This article was downloaded by: [Laurentian University] On: 08 October 2014, At: 10:13 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>

The Construction of Halido-Bridged Dinuclear Copper(II) Complexes With Tridentate Schiff Bases

Shao-Song Qian $^{\rm a}$, Yao Lu $^{\rm b}$, Zhong-Lu You $^{\rm b}$ & Hai-Liang Zhu $^{\rm a}$

^a School of Life Sciences , Shandong University of Technology , ZiBo , P. R. China

^b Department of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian, P. R. China

Accepted author version posted online: 12 Sep 2012. Published online: 03 Dec 2012.

To cite this article: Shao-Song Qian , Yao Lu , Zhong-Lu You & Hai-Liang Zhu (2013) The Construction of Halido-Bridged Dinuclear Copper(II) Complexes With Tridentate Schiff Bases, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 43:1, 107-110, DOI: <u>10.1080/15533174.2012.684237</u>

To link to this article: <u>http://dx.doi.org/10.1080/15533174.2012.684237</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



The Construction of Halido-Bridged Dinuclear Copper(II) Complexes With Tridentate Schiff Bases

Shao-Song Qian,¹ Yao Lu,² Zhong-Lu You,² and Hai-Liang Zhu¹

¹School of Life Sciences, Shandong University of Technology, ZiBo, P. R. China ²Department of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian, P. R. China

Two new halido-bridged dinuclear copper(II) complexes, $[Cu_2Cl_2L_2]$ ·1.5H₂O (1) and $[Cu_2Br_2L_2]$ ·H₂O (2), where L is the deprotonated form of the Schiff base 4-bromo-2-[(2hydroxypropylimino)methyl]phenol, have been prepared and structurally characterized by elemental analysis, IR spectra, and single-crystal X-ray crystallography. Each Cu atom in the complexes is coordinated by three donor atoms of Schiff bases and by two halide atoms, forming a square pyramidal geometry. The Cl and Br atoms are preferred bridging groups for the construction of dinuclear copper complexes with Schiff bases.

Keywords crystal structure, Cu complex, dinuclear complex, Schiff base

INTRODUCTION

Dinuclear complexes with bridging groups are currently attracting much attention for their interesting structures and wide applications.^[1-3] The Schiff bases derived from salicylaldehyde and its derivatives are a kind of versatile ligands in coordination chemistry. The rational design and construction of dinuclear complexes with Schiff bases are of particular interest in coordination and structural chemistry. As is well known, the halide and pseudohalide groups can link two or more metal atoms, yielding various polynuclear complexes.^[4–8] The search in the Cambridge Crystallographic Database (CSD; version 5.32 with addenda up to February 2011)^[9] has revealed that only 19 chlorido-bridged dinuclear copper complexes with Schiff bases derived from salicylaldehyde and its derivatives have been reported, and no such complexes with bromide bridges. In this paper, two new dinuclear Schiff base copper(II) complexes with chloride and bromide bridges, $[Cu_2Cl_2L_2] \cdot 1.5H_2O(1)$ and $[Cu_2Br_2L_2] \cdot H_2O$ (2), where L is the deprotonated form of the Schiff base 4-bromo-2-[(2-hydroxypropylimino)methyl]phenol (HL) (Scheme 1), were successfully prepared and characterized.



SCH. 1. The Schiff base HL.

EXPERIMENTAL

Materials and Measurements

Starting materials, reagents, and solvents with AR grade were purchased from commercial suppliers and were used without further purification. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer (Nanjing University, China). The IR spectra were recorded on a Jasco FT/IR-4000 spectrometer (Liaoning Normal University, China) as KBr pellets in the 4000–200 cm⁻¹ region. Single-crystal structural X-ray diffraction was carried out on a Bruker SMART 1000 CCD area diffractometer (Shandong University of Technology, China).

Synthesis of the Schiff Base

To the methanolic solution (30 mL) of 5-bromosalicylaldehyde (1.0 mmol, 0.201 g) was added a methanolic solution (30 mL) of 1-aminopropan-2-ol (1.0 mmol, 0.075 g) with stirring. The mixture was stirred for 30 min at room temperature to give yellow solution. The solvent was evaporated to give yellow powder, which was washed with cold methanol and dried in air. Yield 92%. Characteristic IR data: 1635 cm⁻¹. Anal. Calcd. for C₁₀H₁₂BrNO₂: C, 46.5; H, 4.7; N, 5.4. Found (%): C, 46.6; H, 4.8; N, 5.5.

Synthesis of the Complexes

For $[Cu_2Cl_2(L^4)_2]\cdot 1.5H_2O$ (1), to the methanolic solution (5 mL) of HL (0.1 mmol, 0.026 g) was added a methanolic solution (5 mL) of CuCl_2·2H_2O (0.1 mmol, 0.017 g) with stirring. The mixture was stirred for 10 min at room temperature, and then transferred to a stainless steel bomb, which was sealed, heated at 150°C for 12 h, and cooled gradually to room temperature. Blue block-shaped crystals of 1, suitable for X-ray crystal structural determination, were formed at the bottom of the bomb. The crystals were isolated by filtration, washed three times with methanol, and dried in air. Yield: 47%. Characteristic IR data (cm⁻¹): 1643 (s), 1180 (m). Anal. Calcd. for

Received 22 February 2012; accepted 8 April 2012.

Address correspondence to Hai-Liang Zhu, School of Life Sciences, Shandong University of Technology, ZiBo 255049, P. R. China. E-mail: hailiang_zhu@163.com

Complex

2

C₂₀H₂₅Br₂Cl₂Cu₂N₂O_{5.5}: C, 32.5; H, 3.4; N, 3.8. Found (%): C, 32.4; H, 3.6; N, 3.6.

For $[Cu_2Br_2(L^4)_2] \cdot H_2O$ (2), complex 2 was synthesized by the similar method as that described for 1, with $CuCl_2 \cdot 2H_2O$ replaced by $CuBr_2$ (0.022 g, 0.1 mmol). The blue blockshaped single crystals of 2 were isolated, washed three times with methanol, and dried in air. Yield: 33%. Characteristic IR data (cm^{-1}) : 1643 (s), 1179 (m). Anal. Calcd. for C₂₀H₂₄Br₄Cu₂N₂O₅: C, 29.3; H, 3.0; N, 3.4. Found (%): C, 29.5; H, 3.1; N, 3.3.

TAI	BLE	1		
	. 1	1	c	

Crystallographic and experimental data for complexes 1 and 2 1

X-Ray Crystallography

Diffraction intensities for the complexes were collected at 298(2) K using a Bruker SMART 1000 CCD area-detector diffractometer (Shandong University of Technology, China) with MoK α radiation ($\lambda = 0.71073$ Å). The collected data were reduced with the SAINT program,^[10] and multiscan absorption correction was performed using the SADABS.^[11] The structures were solved by direct methods. The complexes were refined against F^2 by full-matrix least-squares method using the SHELXTL package.^[12] All of the non-hydrogen atoms were refined anisotropically. The water H atoms in 1 were located from difference Fourier maps and refined isotropically, with O-H and H…H distances restrained to 0.85(1) and 1.37(2) Å, respectively. The remaining hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The crystallographic data for the complexes are summarized in

-			Table 1. Select	ed bond lengths	and angles are give	en in Table 2.		
Formula	$C_{40}H_{50}Br_4$	$C_{20}H_{24}Br_4$	Table 1. Selected bond lengths and angles are given in Table 2.					
	$Cl_4Cu_4N_4O_{11}$	$Cu_2N_2O_5$						
Mr	1478.4	819.1	TABLE 2					
T (K)	298(2)	298(2)	Selected bond lengths (Å) and angles (°)					
Crystal	Block/blue	Block/blue	1					
shape/color			\mathbf{I}	1 976 (7)	$C_{\rm H}1$ O2	1 005 (7)		
Crystal size	$0.23 \times 0.21 \times 0.18$	$0.10 \times 0.08 \times 0.07$	Cul-Ol	1.070(7)	Cu1-02	1.995(7)		
(mm^3)			Cut-Nt	1.930(8)	Cur-Crr	2.720 (3)		
Crystal system	Monoclinic	Monoclinic	Cu1-Cl2	2.201(3)	Cu2-03	1.879 (8)		
Space group	$P2_1/n$	$P2_1/n$	Cu2-04	1.900 (7)	Cu2-N2	1.937 (9)		
a (Å)	14.513(3)	14.593(3)		2.257(3)	Cu2-Cl2	2.718 (3)		
<i>b</i> (Å)	7.818(2)	8.037(2)	OI-CuI-NI	93.2 (3)	01-Cu1-02	1/6.0 (3)		
<i>c</i> (Å)	23.689(3)	23.549(3)	N1-Cu1-O2	82.8 (3)	OI-CuI-Cl2	93.4 (2)		
β (°)	92.218(2)	90.03(2)	NI-CuI-Cl2	159.6 (3)	02-Cu1-Cl2	90.4 (2)		
$V(Å^3)$	2685.8(10)	2761.8(9)	OI-CuI-CII	94.4 (2)	NI-CuI-CII	105.5 (2)		
Z	2	4	O2-Cu1-CII	86.4 (2)	Cl2-Cu1-Cl1	93.2 (1)		
D_{2} (g cm ⁻³)	1.828	1.970	O3-Cu2-N2	94.1 (4)	O3-Cu2-O4	175.3 (3)		
μ (Mo-K α)	4 793	7.359	N2-Cu2-O4	81.2 (4)	O3-Cu2-Cl1	92.4 (2)		
(mm^{-1})	1.775		N2-Cu2-Cl1	161.7 (3)	O4-Cu2-Cl1	92.1 (2)		
F(000)	1460	1584	O3-Cu2-Cl2	91.9 (2)	N2-Cu2-Cl2	103.4 (2)		
Independent	5754	3565	O4-Cu2-Cl2	89.1 (2)	Cl1-Cu2-Cl2	93.5 (1)		
reflections	5754	5505	2					
Observed	2141	1553	Cu1-O1	1.892 (9)	Cu1-O2	1.989 (8)		
reflections $(I >$	2141	1555	Cu1-N1	1.944 (11)	Cu1-Br3	2.415 (2)		
$2\sigma(I)$			Cu1-Br4	2.837 (2)	Cu2-O3	1.910 (10)		
20(1)	0.405 and 0.470	0.526 and 0.627	Cu2-O4	1.986 (8)	Cu2-N2	1.945 (13)		
transmission	0.403 and 0.479		Cu2-Br3	2.834 (2)	Cu2-Br4	2.407 (2)		
Demonstration	210	200	O1-Cu1-N1	93.4 (5)	O1-Cu1-O2	175.6 (4)		
Parameters	518	300	N1-Cu1-O2	82.4 (4)	O1-Cu1-Br3	94.1 (3)		
Restraints	19	0 0 0 0	N1-Cu1-Br3	156.7 (3)	O2-Cu1-Br3	90.2 (2)		
Goodness-oi-fit	0.950	0.819	O1-Cu1-Br4	93.0 (3)	N1-Cu1-Br4	105.2 (3)		
on F ²	0.0000.0.1705	0.0604.0.1000	O2-Cu1-Br4	86.8 (2)	Br3-Cu1-Br4	96.4 (1)		
$R_1, WR_2 [I \ge 2]$	0.0688, 0.1725	0.0604, 0.1202	O3-Cu2-N2	93.7 (5)	O3-Cu2-O4	175.3 (4)		
$2\sigma(I)$] ^a	0 1001 0 00 17	0.1386, 0.1405	N2-Cu2-O4	81.6 (5)	O3-Cu2-Br4	92.9 (3)		
$\kappa_1, w\kappa_2$ (all	0.1981, 0.2347		N2-Cu2-Br4	159.6 (4)	O4-Cu2-Br4	91.7 (3)		
data) ^a			O3-Cu2-Br3	92.0 (3)	N2-Cu2-Br3	102.4 (3)		
$^{3}D = E / E = 2 D = (\sum 12) (\sum 22) (\sum 12) (\sum 12) (2) (2) (2) (2) (2) (2) (2) (2) (2) ($			04-Cu2-Br3	88 7 (2)	Br4-Cu2-Br3	96 7 (1)		

 $K_1 = F_o - F_c/F_o, WR_2 = [\sum W(F_o^2 - Fc^2)/\sum W(F_o^2)^2]$

Br2



C13

FIG. 1. A perspective view of the molecular structure of 1 with the atom labeling scheme. The thermal ellipsoids are drawn at the 30% probability level.

RESULTS AND DISCUSSION

Chemistry

Br

The Schiff base HL was synthesized by the reaction of equimolar quantities of 5-bromosalicylaldehyde with 1aminopropan-2-ol in methanol. The air-stable yellow product of the Schiff base is soluble in DMSO, DMF, methanol, ethanol, acetonitrile, and chloroform, and insoluble in water. The elemental analyses are in good agreement with the chemical formula proposed for the compound. The complexes **1** and **2** were synthesized by the reaction of the Schiff base with CuCl₂·2H₂O or CuBr₂ in methanol at solvothermal condition. All the complexes are stable in air at room temperature for at least two months.

Structure Description of the Complexes

The single-crystal X-ray diffraction shows that the complexes are structurally similar halido-bridged dinuclear copper(II) compounds (Figure 1 for 1, Figure 2 for 2). The asymmetric unit of the complex 1 contains a dichlorido-bridged dinuclear copper(II) complex molecule and 1.5 water molecules of crystallization. The asymmetric unit of the complex 2 contains a dibromido-bridged dinuclear copper(II) complex molecule and a water molecule of crystallization. The Cu…Cu distances are 3.377(1) Å in 1, and 3.434(1) Å in 2, which are within the values observed in the 19 chlorido-bridged Schiff base copper(II) complexes in CSD.

In the complexes, the Schiff bases behave as monoanionic and tridentate ligands, which coordinate to the Cu atoms through the three NNO donor atoms. Each Cu atom in the complexes is five-coordinated in a square pyramidal geometry, with the basal plane defined by the NNO donor atoms of the Schiff base ligand, and by one Cl or Br atom, and with the apical position occupied by another halide atom. The average trans angles are 167.8(2)° for Cu1 and 168.5(2)° for Cu2 in 1, and 166.2(3)° for Cu1 and 167.4(3)° for Cu2 in 2. The Cu atoms deviate from the least-squares planes defined by the four basal donor atoms by 0.178(1) Å for Cu1, and 0.159(1) Å for Cu2 in 1, and 0.201(1) Å for Cu1, and 0.183(1) Å for Cu2 in 2, toward the apical donor atoms. The coordinate bond lengths related to the Cu atoms in both complexes are comparable to each other and also comparable to the corresponding values observed in other similar halido-bridged copper(II) complexes with Schiff bases.[4,13-17]

The coordination number 5 for copper(II) complexes is very common. The question arises as to whether the coordination polyhedra around the Cu atoms can be described as distorted square pyramid or trigonal bipyramid. Further information can be obtained by determining the structural index τ ,^[18] which represents the relative amount of trigonality (square pyramid, $\tau = 0$; trigonal bipyramid, $\tau = 1$); $\tau = (\beta - \alpha)/60^\circ$, α and β



FIG. 2. A perspective view of the molecular structure of 2 with the atom labeling scheme. The thermal ellipsoids are drawn at the 30% probability level.

being the two largest angles around the metal atom. The values of τ are 0.27 (Cu1) and 0.23 (Cu2) in **1**, and 0.32 (Cu1) and 0.26 (Cu2) in **2**. From the τ values, it can be concluded that all the Cu atoms in the complexes adopt distorted square pyramidal coordination.

IR Spectra

In the IR spectra of the complexes, the strong absorption bands at *ca.* 1644 cm⁻¹ for **1** and **2** can be assigned to the azomethine stretching frequencies of the Schiff base ligands, whereas for the free Schiff bases the corresponding bands are observed at 1635 cm⁻¹. The shift of these bands toward lower frequencies on complexation suggests coordination to the Cu atoms through the imine N atoms. The ν (C–O) mode is present as middle bands at 1178–1180 cm⁻¹ for the complexes. The weak bands indicative of the Cu–O, Cu–N, Cu–Cl, and Cu–Br bonds are located in the region 600–300 cm⁻¹.

CONCLUSION

Here we reports the synthesis and crystal structures of two new halido-bridged dinuclear copper(II) complexes with a tridentate Schiff base ligand. Complex **2** is the first reported bromido-bridged dinuclear Schiff base copper(II) compound. The Cl and Br anions are preferred bridging groups for the construction of dinuclear copper(II) complexes with tridentate Schiff bases.

SUPPLEMENTARY MATERIALS

CCDC 843683 (1) and 843684 (2) contain the supplementary crystallographic data for this paper. 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.

REFERENCES

- Yildiz, E.; Cetinkol, T.; Serindag, O. Synthesis and characterization of mono- and dinuclear metal complexes with novel azo compounds and their dyeing properties. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* 2010, 40, 19–26.
- Hui, R.-H.; Zhou, P.; You, Z.-L. Syntheses and crystal structures of two end-on thiocyanato-bridged dinuclear copper(II) complexes derived from 2–[(2-ethylaminoethylimino)methyl]phenol and 2,4-dichloro-6-[(2methylaminoethylimino)methyl]phenol. Synth. React. Inorg. Met.-Org. Nano-Met. Chem. 2009, 39, 495–499.

- Peng, S.-J.; Zeng, J.-L.; Wei, C.; Fang, F. Synthesis and crystal structure of a phenolato-bridged dinuclear oxovanadium(V) complex derived from N'-[1-(2-hydroxyphenyl)ethylidene]-1H-indole-3-carbohydrazide. Synth. React. Inorg. Met.-Org. Nano-Met. Chem. 2011, 41, 1052–1055.
- Thakurta, S.; Roy, P.; Rosair, G.; Gómez-García, C.J.; Garribba, E.; Mitra, S. Ferromagnetic exchange coupling in a new bis(mu-chloro)-bridged copper(II) Schiff base complex: Synthesis, structure, magnetic properties and catalytic oxidation of cycloalkanes. *Polyhedron* 2009, 28, 695–702.
- Nepveu, F.; Bormuth, F.-J.; Walz, L. Synthesis, X-ray structure, and magnetic-properties of di-µ-chloro-bis-[N-(2-hydroxy-2-phenylethyl)salicylideneiminatocopper(II)]. J. Chem. Soc., Dalton Trans. 1986, 1213–1216.
- Bluhm, M.E.; Ciesielski, M.; Gorls, H.; Walter, O.; Doring, M. Complexes of Schiff bases and intermediates in the copper-catalyzed oxidative heterocyclization by atmospheric oxygen. *Inorg. Chem.* 2003, 42, 8878– 8885.
- You, Z.-L.; Zhu, H.-L. Syntheses, crystal structures, and antibacterial activities of four Schiff base copper(II), zinc(II), and cadmium(II) complexes derived from 2–[(2-dimethylaminoethylimino)methyl]phenol. Z. Anorg. Allg. Chem. 2006, 632, 140–146.
- Manzur, J.; Garcia, A.M.; Vega, A.; Ibanez, A. Synthesis and structure of copper (II) complexes with L-OH (L-OH = 2,6-bis–[*N*-(2-pyridylethyl)formidoyl]-4-methyl-phenol). *Polyhedron* 2007, *26*, 115–122.
- Allen, F.H. The Cambridge Structural Database: a quarter of a million crystal structures and rising. *Acta Crystallogr.* 2002, *B58*, 380–388.
- 10. Bruker. SMART and SAINT; Bruker AXS Inc., Madison, WI, 2002.
- 11. Sheldrick, G.M. SADABS: Program for Empirical Absorption Correction of Area Detector; University of Göttingen, Göttingen, Germany, **1996**.
- Sheldrick, G.M. SHELXTL V5.1 Software Reference Manual; Bruker AXS, Inc., Madison, WI, 1997.
- Liu, H.-Y.; Gao, F.; Niu, D.-Z.; Tian, J.-L. Chlorido-bridged polymeric and dinuclear copper(II) complexes with tridentate Schiff base: synthesis, crystal structure and magnetic properties. *Inorg. Chim. Acta* 2009, 362, 4179– 4184.
- Chumakov, Y.M.; Tsapkov, V.I.; Filippova, I.G.; Bocelli, G.; Gulea, A.P. Crystal structures of copper(II) and nickel(II) nitrate and chloride complexes with 4-bromo-2–[(2-hydroxyethylimino)-methyl]phenol. *Crystallogr. Rep.* 2008, 53, 619–625.
- Zhang, N.; You, Z.-L. Syntheses and crystal structures of two tetranuclear copper(II) complexes with Schiff bases. *Transition Met. Chem.* 2010, *35*, 437–440.
- Nayak, S.; Gamez, P.; Kozlevcar, B.; Pevec, A.; Roubeau, O.; Dehnen, S.; Reedijk, J. Coordination compounds from the planar tridentate Schiffbase ligand 2-methoxy-6-((quinolin-8-ylimino)methyl)phenol (mqmpH) with several transition metal ions: Use off [Fe^{III}(mqmp)(CH₃OH)Cl₂] in the catalytic oxidation of alkanes and alkenes. *Polyhedron* 2010, 29, 2291– 2296.
- Adams, H.; Fenton, D.E.; Haque, S.R.; Heath, S.L.; Ohba, M.; Okawa, H.; Spey, S.E. Diversity in the reactions of unsymmetric dinucleating Schiff base ligands with Cu-II and Ni-II. *J. Chem. Soc., Dalton Trans.* 2000, 1849–1856.
- Addison, A.W.; Rao, T.N.; Reedijk, J.; van Rijn, J.; Verschoor, G.C. Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen sulfur donor ligands The crystal and molecular-structure of aqua[1,7-bis(*N*-methylbenzimidazol-2'-yl)-2,6-dithiaheptane]copper(II) perchlorate. *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356.