

Synthesis, structure, and luminescent properties of 2 novel 5-chlorhydroxybenzoate-imidazole metal-organic complexes

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Received: 28.03.2013 • Accepted: 27.06.2013 • Published Online: 16.12.2013 • Printed: 20.01.2014

Abstract: Two novel Zn and Cu complexes with 5-chlorhydroxybenzoate and imidazole ligands, $C_{41}H_{36}Zn_2N_8O_{13}Cl_4$ (**1**) and $C_{26}H_{22}Cl_2Cu_2N_8O_6$ (**2**), were prepared by slow evaporation method. Single crystal X-ray diffraction analysis was used to determine their structures. The purity of the complexes was confirmed by powder X-ray diffraction analysis. In **1** the Zn^{2+} cation is tetraordinated with 2 nitrogen atoms from 2 imidazoles and 2 oxygen atoms from the 2 carboxyl groups in 5-chlorhydroxybenzoate. In **2** the coordination polyhedrons of Cu^{2+} center can be described as distorted square pyramidal geometry sharing common edges, with an oxygen atom on the top of the pyramid. The hydrogen bonds and $\pi - \pi$ interactions between the 2 ligands contribute to the presence of the infinite one-dimensional chain in the structure. Furthermore, solid-state fluorescence spectra indicate that both complexes show violet-blue fluorescence and can be potentially used as violet-blue fluorescence materials.

Key words: Metal-organic complex, X-ray diffraction, crystal structure, photoluminescent

1. Introduction

The design and synthesis of luminescent metal-organic hybrid complexes have received general interest in the field of material and chemistry science, due to their intriguing architecture and various applications in chemical sensors,¹ and photophysical² and light emitting devices.³ In order to investigate the electronic properties and enhance the fluorescence emission performance, carefully choosing the molecular frame and composition is a good way to construct luminescent materials.⁴ In this research area, measures such as enhancing the rigidity in the complexes structure⁵ and modulating of the HOMO–LUMO levels of ligands⁶ have been explored to improve the fluorescence emission property of materials.

The selection of suitable ligands that are inflexible or contain an aromatic π system is not only crucial to the construction of luminescent complexes materials, but also guides the assembly of molecular coordination complexes into extended organized networks.⁷ Among all the ligands containing aromatic π systems, benzoic derivatives and imidazole derivatives are more likely to construct metal-organic hybrid materials and many of them have good photoluminescent (PL) properties because of the proper HOMO–LUMO energy gap.⁸ Since 5-chlorhydroxybenzoic acid and its anions can adopt a wide variety of coordination modes with metal centers, 5-chlorhydroxybenzoic anions were used as connectors.

Generally, the main emission mechanism of metal-organic hybrid complexes can be divided into 3 different

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kinds: ligand-to-ligand charge transfer (LLCT), ligand-to-metal charge transfer (LMCT), and metal-to-ligand transfer (MLCT).^{9–11} As a coordination center atom, Zn^{2+} is a d^{10} configuration metal ion with saturated d-orbital electrons and Cu^{2+} shows d^9 configuration, which is known to effectively quench fluorescence.¹² Combining with imidazole groups and 5-chlorhydroxybenzoic acid as synergistic organic ligands, 2 new metal-organic complexes, $\text{Zn}_2(\text{C}_7\text{H}_4\text{O}_3\text{Cl})_4(\text{C}_3\text{H}_4\text{N}_2)_4 \cdot \text{CH}_3\text{OH}$ and $\text{Cu}_2(\text{ClOC}_6\text{H}_3\text{COO})_2(\text{C}_3\text{H}_4\text{N}_2)_4$, were synthesized. Both of them exhibited violet-blue PL characterization, making them new promising photoluminescence materials.

2. Experimental

All chemicals used were purchased in analytical reagent grade and used directly without further purification. Elemental analyses were performed on a PerkinElmer 240C automatic analyzer. Infrared spectra, taken on KBr pellets, were recorded on a Nicolet FT-IR 360 spectrometer in the range of 4000–400 cm^{-1} . Photoluminescence excitation and emission spectra were recorded by F-4500 FL spectrophotometer at room temperature with a spectral resolution of 1 nm. Powder X-ray diffraction (XRD) measurements were performed using an X'Pert PRO diffractometer from Spectris Pte Ltd. using monochromatized Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The structural figures in this paper were drawn using the programs PLATON and Mercury 1.4.2.

2.1. Synthesis of $\text{Zn}_2(\text{C}_7\text{H}_4\text{O}_3\text{Cl})_4(\text{C}_3\text{H}_4\text{N}_2)_4 \cdot \text{CH}_3\text{OH}$ (1)

A mixture of 5-chlorhydroxybenzoic acid (0.172 g, 1 mmol), imidazole (0.066 g, 1 mmol), and zinc nitrate (0.146 g, 0.5 mmol) was dissolved in 20 mL of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ ($v/v = 1:1$) solvent mixture with stirring at room temperature for 1 h. The pH value of the mixture was adjusted to 6 by adding a NaOH solution (6 mol/L). After stirring for another 0.5 h, the insoluble solid was filtered off. The colorless filtrate was kept at room temperature for 4 days and the colorless single crystals of **1** were isolated. Anal. Found (%): C 49.10, H 3.38, N 10.07. Calcd. (%) for $\text{C}_{41}\text{H}_{36}\text{Zn}_2\text{N}_8\text{O}_{13}\text{Cl}_4$: C 49.24, H 3.24, N 9.99.

IR data (KBr, cm^{-1}): 2560 (*m*), 3540 (*m*), 3500 (*m*), 3490 (*m*), 3460 (*m*), 3420 (*m*), 3410 (*m*), 3390 (*m*), 2944 (*w*), 2880 (*w*), 2830 (*w*), 2630 (*w*), 2080 (*m*), 1640 (*vs*), 1460 (*m*), 1420 (*m*), 1350 (*m*), 1330 (*w*), 1300 (*w*), 1250 (*w*), 1190 (*s*), 1100 (*s*), 827 (*w*), 781 (*w*), 727 (*w*), 660 (*w*), 611 (*w*).

2.2. Synthesis of $\text{Cu}_2(\text{ClOC}_6\text{H}_3\text{COO})_2(\text{C}_3\text{H}_4\text{N}_2)_4$ (2)

5-Chlorhydroxybenzoic acid (0.345 g, 2.0 mmol), imidazole (0.134 g, 2.0 mmol), and copper chlorinate (0.171 g, 1.0 mmol) were added to 20 mL of $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ ($v/v = 1:1$) at room temperature with stirring at room temperature over 1 h. The pH value of the mixture was adjusted to about 7 with NaOH solution (6.0 mol/L). The blue green solution was continually stirred for 1 h and an insoluble dark green solid was filtered off. The blue green filtrate was kept at room temperature for 2 weeks and blue green crystals suitable for X-ray analysis were obtained. The crystals were washed with ethanol and water, and dried in air. Anal. Found (%): C, 42.11; H, 3.10; N, 15.26. Calcd. (%) for $\text{C}_{26}\text{H}_{22}\text{Cl}_2\text{Cu}_2\text{N}_8\text{O}_6$: C, 42.17; H, 2.99; N, 15.13.

IR data (KBr, cm^{-1}): 3488 (*m*), 3476 (*m*), 3430 (*m*), 2880 (*w*), 2090 (*w*), 1626 (*w*), 1582 (*vs*), 1474 (*vs*), 1434 (*s*), 1365 (*s*), 1312 (*m*), 1277 (*w*), 1180 (*s*), 1147 (*w*), 1099 (*m*), 1071 (*m*), 1052 (*w*), 821 (*s*), 722 (*m*), 651 (*s*), 614 (*w*), 561 (*w*), 537 (*w*).

2.3. Structure determination

Three-dimensional X-ray data were collected on a Bruker SMART CCD detector using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) in the φ and ω scan modes at room temperature (298 K). The structure was solved by direct methods¹³ and refined by the full-matrix least-squares method on F^2 using the SHELXS-97 and SHELXL-97 programs, respectively.^{14,15} Nonhydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions.

The crystallographic data and experimental refinement parameters of complexes **1** and **2** are given in the Table.

Table. Crystal data and structure refinement for complexes **1** and **2**.

	1	2
Empirical formula	C ₄₁ H ₃₆ Zn ₂ N ₈ O ₁₃ Cl ₄	C ₂₆ H ₂₂ Cl ₂ Cu ₂ N ₈ O ₆
Formula weight	1121.32	740.52
Temperature (K)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> 1	<i>P</i> 1
<i>a</i> (Å)	11.8585(11)	8.2318(6)
<i>b</i> (Å)	11.9189(11)	10.0460(8)
<i>c</i> (Å)	17.9373(17)	10.2004(8)
α (°)	76.795(2)	119.1130(10)
β (°)	73.646(2)	94.6070(10)
γ (°)	80.861(2)	105.3280(10)
Volume (Å ³)	2356.2(4)	688.55(9)
<i>Z</i>	2	1
Density (calculated) (Mg/m ³)	1.58	1.786
Absorption coefficient (mm ⁻¹)	1.316	1.798
<i>F</i> (000)	1140	374
Crystal size (mm)	0.12 × 0.10 × 0.10	0.16 × 0.13 × 0.10
Theta range for data collection	1.80 ~ 26.00°.	2.35 ~ 28.29°.
Reflections collected	15,807	8534
Independent reflections	9123 [<i>R</i> (int) = 0.0531]	3384 [<i>R</i> (int) = 0.0469]
Completeness to theta = 28.32°	98.30%	98.70%
Absorption correction	None	None
Max. and min. transmission	0.8796 and 0.8580	0.8407 and 0.7618
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	9123 / 13 / 630	3384 / 0 / 199
Goodness-of-fit on F^2	0.99	0.976
Final <i>R</i> indices [<i>I</i> > 2 sigma (<i>I</i>)]	<i>R</i> ₁ = 0.0558, <i>wR</i> ₂ = 0.1057	<i>R</i> ₁ = 0.0351, <i>wR</i> ₂ = 0.0828
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0867, <i>wR</i> ₂ = 0.1152	<i>R</i> ₁ = 0.0439, <i>wR</i> ₂ = 0.0853
Largest diff. peak and hole(e. Å ⁻³)	0.675 and -0.304	0.513 and -0.276

3. Results and discussion

3.1. Powder X-ray diffraction

The phase purity of complexes **1** and **2** was confirmed by powder XRD analysis (see Figures 1 and 2). The experimental XRD patterns are consistent with the simulated ones based on the single-crystal analyses of the

compounds at room temperature. These results confirm that both of these complexes are pure phase. The intensity differences may be due to the preferred orientation of the powder samples.¹⁶

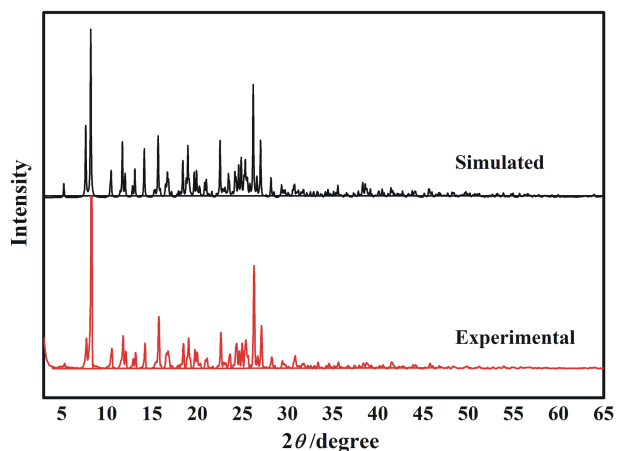


Figure 1. Powder XRD patterns for **1** from experiment and simulated.

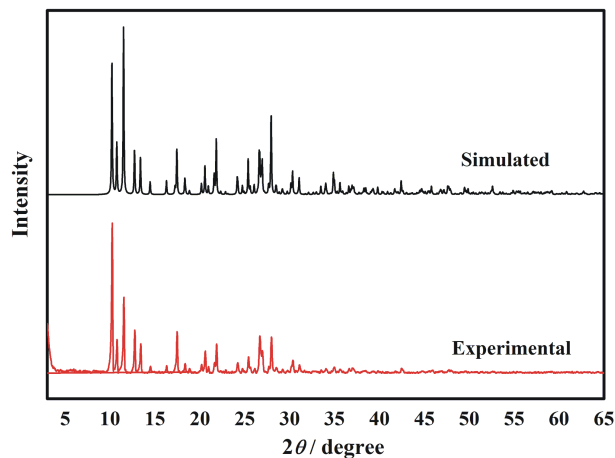


Figure 2. Powder XRD patterns of **2** from experiment and simulated.

3.2. Crystal structure of **1**

The crystal structure of complex **1** is shown in Figure 3. The asymmetric unit contains $2 \text{ Zn}(\text{C}_7\text{H}_4\text{O}_3\text{Cl})_2(\text{C}_3\text{H}_4\text{N}_2)_2$ and 2 distorted methanol molecules. The zinc(II) atom coordinates with 2 nitrogen atoms from 2 imidazole molecules and 2 oxygen atoms from 2 carboxylate groups in 5-chlorhydroxybenzoate, showing a distorted tetrahedral configuration. The average distance of Zn–O is 1.965 Å, while that of Zn–N is 1.995 Å. The π – π stacking interaction involves 2 imidazole rings (N1–C15A–N2–C16A–C17A–C18A and N5–C15B–N6–C16B–C17B–C18B) from different symmetric units, where the interplanar spacing is 3.334 Å and the ring-centroid separation of the imidazole rings is 3.709 Å (Figure 3). Two different intermolecular hydrogen bonds are involved in this crystal structure: N6–H6...O2 ($d_{\text{N6}\dots\text{O2}} = 2.838$ Å and $\angle \text{N6-H6}\dots\text{O2} = 149.7^\circ$) and N2–H2...O1S ($d_{\text{N2}\dots\text{O1S}} = 2.797$ Å and $\angle \text{N2-H2}\dots\text{O1S} = 171.6^\circ$). Moreover, the intramolecular hydrogen bonds between the hydroxyl group and carboxyl group (O9–H9...O4, $d_{\text{O9}\dots\text{O4}} = 2.478$ Å) and halogen bonds (C12A–Cl2...O6, $d_{\text{Cl2}\dots\text{O6}} = 3.206$ Å) also play very important roles in the self-assembly and crystallization processes in the molecules. Because of the π – π stacking interaction between imidazole rings (Figure 4a) and intermolecular hydrogen bonds (Figure 4b), an infinite zigzag chain extends along the [010] direction.

3.3. Crystal structure of **2**

Single crystal X-ray structural analysis reveals that complex **2** also crystallizes in the triclinic centrosymmetric space group $P\bar{1}$. The Cu(II) coordinate environment involves 2 nitrogen atoms from 2 imidazole ligands and 3 oxygen atoms from 2 5-chlorhydroxybenzoates (2 of them from hydroxyl groups and 1 from carboxylate group) (Figure 5). The coordination polyhedrons of the copper(II) center can be described as 2 distorted square pyramidal geometry sharing common edges.¹⁷ The Cu1–O3a distance is 2.3172(16) Å, which is significantly longer than other Cu–O bond distances [Cu1–O3 1.9360(15) Å, Cu1–N3 2.0108(19) Å, Cu1–O1 1.9670(16) Å and Cu1–N1 2.0060(19) Å]. On the other hand, bond distance Cu1–O1 1.9670(16) Å is similar to the average

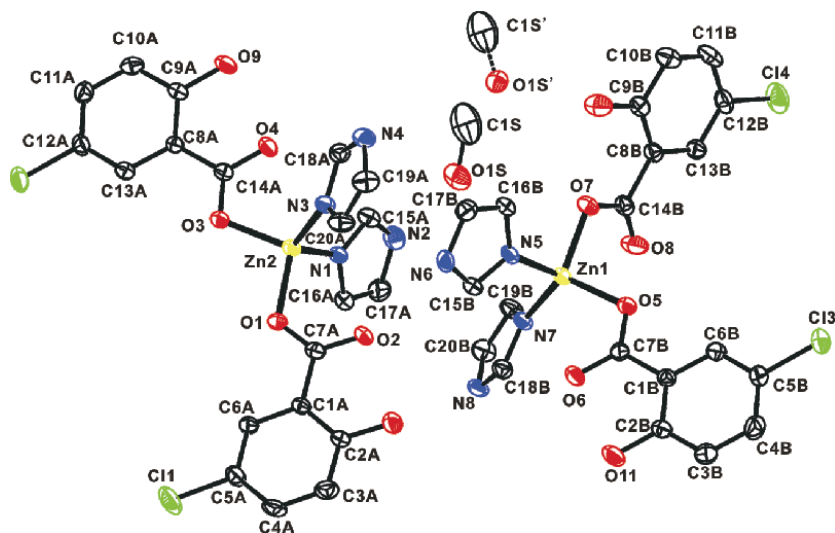


Figure 3. Crystallographic independent structure fragment in complex 1 (diagram drawn with 30% thermal ellipsoid).

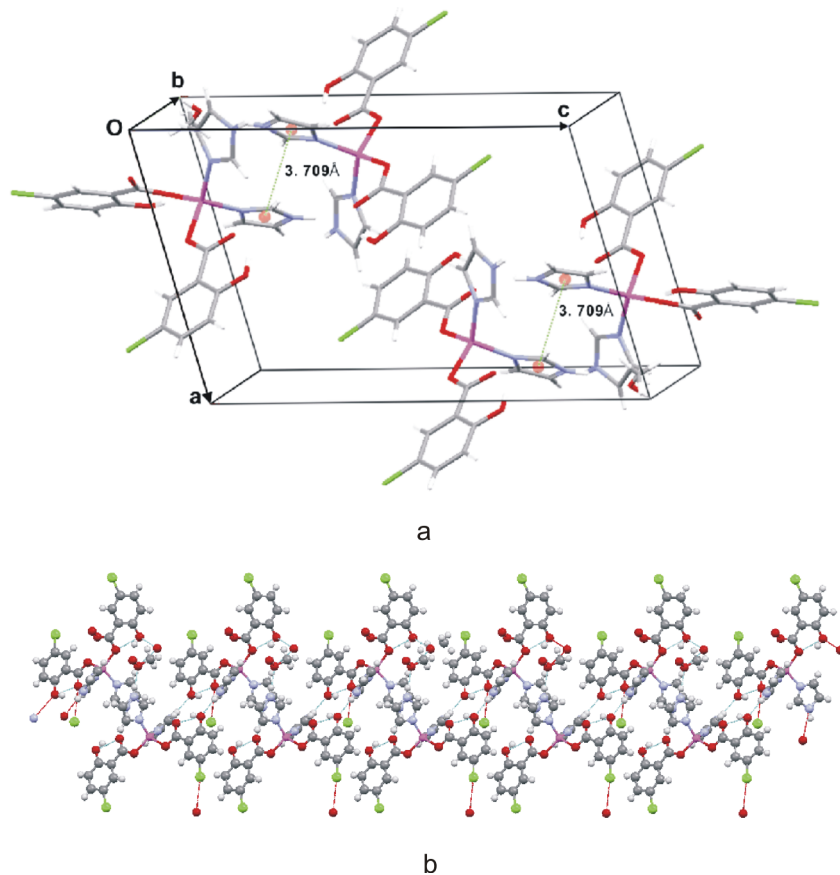


Figure 4. The crystal structure and intermolecular interaction of complex 1: (a) $\pi - \pi$ interaction between imidazole ring-centroid and (b) intermolecular hydrogen bond and halogen bonding in the structure.

distance of Zn–O 1.965 Å, indicating that the categories of the coordination center almost make no difference to the coordinate carboxyl group bond length. Two copper(II) atoms are connected via 2 μ -oxo bridges, forming a nearly planar 4-membered heteroring. Furthermore, the Cu1...Cu2 distance 3.184 Å is slightly longer than that of a similar heteroring Cu₂O₂ observed in [C₄₈H₅₂Cu₂N₁₀O₂] [ClO₄]₂·CH₃CN·(C₂H₅)₂O.¹⁸

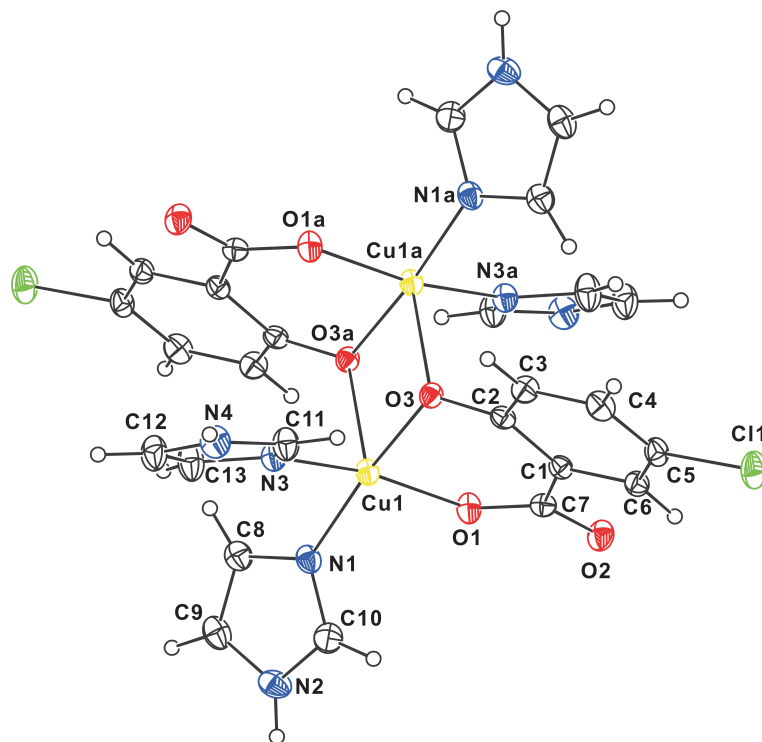


Figure 5. Crystallographic independent structure fragment in complex **2** (diagram drawn with 30% thermal ellipsoid).

Square-pyramidal complexes can participate in intermolecular $\pi - \pi$ interactions and hydrogen bonds to form one-dimensional infinite chain structures.¹⁹ Similarly, in complex **2**, the 5-chlorohydroxybenzoate rings in adjacent molecules participate in the $\pi - \pi$ interactions (Figure 6), where the distance between the centroids of the overlapping rings [C1–C2–C3–C4–C5–C6] is 3.695 Å. In addition, a pair of N–H...O hydrogen bonds (nitrogen atoms from imidazole as the donor and carboxylate oxygen atoms from 5-chlorohydroxybenzoate as the acceptor) contribute to the formation of the infinite one-dimensional chains. The N...O distance and the N–H...O angle are 2.761(3) Å and 171.4°, respectively. Furthermore, the intramolecular CH– π interaction with the distance 3.119 Å also stabilizes the packing structure of molecules.

4. Solid-state fluorescence emission spectrum

The room temperature solid state fluorescence emission spectrum of complex **1** shows strong violet-blue fluorescence (Figure 7a). When excited at 330 nm, strong luminescence was observed with the wavelength centered at ca. 430 nm. Since the Zn²⁺ has saturated d-layer electrons, this emission band probably originates from the $\pi_L - \pi_L^*$ LLCT transition emission. Furthermore, assembling of the Zn(II) ion with the 2 ligands may decrease the intra-ligand HOMO–LUMO energy gap, which is an important factor for the enhancement of the fluorescence phenomenon. There is a similar situation in complex **2**. Herein, the photoluminescence of complex

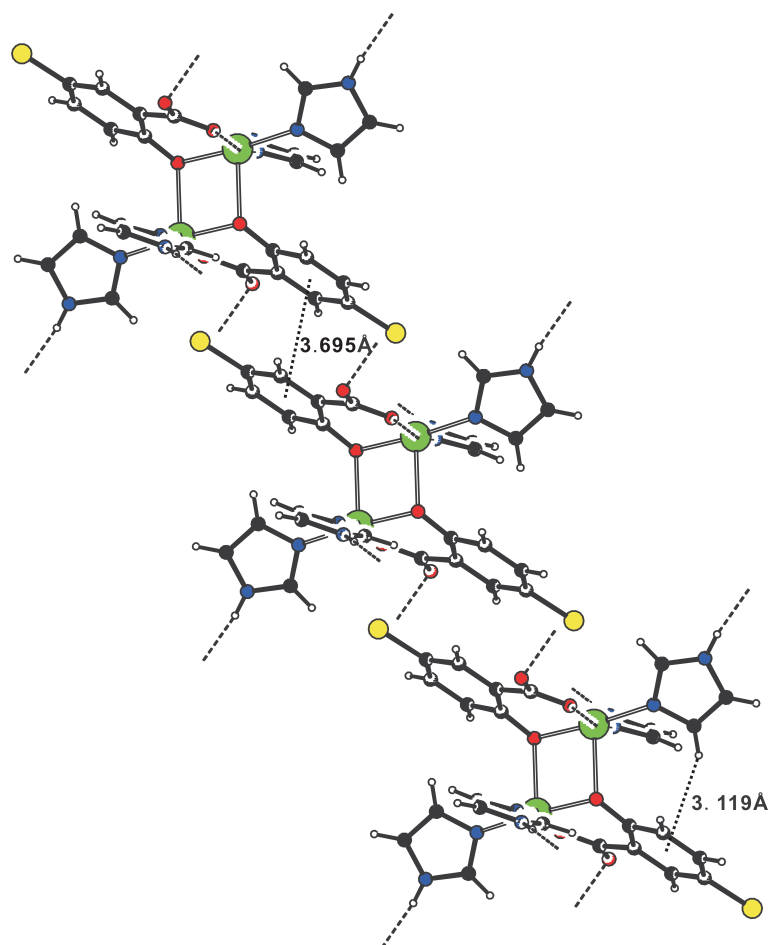


Figure 6. Fragment of one-dimensional chain formed through hydrogen bonding and $\pi - \pi$ interactions.

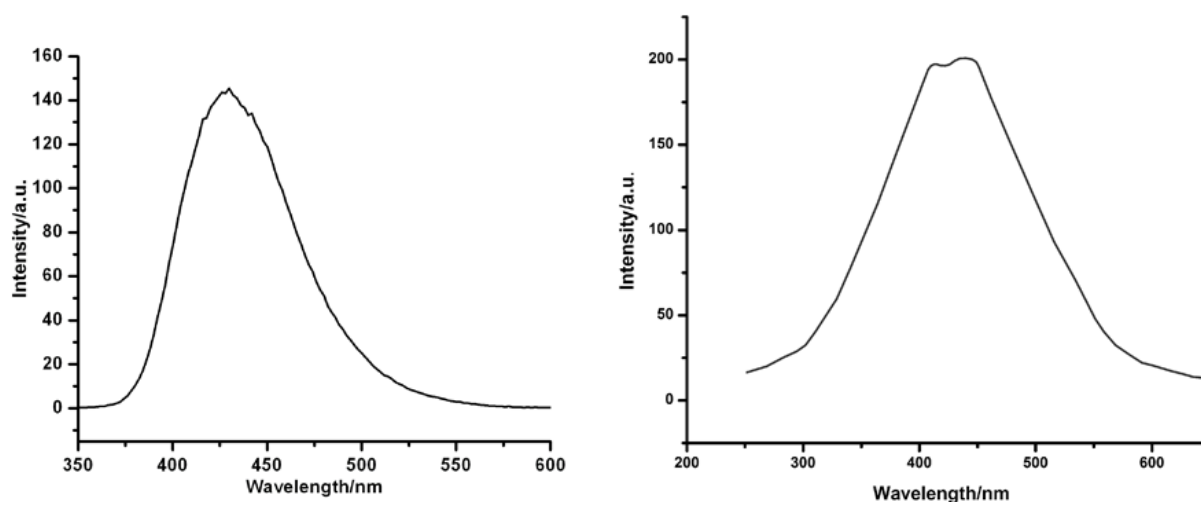


Figure 7. The fluorescence emission spectra of complexes 1 and 2, respectively. (a) $\lambda_{ex} = 330$ nm, (b) $\lambda_{ex} = 364$ nm.

2 in the solid state at room temperature depicted in Figure 7b exhibits 2 luminescence peaks at ca. 420 and ca. 443 nm upon excitation at 364 nm. The appearance of the 2 slight fluorescence emission peaks may be due to the mutual effects of the $\pi_L - \pi_L^*$ LLCT transition emission and the LMCT transition between the Cu^{2+} and imidazole. Compared with the Cu(II) compound based on (8-quinolinyloxy)acetate²⁰, whose fluorescence is in the greenish-blue region, complex **2** can be used for violet-blue fluorescent materials in the future.

5. Conclusion

Two novel metal-organic complexes, **1** and **2**, were prepared by slow evaporation method and characterized by XRD, PL, and FT-IR spectrum. The crystal structure of **1** shows a one-dimensional infinite zigzag chain, interlinked through $\pi - \pi$ stacking interactions and hydrogen bonds. In complex **2**, 2 copper(II) ions in the molecule were coordinated in distorted square-pyramids environment, with the Cu1...Cu2 distance 3.184 Å. Fluorescence properties of the complexes were also studied, which is helpful for the further study of the fluorescence intensity of the complexes using other ortho-hydroxybenzoic derivatives as ligands.

5.1. Supplementary material

CCDC 782970 and 789558 contain the supplementary crystallographic data for complexes **1** and **2**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

We thank Dr Xiang-Gao Meng from the College of Chemistry, Huazhong Normal University, for providing the crystal data with a Bruker Smart Apex CCD diffractometer. This work was supported by the National Natural Science Foundation of China (Nos. 41172051 and 40872039), the Specialized Research Fund for the Doctoral Program of Higher Education of China (No. 20060491504), and the Special Fund for Basic Scientific Research of Central Colleges, China University of Geosciences (Nos. CUGL090308 and CUGL110201).

References

1. Wang, S.; Men, G.; Zhao, L.; Hou, Q.; Jiang, S. *Sensor. Actuat B-Chem.* **2010**, *145*, 826–831.
2. Yan, B.; Wang, X. L.; Qian, K.; Lu, H. F. *J. Photoch. Photobio A.* **2010**, *212*, 75–80.
3. Wang, G.; He, Y. *Mater. Lett.* **2009**, *63*, 470–472.
4. Purkayastha, P.; Chattopadhyay, N.; Patra, G. K.; Datta, D. *Indian. J. Chem A.* **2000**, *39*, 375–377.
5. Cai, L. Z.; Chen, W. T.; Wang, M. S.; Guo, C. G.; Huang, J. S. *Inorg. Chem. Commun.* **2004**, *7*, 611–613.
6. Selvi, S.; Pu, S. C.; Cheng, Y. M.; Fang, J. M.; Chou, P. T. *J. Org. Chem.* **2004**, *69*, 6674–6678.
7. Aghabozorga, H.; Manteghi, F.; Sheshmani, S. *J. Iran. Chem. Soc.* **2008**, *5*, 184–227.
8. Zheng, F. K.; Wu, A. Q.; Li, Y.; Guo, C. G.; Wang, M. S.; Li, Q.; Huang, J. S. *J. Mol. Struct.* **2005**, *740*, 147–151.
9. Zhang, J. Z.; Cao, W. R.; Pan, J. X.; Chen, Q. W. *Inorg. Chem. Commun.* **2007**, *10*, 1360–1364.
10. Reguera, E.; Marin, E.; Calderon, A.; Rodriguez-Hernandez, J. *Spectrochim. Acta Part A.* **2007**, *68*, 191–197.
11. Li, X.; Wang, X. W.; Zhang, Y. H. *Inorg. Chem. Commun.* **2008**, *11*, 832–834.
12. Garzon-Rodriguez, W.; Yatsimirsky, A. K.; Glabe, C. G. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 2243–2248.

13. Sheldrick, G. M. *Acta Crystallogr. Sect. A*. **1990**, *46*, 467–473.
14. Sheldrick, G. M. *SHELXS-97, Program for the solution of crystal structure*; University of Göttingen, Germany, 1997.
15. Sheldrick, G. M. *SHELXL-97, Program for the refinement of crystal structure*; University of Göttingen, Germany, 1997.
16. Xu, G. J.; Zhao, Y. H.; Shao, K. Z.; Yuan, G.; Su, Z. M.; Yan, L. K. *Inorg. Chem. Commun.* **2009**, *12*, 969–971.
17. Addison, A. W.; Rao, T. N.; Reedijk, J.; Verschoor, G. C. *J. Chem. Soc. Dalton Trans.* **1984**, 1349–1356.
18. Battaini, G.; Monzani, E.; Perotti, A.; Para, C.; Casella, L.; Santagostini, L.; Gullotti, M.; Dillinger, R.; Näther, C.; Tuzcek, F. *J. Am. Chem. Soc.* **2003**, *125*, 4185–4198.
19. Ghosh, T.; Mukhopadhyay, A.; Dargaiah, K. S. C.; Pal, S. *Struct. Chem.* **2010**, *21*, 147–152.
20. Liu, D. S.; Sui, Y.; Chen, W. T.; Chen, J. Z.; Huang, C. C. *J. Iran. Chem. Soc.* **2012**, *9*, 827–831.