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Preparation, crystal structures and properties of zinc complexes containing Bis(oxazoline) ligand

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Three zinc complexes ([(DMOX)ZnX$_2$], X = Cl **(1)**, Br **(2)** or I **(3)**), where DMOX is 4,5-dihydro-2-(4,5-dihydro-4,4-dimethyloxazol-2-yl)-4,4-dimethyloxazole), have been fully characterized by single crystal X-ray diffraction, UV–vis, NMR and IR spectroscopy. Moreover, all zinc complexes showed activities in catalyzing hydrolysis of 4-nitrophenyl acetate (4-NA). And active species have been determined by pH titrations of [(DMOX)ZnI$_2$] in catalyzing hydrolysis of 4-NA.

1. Introduction

Zinc is an important element in our body, and the zinc complexes with different biological ligands and coordination environment have been proven to be highly efficient catalysts for the hydrolysis of carboxyester and phosphoester [1–3]. Extensive studies have been carried out using zinc complexes containing pyridine [4,5], pyrazolate [6], hydroxyl [7] or macrocyclic cyclen [8–10] ligands to promote the ester hydrolysis, and the ligands have a great effect on the complexes properties [11–13]. Bisoxazolines compounds have been widely used in modern chemistry due to their easily modified to get vary steric and electronic properties through using an appropriate amino alcohol precursors [14,15]. Transition metal complexes with bisoxazolines ligands turned out to be very efficient and reliable catalysts in organic transformation [16]. In previous studies, we synthesized Cu, Ni and Zn complexes based on oxazoline ligands and studied their catalytic activities in C–N or C–C coupling [17–19]. To the best of our knowledge, the zinc complexes with bis(oxazoline) ligand are rarely reported in hydrolysis procedure. In this work, in order to investigate the halide coordination behavior of such zinc complexes containing bis(oxazoline) ligand on the catalytic activities in the 4-NA hydrolysis, we synthesized three new zinc complexes ([(DMOX)ZnX$_2$], X = Cl (**1**), Br (**2**) or I (**3**)). In addition, the hydrolysis reaction of 4-nitrophenyl acetate (4-NA) promoted by these zinc complexes were also investigated. A zero-point experiment have been performed in the absence of any zinc complex, the results show that the hydrolysis of 4-NA can occurred, the conversion was 40%, while the zinc catalyst can improve hydrolysis of 4-NA to 90% yields. The active species in catalyzing the hydrolysis of 4-NA have also been confirmed by potentiometric pH titrations.

2. Experimental

2.1. Materials and methods

All solvents were purified and degassed by standard procedures. The starting material, 4,5-Dihydro-2-(4,5-dihydro-4,4-dimethyloxazol-2-yl)-4,4-dimethyloxazole) (DMOX) was synthesized according to procedures described in the literature [20]. Other chemicals were analytical grade and used without further purification. The UV measurements were carried out on U-3010 UV–visible spectrophotomer. ^{1}H and ^{13}C NMR were recorded on a 300 MHz or 500 MHz NMR spectrometer at room temperature. Chemical shifts (δ) are given in ppm relative to CDCl$_3$ (7.26 ppm for ^{1}H and 77 ppm for ^{13}C) or internal TMS. IR spectra were recorded on

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a Niclolet AVATAR-360IR spectrometer. Element analyses were performed on an Elementar III vario EI Analyzer.

2.2. Synthesis

2.2.1. Synthesis of [(DMOX)ZnCl$_2$] (**1**)

A 50 mL round-bottomed flask was filled with DMOX (39 mg, 0.2 mmol), ZnCl$_2$ (28 mg, 0.2 mmol), 10 mL MeOH and 10 mL CH$_2$Cl$_2$ as solvent. The mixture was stirred at room temperature for 5 h and then the solvent was removed with a rotary evaporator; the resulting solid was washed with Et$_2$O. The product was dried under vacuum to give the corresponding white complex [(DMOX)ZnCl$_2$] (**1**) (63 mg, 95%). Anal. Calc. for $C_{10}H_{16}Cl_2N_2O_2Zn$ (332.54): C, 36.12; H, 4.85; N, 8.42. Found: C, 36.58; H, 4.70; N, 8.53%. ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.61 (s, 4H), 1.59 (s, 12H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 156.10, 85.42, 68.45, 28.23. IR (KBr cm^{-1}): 2974(m), 2916(w), 1644(vs), 1483(vs), 1445(s), 1359(vs), 1330(vs), 1280(vs), 1191(vs), 995(s), 931(vs), 843(w), 632(s).

2.2.2. Synthesis of [(DMOX)ZnBr$_2$] (**2**)

Prepared by the same procedure as described above for **1**, using DMOX (39 mg, 0.2 mmol) and ZnBr$_2$ (44 mg, 0.2 mmol). Yield: (77 mg, 91%). Anal. Calc. for $C_{10}H_{16}Br_2N_2O_2Zn$ (421.44): C, 28.50; H, 3.83; N, 6.65. Found: C, 28.35; H, 3.94; N, 6.70%. ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.59 (s, 4H), 1.60 (s, 12H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 156.07, 85.40, 68.41, 28.21. IR (KBr cm^{-1}): 2975(m), 2914(w), 1643(vs), 1488(vs), 1447(s), 1357(vs), 1331(vs), 1284(vs), 1192(vs), 993(s), 930(vs), 841(w), 633(s).

2.2.3. Synthesis of [(DMOX)ZnI$_2$] (**3**)

Prepared by the same procedure as described above for **1**, using DMOX (39 mg, 0.2 mmol) and ZnI$_2$ (64 mg, 0.2 mmol). Yield: (94 mg, 92%). Anal. Calc. for $C_{10}H_{16}I_2N_2O_2Zn$ (515.44): C, 23.30; H, 3.13; N, 5.43. Found: C, 23.30; H, 3.42; N, 5.55%. ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.61 (s, 4H), 1.65 (s, 12H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 156.09, 85.41, 68.49, 28.25. IR (KBr cm^{-1}): 2975(m), 2916(w), 1643(vs), 1483(vs), 1447(s), 1359(vs), 1331(vs), 1280(vs), 1192(vs), 995(s), 930(vs), 843(w), 632(s).

2.3. Hydrolysis of 4-nitrophenyl acetate by zinc complexes

The rate of hydrolysis of 4-NA promoted by zinc complexes in H$_2$O/CH$_3$CN (90:10 v/v) in the pH range 7.72–9.15 was measured by an initial rate method at 25 °C. The reaction was monitored by following the increase in absorbance at 400 nm, corresponding to the appearance of the product 4-nitrophenolate (4-NP), up to 5% yield of 4-NP. The pH was maintained by using tris (pH 7.2–9.2) buffer at 50 mM. Ionic strength was maintained by NaClO$_4$ at 100 mM. A typical experiment consisted of loading a UV–vis cell (3.0 mL) with 50 μL of a 4-NA stock solution (60 mM in CH$_3$CN) and then simultaneously injecting a stock solution containing the appropriate buffer and NaClO$_4$ and a stock solution of zinc complexes. All stock solutions used in the kinetic runs was prepared within one week of taking measurements to avoid any decomposition. The concentration of zinc complexes were varied (0.00–0.10 mM) with constant 4-NA (1 mM), and a stock solution containing the appropriate buffer and NaClO$_4$ were varied (2.95–2.70 mL) to keep the same volume (3.00 mL). A plot of absorbance (400 nm) *vs* time was linear in all cases, and the slope of the best-fit line gave the observed reaction rate, dA/dt. The observed second-order rate constants k_{obs} (M^{-1} s^{-1}) were determined as described in the results and discussion.

2.4. Potentiometric pH titrations of [(DMOX)ZnI$_2$]

The pH titrations were carried out under nitrogen at 25 °C with a computer-controlled pH meter (E-201-C) and automatic potentiometric titrator (ZDJ-4A) according to the literature method [3,21]. Aqueous or methanol (water/methanol, 9:1) solutions of the 0.5 mM [(DMOX)ZnI$_2$] (**3**) were titrated with a 0.1 M NaOH aqueous solution. The ionic strength was adjusted to I = 0.1 with NaClO$_4$. The NaOH solutions were calibrated with potassium hydrogen phthalate. A titration of 0.01 M HClO$_4$ with a NaOH solution was used for calibration and to determine logK$_W$. 0.5 M of HClO$_4$ was added to the titration solution in order to determine values in the pH range of 2–8 in [(DMOX)ZnI$_2$] solution. Two independent titrations were made for [(DMOX)ZnI$_2$] solution at least.

The titration data were fitted with the Hyperquad 2000 program (version 2.1, P. Gans) to calculate the ligand protonation constants K$_n$, the complex formation constant K$_{ML}$, and the deprotonation constants of the coordinated water pK$_a$.

2.5. X-ray structure determination

Diffraction data of **1**, **2** and **3** were collected on a Bruker AXS SMART APEX diffractometer, equipped with a CCD area detector using Mo Kα radiation (λ = 0.71073 Å). All the data were collected at 298 K and the structures were solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL) [22], SADABS [23] absorption corrections, scaling and optimal weights were applied to the data, all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions. All calculation was performed using the Bruker product SHELXTL [22]. A summary of the crystallographic data and selected experimental information are given in Table 1, selected bond angles and distances are given in Table 2.

3. Results and discussion

3.1. Structural description of 1 and 3

Dichloromethane and methanol solutions of equimolar amounts of DMOX and each of the zinc halides were stirred at room temperature for 5 h to produce compounds [(DMOX)ZnX$_2$] (X = Cl **(1)**, Br **(2)** or I **(3)**) in high yields of 95%, 91% and 92%, respectively. Complexes **1**, **2** and **3** were fully characterized by IR, NMR spectroscopy and elemental analysis. All zinc complexes are stable to air and moisture and moderately soluble in most solvents such as MeCN, DMSO, CHCl$_3$ and DMF. The ^{1}H NMR spectra of **1** in CDCl$_3$ show singlet resonances due to methyl fragment at δ 1.59 ppm, and the signals of the methylene in the oxazoline rings appear at δ 4.61 ppm range. The ^{13}C NMR spectra of **1** show signals at 156.10, 85.42, 68.45 and 28.23 ppm.

The finely white crystals of **1** and **3** were obtained by vapor diffusion of Et$_2$O solution into MeCN or CH$_2$Cl$_2$ solution. The molecular structures of **1** and **3** are shown in Fig. 1.

The structure of **1** is solved in the orthorhombic crystal system and *Pbca* space group. As can be seen, the coordination geometry of the central zinc center can be best described as a distorted tetrahedron with two Cl atoms and two N atoms. The Zn–N distances (2.072(2) and 2.1081(19) Å) in **1**, which are compatible with a typical single bond length between the zinc center and the nitrogen atom reported in the previous literature, and longer than those of Zn complexes with box ligands [ZnCl$_2${(S,S)-Ph-BOX} [24] (2.032 and 2.022 Å) and [ZnCl$_2${(S,S)-*t*BuBOX}[24] (2.068 and 2.042 Å) containing the six-membered ring. The solid structure of **3** (Fig. 1b) is very similar to that of complex **1**. As expected, the coordination geometry around the Zn center can be seen as a distorted