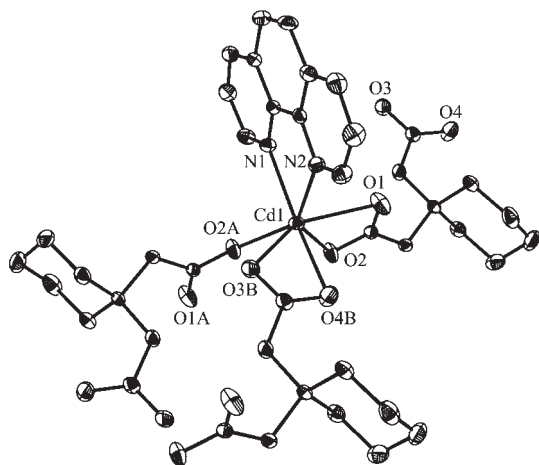


Scheme 1 Coordination modes of  $\text{chdc}^{2-}$  ligands in complexes 1 and 2



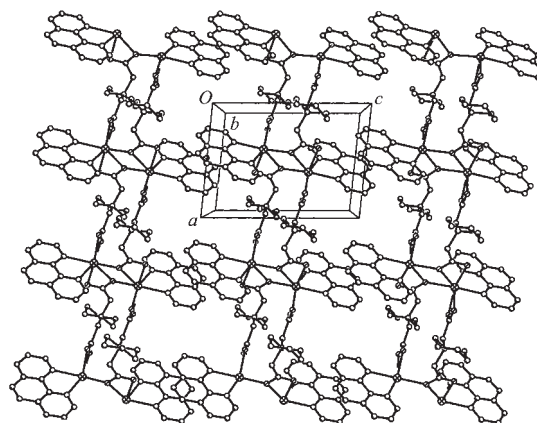
All the phen ligands and H atoms are omitted for clarity

Fig.2 View of the double-chain structure of complex 1



All the H atoms are omitted for clarity

Fig.1 Coordination environment of Cd(II) ions in complex 1



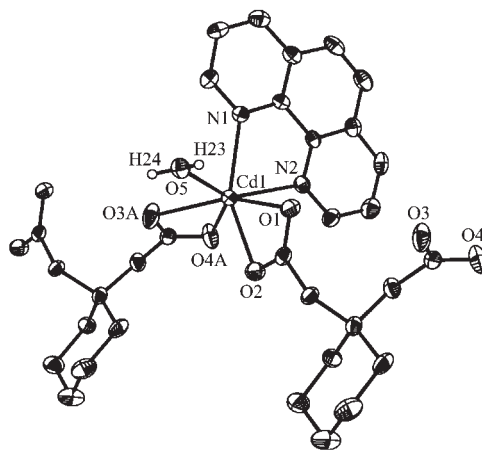
All the H atoms are omitted for clarity

Fig.3 View of the layer structure of complex 1

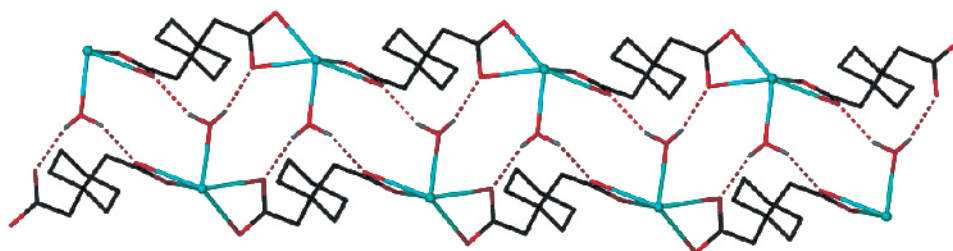
### 2.3 Crystal structure of complex **2**

The selected bond lengths and angles of complex **2** are listed in Table 3. The asymmetric unit of **2** consists a unique Cd(II) ion, which is also seven-coordinated by two nitrogen atoms and five oxygen atoms in a highly distorted pentagonal bipyramid coordination geometry, while four of the oxygen atoms from two chdc ligands and one from coordinated water. The Cd-O(N) bond distances are in the range of 0.227 4~0.253 9 nm, with an average value of 0.237 9 nm. As shown in Scheme 1(b), each carboxyl group of the chdc<sup>2-</sup> ligand chelates a Cd(II) ion, and in this way the ligand links the Cd(II) ions to form the single chains along the *c* axis, with the Cd...Cd distance of 0.816 3 nm, and the phen ligand are attached to one side of chains. The single chains are further linked through the hydrogen bonding (O5-H23...O1# and O5-H24...O3#, symmetry code: #:  $-x+1, y, -z+5/2$ ) to form the double chains, as shown in Fig.5. It is interesting that unlike the usual alternately arranging mode, all the phen ligands are on one side of the double chains, and the chdc<sup>2-</sup> ligands are on the other side. This ar-

ranging mode facilitates the form of the face-to-face  $\pi$ - $\pi$  interaction of phen ligand from two double chains, and this  $\pi$ - $\pi$  interaction combined with the hydrogen bonding makes four single chains to link together to form the 1D supramolecular chains, and these supramolecular chains stack along *c* axis direction to form the final structure of the complex, as shown in Fig.6.



All the H atoms bonded to C atoms are omitted for clarity  
Fig.4 Coordination environment of Cd(II) ions in complex **2**



All the phen ligands and H atoms bonded to C atoms are omitted for clarity  
Fig.5 View of the double-chain of complex **2** formed by the hydrogen bonding linkage of single chains

Table 3 Selected bond lengths and angles of complex **2**

Cd(1)-O(2)	2.274(4)	Cd(1)-O(4)#1	2.379(5)	Cd(1)-O(5)	2.344(4)
Cd(1)-N(2)	2.392(4)	Cd(1)-O(3)#1	2.361(4)	Cd(1)-O(1)	2.539(4)
Cd(1)-N(1)	2.365(4)				
O(2)-Cd(1)-O(5)	98.0(2)	N(1)-Cd(1)-O(4)#1	110.2(2)	O(2)-Cd(1)-O(3)#1	102.8(2)
O(2)-Cd(1)-N(2)	94.0(2)	O(2)-Cd(1)-N(1)	150.6(2)	N(1)-Cd(1)-N(2)	69.7(2)
O(5)-Cd(1)-N(1)	83.0(2)	O(4)#1-Cd(1)-N(2)	81.5(2)	O(3)#1-Cd(1)-N(1)	106.3(2)
O(2)-Cd(1)-O(1)	53.7(2)	O(2)-Cd(1)-O(4)#1	90.4(2)	O(5)-Cd(1)-O(1)	76.9(2)
O(5)-Cd(1)-O(3)#1	79.8(2)	N(1)-Cd(1)-O(1)	98.7(2)	O(3)#1-Cd(1)-O(4)#1	54.0(2)
N(2)-Cd(1)-O(1)	82.0(2)				

Symmetry transformations used to generate equivalent atoms: #1:  $x, y, z-1$ .

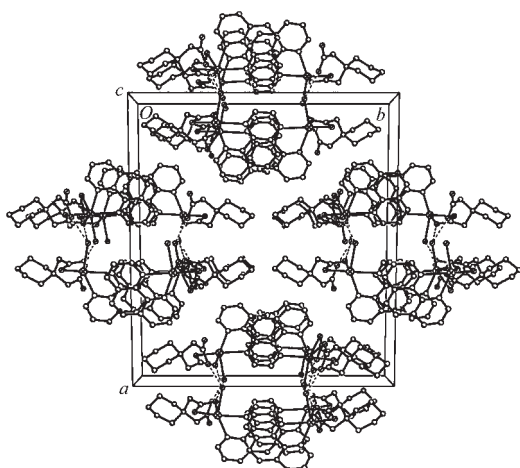


Fig.6 View of the stacking diagram of complex **2** along *c* axis

## 2.4 Thermogravimetry analyses of Complexes **1** and **2**

Thermal gravimetric analysis (TGA) of complex **1** indicates that **1** loses 36.28% of total molecular weight from 157 °C to 244 °C, corresponding to the loss of the phen ligand (Calc. 36.67%). The second weight loss begins at 362 °C and the complex decomposed completely. For **2**, the first weight loss of 3.41% from 78 °C to 133 °C is attributed to the release of the coordinated water molecules (Calc. 3.54%). Then the complex is stable till 339 °C and then starts to decompose.

## 2.5 Fluorescence

The emission spectra of **1** and **2** in the solid state at room temperature are shown in Fig.7. It should be noted although **1** and **2** are constructed from the same ligands and metal ions, they exhibit different fluorescence, which may be resulted from the different coordination and stacking modes of the two complexes.

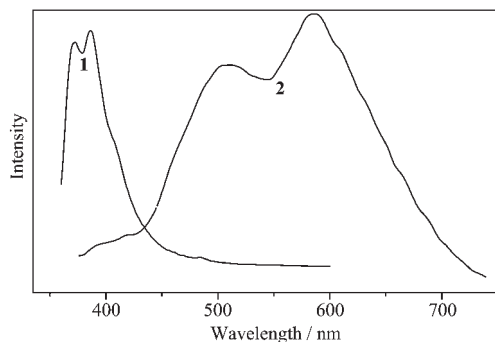


Fig.7 Emission spectrum of **1** and **2** in the solid state

Complex **1** exhibits an intense photoluminescence

emission band from 350 nm to 450 nm, with  $\lambda_{\text{max}}=373$  nm and  $\lambda_{\text{max}}=387$  nm ( $\lambda_{\text{ex}}=340$  nm). The emission of **1** probably can be assigned to the intraligand fluorescent emission, since a very similar emission is observed for the free phen ligand<sup>[31,32]</sup>. The enhancement and significant blue-shift of the emission of the coordinated phen compared with the free phen may be attributed to the chelating of the phen ligand to the metal ion, which effectively increase the rigidity of the ligands and reduce the loss of energy by radiationless decay of the intraligand emission excited state<sup>[33,34]</sup>. **2** exhibits an intense emission band ranges from 400 to 700 nm, with  $\lambda_{\text{max}}=512$  and 586 nm ( $\lambda_{\text{ex}}=280$  nm). Since no emission of free ligands is found in the range of 500~600 nm. Thus, the emission of **2** may be assigned as ligand-to-metal-charge-transfer (LMCT) or metal-to-ligand-charge-transfer (MLCT)<sup>[35]</sup>.

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