This article was downloaded by: [Case Western Reserve University] On: 03 December 2014, At: 10:49 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsrt20</u>

A Linear Piperazine-Containing Ligand and Its Hg Coordination Polymer

Wen-Juan Chu^a, Rui-Jun Li^a, Yao-Ting Fan^a & Hong-Wei Hou^a ^a Department of Chemistry, Zhengzhou University, Zhengzhou, P. R. China Published online: 31 Jan 2012.

To cite this article: Wen-Juan Chu, Rui-Jun Li, Yao-Ting Fan & Hong-Wei Hou (2012) A Linear Piperazine-Containing Ligand and Its Hg Coordination Polymer, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 42:1, 9-13, DOI: <u>10.1080/15533174.2011.609220</u>

To link to this article: <u>http://dx.doi.org/10.1080/15533174.2011.609220</u>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions



A Linear Piperazine-Containing Ligand and Its Hg Coordination Polymer

Wen-Juan Chu, Rui-Jun Li, Yao-Ting Fan, and Hong-Wei Hou

Department of Chemistry, Zhengzhou University, Zhengzhou, P. R. China

Reactions of piperazine hexahydrate with triazol and paraformaldehyde afford a new piperazine-containing ligand: (N,N'-bis(1-H-1,2,4-triazole-1-yl)piperazine) (btp). X-ray crystal diffraction reveals that btp is an overall linear structure. Its Hg²⁺ polymer displays a zigzag chain in which piperazine is held in the chair conformation. In addition, the spectra properties of the btp and 1 are investigated, the strong luminescence characteristics of btp and 1 are found.

Keywords crystal structure, luminescence property, polymer, solid-state UV-Vis

INTRODUCTION

In recent years, nitrogen-containing heterocycles are frequently employed as building blocks such as triazole, tetrazole, piperazine, triazine, and tetrazine have been widely used for the construction of MOFs as a result of their variety of intriguing structure and potential applications in the areas of catalysis, magnetism, luminescence, and gas storage.^[1-13] As is known to us all, substituted 1,4-piperazine can assume different types of bridging conformations in both boat and chair forms, of which the latter is thermodynamically more favorable, though the boat form can coordinate one or bridge two metal ions to give mononuclear and cis-dinuclear complexes, respectively.^[11–17] Compared with the rigid nitrogen heterocycle ligands, the incorporation of flexible units, for example, -CH2group, has recently received increasing attention because the freedom of the C-C single-bond connection between two nitrogen heterocycles in favor of the ligands serving as useful building blocks.[18]

Taking the previous into consideration, we are exploring the design and preparation of nitrogen heterocycles ligands with flexible units. In this article, we synthesized the bidentate ligand: (N,N'-bis(1-H-1,2,4-triazole-1-yl)piperazine) (btp), in which the two triazole groups are held in transconformation in the equatorial position to the piperazine. The btp ligand adopts didentate bridging mode to connect Hg ions leading to a 1D infinite zigzag chain. In addition, polymer **1** and btp are synthesized and characterized by X-ray single crystal diffraction analysis, elemental analysis, IR, solid-state UV-Vis, and so on in the context.

EXPERIMENTAL

Materials and Physical Measurements

All chemicals were of reagent-grade quality and obtained from commercial sources and used without further purification. Elemental analyses (C, H, N) were performed on a Carlo-Erba 1160 Elemental Analyzer. IR spectra were recorded in the region of 4000–400 cm⁻¹ on a FTS-40 infrared spectrophotometer with pressed KBr pellets. Powder XRD patterns were recorded with CuKa1 radiation by using a PANalytical X'Pert PRO diffractometer. Emission spectra were recorded on an F-4500 HITACHI fluorescence spectrophotometer. UV-Vis absorption spectra in the solid state were taken using a Cary 5000 UV-Vis-NIR spectrophotometer.

Synthesis of Ligand

(*N*,*N*'-bis(1-H-1,2,4-triazole-1-yl)piperazine) (btp)

Mixture of triazole (3.04 g, 44 mmol), paraformaldehyde (1.47 g, 49 mmol), and 3 drops of triethylamine were heated at 80° several hours until viscous residues appear. Then the residues were dissolved by methanol and stirred with piperazine (1.85 g, 22 mmol). Coreless crystals (4.22 g) were obtained by filtration and recrystallization in methanol. (yield: 77.34%). Anal. Calcd. for $C_8H_{14}N_8$ (%): C, 48.37; H, 6.50; N, 45.13; Found: C, 47.93; H, 6.96; N, 45.11. M.P.: 228~230°C. IR (KBr, cm⁻¹): 3430(s), 3117(s), 3079(m), 2960(s), 2837(s), 11511(m), 1453(m), 1360(s), 1322(m), 1171(s), 1130(m), 1033(m), 1011(s), 959(w), 889(w), 797(s), 639(s). ¹HNMR(CDCl3): δ 2.687 (8H), 5.480 (4H), 8.531 (4H). Scheme 1

Complex 1 is synthesized by the reactions of HgI_2 (454.4 mg, 1 mmol) and btp (25.0 mg, 0.1 mmol) in methanol (8 mL), then colorless rod-like crystals were obtained upon slow evaporation

Received 10 May 2011; accepted 4 June 2011.

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (No. 20871106 and 90610001).

Address correspondence to Yao-Ting Fan, Department of Chemistry, Zhengzhou University, Henan 450052, P. R. China. E-mail: yt.fan@zzu.edu.cn



SCH. 1. Synthesis of [Hg(btp)₂I₂]_n.

of the solution at ambient temperature. Yield: 48% based on Hg. Anal. Calc. for $C_{10}H_{16}HgN_8I_2$ (1): C, 17.08; H, 2.28; N, 15.94%. Found: C, 17.12; H, 2.34; N, 16.02%. IR data (KBr, cm⁻¹): 3423(s), 3112(s), 2946(m), 2836(s), 1510(s), 1448(m), 1369(s), 1330(m), 1170(s), 1120(m), 1032(m), 1013(s), 978(w), 903(w), 795(s), 632(s).

Crystallographic Data Collection and Structure Determination

Single crystal of btp and complex **1** were put on a Bruker SMART APEX II CCD diffractometer equipped with a graphitemonochromated Mo K α radiation ($\lambda = 0.71073$ Å) by using ω - 2θ scan technique at 293(2) K. Raw data were corrected and the structure was solved by direct method using the SHELXS-97 program.^[19] Non-hydrogen atoms were located by direct phase determination and subjected to anisotropic refinement. The fullmatrix least-squares calculation on F² was applied on the final refinement. The refinement converged at R₁ = 0.0508 and R₁ = 0.0527 values for reflection with I > 2σ for the btp ligand and **1**. Details of crystal structure determination are summarized in the Table 1. Full atomic data are available as a file in CIF format. The selected bond lengths and angles are shown in Table 2.

Determination of Fluorescent Properties

Steady-state fluorescence measurements were performed using spectrofluorimeter Hitachi F-4500 at ambient temperature in solid state. The excitation and emission slit width are both 5 nm, and response time is 0.5 s.

RESULTS AND DISCUSSIONS

Crystal Structure

Crystallographic analysis reveals that btp depicts a linear structure and crystallizes in the monoclinic system, space group $P2_1c$. As shown in Figure 1, the piperazine six-membered ring displays a chair-like conformation. The lone electron pairs of piperazine-N are away from the center of piperazine ring (Scheme 2), hence, it is not in favor of chelation but for polymerization.



SCH. 2.

TABLE 1Crystallographic data for btp and 1

	btp	1
empirical formula	$C_{10}H_{16}N_8$	C ₂₂ H ₂₂ ZnN ₁₀ O ₈ S ₂
Mr	248.31	702.70
crystal system	monoclinic	orthorhombic
space group	$P2_1c$	Pnma
a (Å)	10.296(2)	10.640(2)
<i>b</i> (Å)	9.1917(18)	16.377(3)
<i>c</i> (Å)	6.9092(14)	10.504(2)
α (°)	90.00	90.00
β (°)	104.84(3)	90.00
γ (°)	90.00	90.00
V (Å ³)	632.1(2)	1830.3(6)
Ζ	2	4
$\mu \text{ (mm}^{-1}\text{)}$	0.09	11.79
$D_{\rm c}~({\rm g}\cdot{\rm cm}^{-3})$	1.305	2.550
<i>F</i> (000)	264	1272
Goodness of fit	1.155	1.077
$R_1 (I > 2\sigma(I))$	0.0508	0.0527
wR_2 (all data)	0.1411	0.1608

 $R_{1} = \sum_{w \in F_{0}^{2}} ||F_{0}| - |F_{c}|| / \sum |F_{0}|; wR_{2} = \left[\sum_{w \in F_{0}^{2}} |F_{0}|^{2} - |F_{c}|^{2}\right]^{2} / \sum_{w \in F_{0}^{2}} |F_{0}| - |F_{c}|| / \sum_{w \in F_{0}^{2}} |F_{0}||^{2} + |F_{0$

 TABLE 2

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

btp		
1.4319 (18)	N4-C5	1.4559 (18)
1.4565 (17)	N2-C2	1.3153 (18)
1.3597 (15)	N1-C1	1.3284 (17)
1.4786 (17)	C1-N3	1.3213 (19)
1.518 (2)	N3-C2	1.353 (2)
1.518 (2)		
1		
2.367 (4)	Hg1–N4A	2.367 (4)
2.6644 (13)	Hg1–I2	2.6512 (13)
9) 100.8 (4)	N4-Hg1-I2	102.72 (17)
102.72 (17)	N4-Hg1–I1	103.08 (17)
103.08 (17)	I1-Hg1–I2	139.00 (5)
	btp 1.4319 (18) 1.4565 (17) 1.3597 (15) 1.4786 (17) 1.518 (2) 1.518 (2) 1 2.367 (4) 2.6644 (13) 100.8 (4) 102.72 (17) 103.08 (17)	btp 1.4319 (18) N4-C5 1.4565 (17) N2-C2 1.3597 (15) N1-C1 1.4786 (17) C1-N3 1.518 (2) N3-C2 1.518 (2) 1 2.367 (4) Hg1–N4A 2.6644 (13) Hg1–I2 100.8 (4) N4-Hg1–I2 102.72 (17) N4-Hg1–I1 103.08 (17) I1-Hg1–I2

Symmetry code. For btp: 1 - x + 1, -y + 1, -z + 2; For 1: 1 x, -y + 1/2, z; 2 - x + 1, -y + 1, -z



FIG. 1. The crystal structure of btp (hydrogen atoms are omitted for clarity).

As revealed in Figure 2, in polymer 1, Hg atoms in a distorted tetrahedral environment, coordinating to two N atoms (N4, N4A) from two different btp ligands and two iodide atoms (I1, I2). N-Hg-I bond angles range from 102.72 to 103.08° , I-Hg-I bond angle is calculated 139.00° , and N-Hg-N bond angle is only 100.80° . This distortion leads to a slight difference between two Hg-I bond lengths (2.6644(13) and 2.6512(13) Å). Moreover, the btp in 1 is held in a stable chair conformation and adopted bidentate bridging mode to link Hg centers, leading to an infinite zigzag chain (Figure 3).

Spectra Properties

The luminescent property of free ligand btp and 1 were investigated in the solid state at room temperature. The purity of 1



FIG. 2. The tetrahedral coordination environment of Hg ions in 1 (hydrogen atoms are omitted for clarity).

is confirmed by X-ray powder diffraction (XRPD) patterns (Figure 4). As it can be seen from Figure 5, the ligand btp displays an intense emission band centered at about 371 nm upon photoexciation at 254 nm, which can be attributed to the intraligand $\pi^* \rightarrow \pi$ transition. In comparison, **1** exhibits a relatively weak emission band centered at 378 nm (ex = 250 nm). It can be presumed that the significantly weakened intensity of the emission band for **1** is attributed to the competitive quenching effect of iodide ions.^[20,21] By comparing the luminescence of **1** with free



FIG. 3. The 1D infinite zigzag chain in 1 along c direction (hydrogen atoms are omitted for clarity) (color figure available online).

3500

3000

2500

1500

1000

500

0

online).

240

Intensity 2000

FIG. 4. PXRD patterns: simulated pattern of 1 (a); as-synthesized 1 (b) (color figure available online).

ligand, the effective bands of 1 indicate a slight red shift about 7 nm. Thus the fluorescent emissions of 1 can be tentatively assigned to the ligand-to-ligand charge transfer (LLCT).

The solid-state UV-Vis spectra of ligand btp and the corresponding complexes 1 are further determined (Figure 6). The ligand btp gives characteristic absorptions at approximately 230 nm, which may be attributed to the intraligand $\pi \rightarrow \pi^*$ transition of the ligand. The effective bands at approximately 248 nm for complex 1 indicates an obvious red-shift compared to free ligand, presumably due to increase of the π electron density induced by the coordination of nitrogen heterocyclic group with metal ions.

Wavelength (nm) FIG. 5. The solid-state photoluminescence of btp and 1 (color figure available

320

340

360

400

380

420

btp

SUPPLEMENTARY MATERIALS

260

280

300

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center, CCDC Nos.819064 and 819063. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

REFERENCES

- 1. Mir, M.H.; Kitagawa, S.; Vitzl, J.J. Two- and Three-fold Interpenetrated Metal-Organic Frameworks from One-Pot Crystallization. Inorg. Chem. 2008, 47, 7728.
- 2. Zhai, Q.G.; Lu, C.Z.; Wu, X.Y.; Batten, S.R. Cryst. Growth Des. 2007, 7, 2332



FIG. 6. The solid state UV-Vis spectra btp and 1 (color figure available online).



- Batten, S.R.; Robson, R. Interpenetrating nets: ordered, periodic entanglement. Angew. Chem., Int. Ed. 1998, 37, 1460.
- Eddaoudi, M.; Moler, D.B.; Li, H.L.; Chen, B.L.; Reineke, T.M.; O'Keeffe, M.; Yaghi, O.M. Modular chemistry: secondary building units as a basis for the design of highly porous and robust metal—organic carboxylate frameworks. *Acc. Chem. Res.* 2001, *34*, 319.
- Lee, E.; Kim, J.; Heo, J.; Whang, D.; Kim, K. A two-dimensional polyrotaxane with large cavities and channels: a novel approach to metal-organic open-frameworks by using supramolecular building blocks. *Angew. Chem. Int. Ed.* 2001, 40, 399.
- Zhang, J.P.; Lin, Y.Y.; Zhang, W.X.; Chen, X.M. Temperature- or guest-induced drastic single-crystal-to-single-crystal transformations of a nanoporous coordination polymer. J. Am. Chem. Soc. 2001, 127, 14162.
- Zheng, X.J.; Sun, C.Y.; Lu, S.Z.; Liao, F.H.; Gao, S.; Jin, L.P. New porous lanthanide-organic frameworks: synthesis, characterization, and properties of lanthanide 2,6-naphthalenedicarboxylates. *Eur. J. Inorg. Chem.* 2004, *16*, 3262.
- Yang, J.; Yuo, Q.; Li, G.D.; Cao, J.J.; Li, G.H.; Chen, J.S. Structures, photoluminescence, up-conversion, and magnetism of 2D and 3D rareearth coordination polymers with multicarboxylate linkages. *Inorg. Chem.* 2006, 45, 2857.
- Herr, R.J. 5-Substituted-1H-tetrazoles as carboxylic acid isosteres: medicinal chemistry and synthetic methods. *Bioorg. Med. Chem.* 2002, 10, 3379.
- Xue, H.; Gao, Y.; Twamley, B.; Shreeve, J.N.M. Energetic azolium azolate salts. *Inorg. Chem.* 2005, 44, 5068.
- Ye, C.F.; Xiao, J.C.; Twamley, B.; Shreeve, J.N.M. Energetic salts of azotetrazolate, iminobis(5-tetrazolate) and 5,5'-bis(tetrazolate). *Chem. Commun.* 2005, 21, 2750.
- Lu, Z.Z.; Zhang, R.; Li, Y.Z.; Guo, Z.J.; Zheng, H.G. Solvatochromic behavior of a nanotubular metal-organic framework for sensing small molecules. *J. Am. Chem. Soc.* 2011, 133, 4172.

- Lu, Z.Z.; Zhang, R.; Li, Y.Z.; Guo, Z.J.; Zheng, H.G. [WS₄Cu₃I₂] and [WS₄Cu₄]²⁺ secondary building units formed a metal–organic framework: large tubes in a highly interpenetrated system. *Chem. Commun.* 2011, 47, 2919.
- Boiocchi, M.; Bonizzoni, M.; Fabbrizzi, L.; Foti, F.; Licchelli, M.; Taglietti, A.; Zema, M. The influence of the boat-to-chair conversion on the demetallation of the nickel(II) complex of an open-chain tetramine containing a piperazine fragment. *Dalton Trans.* 2004, 653.
- Mukhopadhyay, S.; Mukhopadhyay, D.; Chatterjee, P.B.; Desplanches, C.; Sutter, J.P.; Butcher, R.J.; Chaudhury, M. Bi- and trinuclear copper(II) complexes of a sterically constrained phenol-based tetradentate ligand: syntheses, structures, and magnetic studies. *Inorg. Chem.* 2004, *43*, 8501.
- Massoud, S.S.; Mautner, F.A. Synthesis, characterization and crystal structure of 1,4-Bis(3-aminopropyl)piperazineperchlorato-copper(II) perchlorate. *Inorg. Chem. Commun.* 2004, 7, 559.
- Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P.F. Exchange interaction in multinuclear transition-metal complexes. 6. nature of metal-metal coupling in dinuclear iron(III) systems containing FeOFeO bridging units. *Inorg. Chem.* **1984**, *23*, 3398.
- Sathiyendiran, M.; Chang, C.H.; Chuang, C.H.; Luo, T.T.; Wen, Y.S.; Lu, K.L. Rigidity-modulated conformation control: a strategy for incorporating flexible building motifs into metallacycles, *Dalton Trans.* 2007, 1872.
- Sheldrick, G.M. SHELXL-97, Program for the solution and refinement of crystal structures. University of Göttingen, Germany, 1997.
- Ng, P.L.; Lee, C.S.; Kwong, H.L.; Chan, A.S.C. Zinc complex of bipyridine crown macrocycle: luminescence sensing of anions in aqueous media via the cooperative action of metal-ligand and hydrophobic interactions. *Inorg. Chem. Commun.* 2005, *8*, 769.
- Xiao, B.; Hou, H.W.; Fan, Y.T.; Tang, M.S. Impact of counteranion on the self-assembly of Cd(II)-containing MOFs: syntheses, structures and photoluminescent properties. *Inorg. Chim. Acta.* 2007, *360*, 3019.