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Synthesis, Crystal Structure, and Fluorescence Properties of Dinuclear and Tetranuclear Zinc(II) Complexes Based on 2-(2'-Hydroxyphenyl)-2-oxazoline

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Abstract: *Two new zinc(II) complexes have been prepared by reaction of 2-(2'-Hydroxyphenyl)-2-oxazoline(Hoz) with Zn(acac)2 and ZnCl2 respectively. The complexes are characterized by IR and X-ray crystallography. Complex 1 is dinuclear zinc structure bridged by the oxygen atoms from oz- ligand and acac- ligand as terminal chelating ligand. Complex 2 is tetranuclear zinc structure bridged by both μ2-oxygen from oz- ligand and μ3-methoxide. 1 crystalizes in P21 space group with crystallographic parameters: a=9.3842Å19), b=13.5840 Å30), c=11.1380 Å20), β=96.250°(30). 2 crystalizes in P-1 space group with crystallographic parameters: a=9.5517Å(19), b=11.1234Å(22), c=11.1826Å(22), α=102.820°(30), β=114.988°(30), γ=100.806°(30). The UV absorption and fluorescence emission spectra are measured on the methanol solution and solid state of complex 1 and it shows strong luminescence.*

Keywords: 2-(2'-Hydroxyphenyl)-2-oxazoline, Dinuclear metal complex, Tetranuclear metal complex, Crystal structure

1. INTRODUCTION

Complexes formed by transition metals with d^{10} electronic structure and organic molecules exhibit interesting luminescent properties[1]. A complex that consists of a metal with a d^0 or d^{10} electronic structure exhibits luminescence because of $\pi\rightarrow\pi^{*}$ or $n\rightarrow\pi^{*}$ electronic transitions in a ligand[2]. However, a corresponding free ligand does not exhibit strong photoluminescence in the visible range[3]. Moreover, quantum yield of fluorescence is extremely low[4] in this region. Stiffness and stability of molecules increase when a molecule complexes with a metal ion[5]. During a radiation jump, energy dissipation free of ration is decreased and luminescence effect is enhanced. Compounds with d^0 or d^{10} metals[6] that exhibit fluorescence are mainly complexes of aluminum(III), boron(III), zinc(II), cadmium(II), and copper(I) with eight oxychinolin derivatives, including azaindole, bipyridine, amino pyridine, Schiff base, and bi-N_2 thiazole derivatives[7]. These complexes usually have mononuclear or multinuclear structures that can form films by vacuum evaporation. Moreover, these complexes are widely used in organic light-emitting diode elements. These substances exhibit excellent electronic transfer properties[7], and they emit light bands ranging from blue to green. Therefore, these complexes are often used as materials for electronic transfer, blue and green light, and chief luminescence in doped light-emitting diode elements[8]. However, different products with similar components but different structures may be generated because of different reaction conditions during the syntheses of complexes[9]. For instance, three (eight-oxychinolin) aluminum complexes form meridian and face structures. In addition[10], different mononuclear and multinuclear complexes that have similar metal ions and ligand ratio, such as mononuclear complex of $Zn(BTZ)_2$ [bis(2-(2-hydroxy- phenyl)benzothiazolate)zinc] and dinuclear complex of $[Zn_2(BTZ)_4]$[11][12] can also be formed. These isomers exhibit different luminescence and electronic transfer properties; thus, synthesis routes of these complexes should be investigated. In addition, special reaction conditions are necessary to produce complex materials of high purity. In a previous work , we reported the luminescence properties of a $Zn_2(oz\ )_4$ dinuclear molecule. Results showed that this molecule exhibits excellent electronic transfer and produces bright blue light when used as a light-emitting diode element[13]. As an extension of our previous

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work, 2-(2'-hydroxyphenyl)-2-oxazoline (Hoz) was used as ligand in this study. This ligand was allowed to react with Zn acetylacetonate [Zn(acac)2] and $ZnCl_2$[14]; a dinuclear zinc complex 1 $[Zn(oz)(acac)]_2$ and a tetranuclear zinc complex 2 $[Zn_4(oz)_4(CH3O)_2Cl_2]$ were synthesized. Reaction conditions, structures of multinuclear complexes formed by the Hoz ligand, and different Zn salts were investigated[15]. The UV absorption and fluorescence emission spectra of the dinuclear complex were also examined.

2. EXPERIMENTAL

2.1. Materials and instruments

All of the reagents were purchased from Alfa-Aesar Company. The Hoz ligands were synthesized in accordance with a procedure described in a previous study[16]. The test instruments used included a Carlo Erballo-type instrument for chemical element analysis (Germany), ECTOR22 Fourier transform infrared spectrophotometer (FT-IR, Nicolet, USA), RINT2000 diffractometer (Cu-Kα, RIGAKU, Japan), 8453 UV–visible spectrophotometer (Agilent, USA), and a FLS920 steady and transient fluorescence spectroscope (Edinburgh Instruments Ltd., England)[17].

2.2. Synthesis of complexes

2.2.1. Synthesis of $[Zn(oz)(acac)]_2$, dinuclear complex 1

An equimolar concentration of triethylamine was added to 20 mL of methanol (MeOH) solution containing 1 mmol of Hoz. The resulting solution was filtered and stored under static conditions. A large number of colorless crystals formed in the solution after 2 d of storage[18]. The chemical elements present in the molecule showed the following composition (%): $C_{28}H_{30}N_2O_8Zn_2$ (653.28); the calculated results are C (51.69), H (4.65), and N (4.31); and the measured values are C (52.41), H (4.71), and N (4.27).

FTIR results (KBr, cm^{-1}): 3436 (m), 2981 (w), 2912 (w), 1631 (s), 1600 (s), 1551 (m), 1520 (s), 1477 (m), 1442 (m), 1400 (s), 1323 (m), 1157 (m), 1072 (m), 1018 (w), 949 (w), 930 (m), 845 (m), 760 (m), 690 (m), 578 (w), and 536 (w).

2.2.2. Synthesis of $[Zn_4(oz)_4(CH_3\ Os)_2Cls_2]$, tetranuclear complex 2

An equimolar concentration of NaOH was added to 20 mL of MeOH solution containing 1 mmol of Hoz. The resulting solution was stirred for 1 h, and then 5 mL of MeOH solution containing 1 mmol of $ZnCl_2$ was added to the solution[19]. The white precipitates that formed in the solution were removed by filtration, and the solution was stored in static conditions. A large number of colorless crystals formed after 7 d of storage[20]. The chemical elements present in the sample showed the following composition (%): $C_{38}H_{38}N_4O_{10}Cl_2Zn_4$ (1035.91); the calculated results are C (44.02), H (3.70), N (5.41); and the measured values are C 44.11, H 3.66, and N (5.35)[21].

FTIR (KBr, cm^{-1}): 2980 (w), 2908 (w), 2890 (w), 1627 (s), 1554 (m), 1537 (m), 1470 (s), 1443 (m), 1389 (m), 1359 (m), 1323 (m), 1234 (m),1159 (m),1139 (m), 1066 (m), 950 (w), 930 (m), 850 (m), 780 (m), and 690 (m).

2.3. Measurement of crystal structure

A crystal of proper size was selected, and its structure was analyzed using a Nonius Kappa CCD surface detector. Single-crystal diffraction data were then collected. All of the structures were analyzed by direct and heavy-atom methods. The results obtained were modified via a SHELX 97 program based on F^2 full matrix least-squares technique[15]. The crystal data of complexes 1 and 2 are shown in Table 1.

3. RESULTS AND DISCUSSION

3.1. Crystal structure description

Complex 1 exhibited a dinuclear structure (Fig. 1). The O_2 atoms of oz in the phenolic hydroxyl group served as a bridge that con-

Table 1. Crystal data for complexes 1 and 2[5].

Formula	1 C28H30N2O8Zn2	2 C38H38N4O10Cl2Zn4
MR	653.28	1043.17
λ[Å]	0.71073	0.71073
T[K]	293(2)	293(2)
Crystal system	Monoclinic	Triclinic
Space group	P21	P1a
a[Å]	9.3842(19)	9.5517(19)
b[Å]	13.584(3)	11.123(2)
c[Å]	11.138(2)	11.183(2)
α[°]	90	102.82(3)
β[°]	96.25(3)	114.99(3)
γ[°]	90	100.81(3)
V[Å3]	1411.4(5)	995.5(3)
Z	2	2
Reflections collected	6164	8158
Independent reflections	6164	4313
Refinement method	Full-matrix least-aquares on F2	Full-matrix least-aquares on F2
Parameters	362	263
Goodness-of-fit	1.027	0.970
Final R indices[I>2σ(I)]	R1=0.0507,wR2=0.1317	R1=0.0402,wR2=0.0854
Largest diff. Peak:hole[eÅ-3]	0.340/-0.394	0.373/-0.333

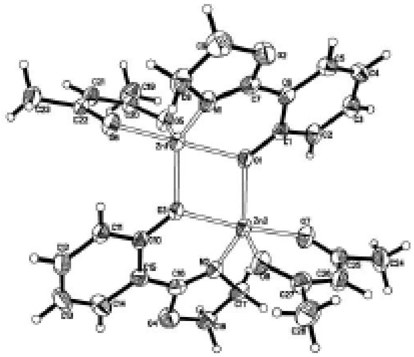

Figure 1. Dinuclear structure of complex 1.

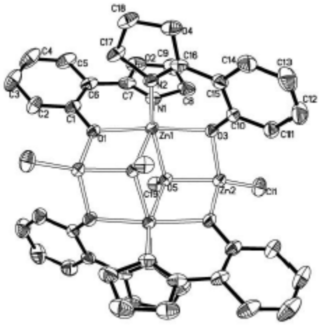

Figure 2. Tetranuclear structure of complex 2

nected the two Zn ions. Meanwhile, the acac anion behaved as a terminal group of the chelating ligand[22]. The two Zn ions in the dinuclear molecule were independent of each other in crystallography . Both of these ions contained five coordinates that assumed a trigonal bipyramidal structure[20]. The lengths of the bonds present in Zn–Ooz were 2.005, 2.108, 2.100, and 2.115 . Meanwhile, the lengths of the bonds present in Zn–Oacac were slightly smaller than those of Zn–Ooz, which were 1.984, 1.985, 2.027, and 2.046. Packing of the crystal structure of complex 1 was analyzed. The result showed that π–π stacking of oz existed between the adjacent dinuclear molecules (d = 3.67).

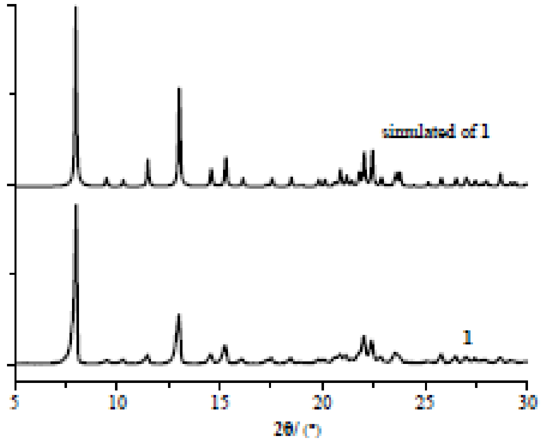

Figure 3. XRD spectrum of complex 1 and its simulated spectrum.

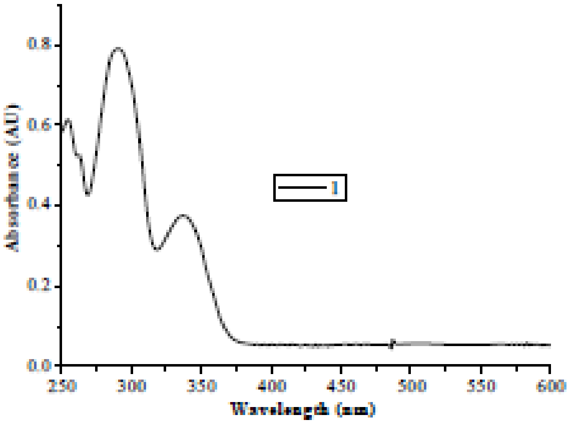

Figure 4. UV–vis spectrum of complex 1 in MeOH.

Complex 2 was different from complex 1 because complex 2 exhibited a tetranuclear structure (Fig. 2). The independent units of the complex contained two Zn ions with different coordination environments, namely, Zn (1) and Zn (2). Zn (1) was located in an octahedral coordination environment that was formed by methoxyl and phenolic hydroxyl groups and N_2 atoms of oz. Zn (2) was present in a tetrahedral coordination environment composed of methoxyl, phenolic hydroxyl group of oz, and chloride (Cl^{-1}) ions [23]. These two independent Zn ions formed a tetranuclear structure that was similar to a coplanar missing-angle double cubane by symmetry-related effects. The O_2 atoms of the phenolic hydroxyl group in the ligand served as a μ_2 bridge, and O_2 atoms of the methoxyl group behaved as a μ_3 bridge. Meanwhile, the Cl^{-1} ions served as terminal groups; therefore, a neutral tetranuclear molecule was formed. The lengths of the Zn–O bonds in the octahedral coordination environment were ~2.1 [Zn(1)–O(5)=2.115, Zn(1)–O(1)=2.118, Zn(1)–O(3)=2.131, Zn(1)–O(5A)=2.181] . In addition, the lengths of the Zn–O bonds in the tetrahedral coordination environment were small (i.e., ~2.0) [Zn(2)–O(1A)=1.963, Zn(2)–O(5)=1.980, Zn(2)–O(3)=1.982] . In this study, the interactions of different molecules were investigated by analyzing the packing in a crystal structure. The results showed that different tetranuclear molecules formed a three-dimensional supramolecular structure via H_2 bond.

3.2. XRD analysis

Sample 1 powder was prepared at room temperature and was subjected to XRD analysis. The data obtained from the experiments were compared with the fitting results provided by an XRD software. Comparison was performed according to the crystal structures formed. The diffraction peaks obtained from the experimental data agreed well with those provided by the fitting data. This result, together with other test results obtained, indicates that sample 1 was highly pure.

3.3. UV–vis absorption spectrum

The UV–vis absorption spectra of complex 1 were obtained at

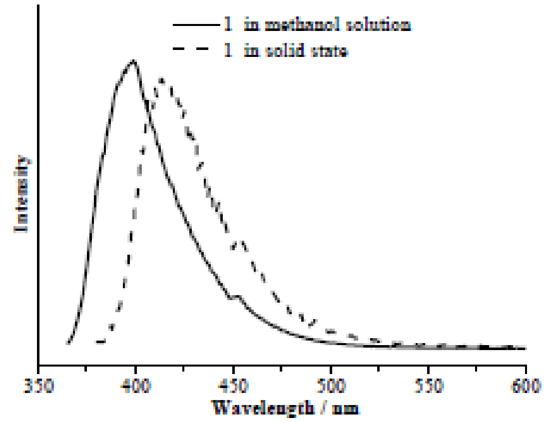

Figure 5. Fluorescence spectrum of complexes 1 and 2 in MeOH.

room temperature. MeOH was used as solvent in this analysis. As shown in Fig. 4, three obvious absorption peaks between 250 and 400 nm are present. The strongest peak is observed at 290 nm, whereas the second strongest peak is at 254 nm. The third peak is present at 337 nm. By comparing the spectra obtained in this study with those of Zn(acac)$_2$ reported in previous studies, the presence of peaks at 254 and 285 nm were attributed to the π–π* transitions of the acac ligand[24]. The absorption peak at 337 nm was due to the π–π* transitions of the oz ligand.

3.4. Fluorescence spectrum

The excitation wavelengths employed were 362 and 369 nm. The fluorescence spectra of sample 1 in a MeOH solution and a solid-state sample were obtained. As shown in Fig. 5, the [Zn(oz)(acac)]$_2$ in a MeOH solution exhibits a strong emission peak at 399 nm; however, the strongest emission exhibited by the solid-state sample was at 413 nm. According to our previous report, the strongest emission peak of the [Zn$_2$(oz)$_4$] in MeOH solution [Zn$_2$(oz)$_4$] is at 404 nm and that of the solid sample is located at 415 nm[21]. By comparing these two results, the emission spectra of [Zn(oz)(acac)]2 showed only a small blueshift.

4. CONCLUSIONS

In this study, dinuclear and tetranuclear complexes with novel structures were synthesized. These complexes were prepared by reacting Hoz with Zn(acac)$_2$ and ZnCl$_2$. Complex 1 was synthesized using Zn(acac)$_2$ as the reactant. A dinuclear complex with acac anions as terminal ligands was formed because of the strong chelating effect of acac with Zn ion. The synthesis of complex 2 involved the removal of Hoz protons using NaOH. A methoxy anion formed as a μ_3 O_2 bridge because of the strong alkalinity exhibited by NaOH. Therefore, when NaOH is used to remove the protons of Hoz zinc, a methoxy group is introduced as a ligand. The anions of the Zn salt, such as acac or Cl^{-1} ions, in the reactants were easily introduced as terminal ligands in the product. The adsorption peaks of acac and oz ligands were present in the UV–vis spectra of complex 1 in solution. The spectrum of the solid-state sample was similar to the emission spectrum of [Zn$_2$(oz)$_4$]; these observed emissions were induced by the π–π* transitions of the oz ligand. Various polynuclear complexes with diverse structures can be produced during the synthesis of a Hoz Zn complex by varying the reactants and using an alkaline substance. In this study, the obtained dinuclear complexes exhibited similar spectral properties with [Zn$_2$(oz)$_4$].

REFERENCES

[1] Yang W, Schmider W, Zang YS, et al., J. Inorg. Chem., 39, 2397 (2000).
[2] Iván B, Javier V, Cárdenas A,et al., J. Inorganic Chemistry Communications, 14, 897 (2011).
[3] Aslanidis P, Cox P, Kapetangiannis K, et al., J. Eur. J. Inorg. Chem., 32, 5029 (2008).
[4] Sabin F, Ryu CK, Ford PC, et al., J. Inorg. Chem., 31, 1941 (1992).
[5] Cöle M, Dinnebier RE, Brütting W., J. Chem. Commun., 23, 2908 (2002).
[6] Wu QG, Esteghamatian M, Hu NX, et al., J. Chem. Mater., 12, 79(2000).
[7] Hassan A, Wang SN., J. Chem. Commun., 211 (1998).
[8] Ma YG, Chao HY, Wu Y, et al., J. Chem. Commun., 22, 2491 (1998).
[9] Wang G, Zhang YG, Cheng YX, et al., J. Synthetic Met., 137, 1119 (2003).
[10]Zhang LY, Liu GF, Zheng SL, et al., J. Eur. J. Inorg. Chem., 16, 2965 (2003).
[11]Jing J, Chen JJ, Hai Y, et al., J. Chem. Sci., 3, 3315 (2012).
[12]Yu G, Yin SW, Liu YQ, et al., J. Am. Chem. Soc., 125, 14816 (2003).
[13]Zhang J, Gao S, and Che CM., J. Eur. J. Inorg. Chem., 5, 956 (2004).
[14]Cwik A, Hell Z, Hegedüs A, et al., J. Tetrahedron Letters, 43, 3985 (2002).
[15]Yang X L, Xie M H, Zou C, et. al., J. Am. Chem. Soc., 134, 10638 (2012).
[16]Xu G, Yamada T, Otsubo K, et. al., J. Am. Chem. Soc., 134, 16524 (2012).
[17]Johnson J A, Lin Q, Wu L C, et. al., Chem. Commun., 49, 2828 (2013).
[18]Lvova L, Galloni P, Floris B, et. al., Sensors, 13, 5841 (2013).
[19]Zhang J L, Che C M, Organic Letters, 4, 1911 (2002).
[20]Moore G F, Konezny S J, Song H E, et.al., J. Phys. Chem. C, 116, 4892 (2012).
[21]Meng L, Cheng Q G, Kim C, et. al., Angew. Chem. Int. Ed., 51, 10082 (2012).
[22]Matsunaga S, Endo N, Mori W., Eur. J. Inorg. Chem., 4550 (2011)
[23]Choi E Y, Wray C A, Hu C, et. al., Cryst Eng Comm., 11, 553 (2009).
[24]Wang X S, Chrzanowski M, Gao W Y, et. al. Chem. Sci., 3, 2823 (2012).

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