ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 12, pp. 874–878. © Pleiades Publishing, Ltd., 2009.

Synthesis, Crystal Structure, and Photoluminescence of Zinc Complex $[Zn(Qina)_2(DMSO)_2] \cdot 2DMSO$[1]

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Received March 23, 2009

Abstract—A novel complex $[Zn(Qina)_2(DMSO)_2] \cdot 2DMSO$ (**I**) (Qina = quinaldic acid, DMSO = dimethyl sulfoxide) has been synthesized and characterized by X-ray diffraction, elementary analysis, and IR spectrum. The unit cell parameters for complex **I**: a = 8.2884(11), b = 22.015(3), c = 9.0685(12) Å, β = 100.61(0)°, V = 1626.41(40) Å^3, Z = 2, space group, $P2_1/n$. In the complex **I**, the Zn(II) atom was six-coordinated to form a distorted octahedral geometry by two Qina ligands and two dimethyl sulfoxide molecules. The crystal structure is stabilized by hydrogen bonds, C–H···π, π–π stacking interaction between adjacent complexes. The binding of the complex **I** with calf thymus DNA has been investigated by fluorescence spectroscopic studies. The result suggested that the complex intercalates into DNA base pairs.

DOI: 10.1134/S1070328409120021

INTRODUCTION

In recent years, inorganic-organic hybrid crystal engineering has captured the interest of researchers [1–5]. The crystal structures mainly depend on both the metal ions and ligands. However, the complexes with the same ion and ligand may form different structures in diverse coordination under different chemical environments [6, 7]. Quinaldine acid (**Qina**) is structurally similar to picolinic acid and pipecolinic acid, which has potentially three coordination sites, two oxygens of carboxylate groups, and pyridinic nitrogen, displaying many different coordinate modes with central metal ions. We and other teams synthesized and structurally characterized a series of transition metal complexes with these ligands and found that the ligands have single coordination mode, chelating to central ions by carboxylate and pyridinic nitrogen [8–12]. To date four zinc(II) quinaldic acid complexes were obtained and characterized by structural and spectroscopic study: [Zn(MEDA)(Qina)] (MEDA = N-(2-mercaptoethyl)picolylamine) [13], $[Zn(Qina)_2(1\text{-MeIm})_2]$ (MeIm = 1-methylimidazole) [14], $[Zn(Qina)_2(H_2O)_2]$ [15], and $[Zn(Qina)_2(HIm)_2]$ (HIm = imidazole) [16]. In continuation of our interest in the systhesis, characterization, and biological activity of zinc(II) quinaldic acid complexes, we have synthesized $[Zn(Qina)_2(DMSO)_2] \cdot 2DMSO$ (**I**) (DMSO = dimethyl sulfoxide) and investigated its crystal structure. In this mononuclear complex, Zn^{2+} ion is six coordinition and Qina binds to zinc in a chelate mode by carboxylate O atom and the Qina N atom. Interestingly, a solvent molecule DMSO was dissociative in disorder [17, 18]. Intramolecular weak interaction, such as hydrogen bonds, C–H···π, and π–π stacking, was found in complex **I**, 3D supramolecular framework was constructed by intermolecular weak interaction mentioned above.

EXPERIMENTAL

Materials and measurements. All chemicals were of reagent grade and purchased from commercial vendors. They were used as purchased without further purification unless otherwise noted. Calf thymus DNA (**CT-DNA**) (Huamei Co.) and ethidium bromide (**EB**) (Fluka, Switzerland). Other chemicals used were of analytical reagent or high purity grade.

Synthesis of complex I. The mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.1 mmol), and Qina (0.2 mmol) was stirring evenly. A KOH solution (0.5 mol/l) was added to adjust pH value to 7.17. After 3 h stirring, remove the above clear solution, leaving the precipitation to be dissolved in 30 ml of DMSO–H_2O ($V_{DMSO} : V_{H_2O} = 2 : 1$) mixed solvent. Colorless transparent crystals were obtained after one week.

For $C_{28}H_{36}N_2O_8S_4Zn$			
anal. calcd, %:	C, 46.57;	H, 5.02;	N, 3.89.
Found, %:	C, 46.93;	H, 5.31;	N, 3.56.

IR spectrum (ν, cm^{-1}): 3421 w, 3060 w, 1632 s, 1565 m, 1511 w, 1463 w, 1385 s, 1268 w, 1216 w, 1162 w, 806 m, 776 m, 636 w, 605 w.

X-ray structure determination. A crystal **I** with dimensions of 0.37 × 0.3 × 0.12 mm was put on a Bruker

[1] The article is published in the original.

Table 1. Crystal data and structure refinement for complex **I**

Parameter	Value
Temperature, K	273(2)
Formula weight	722.20
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	8.2884(11)
b, Å	22.015(3)
c, Å	9.0685(12)
β, deg	100.613(2)
V, Å^3	1626.4(4)
Z	2
ρ_{calcd}, g/cm^3	1.475
Absorption coefficient, mm^{-1}	1.061
F(000)	752
Crystal size, mm^3	0.37 × 0.32 × 0.12
θ range for data collection, deg	1.85–26.04
Index ranges	$-10 \le h \le 10$, $-25 \le k \le 27$, $-5 \le l \le 11$
Reflections collected/unique	3205/2801
Refined parameters	184
Goodness-of-fit on F^2	1.027
Final R indices ($I > 2\sigma(I)$)	0.0604
R indices (all data)	0.0674

Table 2. Selected bond lengths and bond angles for complex **I**

Bond	d, Å	Bond	d, Å
Zn(1)–O(1)	2.010(3)	C(14)–S(2)	1.783(5)
Zn(1)–N(1)	2.219(3)	O(3)–S(2)	1.511(3)
Zn(1)–O(3)	2.232(3)	S(1)'–C(12)'	1.422(14)
C(1)–C(2)	1.410(5)	S(1)'–C(11)'	1.493(13)
C(1)–C(10)	1.522(5)	S(1)'–O(4)	1.663(12)
C(2)–C(3)	1.355(6)	C(9)–N(1)	1.373(5)
C(3)–C(4)	1.416(6)	C(10)–O(2)	1.230(5)
C(4)–C(5)	1.415(6)	C(10)–O(1)	1.265(4)
C(4)–C(9)	1.428(5)	C(13)–S(2)	1.775(5)
C(5)–C(6)	1.356(6)	S(1)–C(12)	1.456(11)
C(6)–C(7)	1.412(6)	S(1)–C(11)	1.535(28)
C(7)–C(8)	1.369(6)	S(1)–O(4)	1.733(12)
C(8)–C(9)	1.403(5)		
Angle	ω, deg	Angle	ω, deg
O(1)Zn(1)N(1)	78.79(10)	O(1)Zn(1)O(3)	90.76(11)

SMART 1000 CCD diffractometer equipped with a graphite-monochromatic MoK_a radiation (λ = 0.71073 Å) by using an ω-2θ scan mode. Corrections for Lp factors and empirical adsorption were applied. Out of the 9038 total reflections collected in the range of 1.85° ≤ θ ≤ 26.04°, 3205 were independent with R_{int} = 0.0267, of which 2801 were considered to be observed ($I > 2\sigma(I)$) and used in the succeeding refinements. The structure was solved by direct methods using SHELXS-97 program [19, 20]. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were located at the theoretical positions. The crystallographic details are listed in Table 1, selected bond lengths and angles – in Table 2.

The atomic coordinates and other parameters of structure I have been deposited with the Cambridge Crystallographic Data Center (no. 660409; deposit@ccdc.cam.ac.uk).

Physical measurements. Elemental analysis (C, H, and N) were performed on a model Finnigan EA 1112. IR spectrum was recorded on a Nicolet IR-470 spectrophotometer using KBr pellets in the 4000–400 cm^{-1} region. Fluorescence quenching experimental were conducted by adding complex **I** to solutions of DNA-EB in 50 mM NaCl/10 mM Tris-HCl at pH 7.2 (where Tris is tris(hydroxymethyl)aminomethane). Fluorescence survey was performed on a Perkin Elmer LS55 fluorescence spectrofluorometer.

RESULTS AND DISCUSSION

The X-ray crystal structure of centrosymmetric complex **I** reveals that the coordination number of Zn^{2+} ion is six distorted octahedral geometry (Fig. 1). Two Qina-ligands coordinate to the central Zn^{2+} ion with

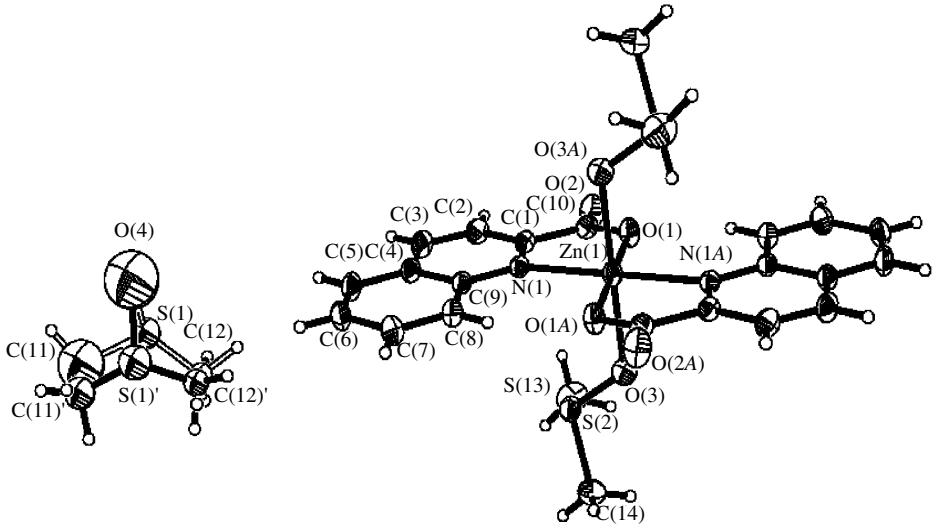

Fig. 1. Molecular structure of $[Zn(Qina)_2(DMSO)_2] \cdot 2DMSO$.

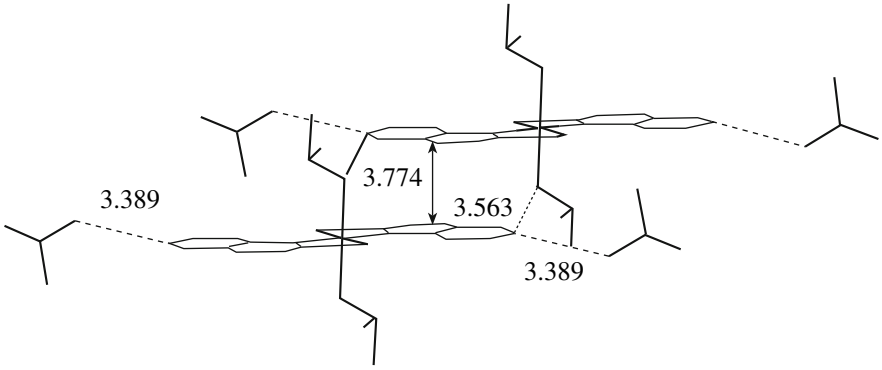

Fig. 2. C–H···π bonding, π–π stacking, hydrogen bonding interactions of intermolecular (hydrogen atoms are omitted for clarity).

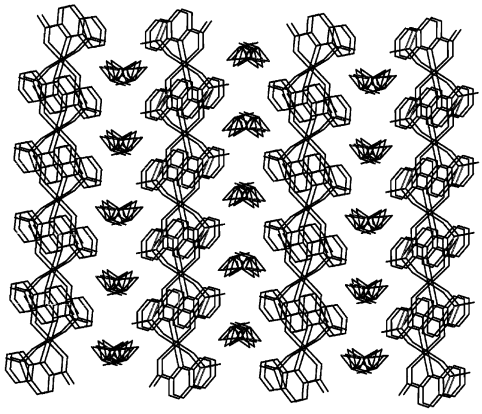

Fig. 3. Three-dimensional structure of the complex $[Zn(Qina)_2(DMSO)_2] \cdot 2DMSO$ (hydrogen atoms are omitted for clarity).

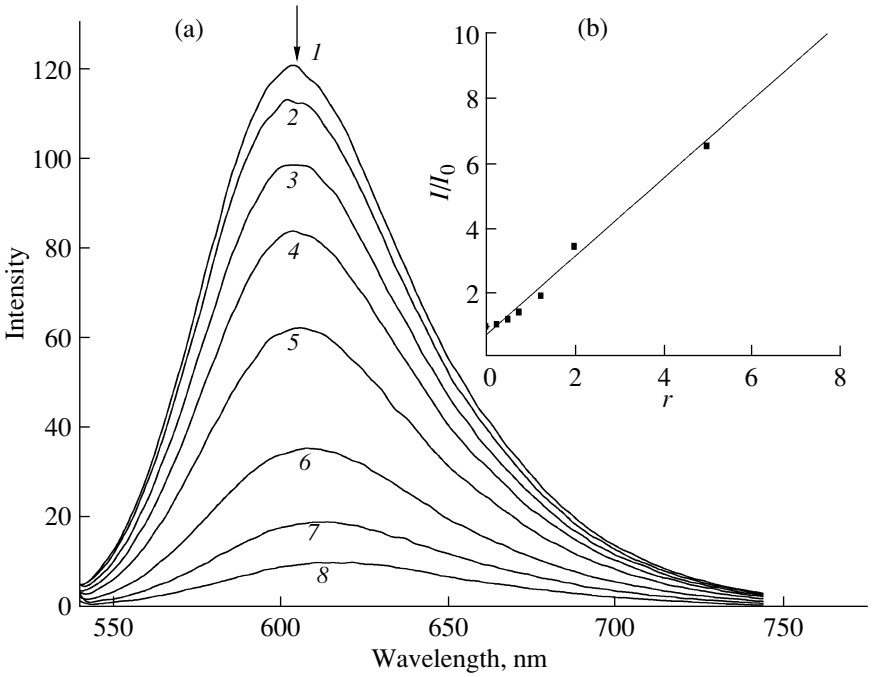

Fig. 4. Fluorescence spectra of the binding of EB to DNA in the absence (*1*) and presence of increasing amounts of complex **I**: c_{compl} = 1.25 (*2*), 2.5 (*3*), 3.75 (*4*), 6.25 (*5*), 10 (*6*), 25 (*7*), and 40 μmol/l (*8*), λ_{ex} = 526 nm, c_{EB} = 50, c_{DNA} = 50 μmol/l (a); the inset is the Stern–Volmer quenching plots (b).

nitrogen atoms and carboxyl oxygen atoms, forming two five-membered chelating rings with O,O, and N,N in *trans*-coordination. Bond length: O(1)–Zn(1) 2.010, Zn(1)–N(1) 2.219, Zn(1)–O(3) 2.232 Å. As common mixed solvent molecules, such as DMSO, DMF, H_2O, EtOH, and so on, the coordination modes are not the same when the central ion and coordination environment are different [21]. In this complex, the oxygen atoms of two DMSO coordinate to the central Zn^{2+} ion, while other two DMSO are dissociative in disorder, this is much similar to the complex [22].

The C–H···π bonding interactions [23, 24] (C(12)'···C(6) 3.389 Å, angle C(12)'–H(12*B*)···C(6) 131°) and hydrogen bonds (C(5)···O(3) 3.536 Å, angle C(5)–H(5)···O(3) 148.42°) are formed between oxygen atom of uncoordinated DMSO and carbon atom in the coordinated aromatic ring, thus generating the one-dimensional chain structure. There exist π–π stacking interactions of adjacent quinaldic acid aromatic ring with the centroid-to-centroid distance of 3.774 Å (Fig. 2). Under the cooperation of C–H···π bonds and π–π stacking interactions, a three-dimensional net structure is formed, as shown in Fig. 3.

The zinc complex can emit luminescence in Tris buffer at room temperature with maxima at about 600 nm, excited in 502 nm. Its interaction with CT-DNA was monitored with luminescence. Competitive EB binding study was undertaken to understand the mode of DNA interaction of the zinc complex. The molecular fluorophore EB emits intense fluorescence in the presence of CT-DNA due to its strong intercalation between the adjacent DNA base pairs ($K_b = 1.4 \times 10^6$ M^{-1}) [25]. Addition of the second molecule, which binds to DNA more strongly than EB, would quench the DNA-induced EB emission [26]. The quenching extent of fluorescence of EB bound to DNA is used to determine the relative DNA binding affinities of the second molecule. The emission spectra of EB and DNA-bound EB in the absence and presence of the complex is given in Fig. 4. According to the classical Stern–Volmer equation [27]: $I_0/I = 1 + K_{sq}r$, where I_0 and I represent the fluorescence intensities in the absence and presence of the complex, respectively, and r is the ratio of the total concentration of the complex to that of DNA([Zn]/[DNA]), K_{sq} is the linear Stern–Volmer quenching constant dependent on the ratio of the bound concentration of EB to the concentration of DNA (Fig. 4). The K_{sq} value is obtained as the slope of I_0/I versus r linear plot. The K_{sq} value for zinc complex **I** is 1.199. Such a value of the quenching constant suggests that the interaction of the title complexes displace DNA-bound EB and bind to DNA with a strong at the intercalative mode, which is due to partial intercalation of the aromatic ring.

ACKNOWLEDGMENTS

We gratefully acknowledge the Natural Science Foundation of China (no. 20671064), the Natural Science Foundation of Liaoning Province (no. 20052014), the Foundation of Educational Department of Liaoning Province (no. 20060679), and the Foundation of Liaoning Bai Qian Wan Talents Program (no. 2008921054).

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