Synthesis, Crystal Structure, and Fluorescence of a Novel Trinuclear Zinc(II) Complex Derived from 2-Ethoxy-6-[(2-phenylaminoethylimino)methyl]phenol

Xiao-Ming Hu[a], **Ling-Wei Xue**[a,*], **Cai-Xia Zhang**[b], **Wei-Chun Yang**[a]

[a] College of Chemistry and Chemical Engineering, Pingdingshan University, Pingdingshan Henan 467000, P.R. China

[b] Coal Chemical Industry Branch of Shenhua Ningxia Coal Group, Yinchuan Ningxia 750411, P.R. China

* Corresponding author. E-mail: pdsuchemistry@163.com

Abstract

A novel trinuclear zinc(II) complex, $[Zn_3L_3(\mu_3\text{-}O)]\cdot ClO_4\cdot H_2O$, where L is the anionic form of 2-ethoxy-6-[(2-phenylaminoethylimino)methyl]phenol, has been synthesized and characterized by elemental analysis, FT-IR spectra, and single crystal X-ray determination. The crystal of the complex is cubic: space group $P2_13$, $a = b = c = 17.6479(2)$ Å, $V = 5496.4(1)$ Å^3, $Z = 4$, $R_1 = 0.0759$, $wR_2 = 0.1963$. The Zn···Zn distance is 3.134(1) Å. The Zn atom is coordinated by one imino N, one amino N, and two phenolate O atoms from the Schiff base ligand, and one bridging O atom, forming distorted trigonal-bipyramidal geometry. Fluorescence of the complex was also studied.

Keywords zinc complex, trinuclear complex, Schiff base, crystal structure, fluorescence

INTRODUCTION

Schiff bases are a kind of versatile ligands which have widely been used in coordination chemistry.[1–3] It has been shown that the Schiff base complexes derived from salicylaldehyde and its derivatives with primary amines, bearing the N_2O, N_2S, NO_2, or NSO donor sets, have interesting biological activity.[4–7] In addition, metal complexes with Schiff bases have also been widely studied for their catalytic properties of various organic reactions,[8-10] magnetic exchange materials,[11-13] as well as photoluminescence applications.[14-16] As an extension of work on the structures and photoluminescence of Schiff base complexes, in the present paper, a novel trinuclear zinc(II) complex, $[Zn_3L_3(\mu_3\text{-}O)]\cdot ClO_4\cdot H_2O$, where L is the anionic form of 2-ethoxy-6-[(2-phenylaminoethylimino)methyl]phenol (HL), has been prepared, characterized, and investigated for its luminescence property.

EXPERIMENTAL

Materials and methods

3-Ethoxysalicylaldehyde and *N*-phenylethane-1,2-diamine were purchased from Fluka. Other reagents and solvents were analytical grade and used without further purification. Zinc perchlorate was prepared by the reaction of perchloric acid with zinc carbonate in water. Elemental (C, H, and N) analyses were made on a Perkin-Elmer Model 240B automatic analyzer. IR spectra were recorded on an IR-408 Shimadzu 568 spectrophotometer. Luminescence was reported on a JASCO FP-6500 spectrofluorimeter (solid) in the range of 200–850 nm.

Synthesis of the complex

3-Ethoxysalicylaldehyde (0.1 mmol, 16.6 mg) and *N*-phenylethane-1,2-diamine (0.1 mmol, 13.6 mg) were reacted in methanol (10 mL). To the solution was added with stirring a methanolic solution (10 mL) of $Zn(ClO_4)_2 \cdot 7H_2O$ (0.1 mmol, 39.0 mg). The mixture was stirred at refluxed for 30 min to give a clear solution. The solution was left still at room temperature in air to give colorless block-shaped single crystals, which were collected by filtration and dried in air. The yield is 28.3 mg (72%). Elemental analysis found: C, 51.7; H, 5.1; N, 7.3%, $C_{51}H_{59}ClN_6O_{12}Zn_3$ calcd: C, 51.9; H, 5.0; N, 7.1%.

X-ray diffraction

Data were collected from a selected crystal mounted on a glass fiber. The data for the complex were processed with SAINT[17] and corrected for absorption using SADABS.[18] Multi-scan absorption corrections were applied with ψ scans.[19] The structure of the complex was solved by direct method using the SHELXS-97 program and refined by full-matrix least-squares techniques on F^2 using anisotropic displacement parameters.[20] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at the calculated positions. Crystallographic data for the complexes are listed in Table 1. Selected bond lengths and angles are given in Table 2.

RESULTS AND DISCUSSION

Reaction of the Schiff base ligand with zinc perchlorate in methanol affords the complex (Scheme 1). The complexes are soluble in DMF, DMSO, methanol, ethanol, and acetonitrile. We have attempted to grow diffraction quality crystals from various solvents. However, well-shaped single crystals suitable for X-ray diffraction were finally obtained from methanol.

Crystal structure description of the complex

The asymmetric unit of the complex contains a trinuclear $[Zn_3L_3(\mu_3\text{-}O)]^+$ cation (Fig. 1), a disordered perchlorate anion, and a disordered water molecule of crystallization. The trinuclear zinc complex cation has a crystallographic three-fold rotation axis symmetry, with the axis passing through the central O bridging atom. The Zn···Zn distance is 3.134(1) Å. The Schiff base ligands coordinate to the Zn atoms through phenolate O, imino N, and amino N atoms, forming a six- and a five-membered chelate rings with Zn atoms. Each Zn atom has a trigonal-bipyramidal coordination, with the equatorial atoms defined by one imino N atom of one Schiff base ligand, one phenolate O atom of another Schiff base ligand, and the bridging O atom, and with the two axial positions defined by the amino N and phenolate O atom of the Schiff base ligand. The three equatorial donor atoms show a high degree of planarity. The Zn1 atom deviates from the least-squares plane defined by the three equatorial donor atoms by 0.004(2) Å. The angular distortion in the trigonal-bipyramidal coordination comes from the bites O1A-Zn1-O4 (80.5(2)º), O1-Zn1-O4 (79.2(2)º) and O1-Zn1-N2 (80.8(5)º). The bond values related to the coordination are within normal ranges when compared to other zinc(II) complexes with Schiff bases.[21,22]

Infrared spectra

For the IR spectrum of the complex, the medium band centered at 3568 cm^{-1} can be assigned to O-H stretching vibrations of the disordered water molecule. The sharp band at 3283 cm^{-1} is clearly attributed to the N-H stretching vibrations. The strong band observed at 1635 cm^{-1} is assigned to the typical azomethine group vibration.[23] The intense absorption at 1090 cm^{-1} is aroused by the perchlorate anion.[24]

Fluorescence property

The fluorescence property of the complex was studied at room temperature (298 K) in the solid state. Figure 2 is the emission spectrum of the complex. The emission band of the complex is from 400 nm to 570 nm, with $\lambda_{max} = 453$ nm ($\lambda_{ex} = 360$ nm). For zinc(II) complexes, no emission originating from metal-centered MLCT/LMCT excited states are expected, since the Zn(II) ion is difficult to oxidize or reduce due to its stable d^{10} configuration. Thus, the emission observed in the complex is tentatively assigned to the π–π* intra-ligand fluorescence.[25]

SUPPLEMENTARY MATERIALS

CCDC-967474 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge at http://www.ccdc.cam.ac.uk/const/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

ACKNOWLEDGEMENTS

This research was supported by the National Sciences Foundation of China (No. 20676057 and 20877036) and Top-class foundation of Pingdingshan University (No. 2008010).

REFERENCES

1. Pradeep, C.P.; Das, S.K. Coordination and supramolecular aspects of the metal complexes of chiral N-salicyl-beta-amino alcohol Schiff base ligands: Towards understanding the roles of weak interactions in their catalytic reactions. *Coord. Chem. Rev.* **2013**, *257*, 1699-1715.
2. Ourari, A.; Aggoun, D.; Ouahab, L. A novel copper(II)-Schiff base complex containing pyrrole ring: Synthesis, characterization and its modified electrodes applied in oxidation of aliphatic alcohols. *Inorg. Chem. Commun.* **2013**, *33*, 118-124.
3. Ghosh, S.; Biswas, S.; Bauza, A.; Barcelo-Oliver, M.; Frontera, A.; Ghosh, A. Use of metalloligands [CuL] (H_2L = Salen type di-Schiff bases) in the formation of heterobinnetallic copper(II)-uranyl complexes: Photophysical investigations, structural variations, and theoretical calculations. *Inorg. Chem.* **2013**, *52*, 7508-7523.
4. Paiva, I.L.; de Carvalho, G.S.G.; da Silva, A.D.; Corbi, P.P.; Bergamini, F.R.G.; Formiga, A.L.B.; Diniz, R.; do Carmo, W.R.; Leite, C.Q.F.; Pavan, F.R.; Cuin, A. Silver(I) complexes with symmetrical Schiff bases: Synthesis, structural characterization, DFT studies and antimycobacterial assays. *Polyhedron* **2013**, *62*, 104-109.
5. Fleck, M.; Layek, M.; Saha, R.; Bandyopadhyay, D. Synthetic aspects, crystal structures and antibacterial activities of manganese(III) and cobalt(III) complexes containing a tetradentate Schiff base. *Transition Met. Chem.* **2013**, *38*, 715-724.
6. Farag, A.M.; Guan, T.S.; Osman, H.; Majid, A.M.S.A.; Iqbal, M.A.; Ahamed, M.B.K. Synthesis of metal(II) [M = Cu, Mn, Zn] Schiff base complexes and their Pro-apoptotic activity in liver tumor cells via caspase activation. *Med. Chem. Res.* **2013**, *22*, 4727-4736.

7. Lee, S.M.; Ali, H.M.; Sim, K.S.; Malek, S.N.A.; Lo, K.M. Synthesis, characterization and biological activity of diorganotin complexes with ONO terdentate Schiff base. *Inorg. Chim. Acta* **2013**, *406*, 272-278.
8. Banerjee, A.; Guha, A.; Adhikary, J.; Khan, A.; Manna, K.; Dey, S.; Zangrando, E.; Das, D. Dinuclear cobalt(II) complexes of Schiff-base compartmental ligands: Syntheses, crystal structure and bio-relevant catalytic activities. *Polyhedron* **2013**, *60*, 102-109.
9. Pasa, S.; Ocak, Y.S.; Temel, H.; Kilicoglu, T. Synthesis, characterization and catalytic behavior in the Suzuki reaction of Schiff base and its complexes and the optical properties of nickel complex used in the fabrication of a photodiode. *Inorg. Chim. Acta* **2013**, *405*, 493-504.
10. Pattanayak, P.; Pratihar, J.L.; Patra, D.; Brandao, P.; Mal, D.; Felix, V. Synthesis, crystal structure, spectral properties and catalytic activity of a binuclear copper(II) complex containing a Schiff base ligand. *Polyhedron* **2013**, *59*, 23-28.
11. Shit, S.; Nandy, M.; Rosair, G.; Gomez-Garcia, C.J.; Almenar, J.J.B.; Mitra, S. A ferromagnetically coupled single hydroxido bridged tetranuclear nickel(II) Schiff base complex incorporating a Ni4O4 cubane core: Crystal structure and magnetic study. *Polyhedron* **2013**, *61*, 73-79.
12. Puterova-Tokarova, Z.; Mrazova, V.; Boca, R. Magnetism of novel Schiff-base copper(II) complexes derived from aminoacids. *Polyhedron* **2013**, *61*, 87-93.
13. Shaabani, B.; Khandar, A.A.; Dusek, M.; Pojarova, M.; Mahmoudi, F.; Feher, A.; Kajnakova, M. Two coordination polymers based on semicarbazone Schiff base and azide:

synthesis, crystal structure, electrochemistry, magnetic properties and biological activity. *J. Coord. Chem.* **2013**, *66*, 748-762.

14. Feng, X.; Zhou, L.L.; Shi, Z.-Q.; Shang, J.-J.; Wu, X.-H.; Wang, L.-Y.; Zhou, J.-G. Synthesis, crystal structure, and luminescence property of a new zinc(II) complex with Schiff-base containing triazole propane ancillary ligand. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **2013**, *43*, 1093-1098.
15. Roy, S.; Sarkar, B.N.; Bhar, K.; Satapathi, S.; Mitra, P.; Ghosh, B.K. Syntheses, structures and luminescence behaviors of zinc(II) complexes containing a tetradentate Schiff base: Variation in nuclearity and geometry with the change of halide/pseudohalide/carboxylate and counter anion. *J. Mol. Struct.* **2013**, *1037*, 160-169.
16. Marinescu, G.; Madalan, A.M.; Tiseanu, C.; Andruh, M. New d(10) heterometallic coordination polymers based on compartmental Schiff-base ligands. Synthesis, structure and luminescence. *Polyhedron* **2011**, *30*, 1070-1075.
17. Bruker, SMART and SAINT. *Area Detector Control and Integration Software*; Bruker Analytical X-ray Instruments Inc.: Madison, WI, USA, **1997**.
18. Sheldrick, G. M. SADABS. *Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Göttingen, Germany, **1997**.
19. North, A. C. T.; Phillips, D. C.; Mathews, F. S. A semi-empirical method of absorption correction. *Acta Crystallogr.*, **1968**, *A24*, 351-359.
20. Sheldrick, G. M. SHELXL-97. *Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, **1997**.

21. Tandon, S.S.; Chander, S.; Thompson, L.K. Ligating properties of tridentate Schiff base ligands, 2-[[(2-pyridinylmethyl)imino]methyl] phenol (HSALIMP) and 2-[[[2-(2-pyridinyl)ethyl]imino]methyl]phenol (HSALIEP) with zinc(II), cadmium(II), nickel(II) and manganese(III) ions. X-ray crystal structures of the $[Zn(SALIEP)(NO_3)]_2$ dimer, $[Mn(SALIEP)_2](ClO_4)$, and $[Zn(AMP)_2(NO_3)_2]$. *Inorg. Chim. Acta* **2000**, *300*, 683-692.

22. Garcia-Raso, A.; Fiol, J.J.; Lopez-Zafra, A.; Mata, I.; Espinosa, E. Synthesis of ZnN-salicylidene-L-aminoacidatos: X-ray structure of [(N-salicylidene-L-alaninato) (aqua)zinc(II)]$\cdot 0.25H_2O$ and [(N-salicylidene-L-valinato) (aqua)zinc(II)]. *Polyhedron* **2000**, *19*, 673-680.

23. Lal, R.A.; Choudhury, S.; Ahmed, A.; Chakraborty, M.; Thakur, R.B.; Kumar, A. Synthesis and spectral studies of nickel(II) complexes derived from disalicylaldehyde oxaloyldihydrazone. *J. Coord. Chem.* **2009**, *62*, 3864-3874.

24. Qian, J.; Tian, J.-L.; Feng, L.; Gu, W.; Zhao, X.-J.; Yan, S.-P. Syntheses, structures, and spectroscopic properties of binuclear copper(II) complexes containing N,N-bis(2-pyridylmethyl)amine ligands. *J. Coord. Chem.* **2009**, *62*, 3276-3283.

25. Das, D.; Chand, B.G.; Sarker, K.K.; Dinda, J.; Sinha, C. Zn(II)-azide complexes of diimine and azoimine functions: Synthesis, spectra and X-ray structures. *Polyhedron*, **2006**, *25*, 2333-2340.

TABLE 1

Crystal and structure refinement data for the complex

Molecular formula	$C_{51}H_{57}ClN_6O_{12}Zn_3$
Molecular weight	1177.6
Crystal system	Cubic
Space group	$P2_13$
a /Å	17.6479(2)
b /Å	17.6479(2)
c /Å	17.6479(2)
V / ´ ^{3}	5496.4(1)
Z	4
D_{calc} (g cm^{-3})	1.423
Crystal dimensions (mm)	0.20 × 0.20 × 0.18
μ (mm^{-1})	1.411
F000	2432
Radiation λ	Mo Kα (0.71073 ´)
T_{min}/T_{max}	0.7656/0.7853
Reflections measured	27586
Range/indices (h, k, l)	-20, 20; -19, 20; -20, 18
θ limit (°)	1.63–24.65
Unique reflections	3087 [R_{int} = 0.0532]

Observed reflections ($I > 2\sigma(I)$)	2143
Parameters	242
Restraints	64
Goodness of fit on F^2	1.062
R_1, wR_2 [$I \geq 2\sigma(I)$][a]	0.0759, 0.1963
R_1, wR_2 (all data)[a]	0.1101, 0.2385

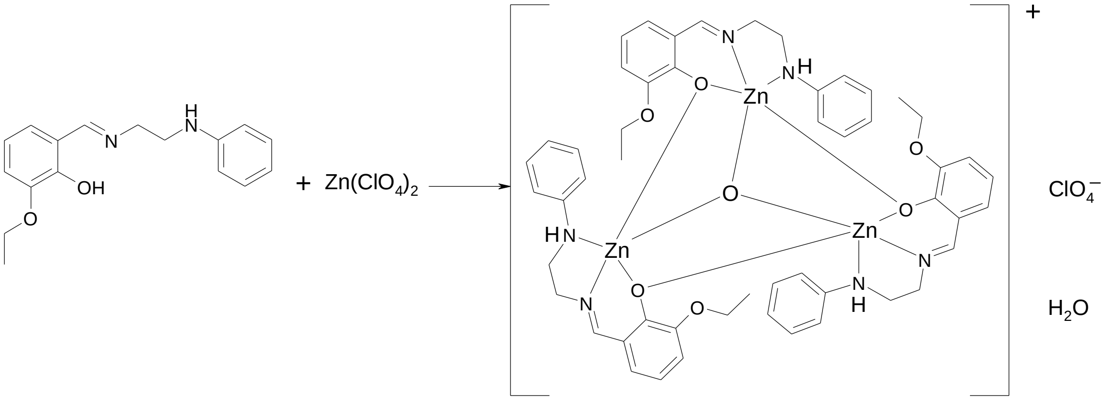
[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

TABLE 2

Selected bond lengths (Å) and angles (°) for the complex

Bond lengths			
Zn1-O1A	1.972(6)	Zn1-N1	1.995(11)
Zn1-O1	2.028(6)	Zn1-O4	2.094(5)
Zn1-N2	2.260(13)		
Bond angles			
O1A-Zn1-N1	139.3(4)	O1A-Zn1-O1	102.7(4)
N1-Zn1-O1	89.2(4)	O1A-Zn1-O4	80.5(2)
N1-Zn1-O4	140.1(4)	O1-Zn1-O4	79.2(2)
O1A-Zn1-N2	101.3(4)	N1-Zn1-N2	80.8(5)
O1-Zn1-N2	152.8(4)	O4-Zn1-N2	92.4(4)

Symmetry operation to generate related atoms: A: 3/2 – *z*, 1 – *x*, 1/2 + *y*.



SCH. 1. The preparation of the complex.

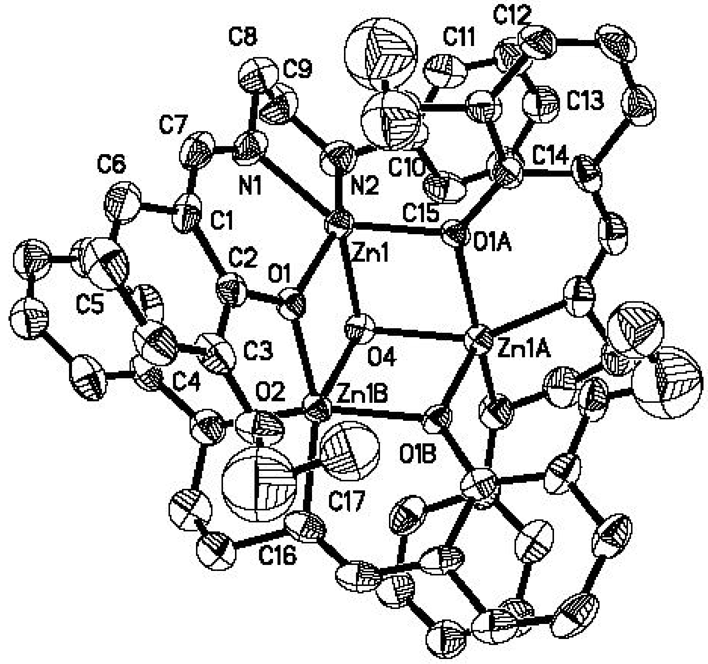


FIG. 1. Molecular structure of the complex at 30% probability displacement. Atoms labeled with the suffix A and B are at the symmetry operations 3/2 – *z*, 1 – *x*, 1/2 + *y* and 1 – *y*, –1/2 + *z*, 3/2 – *x*, respectively.

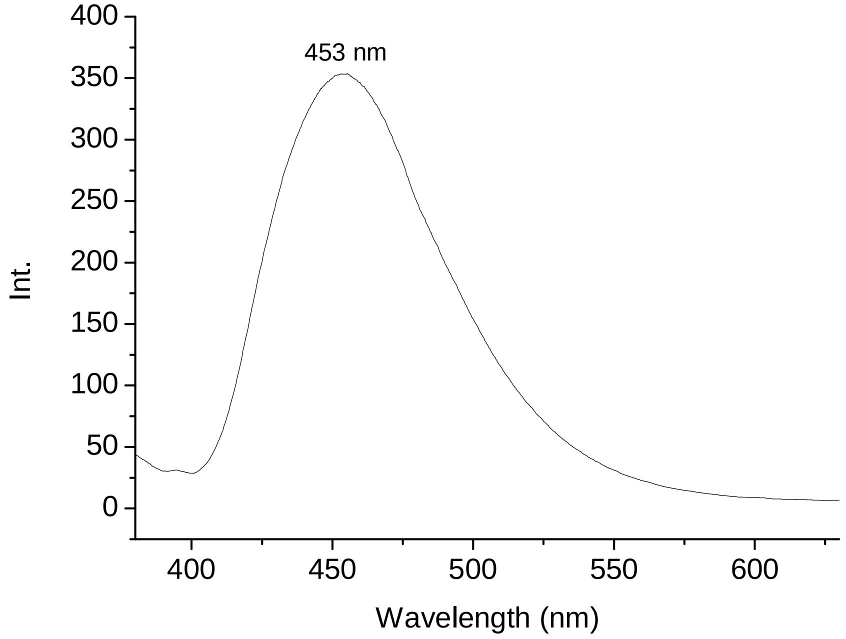


FIG. 2. Emission spectrum of the complex.