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Hydrogen Bonded Supramolecular Framework in Inorganic-Organic Hybrid Compound: Syntheses, Crystal Structure, Thermal Stability, and Photoluminescent Properties

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A novel compound $[Mn(bip)_2Cl_2\cdot 4H_2O]$ (1) $[bip = 2\cdot(4-bromophenyl)\cdot1H-imidazo[4,5\cdotf][1,10]phenanthroline]$ has been synthesized by hydrothermal reactions and characterized by elemental analysis, thermogravimetric (TG) analysis, infrared spectrum (IR), XRD spectra (X-ray powder diffraction), and singlecrystal X-ray diffraction. The title compound crystallizes in orthorhombic, space group *pbcn* with a = 1.4820, b = 0.8961, c =2.8105 nm, $\beta = 90^\circ$. Single-crystal X-ray diffraction reveals that compound 1 is zero-dimensional (0D) architecture, and the existence of hydrogen bonds and $\pi \cdot \pi$ interactions lead the 0D to 2D novel frameworks. Hydrogen bonds and $\pi \cdot \pi$ interactions are powerful interactions for directing supra-molecular architectures. TG analysis shows clear courses of weight loss, which corresponds to the decomposition of different ligands. The luminescent properties for the ligand bip and compound 1 are also discussed.

Keywords coordination compound, fluorescence, hydrogen bond, thermal stability analysis, XRD spectra

INTRODUCTION

Design and construction of metal-involved supra-molecular architectures based on crystal engineering are currently of interest.^[1,2] The increasing interest in this field is justified not only by their intriguing structural motifs, but also their potential applications as various fields such as ion exchange, microelectronics, catalysis, nonlinear optics, and porous materials.^[3–7] Nowadays, the method of hydrothermal synthesis is widely used to synthesis novel crystal structures, because it can solve the problems of ligands solubility and enhance the reactivity of reactants in the crystallization process to obtain perfect crystal. In addition, H-bonds and π - π interactions

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also affect the results. A successful approach to build these supramolecular frameworks is to select suitable multidentate ligands as building blocks. Among them, multidentate ligands such as N-heterocyclic ligands are widely used in the rational design and controlled synthesis of coordination polymers.^[8–10] As for the N-heterocyclic ligand, we chose one long-conjugated unsymmetrical aromatic N-heterocyclic ligands bip (bip =2-(4-bromophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline) in view of the following characteristics: (a) it possesses extended long-conjugated unsymmetrical aromatic system to provide supramolecular interactions; (b) it has two nitrogen atoms, which is similar with 2,2'-bipyridyl-like bidentate chelating molecules; and (c) it possesses strong and rigidity of coordination ability to metal atoms to construct intriguing structures. Manganese compounds with carboxylate are known to exist at the active sites of some Mn(II)-containing metalloenzymes.^[11] Based on the previous reasons, we designed and synthesized the compound, namely, $[Mn(bip)_2Cl_2\cdot 4H_2O]$ 1. The compound 1 exhibits zero-dimensional (0D) structures, and display novel 2D layer structures via hydrogen bonds and inter-chain π - π stacking interactions. The research shows that 1 is luminescent material.

EXPERIMENTAL

Materials

The ligand bip was prepared according to the description in the literature procedures.^[12] The metallic salt, NaOH, were purchased commercially and used without further purification.

Physical Measurements

The FT-IR spectrum was measured with KBr pellets in the range of 4000–400 cm⁻¹ on a Perkin-Elmer 240C spectrometer. TGA was performed using a Perkin-Elmer TG-7 analyzer at the rate of 10°C/min rise of temperature in nitrogen atmosphere. Crystal structures were determined on a Bruker SMART APEX II CCD X-ray diffractometer. Carbon, hydrogen and

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SCH. 1. The synthesis of bip.

nitrogen elemental analyses were performed with a PE-2400 elemental analyzer. X-ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer of Philips with monochromated Co-K α radiation.

Syntheses

Synthesis of bip

A mixture of 4-bromobenzaldehyde, 1,10-phenanthroline-5,6-dione (0.525 g, 2.5 mmol), ammonium acetate (3.88 g, 50 mmol) and glacial acetic acid was refluxed for 5 h, then cooled to room temperature. Yellow precipitate was obtained when addition of concentrated aqueous ammonia to neutralize, which was collected and washed with water. The crude product dissolved in ethanol was purified by filtration on silica gel. The principal yellow band was obtained. Then evaporation of the solution gave yellow products. Yield 0.66 g. m.p. 320–322°C.

Synthesis of $[Mn(bip)_2Cl_2\cdot 4H_2O]$ (1)

A mixture of MnCl₂ (0.037g, 0.3 mmol), bip (0.112 g, 0.3 mmol), and H₂O (18 mL) was stirred at room temperature and adjusted the pH value to about 7.0 with NaOH. We put the cloudy solution into a 30-mL Teflon-lined stainless vessel under autogenous pressure at 443 K for 72 h, and afterwards cooled to room temperature at a rate of 5°C/h. Small yellow crystals of compound **1** were collected in 89% yield based on Mn. $C_{38}H_{30}Br_2Cl_2MnN_8O_4$: Anal. Calcd. (%) C 48.12, H 3.18, N 11.81; Found: C 48.05, H 3.16, N 11.88%. IR (KBr, cm⁻¹): 3369(s), 1509(s), 1277(s), 817(s), 665(m), 531(m), 442(m).

X-Ray Crystallography

Single-crystal X-ray diffraction data were collected at room temperature with a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromatized MoK α radiation ($\lambda = 0.71073$ Å) at 293(2) K in the range of $2.00 \le \theta \le 26.02^{\circ}$ for **1**. Absorption corrections were applied using multi-scan technique and all the structures were solved by direct methods with SHELXS-97^[13] and refined with SHELXL-97^[14] by full-matrix least-squares techniques on F^2 . Non-hydrogen atoms were refined with anisotropic temperature parameters. Experimental details for crystallographic data and structure refinement parameters for **1** are listed in Table 1.

RESULTS AND DISCUSSION

Description of Crystal Structures

The molecular structure is shown in Figure 1, and the 2D layer structure linked hydrogen bonds is suggested in Figure 2. Selected important bond lengths and bond angles for compound 1 are shown in Table 3.

TABLE 1 Crystal data and details of structure refinement parameters for

	1		
Empirical formula	$C_{38}H_{30}Br_2Cl_2MnN_8O_4$		
Formula weight	948.36		
Crystal system	orthorhombic		
Space group	pbcn		
a (nm)	1.48201		
<i>b</i> (nm)	0.89616		
<i>c</i> (nm)	2.80158		
β (°)	90		
Volume (nm ³)	3.7208		
Ζ	4		
Density (Mg/m ³) (calculated)	1.693		
Absorption coefficient (mm^{-1})	2.700		
F(000)	1900		
Crystal size (mm ³)	$0.433 \times 0.371 \times 0.308$		
Theta range (°)	2.00-26.02		
Reflections collected	24270		
Unique reflections $[R_{int}]$	3654 [0.0657]		
Goodness-of-fit on F^2	0.998		
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0343		
	wR2 = 0.0728		
<i>R</i> indices (all data)	R1 = 0.0577		
	wR2 = 0.0811		
Largest difference peak and hole (e. $Å^{-3}$)	0.492, -0.288		



FIG. 1. The molecular structure of compound ${\bf 1}$ (hydrogen atoms were omitted).

As shown in Figure 1, the coordination compound 1 crystallizes in orthorhombic, space group *pbcn*, and the asymmetric unit of 1 consists of one Mn (II) atom, two bip ligands, two chloride ions, and two lattice water molecules. The coordinated chloride ions occupy two coordination points of Mn (II) atom. The Mn (II) atom is hexa-coordinated with four nitrogen atoms from two chelating bip ligands and two chloride ions from metal salts, furnishing a slightly distorted octahedral geometry. The bond distance of Mn–Cl in compound 1 is 2.5159 Å, and those of Mn–N bond distance fall in the 2.275 to 2.288 Å range, which are similar with the values reported.^[15–18]

Hydrogen bonding interactions are usually important in the synthesis of supramolecular architectures, there are six type of hydrogen bonding interactions in compound 1: O-H...O, O-H…Cl, N-H…Cl, C-H…Cl, and the most interesting aspect of the structure in 1 concerns the intermolecular C-H···Cl [H(8A)···Cl(1) = 2.70 Å, C(8)···Cl(1) = 3.593 Å, and C(8)-H(8A)···Cl(1) = 161°], N-H···Cl [H(3A)···Cl(1) = 2.39 Å, N(3)...Cl(1) = 3.212 Å, and C(8)-H(8A)...Cl(1) = 160° interactions, which helps in the construction of the 2D structure (Figure 2). Moreover, there are π - π interactions between the aryl ring of bip ligands and symmetry of the two adjacent equivalent of aromatic ring (symmetry codes: -x, -1 + y, 1.5 - z, 0.5 + x, -1.5 + y, 1.5 - z). The distance between $cg(1) \rightarrow cg(2)$ ring centroid is 3.6070 Å and $cg(3) \rightarrow cg(4)$ is 3.6441Å. Cg(1): C14 \rightarrow C15 \rightarrow C16 \rightarrow C17 \rightarrow C18 \rightarrow C19, Cg(2): $C11 \rightarrow C12, Cg(4): C11 \rightarrow C12 \rightarrow C13 \rightarrow N3 \rightarrow N4.$



FIG. 2. 2D structure of compound 1 linked by hydrogen bonds (dotted lines represent hydrogen bonds).

 TABLE 2

 Selected bond lengths (Å) and bond angles (°) for 1

Bond	Dist.	Bond	Dist.
Mn(1)-N(1)	2.288(2)	Mn(1)-N(2)	2.275(2)
Mn(1)-Cl(1)	2.5159(8)		
Angle	(°)	Angle	(°)
N(2)-Mn(1)-N(1)	72.75(8)	N(2)-Mn(1)-Cl(1)	103.93(6)
N(1)-Mn(1)-Cl(1)	90.57(6)	$N(2)^{#1}-Mn(1)-N(2)$	156.62(12)
$N(1)^{#1}-Mn(1)-N(1)$	88.90(12)	$N(2)-Mn(1)-Cl(1)^{\#1}$	92.06(6)
N(1)-Mn(1)-Cl(1) ^{#1}	164.80(6)	N(2)-Mn(1)-N(1) ^{#1}	90.42(8)
Cl(1) ^{#1} -Mn(1)-Cl(1)	93.87(4)		

IR Spectra

In compound 1, the infrared spectrum exhibited absorption at 3369 cm⁻¹, which is assigned to O–H stretching vibration. The spectrum of compound 1 shows the strong bands at 1509 and 817 cm⁻¹ are due to C=C and C=N stretching vibrations of the coordinated phenanthroline molecules. Below 700 cm⁻¹ it seems to be a lot of bands, which correspond to the Mn–N stretching mode. The IR results are good agreement with their solid structural features from the results of their crystal structures.

XRD Spectra

The simulated and experimental power XRD patterns of **1** are shown in Figure 3. The patterns calculated from the singlecrystal X-ray data of **1** are in good agreement with the observed ones in almost identical peak position but with different peak intensities, which indicates the phase purity of the products. The differences in intensity may be due to the preferred orientation of the powder samples.^[19,20]

Thermal Analysis

To examine the stability of compound 1, we examined the TG curves of crystalline samples in the flowing nitrogen atmosphere at a heating rate of 10° C/min (Figure 4). As expected, in compound 1, the first weight loss of 16.53% corresponds to the loss of chloride ions and two water molecules (calcd. 15.07%). The second weight loss in the temperature range of 245–595°C can be ascribed to the release of bip ligands (obsvd. 77.21%, calcd. 79.12%).

 TABLE 3

 Hydrogen bond lengths (nm) and angles (°) for the compound 1

D–H···A	D–H	H···A	D····A	D−H…A
$O(1W) - H(1W) \cdots O(2W)$	0.0960	0.1770	0.2709	167
$O(2W)-H(3W)\cdots Cl(1)$	0.0900	0.2350	0.3243	171
$N(3)-H(3A)\cdots Cl(1)$	0.0860	0.2390	0.3212	160
$C(8)-H(8A)\cdots Cl(1)$	0.0930	0.2700	0.3593	161



FIG. 3. Experimental and simulated X-ray powder diffraction patterns of compound 1.

Photoluminescent Properties

Luminescence property is very important in photochemistry and photophysics. So in this study, we research the luminescence of compounds **1** and free ligand bip (Figure 5). The free ligand exhibits emission at 579 nm (excitation at 325 nm) for bip. Compound **1** shows one broad emission band with the maximum intensity at 629 nm upon excitation at 325 nm, which is red-shifted by 50 nm relative to the emission wavelength of free ligand bip. The energy of the luminescence suggests that the most possible assignment for the emissions of **1** originates from ligand-to-metal charge transfer.^[21] Compound **1** exhibits strong emission, the reason of which may be attributed to the rigidity of *N*-heterocyclic ligands. The rigidity is favor of energy transfer and reduces the loss of energy through a radiationless pathway. The compound **1** may be good candidate for potential

100 - 80 - 40 - 20 - 0 0 200 400 600 800 Temperature /'C

FIG. 4. TG curve of compound 1.

FIG. 5. Luminescent spectrum of ligand bip and compound **1** in solid state at room temperature.

photoluminescence material because it is highly thermally stable and insoluble in water and common organic solvents.

CONCLUSIONS

In conclusion, one novel compound has been synthesized by using plane multifunctional ligands bip and metallic salt. It is worthy to note that the intermolecular hydrogen bonds play an important role in the supramolecular structure. Here we studied the syntheses, structures, XRD spectra, and TG analysis of compound **1**, and also we investigate the fluorescence properties of title compound, as well as the free ligand bip. The results reveal that the title compound is worthy of further study as candidate of potential photoluminescent material. This material will give new impetus to the construction of novel functional material with potentially useful physical properties.

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SUPPLEMENTAL MATERIAL

Supplemental data for this article can be accessed on the publisher's website. CCDC 927171 contains the supplementary crystallographic data for **1**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest.cif.

REFERENCES

- 1. Batten, S. R.; Robson, R. Angew. Chem. Int. Ed. 1998, 37, 1460.
- Wu, C. D.; Hu, A.; Zhang, L.; Lin, W. B. J. Am. Chem. Soc. 2005, 127, 8940.
- Blake, A. J.; Champness, N. R.; Easun, T. L.; Allan, D. R.; Nowell, H.; George, M. W.; Jia, J. H.; Sun, X. Z. Nat. Chem. 2010, 2, 688.
- Hou, Y.; Yin, W. T.; Xie, X. D.; Chen, X.; Zhou, J. R.; Zuo, H. R.; Huang, Q.; Yang, L. M.; Ni, C. L.; Hu, X. L. *Inorg. Chim. Acta.* 2010, 363, 424.
- 5. Li, J. R.; Kuppler, R. J.; Zhou, H. C. Chem. Soc. Rev. 2009, 38, 1477.
- Williams, K. A.; Boydston, A. J.; Bielawski, C. W. Chem. Soc. Rev. 2007, 36, 729.
- 7. Evans, O. R.; Lin, W. Acc. Chem. Res. 2002, 35, 511.
- Ye, J. W.; Wang, J.; Zhang, J. Y.; Zhang, P.; Wang, Y. CrystEngComm 2007, 9, 515.
- 9. Cui, R. H.; Xu, Y. H.; Jiang, Z. H. Inorg. Chem. Commun. 2009, 12, 934.
- 10. Deng, Y. Y.; Liu, F. Q.; Liu, B. C. Chin. J. Inorg. Chem. 2009, 25, 1396.
- 11. Xu, H. J.; Li, D. P.; Li, G. Q. Chin. J. Inorg. Chem. 2009, 25, 1504.
- 12. Steck, E. A.; Day, A. R. J. Am. Chem. Soc. 1943, 65, 452
- Sheldrick, G. M. SHELXS-97, Program for the Solution of Crystal Structure; University of Göttingen, Germany, 1997.
- 14. Sheldrick, G. M. SHELXS-97, Program for the Refinement of Crystal Structure; University of Göttingen, Germany, 1997.
- 15. Biju, A. R.; Rajasekharan, M. V. J. Mol. Struct. 2008, 875, 457.
- 16. Zhang, S. H.; Feng, C. J. Mol. Struct. 2010, 977, 65.
- Lehleh, A.; Beghidja, A.; Beghidja, C.; Mentre, O.; R. Welter, C. R. Chimie. 2011, 14, 466.
- Pradeep, C. P.; Zacharias, P. S.; Das, S. K. Inorg. Chem. Comm. 2008, 11, 90.
- Fang, S. M.; Peng, D. L.; Chen, M.; Jia, L. R.; Hu, M. J. Coord. Chem. 2012, 65, 668.
- 20. Akhbari, K.; Morsali, A. J. Coord. Chem. 2011, 64, 3521.
- Li, M. X.; Wang, H.; Liang, S. W.; Shao, M.; He, X.; Wang, Z. X.; Zhu, S. R. Cryst. Growth Des. 2009, 9, 4626.

