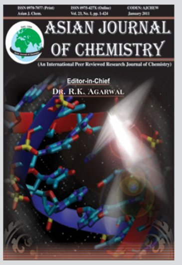
Asian Journal of Chemistry; *Vol. 23, No. 9 (2011), 4212-4214*

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Synthesis and Crystal Structure of A Binuclear Zinc(II) Complex

YA-NING GUO

Department of Chemistry and Chemical Engineering, Baoji University of Arts and Sciences, Baoji, P.R. China

Corresponding author: Tel: +86 917 3566589; E-mail: ggyn1997@163.com

(*Received*: 26 February 2011; *Accepted*: 30 May 2011) AJC-10004

A new binuclear complex $Zn_2L_2ClN_3$ 1 (HL = 2-(1pyridin-2-yl-ethylideneamino)- phenol) has been synthesized and characterized by X-ray single-crystal diffraction analysis. The complex crystallizes in orthorhombic, space group Pbca with a = 13.9620(15) Å, b = 8.7547(11) Å, c = 20.441(2) Å, V = 2498.5(5) Å3, Z = 4, $C_{26}H_{22}N_7O_2ClZn_2$, M_r = 630.70, Dc = 1.677 g cm^{-3}, F(000) = 1280, μ = 2.067 mm^{-1}, the final R = 0.0681 and wR = 0.1535 for 1292 observed reflections with I > 2s(I). The coordination geometry of each Zn(II) atom is trigonal bipyramidal and the two Zn(II) ions are bridged by two phenolic oxygen atoms with Zn…Zn separation of 3.172 Å. The present complex of zinc(II) exhibits a three-dimensional structure through hydrogen bondings and the conformation and packing is also stabilized by them.

Key Words: Schiff base, Synthesis, Crystal structure.

INTRODUCTION

Schiff bases have long been used as organic chelating ligands in the synthesis of metal complexes due to their easy preparation and structural varieties. It make them to coordinate with many metals to form various functional complexes and even to build a super-molecular structure. In recent years, there has been enhanced interest in the synthesis and characterization of Schiff bases and their complexes due to their important catalytic[1], magnetic[2,3], optical[4] and biological properties[5,6]. Although Schiff bases derived from some actively aromatic aldehyde such as salicylaldehyde, vanillin as well as furfural, salicylaldehyde and various amines have extensively been used to synthesize many complexes. The complexes with 2-acetylpyridine as the carbonyl group counterpart of the Schiff base have received very scanty attention.

Furthermore, Schiff base ligands possessed N-donors and phenolic hydroxyl stimulated scientists' interest because they have favourable coordination abilities and they can easily construct hydrogen bondings. Another, phenolate O site of Schiff base ligand containing phenolic hydroxyl can function as a bridging site to furnish dinuclear complexes, which simultaneously having other ancillary ligands in thei coordination positions[7]. So polydentate Schiff bases containing N, O atoms are regarded as a good type of chelating ligands for transition metals. In view of these, more and more scientists give attention to the reaearch on pyridone Schiff base and their complexes[8-10]. In this paper, we report the synthesis and structural characterization of a binuclear Zn(II) complex with a Schiff base derived from the condensation of *o*-aminophenol and 2-acetylpyridine.

EXPERIMENTAL

All chemicals and solvents obtained from commercial sources were of reagent grade and used without further purification. Crystal structure data were collected by a Bruker Smart-1000 CCD diffractometer.

Synthesis of the complex: *o*-Aminophenol (2.2 g, 20 mmol) and an equimolar quantity of 2-acetylpyridine were dissolved in ethanol(50 mL). After stirring for about 3 h at room tempreture, the solution of NaN_3 and $ZnCl_2$ (20 mmol) in 40 mL methanol was added. The mixture was stirred for 0.5 h. The resulting yellow filtrate was left standing at room temperature for slow evaporation for 1 week, yellow block crystals suitable for X-ray analysis obtained.

X-ray crystallographic determination: A yellow block crystal with dimensions of 0.21 mm × 0.19 mm × 0.09 mm was selected for measurement. Diffraction data of **1** were collected at 298(2) K on a Bruker Smart-1000 CCD diffractometer equipped with a graphite-monochromatic MoK_α radiation (λ = 0.71073 Å). A total of 11902 reflections were collected in the range of $1.99 \leq \theta \leq 25.04°$ by using an φ-ω multi-scan mode, of which 2216 were unique with R_{int} = 0.092 and 1292 were observed with $I > 2\sigma(I)$. The structure of **1** was solved by direct methods and refined on F^2 by full-matrix least-squares procedures using the SHELX-97 program package[11]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to carbon atoms were fixed at their

TABLE-1

SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) OF THE COMPLEX

Bond	Dist.	Bond	Dist.	Bond	Dist.
Zn(1)-O(1)#1	2.014(5)	Zn(1)-N(3)	2.07(8)	Zn(1)-N(2)	2.098(6)
Zn(1)-O(1)	2.106(6)	Zn(1)-N(1)	2.136(7)	Zn(1)-Cl(1)	2.32(2)
N(1)-C(7)	1.331(11)	N(1)-C(3)	1.338(10)	N(2)-C(2)	1.283(9)
N(2)-C(8)	1.434(10)	N(3)-N(4)	1.21(7)	N(3)-N(5)	1.20(6)
O(1)-C(9)	1.314(9)	C(2)-C(3)	1.485(11)	C(1)-C(2)	1.504(10)
C(1)-H(1A)	0.9600	C(1)-C(1C)	0.9600	C(13)-H(13)	0.9300
Angle	(°)	Angle	(°)	Angle	(°)
O(1)#1-Zn(1)-N(3)	114(2)	O(1)#1-Zn(1)-N(2)	124.8(2)	O(1)#1-Zn(1)-O(1)	79.3(2)
N(2)-Zn(1)-O(1)	77.9(2)	O(1)-Zn(1)-N(1)	149.7(2)	N(3)-Zn(1)-Cl(1)	15.1(10)
O(1)- Zn(1)-Cl(1)-	111.6(4)	C(7)-N(1)-Zn(1)	126.6(6)	C(3)-N(1)-Zn(1)	114.6(6)
C(2)-N(2)-Zn(1)	118.7(6)	C(8)-N(2)-Zn(1)	112.8(5)	C(1)-O(1)-Zn(1)	113.1(5)
Zn(1) 1-O(1)-Zn(1)	100.7(2)	N(2)-C(2)-C(3)	114.0(7)	N(1)-C(3)-C(4)	121.8(9)
N(1)-C(3)-C2)	115.8(7)	C(3)-C(3)-C(5)	118.1(9)	C(5)-C(6)-C(7)	118.4(10)

Symmetry code: #1 -x+1,-y,-z+1

ideal positions. The final R = 0.0681, wR = 0.1535 (w = 1/[$\sigma^2(Fo^2) + (0.0697P)^2 + 9.6794P$], where P = $(Fo^2 + 2Fc^2)/3$), S = 1.07, $(\Delta/\sigma)_{max}$ = 0.001, $(\Delta\rho)_{max}$ = 1.00 and $(\Delta\rho)_{min}$ = -1.07 e/Å^3. Selected bond lengths and bond angles are listed in Table-1 and the hydrogen bond parameters in Table-2.

TABLE-2

HYDROGEN BOND LENGTHS (Å) AND BOND ANGLES (°) OF COMPLEX

D-H…A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
C1-H1A…O1$^{\#1}$	0.96	2.49	3.418(10)	161.3
C7-H7…N5$^{\#2}$	0.93	2.58	3.19(2)	123.3

Symmetry transformations used to generate the equivalent atoms: #1: -1/2+x, +y, 1/2-z; #2: 3/2-x, -1-y, 1/2+z

RESULTS AND DISCUSSION

The perspective view of the molecular structure of the complex is illustrated in Fig. 1. The dinuclear Zn(II) complex **1** is composed of two zinc(II) ions, two Schiff base L$^-$ ligands, one Cl$^-$ ion and one N$_3^-$ ion, Cl$^-$ ion and N$_3^-$ ion are disorder with the site occupancy of 50 %. Two zinc(II) atoms are held together by two deprotonated phenolic oxygen atoms from two different Schiff base L$^-$ ligands, forming a Zn$_2$O$_2$ parallelogram[12] (∠Zn(1)-O(1)-Zn(1) = 100.7(2)°, which very close to 100.57° in [Zn$_2$(SHSH)$_2$(2Mepy)$_2$]; ∠O(1)-Zn(1)-O(1) = 79.3(2)°, the torsion angle of O(1A)-Zn(1)-O(1)-Zn(1A) is 0.00°) plane with Zn···Zn distance being 3.172 Å, which is consistent with that of 3.150(1) Å in a reported complex[13]. The present of zinc(II) complex is centrosymmetric and two Zn(II) atoms in similar coordination environment. Each Zn(II) ion is coordinated by two N atoms (pyridyl N (Zn(1)-N(1) = 2.136(7) Å) and imine N (Zn(1)-N(2) = 2.098(6) Å) and two phenol O (Zn(1)-O(1) = 2.106(6) Å and Zn(1)-O(1A) = 2.014(5) Å, symmetry code:-x+1,-y,-z+1) from the tridentate chelating Schiff base as well as one Cl$^-$ (Zn(1)-Cl(1) = 2.32(2) Å)or one N atom(Zn(1)-N(3) = 2.07(8) Å) from N$_3^-$, leading to a slightly distorted square-pyramidal geometry. In the square pyramid, two N atoms(N(1) and N(2)) and two O atoms (O(1) and O(1A)) determine the square planeand the N(3) or Cl(1) ion occupies the apical position. The sum of ∠O(1A)-Zn(1)-N(1) (104.1(2)°), ∠N(2)-Zn(1)-N(1) (75.7(3)°), ∠N(2)-Zn(1)-O(1) (77.9(2)°) and ∠O(1)-Zn(1)-O(1A) (79.3(2)°) bond angles is 337.0°, which indicates that N(1), N(2), Cl(1) and O(1) are non-planar. The Zn(II) ion deviates from the least-squares plane of the basal plane N(1)-N(2)-O(1)-O(1A) by 0.6942 Å. The N$_3^-$ ion is nearly linear with the N(3)-N(4)-N(5) angle of 159(10)º.

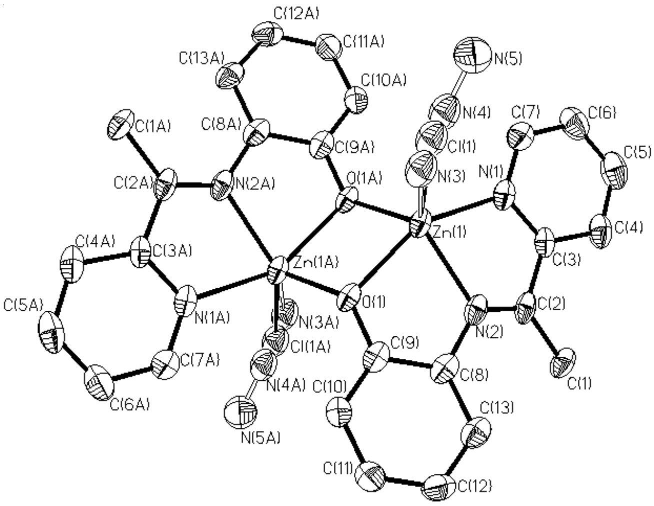


Fig. 1. Molecular structure of the title complex drawn at 30 % probability thermal ellipsoids. H atoms have been omitted for clarity. Symmetry code: (A) -x+1,-y,-z+1

Each tridentate Schiff ligand combines with one Zn(II) atom resulting in two five membered chelating rings. One five membered chelating ring consisting of atoms Zn(1), C(2), C(3), N(1), N(2) is planar, with mean deviation of 0.0426 Å. And another five membered chelating ring involving atoms C(8), C(9)7, N(2), O(1), Zn(1) is planar, confirmed by the mean deviation of 0.0850 Å. The two aromatic rings (phenyl and pyridine rings) in each ligand, N(1)/C(1)~C(6) and C(8)~C(13), make a dihedral angle of 16.83(4), indicating each ligand in the title complex is planar. The C(2)=N(2) bond length of 1.283(9) Å conforms to the value for a double bond.

In the crystal structure, dinuclear units are linked to form an infinite two-dimensional framework by hydrogen bondings (C(1)- H(1A)···O(1) 2.495(3) Å, symmetry code: -1/2+x, +y, 1/2-z) running along the a,b-axes, as shown in Fig. 2. Then the two-dimensional frameworks are further linked through another hydrogen bonding (C(7)-H(7)···N(5) 2.582(3) Å, symmetry code: 3/2-x, -1-y, 1/2+z) to generate a three-dimentional network (Fig. 3, Table- 2). These ineractions stabilized the conformation and packing of the present binuclear zinc(II) complex to give a polymeric arrangement in the solid state.

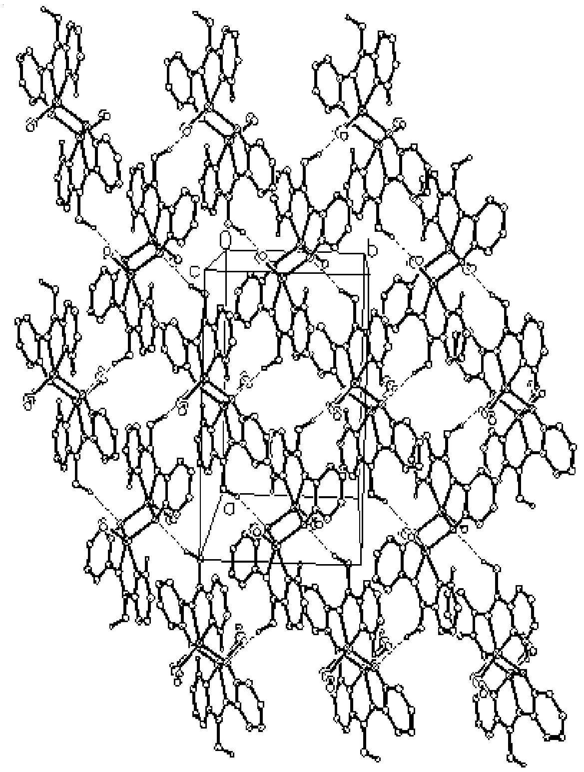


Fig. 2. Two-dimensional framework constructed by strong hydrogen bonds (Some hydrogen atoms are omitted for clarity)

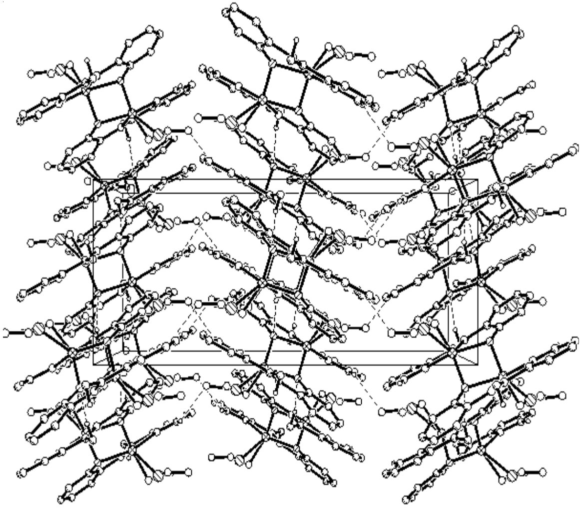


Fig. 3. A 3-D network structure of the complex viewed down the a-axis

Conclusion

In this work, a new three-dimensional supramolecular architecture of Zn(II)-Schiff base complex is successfully synthesized. Zinc(II) ion has a N_2O_2 donor set from tridentate Schiff base. The hydrogen bondings in complex stabilized the conformation and packing of the present complex to give a polymeric arrangement in the solid state and also linked the complex to construct a complicated supramolecule.

ACKNOWLEDGEMENTS

The work was supported by the Special Scientific Research Project of Shaanxi Education Commission (Project No. 2010JS069 and No. 09JS067)

REFERENCES

1. S.A. Schuetz, C.M. Silvernail, C.D. Incarvito, A.L. Rheingold, J.L. Clark, V.W. Day and J.A. Belot, *Inorg. Chem.*, **43**, 6203 (2004).
2. M. He, Q.F. Li, T. Xie, G.M. Xu, J. Yu and W. Li, *Chin. J. Struct. Chem.*, **29**, 582 (2010).
3. H. Liang, X.J. Wang, Y.L. Cong, S.T. Li and J.Q. Zeng, *Chin. J. Struct. Chem.*, **16**, 141 (1997).
4. W. Wang, F.X. Zhang, J. Li, H.X. Li, Y.Q. Huo and G.X. Du, *Acta Chim. Sin.,* **62**, 1529 (2004).
5. D.F. Xu, S.Z. Ma, G.Y. Du, Q.Z. He and D.Z. Sun, *J. Rare Earths*, **26**, 643 (2008).
6. X. Zhong, J. Yi, J. Sun, H.L. Wei, W.S. Liu and K.B. Yu, *Eur. J. Med. Chem.*, **41**, 1090 (2006).
7. H. Li, J.L. Huang and Y.L. Feng, *Chin. J. Struct. Chem.,* **28**, 718 (2009).
8. M.B. Dai, Q.L. Zhang, X.C. Zhu, Y.Q. Zhang and B.X. Zhu, *Chin. J. Inorg. Chem.*, **24**, 1381 (2008).
9. G.X. Du, H. Guo, H. Jiao, J.J. Liu and J. Li, *Acta Chim. Sin*. **65**, 2863 (2007).
10. A. Garoufis, S. Kasselouri, S. Boyatzis and C.P. Ratopoulou, *Polyhedron*, **18**,1615 (1999).
11. G.M. Sheldrick, SHELX-97. Program Package for Crystal Structure Solution and Refinement; University of Gottingen: Germany (1997).
12. Z.Q. Hu, S.M. Shi and H.W. He, *Chin. J. Inorg. Chem.*, **23**, 323 (2007).
13. X.H. Chen, Q.J. Wang and Z.Y. Liang, *Chin. J. Inorg. Chem.*, **25**, 910 (2009).