

研究简报

## 氯桥连 1-甲基-3-羧甲基咪唑镉一维配位聚合物： [Cd<sub>2</sub>(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>Cl<sub>4</sub>]<sub>n</sub>·3nH<sub>2</sub>O 的合成及晶体结构

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关键词: 离子液体; 1-甲基-3-羧甲基咪唑; 配位聚合物; 晶体结构

中图分类号: O614.24<sup>2</sup>

文献标识码: A

文章编号: 1001-4861(2008)10-1709-04

## Synthesis and Crystal Structure of a Chlorine-bridged Cd(II) Polymer with One-dimensional Polymeric Structure: [Cd<sub>2</sub>(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>Cl<sub>4</sub>]<sub>n</sub>·3nH<sub>2</sub>O

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**Abstract:** A metal-organic coordination polymer [Cd<sub>2</sub>(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>Cl<sub>4</sub>]<sub>n</sub>·3nH<sub>2</sub>O [where C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub> is ionic liquid, 1-carboxymethyl-3-methylimidazolium] **1** has been hydrothermally synthesized and characterized by X-ray diffraction single-crystal structure analysis. The complex crystallizes in orthorhombic, space group *Aba2* with *a*=1.747 6(3) nm, *b*=1.933 6(4) nm, *c*=0.692 75(13) nm, *V*=2.340 9(8) nm<sup>3</sup>, *M<sub>r</sub>*=700.96, *D<sub>c</sub>*=1.989 g·cm<sup>-3</sup>, *μ*(Mo *Kα*)=2.312 mm<sup>-1</sup>, *F*(000)=1 368, *Z*=4, the final *R*=0.021 4 and *wR*=0.051 2 for 3 331 observed reflections (*I*>2σ(*I*)). Each Cd(II) atom is in a distorted octahedral environment, surrounded by an uncommon symmetrical bidentate chelating carboxylato group and two pairs of bridging chloro ligands. Successive octahedra related by the *c*-glide of eration share edges to generate a one-dimensional polymeric structure. CCDC: 692298.

**Key words:** ionic liquid; 1-carboxymethyl-3-methylimidazolium; coordination polymer; crystal structure

Crystal engineering of metal-organic materials has drawn great attention because many specific properties such as ion-exchange, sorption, catalysis, and nonlinear optical properties, which can be achieved by molecular design<sup>[1-4]</sup>. Lately, near-ambient temperature ionic li-

quids, or organic molten salts, have been extensively studied owing to their potential synthetic, catalysis, electrochemical, photoelectrochemical, and phase transfer applications<sup>[5-10]</sup>, which can be attributed to their characteristic physicochemical properties such as

收稿日期: 2008-02-18。收修改稿日期: 2008-06-02。

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tunable solvation strength, solubility, negligible vapor pressure, high thermal stability, ionic conductivity, and heating behavior under microwave radiation<sup>[11–14]</sup>. Nowadays, many pyridinium, quaternary ammonium, and dialkylimidazolium salts have been utilized as ionic liquids, which are nonflammable, nonvolatile, and are often considered as environmentally friendly solvents to replace volatile organic compounds (VOC)<sup>[15]</sup>. Ambient-temperature ionic liquids encompassing 1,3-dialkylimidazolium salts have shown great promise as an attractive alternative to conventional solvents<sup>[16,17]</sup>. Their potential for recyclability, ability to dissolve a variety of materials, and importantly their nonvolatile nature with barely measurable vapor pressure are some of their unique attributes responsible for newly found popularity. It has been reported that dialkylimidazolium cations were used as templates in aqueous solution for the synthesis of zeolites and MCM-41<sup>[18]</sup>. Recently, we have synthesized and reported zinc polymer with 1-carboxymethyl-3-methylimidazolium<sup>[19]</sup>. As an extension of our work in this field, we report the preparation and crystal structure of a new cadmium(II) complex of ionic liquid 1-carboxymethyl-3-methylimidazolium namely Catena-[ $\mu$ -Tertachloro-Di (1-carboxymethyl-3-methylimidazolium) dicadmium(II)] trihydrate, in which the ionic liquid ligand acts in a nearly symmetrical bidentate mode.

## 1 Experimental

### 1.1 Materials and instruments

All reagents were of analytical grade quality and were used without further purification. Elemental analyses were carried out on Elementar Vario EL III elemental analyzer. The <sup>1</sup>H NMR spectra were recorded at 400 MHz on a Bruker-400 spectrometer using d<sub>6</sub>-DMSO as solvent, chemical shifts are expressed as  $\delta$  (ppm) with respect to tetramethylsilane as an external reference.

### 1.2 Synthesis of the title compound

A mixture of Cd(OH)<sub>2</sub> (1 mmol), 1-carboxymethyl-3-methylimidazolium chloride (1 mmol) and water (20 mL) was sealed in a 25 mL Teflon-lined stainless steel reactor and heated at 393 K for 48 h. A colourless solution was obtained after cooling the reaction to room temperature, colourless single crystals were obtained after two weeks in 50% yield (based on Cd). Anal. Calcd. for [Cd<sub>2</sub>(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>Cl<sub>4</sub>]<sub>n</sub> · 3nH<sub>2</sub>O (%): C 22.88; H 3.52; N 8.89. Found (%): C 22.76; H 3.61; N 8.79. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>, ppm);  $\delta$  9.04(s, 1H, N-CH=N), 7.68(d, 2H, -CH=CH-), 5.11(s, 2H, -CH<sub>2</sub>-), 3.89(s, 3H, -CH<sub>3</sub>)

### 1.3 Crystal structure determination

A single crystal of the title complex with dimensions of 0.192 mm × 0.161 mm × 0.092 mm was selected for the experiment. Data collection was performed using a Bruker SMART APEX II CCD area detector diffractometer with Mo K $\alpha$  radiation ( $\lambda$ =0.071 073 nm) with an  $\omega$ -scan mode in the range of 2.33° <  $\theta$  < 27.61°. A total of 5 165 reflections were collected and 2 406 were independent with  $R_{\text{int}}$ =0.019 4, of which 3 331 with  $I > 2\sigma(I)$  were considered as observed. The correction for Lp factors was applied. Absorption correction was performed by the SADABS program<sup>[22]</sup>. The structure was solved by direct methods with SHELXS-97 program<sup>[20]</sup> and refined with SHELXL-97<sup>[21]</sup> by full-matrix least-squares techniques on  $F^2$ . All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. The C-bound hydrogen atoms were treated as riding and were included in the refinement with  $U_{\text{iso}}$  (H)=1.2 $U_{\text{eq}}$  (C). The water H atoms were located in the Fourier map and included in the refinement, their  $U_{\text{iso}}$  values were set to 1.5 $U_{\text{eq}}$  of their bound atoms. Crystal data and structure refinement parameters are listed in Table 1.

CCDC: 692298.

Table 1 Crystallographic data for 1

Empirical formula	C <sub>12</sub> H <sub>22</sub> Cd <sub>2</sub> Cl <sub>4</sub> N <sub>4</sub> O <sub>7</sub>	$\mu$ / mm <sup>-1</sup>	2.312
Formula weight	700.96	$F(000)$	1368
Crystal size / mm	0.192 × 0.161 × 0.092	$\theta$ range / (°)	2.33 ≤ $\theta$ ≤ 27.61
Colour / shape	Colourless / block	Limiting indices	-14 ≤ $h$ ≤ 22, -24 ≤ $k$ ≤ 22, -8 ≤ $l$ ≤ 8

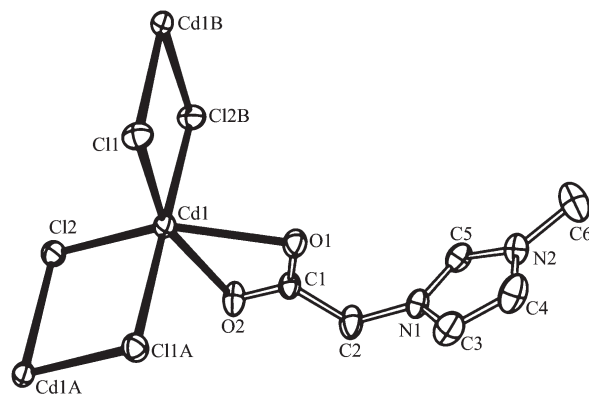
Continued Table 2

Temperature / K	296(2)	Reflections collected	5 165
Crystal system	Orthorhombic	Independent reflections ( $R_{int}$ )	2 406 (0.019 4)
Space group	<i>Aba2</i>	Reflections with $[I > 2\sigma(I)]$	2 260
$a$ / nm	1.747 6(4)	Data / restraints / parameters	2 406 / 5 / 141
$b$ / nm	1.933 6(4)	Goodness of fit on $F^2$	1.041
$c$ / nm	0.692 75(13)	Final $R$ indices $[I > 2\sigma(I)]$	$R_1=0.021\ 4$ , $wR_2=0.051\ 3$
$V$ / nm <sup>3</sup>	2.340 9(8)	$R$ indices (all data)	$R_1=0.023\ 7$ , $wR_2=0.052\ 7$
$Z$	4	$\Delta\rho_{max}$ $\Delta\rho_{min}$ / (e·nm <sup>-3</sup> )	325, -758
$D_c$ / (g·cm <sup>-3</sup> )	1.989		

## 2 Results and discussion

In the crystal structure of **1**, Cd(II) atom is coordinated with one ionic liquid ligand and four chloride ion. The structure of the present complex is different from those of the polymeric Cd(II) complexes of analogous ligands, namely [Cd(4-hydroxy-*L*-proline)Cl<sub>2</sub>]<sub>n</sub><sup>[23]</sup>, and [Cd(proline)Cl<sub>2</sub>]<sub>n</sub>·*n*H<sub>2</sub>O<sup>[24]</sup>, which are all one dimensional polymeric species with each pair of Cd(II) atoms bridged by two chloro ligands and a bridging carboxylato group. As illustrated in Fig.1, the Cd(II) atom is in an elongated octahedral environment, being coordinated by two trans-related chloro ligands [Cd(1)-Cl(1a)=0.264 86(9), Cd(1)-Cl(2b)=0.263 23(9) nm] and two *cis*-related chloro ligands [Cd(1)-Cl(1)=0.253 67(8), Cd(1)-Cl(2)=0.255 64(9) nm], as well as a chelating ionic liquid ligand [Cd-O=0.245 1(2), 0.234 2(2) nm]. The most distorted angle of the octahedron is O(1)-Cd(1)-O(2) at 54.53(7)°. Neighboring Cd(II) atoms are linked by two pairs of bridging chloro ligands [Cd-Cl-

Cd=92.55(3), 92.49(3)°] to build up a one-dimensional polymer running parallel to the *c* axis (see Fig.2). The closest Cd···Cd contact of 0.374 81(8) nm is much larger than that (0.298 nm) in the metal. The selected important bond parameters are given in Table 2.



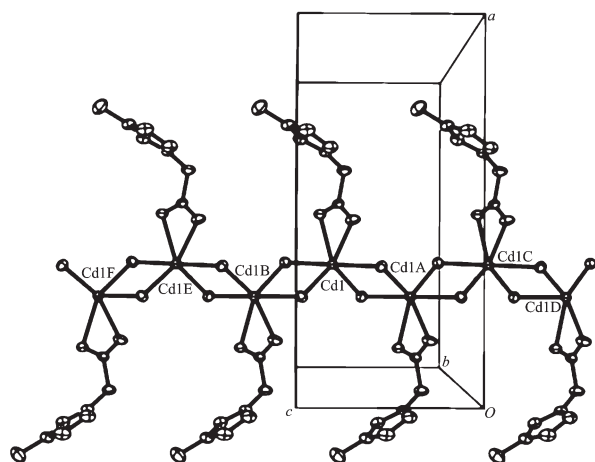
A: 0.5-*x*, *y*, 0.5+*z*; B: 0.5-*x*, *y*, -0.5+*z*

Fig.1 Perspective view showing the coordination geometry of the metal atom, Displacement ellipsoids are drawn at the 30% probability level

Table 2 Selected bond lengths (nm) and bond angles (°) for **1**

Cd(1)-O(2)	0.234 2(2)	Cd(1)-Cl(2)#1	0.263 23(9)	O(1)-C(1)	0.124 6(4)
Cd(1)-O(1)	0.245 1(2)	Cd(1)-Cl(1)#2	0.264 86(9)	O(2)-C(1)	0.125 6(4)
Cd(1)-Cl(1)	0.253 67(8)	Cl(1)-Cd(1)#1	0.264 86(9)		
Cd(1)-Cl(2)	0.255 64(9)	Cl(2)-Cd(1b)i	0.263 23(9)		
O(2)-Cd(1)-O(1)	54.53(7)	O(1)-Cd(1)-Cl(2)#1	89.32(6)	Cl(2a)-Cd(1)-Cl(1)#2	178.89(3)
O(2)-Cd(1)-Cl(1)	153.13(6)	Cl(1)-Cd(1)-Cl(2)#1	87.80(3)	C(1)-O(1)-Cd(1)	88.85(18)
O(1)-Cd(1)-Cl(1)	99.00(6)	Cl(2)-Cd(1)-Cl(2)#1	93.94(3)	C(1)-O(2)-Cd(1)	93.65(19)
O(2)-Cd(1)-Cl(2)	95.02(6)	O(2)-Cd(1)-Cl(1)#2	84.87(7)	O(1)-C(1)-O(2)	123.0(3)
O(1)-Cd(1)-Cl(2)	149.55(6)	O(1)-Cd(1)-Cl(1)#2	90.10(6)	O(1)-C(1)-C(2)	121.5(3)
Cl(1)-Cd(1)-Cl(2)	111.37(3)	Cl(1)-Cd(1)-Cl(1)#2	91.35(3)	O(2)-C(1)-C(2)	115.5(3)
O(2)-Cd(1)-Cl(2a)	95.56(7)	Cl(2)-Cd(1)-Cl(1)#2	87.04(3)		

Symmetry transformation: #1: 0.5-*x*, *y*, 0.5+*z*; #2: 0.5-*x*, *y*, -0.5+*z*.



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

Fig.2 A fragment of the crystal structure of **1**, showing a one-dimensional polymeric chain running along the *c* axis

Herein, water molecule is not only a hydrogen-bond acceptor but also proton donor. The O1w H atoms make intermolecular hydrogen bonds to the O1 atoms [ $d(\text{O}\cdots\text{O})=0.281\,5(4)$  nm and  $\angle \text{O}-\text{H}\cdots\text{O}=168(6)^\circ$ ], O2 atoms [(symmetry:  $x, y, 1+z$ ) with  $d(\text{O}\cdots\text{O})=0.326\,2(5)$  nm and  $\angle \text{O}-\text{H}\cdots\text{O}=133(5)^\circ$ ] and chloride ion [(symmetry:  $0.5-x, y, 0.5+z$ ) with  $d(\text{O}\cdots\text{Cl})=0.345\,4(4)$  nm and  $\angle \text{O}-\text{H}\cdots\text{O}=146(6)^\circ$ ]. The O1w H atoms also make intermolecular hydrogen bonds to the O2w atoms [ $d(\text{O}\cdots\text{O})=0.281\,9(4)$  nm and  $\angle \text{O}-\text{H}\cdots\text{O}=169(6)^\circ$ ]. In combination with strong  $\text{O}-\text{H}\cdots\text{O}$  as well as  $\text{O}-\text{H}\cdots\text{Cl}$  hydrogen interactions between aqua water molecule and Coordinated carboxylate group and chloride ion forming a three dimensional network (Table 3).

Table 3 Hydrogen bonds geometry for **1**

D-H $\cdots$ A	$d(\text{D-H})$ / nm	$d(\text{H}\cdots\text{A})$ / nm	$d(\text{D-H}\cdots\text{A})$ / nm	$\angle \text{DHA}$ / ( $^\circ$ )
O(1W)-H(1WA)-O(1)	0.082 3(19)	0.200(2)	0.281 5(4)	168(6)
O(1W)-H(1WB)-O(2) <sup>i</sup>	0.081 1(19)	0.266(5)	0.326 2(5)	133(5)
O(1W)-H(1WB)-Cl(1) <sup>ii</sup>	0.081 1(19)	0.275(4)	0.345 4(4)	146(6)
O(2W)-H(2WA)-O(1W)	0.085 5(19)	0.198(2)	0.281 9(4)	169(6)

Symmetry transformation: <sup>i</sup>  $x, y, 1+z$ ; <sup>ii</sup>  $0.5-x, y, 0.5+z$ .

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