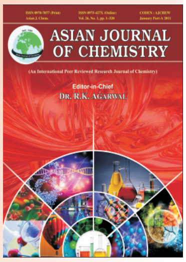
Asian Journal of Chemistry; Vol. 26, No. 15 (2014), 4865-4867

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16263



ASIAN JOURNAL OF CHEMISTRY

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Synthesis, Structure, Properties and Time-Dependent Density Functional Theory Calculations of Cadmium Complex

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Received: 31 August 2013; *Accepted*: 16 December 2013; *Published online*: 16 July 2014; AJC-15587

A cadmium complex $CdCl_2(2,2'\text{-bipy})_2$ (**1**) (bipy = bipyridine) was obtained by a hydrothermal reaction and structurally characterized by single-crystal X-ray diffraction. Photoluminescent study shows that complex **1** exhibits a greenish yellow emission. Theoretical investigations reveal that the emission is ascribed to the ligand-to-ligand charge transfer (LLCT). The spectral data of FT-IR were also reported.

Keywords: Bipyridine, Crystal, Ligand-to-ligand charge transfer, Photoluminescence, Time-dependent density functional theory.

INTRODUCTION

In recent years, metal halide-bipy complexes have attracted increasing interest not only due to their intrinsic aesthetic appeals, but also because of their multifariously potential applications. Bipyridine has a common character-a delocalized π-system of the pyridyl rings, which allows it to be a good candidate for preparing light emitting materials that can be used in different areas, like chemical sensors[1], emitting materials for organic light emitting diodes (OLED)[2] and sensitizers in solar energy conversion[3]. Up to date, a great number of structures of metal halide-bipy complexes have been documented[4] but group-12 (IIB) metal halide-bipy complexes are relatively rare. Our recent efforts in preparing IIB-based complexes are mainly focused on the systems containing a bifunctional ligand, such as 2,2'-bipyridine. We report herein the synthesis, photoluminescence and theoretical investigations of a cadmium complex $CdCl_2(2,2'\text{-bipy})_2$ (**1**).

EXPERIMENTAL

The fluorescent data were collected at room temperature on a computer-controlled JY Fluoro Max-3 spectrometer. Time-dependent density functional theory (TDDFT) calculation was performed by Gaussian03 suite of programs.

Synthesis of $CdCl_2(2,2'\text{-bipy})_2$ (1): This complex was prepared by mixing $CdCl_2$ (1 mmol, 183 mg), 2,2'-bipy (2 mmol, 312 mg) and 10 mL distilled water in a 25 mL Teflon-lined stainless steel autoclave and heated at 453 K for 10 days. After being slowly cooled down to room temperature at 6 K/h, colorless crystals were obtained. Yield: 46 %.

X-ray structure determination: The intensity data set was measured on a Rigaku Mercury CCD X-ray diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å) by using an ω-scan technique. Crystal clear software was used for data reduction and empirical absorption corrections[5]. The structure was solved by the direct method using the Siemens SHELXTLTM Version 5 package of crystallographic software[6]. The difference fourier maps based on the atomic positions yield all non-hydrogen atoms. The structure was refined using a full-matrix least-squares refinement on F^2. All non-hydrogen atoms were refined anisotropically. CCDC 895735 (Table-1).

RESULTS AND DISCUSSION

An ORTEP drawing of **1** together with the atomic numbering scheme is given in Fig. 1. The results of X-ray diffraction analysis illustrate that the crystal structure of **1** consists of isolated $CdCl_2(2,2'\text{-bipy})_2$ molecules. The Cd(II) ion has a distorted octahedral geometry, coordinated by two chlorine atoms and four nitrogen atoms from two 2,2'-bipy ligand. The bond lengths of Cd-Cl are 2.5127(7) Å and 2.5138(7) Å, which are comparable with the counterpart reported in the literature[7]. The 2,2'-bipy ligand coordinates to the cadmium ion in a classical coordination geometry, *i.e.* it chelates to the Cd(II) ion with

TABLE-1
SUMMARY OF CRYSTALLOGRAPHIC DATA AND STRUCTURE ANALYSIS

Molecular formula	$C_{20}H_{16}N_4CdCl_2$
Formula weight	495.67
Color	Colorless
Crystal size (mm^3)	0.32 0.25 0.18
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	8.7456(14)
b (Å)	14.405(2)
c (Å)	15.860(3)
β(°)	98.743(3)
V(Å^3)	1974.8(6)
Z	4
$2\theta_{max}$ (°)	50
Index ranges	$-10 \leq h \leq 10$; $-17 \leq k \leq 14$; $-18 \leq l \leq 18$
Reflections collected	14909
Independent, observed reflections (R_{int})	3485, 3196 (0.0202)
$d_{calcd.}$ (g/cm^3)	1.667
μ (mm^{-1})	1.388
T (K)	296 (2)
F(000)	984
R1, wR2	0.0204, 0.0540
S	1.015
Largest and Mean Δ/σ	0, 0
Δρ (max, min) (e/Å^3)	0.448, -0.238

its two nitrogen atoms. The bite angles of N(1)-Cd(1)-N(2) and N(3)-Cd(1)-N(4) are 68.05 (6)° to 67.44 (7)°, respectively. The bond distances of Cd-N range from 2.3805 (17) Å to 2.463 (2) Å. The bond angle of Cl(1)-Cd(1)-Cl (2) is 103.04 (3)°. For each 2,2'-bipy ligand, the pyridyl rings are approximately coplanar with a small dihedral angle of 5.81° and 9.49°, which are similar to the cases found in the literature[8]. The two 2,2'-bipy ligands are almost perpendicular with a dihedral angle of 88.73°. In **1**, there are two types of hydrogen-bonding interactions, namely, Cl···N and Cl···C hydrogen-bonding interactions. The $CdCl_2(2,2'\text{-bipy})_2$ moieties link together through the hydrogen bonding interactions to yield a 3-D supramolecular network, as shown in Fig. 2. The results of bond valence calculation reveal that the cadmium is in a +2 oxidation state (Cd1: 2.1)[9] (Table-2).

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°)

Cd(1)-Cl(1)	2.5127(7)	N(2)-Cd(1)-N(4)	88.38(6)
Cd(1)-Cl(2)	2.5138(7)	N(3)-Cd(1)-N(4)	67.44(7)
Cd(1)-N(1)	2.4288(18)	N(1)-Cd(1)-Cl(1)	164.28(5)
Cd(1)-N(2)	2.3805(17)	N(2)-Cd(1)-Cl(1)	96.84(5)
Cd(1)-N(3)	2.3918(19)	N(3)-Cd(1)-Cl(1)	102.23(5)
Cd(1)-N(4)	2.463(2)	N(4)-Cd(1)-Cl(1)	88.29(4)
		N(1)-Cd(1)-Cl(2)	85.86(5)
N(1)-Cd(1)-N(2)	68.05(6)	N(2)-Cd(1)-Cl(2)	105.53(5)
N(1)-Cd(1)-N(3)	89.78(6)	N(2)-Cd(1)-Cl(3)	94.51(5)
N(1)-Cd(1)-N(4)	86.99(6)	N(2)-Cd(1)-Cl(4)	160.60(5)
N(2)-Cd(1)-N(3)	148.38(6)	Cl(1)-Cd(1)-Cl(2)	103.04(3)

The fluorescent spectra exhibits that **1** has a greenish yellow emission band with a maximum wavelength at around 573 nm when it was excited at 375 nm (Fig. 3). To reveal the fluorescent nature, we measured the fluorescent spectra of 2,2'-bipy at room temperature. For 2,2'-bipy, the emission spectra shows one emission band at 530 nm upon photo-excitation of 343 nm, as given in the inset of Fig. 3. Obviously, the emission band of **1** is largely red-shifted about 43 nm, comparing with that of pure 2,2'-bipy. The reason for that is probably because of the formation of the complex. For the sake of further understanding the nature of the emission, theoretical in vestigations were also performed. The ground state geometry was adapted from its X-ray data. On the basis of the geometry, time-dependent DFT calculations using the B3LYP functional were conducted. As given in Fig. 4, the calculation results display the characteristics of the highest occupied (HOMO) and the lowest unoccupied (LUMO) frontier orbitals of **1**. Clearly, the electron densities of the singlet state of the HOMO are at the chlorine ligands, while that of the LUMO reside at the 2,2'-bipy ligands, indicating that the emission band should be ascribed to ligand-to-ligand charge transfer (LLCT) (from the HOMO of the chlorine atoms to the LUMO of the 2,2'-bipy ligands).

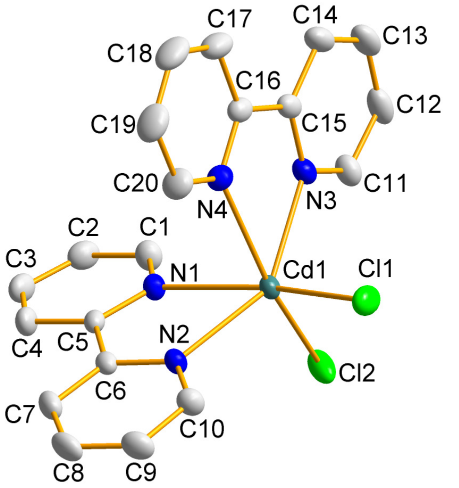

Fig. 1. An ORTEP view of **1** showing 25 % thermal ellipsoids

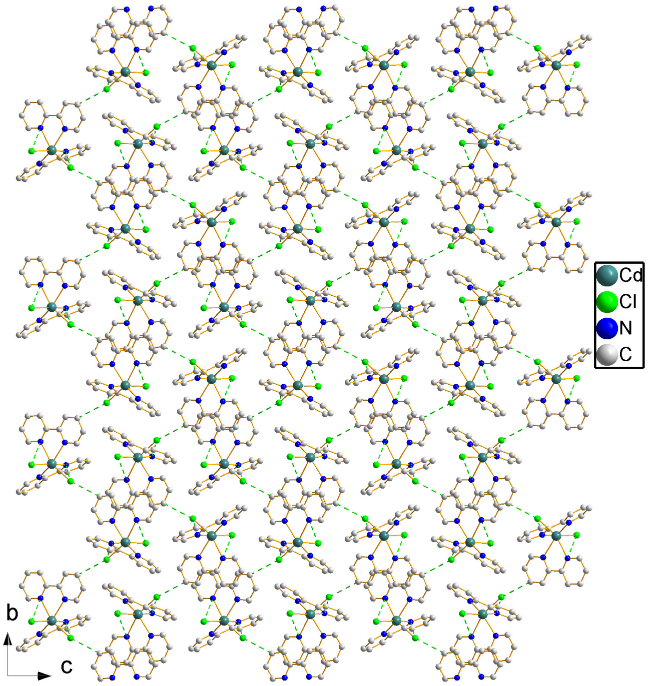

Fig. 2. Crystal packing diagram with the dashed lines representing the hydrogen-bonding interactions (Å): Cl2···N1 3.367, Cl1···N4 3.465 and Cl2···C13(1 - x, -1/2 + y, 1/2 - z) 3.487

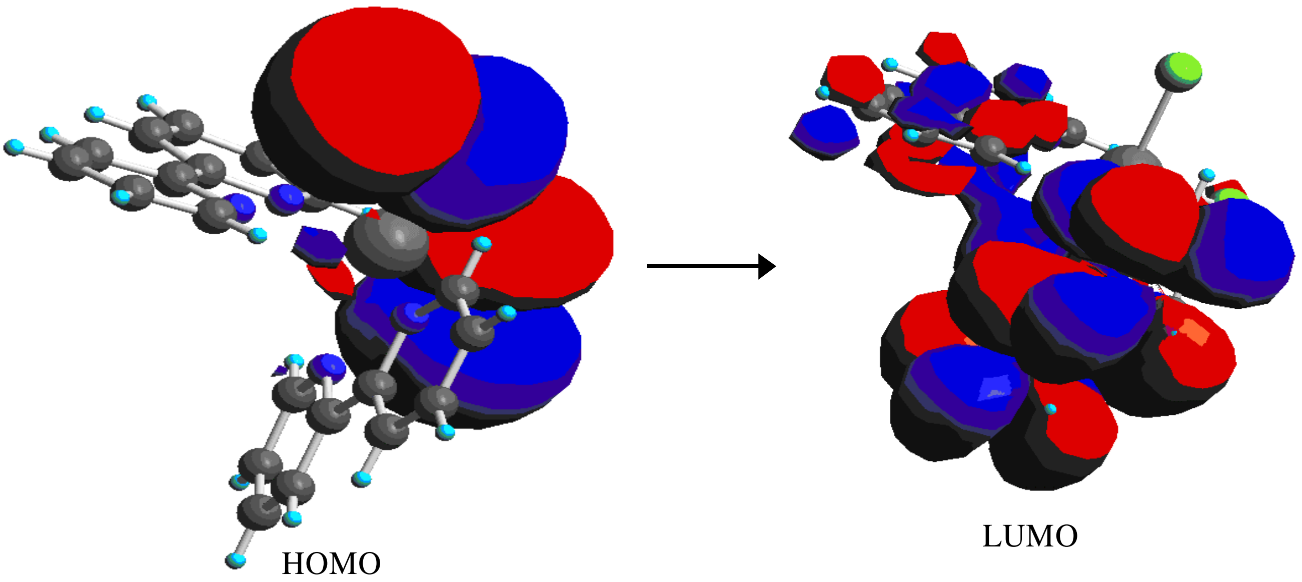

Fig. 4. Electron-density distribution of HOMO (left) and LUMO (right) calculated for **1**

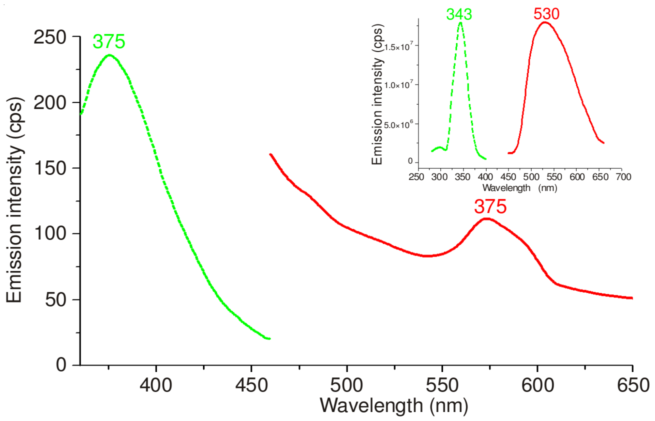

Fig. 3. Emission spectra of **1** at room temperature (Inset: the luminescent spectra of pure 2,2'-bipy). Green dashed lines: excitation spectra; red dashed lines: emission spectra

Conclusion

We synthesized a cadmium complex with an isolated 0-D structure. Photoluminescent investigation reveals that it shows a greenish yellow emission, in combination with the molecular orbital calculations, lead us to conclude that this emission band probably originates from the ligand-to-ligand charge transfer (LLCT) transition.

ACKNOWLEDGEMENTS

This work was supported by the NSF of China (21361013), the NSF of Jiangxi Province (20132BAB203010) and the open foundation (No. 20130014) of the State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences.

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