

UDC 548.737

CRYSTAL STRUCTURES OF [Zn(SALIMP)(CH₃CO₂)₂] AND [Cu(SALIMP)Cl] WITH 2-[[2-PYRIDINYLMETHYL]IMINO]METHYL]PHENOL (HSALIMP) AS A LIGAND

© 2011 R.-P. Liu, M.-Yu. Duan, J. Li*, Z.-P. Su, J.-H. Zhang, F.-X. Zhang

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, The College of Chemistry and Material Science, Northwest University, Xi'an, Shaan xi, 710069, P. R. China

Received November, 27, 2009

Two complexes [Zn(SALIMP)(CH₃CO₂)₂] (**1**) and [Cu(SALIMP)Cl] (**2**) are obtained by the reactions of zinc(II) and copper(II) salts with a tridentate Schiff base ligand 2-[[2-pyridinylmethyl]imino]methyl]phenol (HSALIMP). Their structure is determined by single crystal X-ray diffraction. Data for complex **1**: C₃₀H₂₈N₄O₆Zn₂, CCDC number: 668213, *M_r* = 671.3, monoclinic, *C*2/*c*, with *a* = 34.670(5) Å, *b* = 15.266(2) Å, *c* = 23.464(4) Å, β = 114.045(2)°, *V* = 11341(3) Å³, *Z* = 16, *F*(000) = 5504, GOOF(*F*²) = 0.894, the final *R* = 0.0520 and *wR* = 0.1272 for 10515 observed reflections with *I* > 2σ(*I*); complex **2**: C₁₃H₁₂N₂OCu, CCDC number: 668211, *M_r* = 311.24, triclinic, *P*-1, with *a* = 7.4050(8) Å, *b* = 10.2369(11) Å, *c* = 16.2873(17) Å, α = 87.728(2)°, β = 87.818(2)°, γ = 78.279(2)°, *V* = 1207.4(2) Å³, *Z* = 4, *F*(000) = 632, GOOF(*F*²) = 1.077, the final *R* = 0.0326 and *wR* = 0.0381 for 4209 observed reflections with *I* > 2σ(*I*).

Keywords: zinc(II) complex, copper(II) complex, Schiff base, crystal structure, 2-[[2-pyridinylmethyl]imino]methyl]phenol (HSALIMP).

INTRODUCTION

Transition metal complexes containing Schiff base ligands have been of great interest for many years. These complexes play an important role in the development of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures [1, 2]. 2-[[2-pyridinylmethyl]imino]methyl]phenol (HSALIMP) is a relatively planar and rigid tridentate Schiff base ligand coordinating to a metal ion with the N,N,O donor-atom. Different coordination molecules can be constructed with HSALIMP through variation of metal ions or anions, and consequently, they have different properties. Some complexes with HSALIMP or similar ligands have been reported [3—12], and they showed different coordinating behavior or packing mode when the anion (such as NH₃⁻, ClO₄⁻, Cl⁻, Br⁻) is different or the metal ion is changed. CH₃COO⁻ can act not only as an anion, but also as a ligand, and very few reports is concerned with CH₃COO⁻ in these complexes. In addition, we are interested in square planar copper(II) complexes, in which magnetic exchange occurs exclusively through intermolecular π—π interactions involving the terminal aromatic ligands [13]. In an attempt to design new structures, we report herein the synthesis and characterization of [Zn(SALIMP)×(CH₃CO₂)₂] (**1**) and [Cu(SALIMP)Cl] (**2**) complexes with Schiff base 2-[[2-pyridinylmethyl]imino]methyl] phenol (HSALIMP) as a ligand.

* E-mail: junli@nwu.edu.cn

EXPERIMENTAL

Materials. 2-aminomethyl pyridine used was supplied by Johnson Matthey Company. All chemicals were of analytical or reagent grade available commercially and used as received.

Synthesis of the 2-[[2-(pyridinylmethyl)imino]methyl]phenol (HSALIMP) ligand. 2-aminomethylpyridine (2.16 g, 20 mmol) was dissolved in methanol (10 ml). A solution of salicylaldehyde (2.1 ml, 20 mmol) in methanol (10 ml) was added dropwise with stirring. The color of the solution changed from colorless to yellow. The mixture was stirred at room temperature for 3 h. Then filtered; methanol and water were removed under vacuum. 2-[[2-(pyridinylmethyl)imino]methyl]phenol was obtained as yellow oil.

Synthesis of the [Zn(SALIMP)(CH₃CO₂)]₂ complex (1). HSALIMP (0.422 g, 2.0 mmol), dissolved in warm dry ethanol (15 ml), was added to a solution of Zn(Ac)₂·2H₂O (0.538g, 2.0 mmol) in dry ethanol (10 ml) under stirring at room temperature for 2 h. The color of the reaction mixture immediately changed from light yellow to dark yellow. The resulting mixture was filtered off and left at room temperature for 5 days; then it gave a yellow diamond crystal. Yield: 65.3 %. Anal. Calc. for [C₁₅H₁₄N₂O₃Zn] C, 53.66; H, 4.17; N, 8.38. Found: C, 53.87; H, 4.04; N, 8.57.

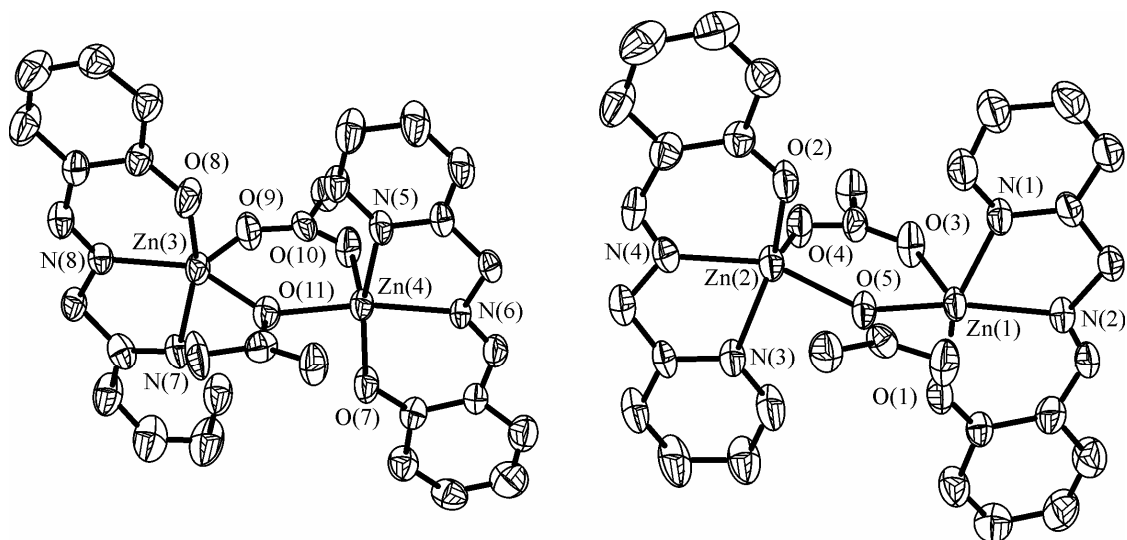
Synthesis of the complex [Cu(SALIMP)Cl] (2). Complex 2 was obtained as a dark green crystal, in a manner similar to complex 1, by replacing Zn(Ac)₂·2H₂O with CuCl₂·2H₂O. Yield: 61.3 %. Anal. Calc. for [C₁₃H₁₁N₂OClCu] C, 9.03; H, 3.54; N, 50.32. Found: C, 8.96; H, 3.42; N, 50.85.

Crystallographic data collection and refinement. The crystals of a suitable fit size and fine shape were placed on a Bruker Smart Apex CCD crystal X-ray diffractometer with graphite monochromatized MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 298 K. The structures were solved by direct methods and refined by full-matrix least-square fitting on F^2 using the SHELXTL-97 crystallographic software package. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in the calculated positions with fixed C—H. The crystal parameters of complexes 1 and 2 are given in Table 1.

Table 1

Crystal parameters of complexes 1 and 2

Complexes	1	2
Empirical formular	C ₃₀ H ₂₈ N ₄ O ₆ Zn ₂	C ₁₃ H ₁₂ N ₂ OClCu
CCDC number	668213	668211
Formular weight	671.3	311.24
Crystal system	Monoclinic	Triclinic
Crystal size, mm	0.30×0.33×0.34	0.40×0.36×0.34
Space group	C2/c	P-1
<i>a</i> , <i>b</i> , <i>c</i> , Å	34.670(5), 15.266(2), 23.464(4)	7.4050(8), 10.2369(11), 16.2873(17)
α , β , γ , deg.	114.045(2)	87.728(2), 87.818(2), 78.279(2)
<i>V</i> , Å ³	11341(3)	1207.4(2)
<i>Z</i>	16	4
μ , cm ⁻¹	1.743	2.016
<i>D</i> _{calc} , g/cm ³	1.573	1.712
θ , deg.	1.61—25.50	2.03—25.00
<i>F</i> (000)	5504	632
Reflections collected	29243	6146
Independed reflections	10515	4209
GOOF (F^2)	0.894	1.077
Data / restraints / parameters	10515 / 0 / 762	4209 / 0 / 325
Final <i>R</i> indices [$I > 2\sigma(I)$]	0.0520	0.0326
<i>R</i> indices(all data)	0.1272	0.0381

Fig. 1. Crystal structure of **1**

RESULTS AND DISCUSSION

Crystal structure of $[\text{Zn}(\text{SALIMP})(\text{CH}_3\text{CO}_2)]_2$ complex (1**).** The crystal structure of complex **1** is shown in Fig. 1, and selected bond distances and angles are given in Table 2.

The smallest independent unit comprises two $[\text{Zn}(\text{SALIMP})(\text{CH}_3\text{CO}_2)]_2$ molecules in complex **1**. They have the same coordination environment with slightly different bond lengths and angles (Table 2). It consists of a dizinc core with two penta-coordinated zinc ions linked by two acetate mole-

Table 2

Selected bond lengths (Å) and bond angles (deg.)

Complex 1					
Zn(1)—O(1)	1.979(5)	Zn(2)—O(5)	2.059(4)	Zn(3)—N(8)	2.063(4)
Zn(1)—O(3)	2.047(4)	Zn(2)—N(3)	2.169(6)	Zn(4)—O(7)	1.982(4)
Zn(1)—O(5)	2.060(3)	Zn(2)—N(4)	2.054(5)	Zn(4)—O(10)	2.059(3)
Zn(1)—N(1)	2.145(5)	Zn(3)—O(8)	1.965(4)	Zn(4)—O(11)	2.059(3)
Zn(1)—N(2)	2.094(5)	Zn(3)—O(9)	1.983(4)	Zn(4)—N(5)	2.156(4)
Zn(2)—O(2)	1.969(5)	Zn(3)—O(11)	2.076(3)	Zn(4)—N(6)	2.093(4)
Zn(2)—O(4)	1.999(4)	Zn(3)—N(7)	2.160(5)		
O(1)—Zn(1)—O(3)	99.70(2)	O(4)—Zn(2)—N(3)	94.40(2)	N(8)—Zn(3)—N(7)	77.21(19)
O(1)—Zn(1)—N(2)	88.30(2)	N(4)—Zn(2)—N(3)	77.70(2)	O(7)—Zn(4)—O(10)	98.63(17)
O(3)—Zn(1)—N(1)	94.13(19)	O(8)—Zn(3)—O(9)	102.65(19)	O(7)—Zn(4)—N(5)	163.50(17)
N(2)—Zn(1)—N(1)	77.50(2)	O(8)—Zn(3)—N(8)	89.01(17)	O(10)—Zn(4)—N(5)	93.77(16)
O(2)—Zn(2)—O(4)	101.90(2)	O(9)—Zn(3)—N(7)	93.58(17)	N(6)—Zn(4)—N(5)	77.20(17)
O(2)—Zn(2)—N(3)	161.80(2)				
Complex 2					
Cu(1)—O(1)	1.902(2)	Cu(1)—Cl(1)	2.2438(7)	Cu(2)—N(3)	2.015(2)
Cu(1)—N(2)	1.943(2)	Cu(2)—O(2)	1.907(2)	Cu(2)—Cl(2)	2.2469(8)
Cu(1)—N(1)	2.023(2)	Cu(2)—N(4)	1.944(2)		
O(1)—Cu(1)—N(2)	92.61(9)	N(1)—Cu(1)—Cl(1)	94.85(7)	O(2)—Cu(2)—Cl(2)	90.06(6)
N(2)—Cu(1)—N(1)	82.13(10)	O(2)—Cu(2)—N(4)	92.66(9)	N(3)—Cu(2)—Cl(2)	95.41(7)
O(1)—Cu(1)—Cl(1)	90.42(6)	N(4)—Cu(2)—N(3)	81.87(10)		

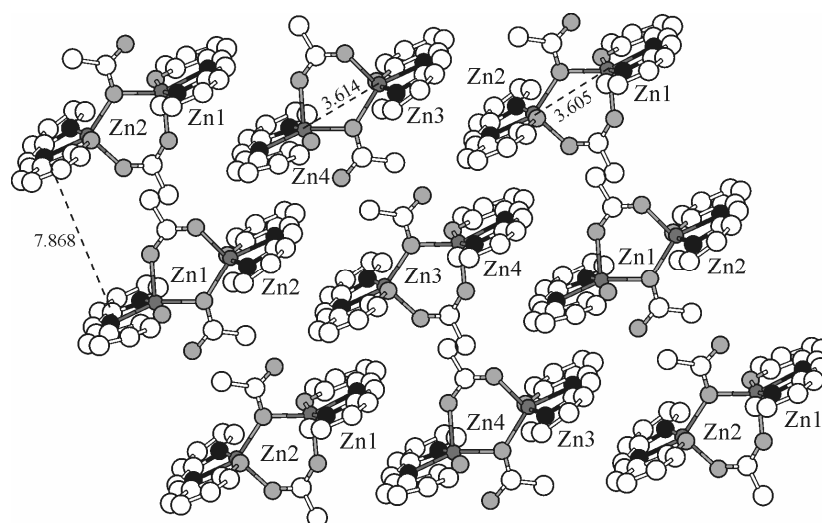


Fig. 2. Crystal packing of **1** (hydrogen atoms are omitted for clarity)

cles. The coordination environment around each zinc ion is a distorted square pyramid with the equatorial plane consisting of two nitrogen atoms, an oxygen atom of the tridentate SALIMP ligand, and an oxygen atom of one acetate bridging ligand. The axial site is occupied by the oxygen atom of another acetate bridging ligand. It is noticeable here that one of the acetate molecules bidentately bridges two zinc ions at the equatorial—axial sites via O(3), O(4), and another acetate molecule monodentately bridges two zinc ion at the equatorial—equatorial sites via O(5). Coordinated to zinc atoms, the ligand formed two adjacent six- and five-membered chelate rings, which are favor of the stabilization of the complex.

Acetate plays an important role in forming the dimer. With Cl^- , NH_3^- , ClO_4^- , Zn(II) usually forms mononuclear complexes with HSAIMP [14, 15]. But with HSAIEP (2-[[[2-(2-pyridinyl)ethyl]imino]methyl]phenol) that has one C atom more than HSAIMP, a dimer zinc complex can be formed using the deprotonated phenolate group as a bridging atom [3]. The O(5) bridge forms an asymmetric linkage to the zinc atoms with similar zinc-oxygen distances (zinc-oxygen distances from 2.059 Å to 2.076 Å) (Table 2), which are markedly different from the zinc-oxygen distances of $[\text{Zn}(\text{SALIEP})(\text{NO}_3)_2]$ (Zn(1)—O(1) 1.994 Å, and O(1)—Zn(1) 2.103 Å). And the Zn—Zn separations in **1** (Zn(1)—Zn(2) 3.605 Å, Zn(3)—Zn(4) 3.614 Å) are also significantly longer than those observed in $[\text{Zn}(\text{SALIEP})(\text{NO}_3)_2]$ (Zn—Zn = 3.184 Å) [3].

The ligand and Zn are approximately coplanar, with an average deviation of 0.120(4) Å. These planes are parallel, but the distance between the two planes is large (7.868 Å), so there is no π — π stacking interactions between the planes. These parallel molecules form a column along the *c* axis, and a stagger arrangement between the columns was constructed (Fig. 2).

Crystal structure of the [Cu(SALIMP)Cl] complex (2). The crystal structure of the [Cu(SALIMP)Cl] complex is shown in Fig. 3 and selected bond distances and angles are given in Table 2.

In complex **2**, the smallest independent unit comprises two [Cu(SALIMP)Cl] molecules. The copper(II) center is in a square-based planar N_2OCl coordination environment constituted by the deprotonated phenolato oxygen, pyridine nitrogen, imine nitrogen, and the chlorine anion. Cu1, O1, N1, N2, and Cl1 are nearly coplanar (a coplanar error is 0.0226 Å). The Cu—O average bond distance of 1.905 Å is shorter than that observed

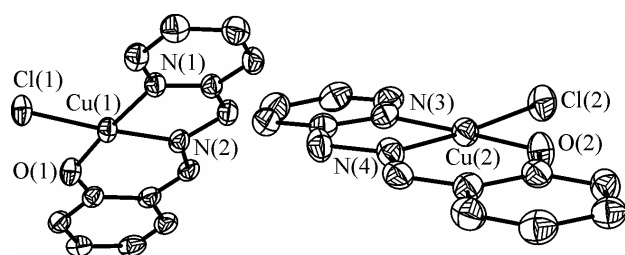
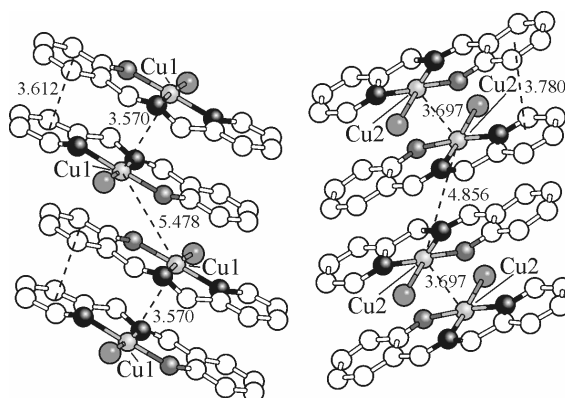


Fig. 3. Crystal structure of **2**

Fig. 4. Intermolecular π — π stacking interaction of **2** (hydrogen atoms are omitted for clarity)



in $[\text{Cu}(\text{L})\text{Cl}](\text{L}=\text{N}-(2\text{-pyridylmethyl})-3\text{-methoxy-salicylaldiminato})$ ($\text{Cu}-\text{O} = 1.915 \text{ \AA}$) [9], whereas the $\text{Cu}-\text{N}$ average bond distance of 2.019 \AA is longer than that observed in $[\text{Cu}(\text{L})\text{Cl}]$ ($\text{Cu}-\text{N} = 1.944 \text{ \AA}$). The distance is observed for the $\text{Cu}-\text{N}$ average bond length involving the pyridine ring ($\text{Cu}-\text{N} = 1.943 \text{ \AA}$), which falls in the range reported for other $\text{Cu}(\text{II})$ square planar complexes [4]. The $\text{Cu}-\text{Cl}$ average bond length (2.245 \AA) is within the range reported for copper(II)—Cl compounds and agrees with the ionic radii.

In square planar based copper(II) complexes, the metal ion is often involved in very weak axial interactions, and in these cases, dinuclear species or polynuclear chains with equatorial-apical bridges are often observed [16]. Such an interaction is likely to stabilize the complex in the solid state [17]. In complex **2**, planar $[\text{Cu}_1(\text{SALIMP})\text{Cl}]$ or $[\text{Cu}_2(\text{SALIMP})\text{Cl}]$ molecules form one-dimensional assemblies via π — π stacking. Planar $[\text{Cu}_1(\text{SALIMP})\text{Cl}]$ and $[\text{Cu}_2(\text{SALIMP})\text{Cl}]$ are stagger arranged (Fig. 4). The corresponding centroid-to-centroid ring distances are 3.612 \AA and 3.780 \AA respectively. The $\text{Cu}\dots\text{Cu}$ distances between two parallel planar are 3.570 \AA ($\text{Cu}_1\dots\text{Cu}_1$) and 3.697 \AA ($\text{Cu}_2\dots\text{Cu}_2$) respectively. Each square planar molecule is involved in two types of π — π stacking interactions involving pyridyl and aldehyde rings of the adjacent molecules. This stacking results in two chain-like arrangements of the metal ion with short ($\text{Cu}_1\dots\text{Cu}_1$) and long ($\text{Cu}_2\dots\text{Cu}_2$) distances.

CONCLUSIONS

One Schiff base ligand 2-[[2-(2-pyridinylmethyl)imino]methyl]phenol (HSALIMP) and its complexes with $\text{Zn}(\text{II})$ and $\text{Cu}(\text{II})$ have been synthesized. The crystal structure of $[\text{Zn}(\text{SALIMP})\times(\text{CH}_3\text{CO}_2)_2]$ **1** is a dinuclear complex; two $[\text{Zn}(\text{SALIMP})]^+$ units are bridged to form a dinuclear coordination unit via oxygens of two acetate bridging ligands. In the two acetate bridging ligands, one supplies two oxygen atoms as a bridge to coordinate and the other supplies one oxygen atom. The structure of $[\text{Cu}(\text{SALIMP})\text{Cl}]$ **2** is mononuclear and square-based planar comprising the HSALIMP ligand and a Cl anion. In complex **2**, a one-dimensional chain is formed by the intermolecular π — π stacking interaction.

REFERENCES

- Gupta K.C., Sutar A.K. // *Coord. Chem. Rev.* – 2008. – **252**. – P. 1420 – 1450.
- Alexeeva Yu.E., Kharisov B.I., Hernández García T.C., Garnovskii A.D. // *Coord. Chem. Rev.* – 2010. – **254**. – P. 794 – 831.
- Tandon S.S., Chander S., Thompson L.K. // *Inorg. Chim. Acta.* – 2000. – **300-302**. – P. 683 – 692.
- Kannappan R., Tanase S., Mutikainen I. et al. // *Inorg. Chim. Acta.* – 2005. – **358**. – P. 383 – 388.
- Sun Y.X., Gao G.Z., Pei H.X., Zhang R. // *Acta Crystallogr.* – 2005. – **E61**. – P. m370 – 372.
- Sun Y.X., Gao Y.Z., Zhang H.L. et al. // *Acta Crystallogr.* – 2005. – **E61**. – P. m1055 – 1057.
- You Zhong-Lu, Chen Bo, Zhua Hai-Liang, Liu Wei-Sheng // *Acta Crystallogr.* – 2004. – **E60**. – P. m884 – 886.
- Sun Yu-Xi // *Acta Crystallogr.* – 2005. – **E61**. – P. m335 – 337.
- Sun Yu-Xi // *Acta Crystallogr.* – 2005. – **E61**. – P. m338 – 340.
- Ma Jun-Ying, Wu Tong-Xing, She Xue-Gong, Pan Xin-Fu // *Acta Crystallogr.* – 2005. – **E61**. – P. m695 – 696.
- Su Z.P., Zhang J.H., Guo H. et al. // *Sci. J. Northwest University Online.* – 2007. – **5**. – P. 5.
- Cucciolito M.E., Litto R.D., Fanizzi F.P. et al. // *Inorg. Chim. Acta.* – 2009. – 2010. – **363**. – P. 741 – 747.
- Amoroso A.J., Jeffery J.C., Jones P.L. et al. // *Angew. Chem. Int. Ed. Engl.* – 1995. – **34**. – P. 1443 – 1446.
- Li Z.X., Zhang X.L. // *Acta Crystallogr.* – 2004. – **E60**. – P. m1017 – 1019.
- Wei Y.J. // *Acta Crystallogr.* – 2005. – **E61**. – P. m1085 – 1087.
- Sangeetha N.R., Pal S. // *Polyhedron.* – 2000. – **19**. – P. 2713 – 2717.
- Subramanian P.S., Suresh E., Dastidar P. et al. // *Inorg. Chem.* – 2001. – **40**. – P. 4291 – 4301.