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Research paper

Synthesis, crystal structure, luminescent properties and antibacterial activities of zinc complexes with bipyridyl and salicylate ligands

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ABSTRACT

Two novel coordination complexes having salicylate and bidentate rigid organodiamine ligands, namely, $[Zn(\mu\text{-bpp})_2(Sal)_2]_n$ (**1**) and $[\{Zn(Sal)_2\}_2(\mu\text{-bpe})]_2$ (**2**) [bpp = 1,3-bis(4-pyridyl)propane, bpe = 1,2-bis(4-pyridyl)ethane, and Sal^- = salicylate anion] were synthesized under solvothermal condition. The complexes were investigated by single crystal X-ray diffraction (SCXRD), elemental analysis, Fourier-transform infrared spectroscopy (FT-IR), powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), and photoluminescence spectroscopy. From structural analyses, **1** is a 1-D structure linked by bpp ligands with each Zn(II) atom in a tetrahedral coordination geometry while **2** is a dinuclear 0-D structure. All complexes were tested for their antibacterial activity by *in vitro* agar diffusion method against *Staphylococcus aureus, Escherichia coli*, and *Pseudomonas aeruginosa*. Both **1** and **2** showed mediocre inhibition activity against the tested bacteria. Both complexes showed strong emission with λ_{em} at 393 nm (λ_{ex} = 350 nm) and 390 nm (λ_{ex} = 350 nm) for **1** and **2**, respectively, in dimethyl sulfoxide (DMSO) solution. Metal ion sensing study showed that both complexes could be applied as a fluorescence sensor for detecting Cu^{2+} ion with good sensitivity and selectivity.

1. Introduction

In the past few decades, coordination complexes have received much interest due to their diverse applications such as catalysis, magnetism, non-linear optics, adsorption, drugs, fluorescent sensing, gas storage, luminescence, and so on [1–7]. The luminescent properties of coordination complexes are widely used as luminescent probes to detect metal ions such as K^+, Fe^{2+}, Zn^{2+}, and Cu^{2+} [8–12], solvent molecules, and nitroaromatic explosives [5] through enhancement or quenching of luminescent intensities of the complexes.

The *N*-donor ligands such as 4,4′-bipyridine, 1,3-bis(4-pyridyl) propane, and 1,2-bis(4-pyridyl)ethane have been widely used for syntheses of coordination complexes due to their capacity to coordinate to metal centers in many different ways as part of crystal engineering leading to numerous different structures [13].

The carboxylic groups of the aliphatic and aromatic acid may use their different coordination modes to coordinate to metal centers to form coordination complexes with different structures and geometries, not only for their structural diversity of topologies, but also for their ability to act as hydrogen bonding acceptors and hydrogen bonding donors for extension of supramolecular architectures [14]. Salicylate ligand can bind to metal center as a monodentate [15], bidentate chelating (hydroxyl oxygen atoms and one carboxylate oxygen [16], two oxygens of carboxylate group [17]), and bridging bidentate carboxylate ligand [18]. In addition, some salicylate complexes may show inhibitory action on the growth of bacterial, anti-inflammatory, antipyretic, and analgesic drugs [19].

In this work, we report the synthesis, structural characterization, and luminescent properties of zinc(II) complexes with 1,3-bis(4-pyridyl)propane or 1,2-bis(4-pyridyl)ethane and salicylate as ligands. Moreover, both complexes were studied for antibacterial activity and as metal ion sensor in aqueous solution. For the latter, the positive result was observed for Cu^{2+} ion.

2. Experimental section

2.1. Materials and general methods

All chemicals and solvents employed in this work were purchased from commercial sources and used without further purification. FT-IR spectra were obtained using KBr pellet on a

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Perkin-Elmer Spectrum One Fourier-transform infrared spectrophotometer between 4000 and 400 cm^{-1}. Thermogravimetric analyses (TGA) were carried out on a Perkin Elmer TGA 7 in the range 50–1000 °C with a heating rate of 10 °C/min under N_2 atmosphere. Elemental analyses (CHN) were performed on a Perkin-Elmer 240 elemental analyzer. Fluorescence spectra were recorded with a Perkin Elmer LS55 Luminescence spectrometer with excitation and emission slit width 10 nm and scan rate 400 nm/min at room temperature. Powder X-ray diffraction measurements were carried out using a X'Pert MPD PHILIPS X-ray diffractometer with Cu Kα radiation in the 2θ range of 5–50° to check the phase purity. ^{1}H NMR spectra were recorded on a Bruker 400 MHz Spectrometer in DMSO-d_6 using $SiMe_4$ as an internal reference.

2.2. Syntheses of complexes

2.2.1. Synthesis of $[Zn(\mu\text{-bpp})(Sal)_2]_n$, 1

A colorless ethanol solution of 1,3-bis(4-pyridyl)propane (0.1982 g, 1 mmol) was added to a solution of $Zn(OAc)_2{\cdot}2H_2O$ (0.2195 g, 1 mmol, in 15 mL of water), stirred for 15 min, then, a solution of acetylsalicylic acid (0.3602 g, 2 mmol, in 15 mL of ethanol) was added. The pH of the mixture was adjusted to 7 with 1 M NaOH. The resultant solution was added to a Parr Teflon-lined stainless steel vessel and heated for 3 days at 120 °C at rate of 5 °C/s and cooled to room temperature. The crystals formed were filtered off and successively washed with H_2O and EtOH, and dried in a vacuum. Block crystals were obtained in 83% yield based on Zn. The elemental analyses were: Calc. for $C_{27}H_{24}N_2O_6Zn$: C, 60.3; H, 4.5; N, 5.2%. Found: C, 59.24; H, 4.02; N, 5.14%. IR (KBr): ν = 3450 (w), 3063(m), 2948(m), 1620(s), 1570(s), 1509(m), 1486(s), 1482 (s), 1396(s), 1309(m), 1257(m), 1261(m), 1249(m), 1193(m), 1184(m), 1070(m), 1033(m), 866(m), 810(m), 761(m), 705(m), 668(m), 562(m), 530(m), 453(m), 425(m) cm^{-1}.

2.2.2. Synthesis of $[\{Zn(Sal)_2\}_2(\mu\text{-bpe})]_2$, 2

The synthesis of **2** was similar to that of **1** except that 1,2-bis(4-pyridyl)ethane (0.1842 g, 1 mmol) was used instead of 1,3-bis(4-pyridyl)propane, yield: 32% based on Zn. Calc. for $C_{52}H_{44}N_4O_{12}Zn_2$: C, 59.6; H, 4.2; N, 5.3%. Found: C, 59.21; H, 4.10; N, 5.35%. IR (KBr): ν = 3450(w), 3060(m), 2951(m), 1619(s), 1570(s), 1552(m), 1490 (s), 1482(s), 1396(s), 1347(m), 1260(m), 1248(m), 1165(m), 1154 (m), 1070(m), 1041(m), 865(m), 852(m), 773(m), 707(m), 659 (m), 563(m), 525(m), 458(m), 424(m) cm^{-1}.

2.3. X-Ray crystallography

Crystals of the complexes **1** and **2** were selected under an optical microscope and glued on glass fiber for single crystal X-ray diffraction experiments. X-ray diffraction data were collected using a Bruker D8 QUEST CMOS using Mo-Kα radiation (λ = 0.71073 Å) and operating at T = 296(2) K. Data were measured using ω and ϕ scans using Mo-Kα radiation (50 kV, 30 mA). The total number of runs and images was based on the strategy calculation from the program APEX3 and unit cell indexing was refined using SAINT (V8.38A). Data reduction and scaling were performed using SAINT (V8.38A) and SADABS-2016/2 was used for absorption correction [20]. The structure was solved with the ShelXT structure solution program using combined Patterson and dual-space recycling methods [21]. The crystal structure was refined by least squares using ShelXL [22]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon atoms were placed at calculated positions and refined using a riding model approximation, with C—H = 0.93 (aromatic CH) or 0.97 (methylene CH_2) Å, and with U_{iso}(H) = 1.2U_{eq}(C). The O—H hydrogen atoms were located in difference Fourier maps but refined with O—H = 0.82 ± 0.02 Å, and with U_{iso}(H) = 1.5U_{eq}(O). For **2**, the 4-ethylpyridine moiety of the 1,2-bis(4-pyridyl)ethane molecule is disordered over two positions (A and B) with a refined occupancy of 0.886(4) and 0.114(4). The crystal data as well as details of data collection and refinements for complexes are listed in Table 1. Selected bond lengths and bond angles are given in Table 2. All packing diagrams and wire frame plots were produced using the Mercury 3.8 software program [23].

2.4. Antibacterial activity experiment

The *in vitro* antibacterial activities of both complexes were tested by using disc diffusion method. The bacterial cultures used were *Staphylococcus aureus ATCC 25923, Escherichia coli ATCC 25922*, and *Pseudomonas aeruginosa ATCC 27853).* The inoculums were prepared using a liquid broth of bacterial and adjusted to a turbidity equivalent of 0.5 McFarland standard containing approximately 10^4–10^6 CFU/mL. Cotton buds were dipped into the inoculums and the surface area of the nutrient agar (NA) was inoculated by streaking the sterile cotton swab. The paper disks impregnated with the test complexes were placed on nutrient agar followed by inoculation at 37 °C for 24 h. Penicillin and gentamicin (10 μg/disc) were used as standards. Each complex was dissolved in DMSO at a concentration of 1 mg/mL. The antibacterial activity was evaluated by measuring growth inhibition zone diameter (IZD, in mm) and classified as high sensitivity if IZD ≥ 20 mm, medium sensitivity for 14–20 mm, low sensitivity for 7–13 mm, and insignificant for <7 mm [6].

2.5. Luminescent sensing for metal ions properties

2.5.1. Effect of metal ions on fluorescence properties of 1 and 2

The sensing experiments were carried out by monitoring the fluorescence quenching behavior of **1** (or **2**) upon the addition of metal ions at room temperature. Aqueous solution of metal chloride (0.5 mM, 200 μL) (MCl or MCl_2; M = Cd^{2+}, Mn^{2+}, Sr^{2+}, K^+,

Table 1
Crystallographic data and structure refinement for **1** and **2**.

	1	**2**
Empirical formula	$C_{27}H_{24}N_2O_6Zn$	$C_{52}H_{44}N_4O_{12}Zn_2$
Formula weight	537.85	1047.65
Temperature/K	296.0	296.0
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	13.1199(4)	11.2840(6)
b/Å	11.2017(4)	11.4948(6)
c/Å	16.9977(6)	12.0972(7)
α/°	90.00	66.129(2)
β/°	94.0160(10)	63.384(2)
γ/°	90.00	63.697(2)
Volume/Å^3	2491.94(15)	1215.26(11)
Z	4	1
ρ_{calc}g/cm^3	1.434	1.432
μ/mm^{-1}	1.030	1.054
F(0 0 0)	1112.0	540.0
Crystal size/mm^3	0.32 × 0.26 × 0.26	0.24 × 0.22 × 0.22
2Θ range for data collection/°	6.02–54	6.34–53.32
Index ranges	$-16 \le h \le 16$, $-13 \le k \le 14$, $-21 \le l \le 21$	$-14 \le h \le 14$, $-14 \le k \le 14$, $-15 \le l \le 15$
Reflections collected	47,678	21,587
Independent reflections	5418 [R_{int} = 0.0657, R_{sigma} = 0.0352]	5062 [R_{int} = 0.0539, R_{sigma} = 0.0450]
Data/restraints/parameters	5418/2/333	5062/285/397
Goodness-of-fit on F^2	1.017	1.040
Final R indexes [I ≥ 2σ (I)]	R_1 = 0.0378, wR_2 = 0.0756	R_1 = 0.0436, wR_2 = 0.0857
Final R indexes [all data]	R_1 = 0.0701, wR_2 = 0.0873	R_1 = 0.0701, wR_2 = 0.0946
Largest diff. peak/hole/e Å^{-3}	0.28/−0.20	0.49/−0.36