

一种 2,2'-联咪唑镉化合物的荧光、理论计算和结构研究

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摘要: 通过水热反应合成了一种新颖的镉-联咪唑化合物 $[\text{Cd}(\text{BIm})_2](\text{ClO}_4)(\text{OH}) \cdot 2\text{H}_2\text{O}$ (**1**) (BIm=2,2'-biimidazole), 并对其进行了单晶 X-射线衍射结构表征。该化合物具有孤立结构特征, 镉原子与 4 个氮原子配位形成 1 个扭曲的四面体。光致发光研究发现该化合物发出蓝色荧光。理论研究结果显示该荧光来自于 LMCT 机理。本文还对其红外光谱进行了报道。

关键词: 联咪唑; 晶体; 水热; 光致发光

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Fluorescent, Theoretical and Structural Investigations of a 2,2'-Biimidazole Cadmium Compound

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Abstract: A novel cadmium-biimidazole compound $[\text{Cd}(\text{BIm})_2](\text{ClO}_4)(\text{OH}) \cdot 2\text{H}_2\text{O}$ (**1**) (BIm=2,2'-biimidazole) has been synthesized via a hydrothermal reaction and structurally characterized by single-crystal X-ray diffraction. Compound **1** features an isolated (0D) structure with the cadmium ions coordinating to four nitrogen atoms to give a distorted tetrahedron. Photoluminescent investigation shows that compound **1** exhibits an emission in the blue region. Theoretical study reveals that the emission is ascribed to ligand-to-metal charge transfer (LMCT). The spectral data of FT-IR are also reported. CCDC: 895386.

Key words: biimidazole; crystal; hydrothermal; photoluminescence

0 Introduction

In recent years, the increasing interest in the area of the crystal engineering of transition metal compounds is justified by their potential applications as magnetic functional materials, zeolite-like materials, catalysts, biological materials and so forth^[1-3]. Transition metal compounds containing a group 12 (II B) metal are very attractive for the following reasons: fluorescent properties, photoelectric properties, the

diversity of the coordination numbers and geometries offered by the d^{10} configuration of the II B metal ions, the broad applications of the II B compounds and the essential role in biological systems of zinc and so on^[4-5]. The 2,2'-biimidazole is an interesting building block in constructing supramolecular or extended structures because it can coordinate to metal ions through its nitrogen atoms. Fluorescent materials, especially blue fluorescent materials, have attracted intensive attention for decades because blue fluorescence is one

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of the key colour for full-color electroluminescent displays (ELDs) and blue fluorescent materials are still rare thus far. My recent efforts in preparing new IIB compounds are mainly focusing on the synthesis of the 2,2'-biimidazole-containing compounds with blue fluorescence. I report herein the preparation, structural characterization and photoluminescence of a new compound $[\text{Cd}(\text{BIIm})_2](\text{ClO}_4)(\text{OH}) \cdot 2\text{H}_2\text{O}$ (**1**) (BIIm=2,2'-biimidazole) with a OD structure and is synthesized via a hydrothermal reaction. The electronic transition in the fluorescent process of **1** is investigated by time-dependent density functional theory (TDDFT) calculations. A search from the CCDC database (the Cambridge Crystallographic Data Centre), hundreds of 2,2'-biimidazole-containing compounds can be found^[6-11], however, amongst which cadmium compounds are rare, especially cadmium perchlorides are even less. To my best knowledge, only one example of cadmium perchloride containing 2,2'-biimidazole has been reported thus far^[12].

1 Experimental

1.1 Synthesis of $[\text{Cd}(\text{BIIm})_2](\text{ClO}_4)(\text{OH}) \cdot 2\text{H}_2\text{O}$ (**1**) (BIIm=2,2'-biimidazole)

All reactants of AR grade were obtained commercially and used without further purification. The title compound was synthesized by mixing $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol, 419 mg), BIIm (2 mmol, 268 mg) and 10 mL distilled water in a 25 mL Teflon-lined stainless steel autoclave and heated at 473 K for 10 d.

After being slowly cooled down to room temperature at a rate of $6 \text{ K} \cdot \text{h}^{-1}$, light yellow crystals suitable for X-ray analysis were obtained. The yield is 35%. $\text{C}_{12}\text{H}_{17}\text{CdClN}_8\text{O}_7$: Calcd. (%): C, 27.00; H, 3.19; N, 21.01; Found (%): C, 26.91; H, 3.23; N, 21.08. IR peaks (KBr, cm^{-1}): 3 238(vs), 3 205(vs), 3 137(w), 3 005(m), 2 912(m), 2 817(m), 1 615(w), 1 520(m), 1 422(s), 1 378(w), 1 339(w), 1 123(s), 1 089(vs), 984(w), 928(w), 851(w), 763(s), 730(m), 668(s), 618(w), and 480(w).

Infrared Spectra were obtained with a PE Spectrum-One FT-IR spectrometer using KBr discs. Elemental analyses of carbon, hydrogen and nitrogen were carried out with an Elementar Vario EL. The fluorescent data were collected at room temperature on a computer-controlled JY FluoroMax-3 spectrometer. Time-dependent density functional theory (TDDFT) calculation was performed by means of Gaussian03 suite of programs. The electron density diagrams of molecular orbital were obtained with the ChemOffice Ultra 7.0 graphics program.

1.2 X-ray structure determination

X-ray diffraction data were collected on Rigaku Mercury CCD X-ray diffractometer with graphite monochromated $\text{Mo } K\alpha$ radiation ($\lambda = 0.071\ 073 \text{ nm}$) using an ω scan technique. CrystalClear software was used for data reduction and empirical absorption correction^[13]. The structure was solved by the direct methods using the Siemens SHELXTL™ Version 5 package of crystallographic software^[14]. The difference Fourier maps based on the atomic positions yield all

Table 1 Summary of crystallographic data and structure analysis for **1**

Formula	$\text{C}_{12}\text{H}_{17}\text{CdClN}_8\text{O}_7$	$2\theta_{\text{max}} / (^\circ)$	50
Formula weight	533.19	Reflections collected	6 662
Colour	Light yellow	Independent, observed reflections (R_{int})	1 631, 1 496 (0.030 9)
Crystal size / mm	0.25×0.10×0.09	$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.921
Crystal system	Monoclinic	μ / mm^{-1}	1.387
Space group	$C2/c$	T / K	296(2)
a / nm	0.687 32(2)	$F(000)$	1 064
b / nm	1.792 13(5)	R_1, wR_2	0.040 4, 0.101 9
c / nm	1.497 03(4)	S	1.041
$\beta / (^\circ)$	91.444(2)	Largest and Mean Δ/σ	0, 0
V / nm^3	1.843 41(9)	$(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}} / (\text{e} \cdot \text{nm}^{-3})$	432, -561
Z	4		

Table 2 Selected bond lengths (nm) and bond angles (°)

Cd1-N1	0.230 5(4)	Cd1-N3	0.232 4(4)	Cd1-N3 ⁱ	0.232 4(4)
Cd1-N1 ⁱ	0.230 5(4)				
N1-Cd1-N1 ⁱ	101.3(2)	N1-Cd1-N3 ⁱ	75.2(1)	N1-Cd1-N3	162.2(1)
N1i-Cd1-N3 ⁱ	162.2(1)	N1i-Cd1-N3	75.2(1)	N3i-Cd1-N3	113.3(2)

Symmetry code: ⁱ $-x-1, y, -z+3/2$.

non-hydrogen atoms. The structure was refined using a full-matrix least-squares refinement on F^2 . All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were generated theoretically, except for those on the lattice water molecules and hydroxyl groups which are yielded by the difference Fourier maps, allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but were not refined. The summary of crystallographic data and structure analysis is given in Table 1. The selected bond lengths and bond angles are listed in Table 2.

CCDC: 895386.

2 Results and discussion

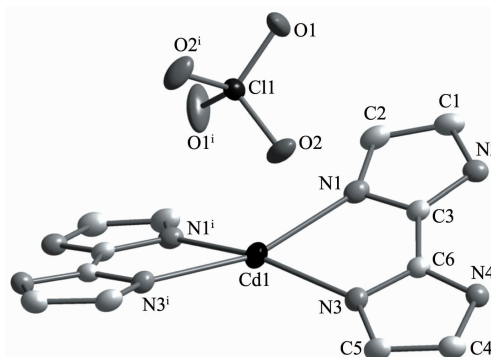
2.1 IR spectrum

The characteristic stretching vibrations of N-H group in imidazole ring were observed at $3\,137\text{ cm}^{-1}$ [15]. The stretching vibration ($\nu_{\text{C=N}}$) of free ligand at $1\,683\text{ cm}^{-1}$ red-shifted to $1\,615\text{ cm}^{-1}$ in **1**. The characteristic stretching vibration of perchloride moieties in compound **1** can be found at $1\,089\text{ cm}^{-1}$.

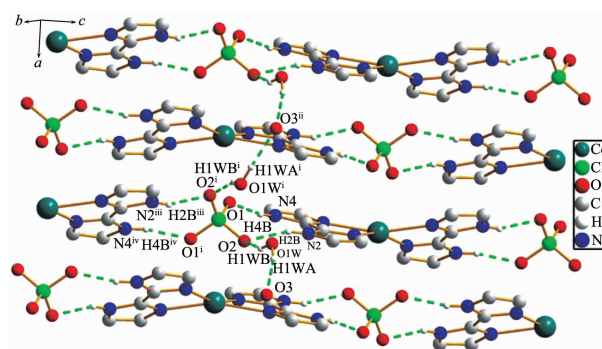
2.2 Crystal structure

Single-crystal X-ray diffraction analysis reveals that compound **1** is characteristic of an isolated (0D) structure, containing discrete $[\text{Cd}(\text{BIm})_2]^{2+}$ cations, ClO_4^- and OH^- anions, and lattice water molecules. An ORTEP drawing of **1** with 20% thermal ellipsoids is shown in Fig.1. The Cd1 atom is surrounded by four nitrogen atoms to form a distorted tetrahedron. The Cd-N bond distances are between $0.230\,5\,(4)$ and $0.232\,4\,(4)$ nm with an average value of $0.231\,4\,(4)$ nm, which is comparable with that reported previously [12,16]. The dihedral angle between two imidazole rings is $4.35\,(2)^\circ$. The displacements of the atoms on the

imidazole rings are $-0.004\,6\sim 0.004\,3$ nm from their ring planes. The $[\text{Cd}(\text{BIm})_2]^{2+}$ cations, perchlorate groups, hydroxyl groups and the lattice water molecules connect to each other via hydrogen-bonding interactions (Table 3) to yield a 2D supramolecular network, as shown in Fig.2. The electrostatic effect and the hydrogen bonding interactions between the $[\text{Cd}(\text{BIm})_2]^{2+}$ cations, perchlorate anions, hydroxyl groups and the lattice water molecules solidify the crystal packing of **1** (Fig.3).



Lattice water molecules, hydroxyl groups and hydrogen atoms were omitted for clarity; Symmetry code: ⁱ $-x-1, y, -z+3/2$

Fig.1 ORTEP drawing of **1** with 20% thermal ellipsoids

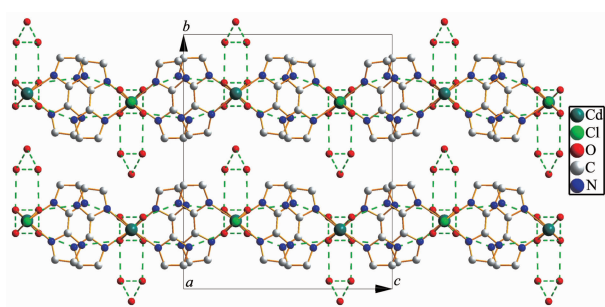
Symmetry codes: ⁱ $1/2+x, -1/2+y, z$; ⁱⁱ $-1+x, y, z$; ⁱⁱⁱ $-1/2-x, 3/2-y, 1-z$; ^{iv} $-1/2-x, 3/2-y, 2-z$

Fig.2 A 2D supramolecular layer of **1** with the dashed lines representing the hydrogen-bonding interactions

Table 3 Hydrogen-bonding interactions in the complex

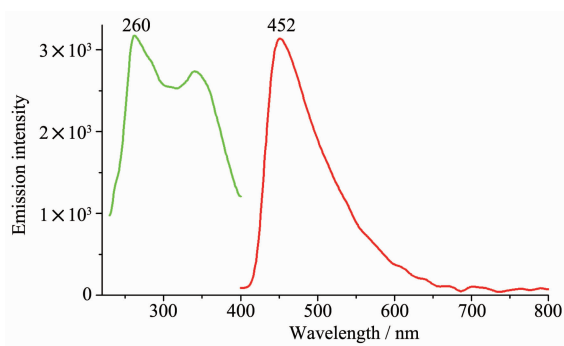
D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H...A}) / \text{nm}$	$d(\text{D...A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$
$\text{N4}^{\text{iv}}-\text{H4B}^{\text{iv}}\cdots\text{O1}^{\text{i}}$	0.086	0.188	0.272 7	169
$\text{N4}-\text{H4B}\cdots\text{O1}$	0.086	0.188	0.272 7	169
$\text{O1W}^{\text{v}}-\text{H1WB}^{\text{i}}\cdots\text{O2}^{\text{i}}$	0.090	0.203	0.287 0	156
$\text{O1W}-\text{H1WB}\cdots\text{O2}$	0.090	0.203	0.287 0	156
$\text{N2}^{\text{iii}}-\text{H2B}^{\text{iii}}\cdots\text{O2}^{\text{i}}$	0.086	0.198	0.280 5	161
$\text{N2}-\text{H2B}\cdots\text{O2}$	0.086	0.198	0.280 5	161
$\text{O1W}-\text{H1WA}\cdots\text{O3}$	0.090	0.192	0.280 7	166
$\text{O1W}-\text{H1WA}\cdots\text{O3}^{\text{ii}}$	0.090	0.192	0.280 7	166

Symmetry codes: ⁱ $1/2+x, -1/2+y, z$; ⁱⁱ $-1+x, y, z$; ⁱⁱⁱ $-1/2-x, 3/2-y, 1-z$; ^{iv} $-1/2-x, 3/2-y, 2-z$.

Fig.3 A crystal packing diagram of **1**

2.3 Luminescent property

Taking into account the excellent luminescent property of Cd^{2+} ion, the solid-state emission spectra of compound **1** are measured at room temperature. The emission spectra are given in Fig.4. The solid-state excitation spectra of the title compound show that the effective energy absorption mainly takes place in the long wavelength ultraviolet region of the range 250~380 nm. The excitation band of compound **1** under the emission of 452 nm possesses one main peak of 260 nm, accompanied by a side band at 339 nm. I further measured the corresponding emission spectra by using



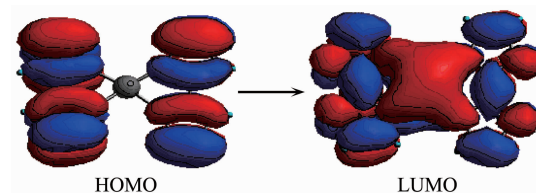
Left: excitation spectra; Right: emission spectra

Fig.4 Emission spectra of **1** at room temperature

the excitation wavelength of 260 nm for the title compound, and I obtained the emission spectra as also shown in Fig.4. For compound **1**, the emission spectra show one broad and strong blue emission band at 452 nm under the excitation of 260 nm.

2.4 Theoretical studies

In order to clarify the nature of the fluorescent emission of **1**, theoretical studies have been performed. The ground state geometry was adapted from the X-ray data of **1**. On the basis of this geometry, time-dependent DFT (TDDFT) calculations using the B3LYP functional were conducted. As shown in Fig.5, the results reveal the features of the highest occupied (HOMO) and the lowest unoccupied (LUMO) frontier orbitals. Obviously, the electron densities of the singlet state of the HOMO reside at the 2,2'-biimidazole molecules, while that of the LUMO are allocated on the metal center and the 2,2'-biimidazole moieties, suggesting that the emission band of **1** can be attributed to ligand-to-metal charge transfer (LMCT) (from the HOMO of the 2,2'-biimidazole molecules to the LUMO of the metal center).



Iso-surfaces correspond to electronic density differences of $-15 \text{ e} \cdot \text{nm}^{-3}$ (dark black) and $+15 \text{ e} \cdot \text{nm}^{-3}$ (light black)

Fig.5 Electron-density distribution of HOMO (left) and LUMO (right) calculated for **1**

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