# Zn(II) Complexes with Quinoline Supported Amidate Ligands: Synthesis, Fluorescence, and Catalytic Activity

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Received June 6, 2019; revised December 11, 2019; accepted December 25, 2019

Abstract—Zn(II) complexes of *N*-(quinolin-8-yl)picolinamide (HL<sup>1</sup>) (1) and  $N^2, N^6$ -di(quinolin-8-yl)pyridine-2,6dicarboxamide (H<sub>2</sub>L<sup>2</sup>) (2) have been synthesized by deprotonation of the ligands and characterized by IR, NMR, and Single crystal X-ray crystallography. The mononuclear [Zn(L<sup>1</sup>)<sub>2</sub>] (3) and homodinuclear [Zn<sub>2</sub>(L<sup>2</sup>)<sub>2</sub>] (4) complexes are characterized by distorted octahedral geometries stabilized by hydrogen bonding and weak  $\pi \cdots \pi$ interaction. The complexes demonstrate intense fluorescence bands in comparison with their corresponding ligands with well-distinguished intensity. The complexes act as efficient catalysts in various transesterification reactions. Among those, the best results have been achieved with complex 3 in conversion of 4-nitrophenylacetate into methyl acetate within 3 h.

Keywords: Zn(II), quinoline, amidate, transesterification, fluorescence

**DOI:** 10.1134/S1070363219120302

#### INTRODUCTION

Photoluminescence properties of transition and main group metal complexes have already been well established [1–3]. Quinoline and most of its derivatives are potentially photoluminescent compounds [4, 5], and their photoluminescence effect increases upon coordination to some metals [6, 7]. Such property makes them photoluminescent detectives for selective probe of various metallic ions in solution both *in vivo* and *in vitro*. Many studies of modification of these compounds have been performed for enhancing the desired selectivity and luminescence properties [8–10]. Highly diverse photoluminescent features and advance applications have been reported for electronic and steric modifications of the ligand in quinoline based zinc complexes [11–14].

Various metal catalyzed transesterification reactions have been cited in literature [15-17]. Zn(II) Complexes of relatively low toxicity characterized by air and moisture stability were found to have real potential for these reactions [18]. Zinc-amidates under moderately tough catalytic conditions could be used in transesterification reactions [19]. Here in, the synthesis and characterization of two new Zn(II) complexes with amidates stabilized by additional pendent quinoline and picoline arms are presented. Their fluorescence properties as well as catalytic activity in various transesterification reactions have been tested.

#### EXPERIMENTAL

Synthetic precursors including picolinic acid, dipicolinc acid, 8-aminoquinoline, zinc(II) acetate, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from Sigma Aldrich. Triphenylphosphite (TPP) and tetrabutylammonium bromide (TBAB) were supplied by Daejung chemicals, Korea. Dichloromethane (DCM) was dried by anhydrous CaO followed by distillation. *N*-(Quinolin-8-yl)picolinamide (HL<sup>1</sup>) (**1**) was prepared according to the reported earlier procedure [20]. IR spectra were recorded on a Thermo Scientific Nicolet-6700 FT-IR spectrophotometer. NMR spectra were measured on a Bruker Avance 300 NMR spectrometer. A Sanyo Gallen Kamp MPD350 apparatus was used for determining melting points. Single crystal X-ray profiles of compounds were accumulated on a Bruker Kappa Apex



II X-ray diffractometer. Steady-state fluorescence (SSF) measurements were carried out on a Shimadzu RF-6000 spectrofluorophotometer using a low-noise photomultiplier detector. The slit width (ex 5.0 nm; em 5.0 nm) was adjusted to obtain good resolution of the bands. Fluorescence spectra of all samples were recorded in DCM in the range of 350–800 nm with excitation at 330 nm.

N<sup>2</sup>, N<sup>6</sup>-di(quinolin-8-yl)pyridine-2, 6-dicarboxamide  $(H_2L^2)$  (2). The reaction mixture of 8-aminoquinoline (1.0 g, 6.94 mmol) with dipicolinic acid (0.58 g, 3.47 mmol), triphenylphosphite (TPP) (2.15 g, 6.94 mmol), and tetrabutylammonium bromide (TBAB) (1.12 g, 3.47 mmol) was heated for 30 min at 120°C till the homogeneous solution was formed. The solution was cooled down to room temperature, and the product was precipitated out upon addition of cold water (10 mL). The precipitate formed was filtered off and washed with cold ethanol to give pure compound 2. Light green solid, yield 83.0%, mp 285°C. IR spectrum, v, cm<sup>-1</sup>: 3320, 3296, 3015, 2970, 1738, 1677, 1592, 1487, 1366, 1022, 852s, 527. <sup>1</sup>H NMR spectrum, δ, ppm: 12.39 s (2H, N-H), 9.05 d (2H, Ar-H), 8.61 d (2H, Ar-H), 8.28 d (2H, Ar-H), 8.25-8.19 m (2H, Ar-H), 7.72-7.63 m (2H, Ar-H), 7.37–7.33 m (1H, Ar-H). Found %: C 71.35; H 3.75; N 16.25. C<sub>25</sub>H<sub>17</sub>N<sub>5</sub>O<sub>2</sub>. Calculated, %: C 71.70; H 4.10; N 16.70.

 $Zn(L^{1})_{2}$  (3). A mixture of  $Zn(OAc)_{2}.2H_{2}O$  (100 mg, 0.46 mmol) with HL1 (227 mg, 0.92 mmol) and DCM (10 mL) was stirred for 10 min at room temperature followed by the addition of DBU (0.206 mL, 1.38 mmol). The resulting mixture was refluxed for 2 h. After cooling down to room temperature, *n*-hexane was added slowly to induce precipitation. The precipitate was filtered off and washed three times with *n*-hexane and diethyl ether to give the product 3 as light green solid, yield 58%, mp 290°C. IR spectrum, v, cm<sup>-1</sup>: 3057, 1613, 1585, 1495, 1382, 1208, 1150, 1041, 829, 749. <sup>1</sup>H NMR spectrum, δ, ppm: 9.68 d (1H, Ar-H), 8.56 d (1H, Ar-H), 8.19 d (1H, Ar-H), 8.09 d (1H, Ar-H), 7.98 d (1H, Ar-H), 7.85–7.73 m (2H, Ar-H), 7.44 d (1H, Ar-H), 7.13-7.08 m (2H, Ar-H). Found, %: C 63.90; H 3.35; N 14.50. C<sub>30</sub>H<sub>20</sub>N<sub>6</sub>O<sub>2</sub>Zn. Calculated, %: C 64.10; H 3.60; N 14.95.

**Zn<sub>2</sub>(L<sup>2</sup>)<sub>2</sub> (4).** A mixture of Zn(OAc)<sub>2</sub>.2H<sub>2</sub>O (100 mg, 0.46 mmol) with H<sub>2</sub>L<sup>2</sup> (193 mg, 0.46 mmol) and DCM (10 mL) was stirred for 10 min at room temperature prior to addition of DBU (0.206 mL, 1.38 mmol). The reaction mixture was refluxed for 2 h. Upon cooling down to ambient temperature the precipitate was filtered off and washed three time with diethyl ether to give the product **4** as a parrot green solid, yield 74%, mp 310°C. IR spectrum, v, cm<sup>-1</sup>: 3053, 1631, 1605, 1568, 1401, 1317, 1238, 1157, 1004, 825, 759. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 9.03 d (2H,

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Fig. 1. ORTEP of  $[Zn(L^1)_2]$ .

Ar-H), 8.95 d (2H, Ar-H), 8.86 d (2H, Ar-H), 8.36 d (2H, Ar-H), 8.11–8.06 m (2H, Ar-H), 8.00–7.52 m (1H, Ar-H). Found, %: C 61.75; H 3.00; N 14.10.  $C_{50}H_{30}N_{10}O_4Zn_2$ . Calculated, %: C 62.20; H 3.15; N 14.50.

**Transesterification.** To a solution of an ester (0.05 mmol) dissolved in methanol/chloroform (1 : 1) (1 mL) the catalyst (2.0  $\mu$ mol) was added, and the mixture was stirred at 50°C (500 rpm). Reaction progress was monitored by GC–MS of 20- $\mu$ L aliquots. All reactions were carried out not less than three times and the average conversion was calculated.

# **RESULTS AND DISCUSSION**

*N*-(Quinolin-8-yl)picolinamide (1) was prepared according to the literature procedure [21] in the presence

Parameter	$[Zn(L^1)_2]$	$[Zn_2(L^2)_2]$
Formula	$\mathrm{C}_{30}\mathrm{H}_{21}\mathrm{N}_{5}\mathrm{O}_{3}\mathrm{Zn}$	$C_{52}H_{32}C_{16}N_{10}O_4Zn_2$
Formula weight	564.89	1204.31
Temperature, K	100(2)	100(2)
Wavelength, Å	1.54178	1.54178
Crystal system	Monoclinic	Trigonal
Space group	$P2_{1}/c$	P3 <sub>2</sub>

**Table 1.** Crystal data for  $[Zn(L^1)_2]$  and  $[Zn_2(L^2)_2]$ 



Fig. 2. ORTEP of  $[Zn_2(L^2)_2]$  molecule.

of triphenylphosphite that acted as a peptide coupling agent. The new and improved approach to the synthesis of  $N^2$ ,  $N^6$ -di(quinolin-8-yl)pyridine-2, 6-dicarboxamide (**2**) involved addition of tetrabutylammonium bromide (TBAB) [22,23] (Scheme 1). Two new zinc complexes, [Zn(L<sup>1</sup>)<sub>2</sub>] (**3**) and [Zn<sub>2</sub>(L<sup>2</sup>)<sub>2</sub>] (**4**), were prepared by deprotonation of compounds **1** and **2** respectively. In the course of these processes 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) was added. It acted as a base but also improved the solubility of ligands.

The IR spectrum of  $[Zn(L^1)_2]$  demonstrated absence of the band at 3421 cm<sup>-1</sup> that indicated N-H deprotonation of the ligand. The shift of the carbonyl band from 1738 to 1613 cm<sup>-1</sup> also indicated formation of the deprotonated ligand. Elemental analysis suggested that the metal to ligand ratio was 1 : 2. <sup>1</sup>H NMR spectrum of compound **3** demonstrated absence of the singlet between 10 and 12 ppm confirming deprotonation of amide. Suitable crystal of **3** for single crystal XRD was obtained by slow evaporation in chloroform solution. According to ORTEP diagram of complex **3** (Fig. 1), it had distorted octahedral geometry in which Zn(II) was surrounded by two L<sup>1</sup>.

IR spectrum of  $[Zn_2(L^2)_2]$  exhibited the absence of N–H band of  $H_2L^2$  ligand at 3320 cm<sup>-1</sup>. Shifting of carbonyl band from 1738 to 1631 cm<sup>-1</sup> indicated the ligand coordination to Zn(II). H<sup>1</sup> NMR spectrum also demonstrated absence of the singlet between 10 and

Bond angle	φ, deg	Bond angle	φ, deg		
[Zn(L <sup>1</sup> ) <sub>2</sub> ]					
$N^{6}Zn^{1}N^{1}$	98.4(2)	N <sup>1</sup> Zn <sup>1</sup> N <sup>5</sup>	91.2(2)		
$N^{6}Zn^{1}N^{2}$	173.9(2)	N <sup>2</sup> Zn <sup>1</sup> N <sup>3</sup>	77.9(2)		
N <sup>6</sup> Zn <sup>1</sup> N <sup>3</sup>	106.6(2)	N <sup>2</sup> Zn <sup>1</sup> N <sup>4</sup>	106.7(2)		
$[Zn_2(L^2)_2]$					
$N^1Zn^1N^{0L}$	74.8(3)	N <sup>0L</sup> Zn <sup>2</sup> N <sup>0M</sup>	93.0(3)		
$N^1Zn^1N^{0M}$	94.1(3)	N <sup>0L</sup> Zn <sup>2</sup> N <sup>5</sup>	94.1(3)		
$N^{1}Zn^{1}N^{2}$	79.6(3)	N <sup>0L</sup> Zn <sup>2</sup> N <sup>6</sup>	80.7(3)		

Table 2. Selected bond angles in  $[Zn(L^1)_2]$  and  $[Zn_2(L^2)_2]$  structures

12 ppm attributed to deprotonated amide. Elemental analysis indicated the metal to ligand ratio 1 : 1. ORTEP (Fig. 2) showed that the complex 4 consisted of homodinuclear Zn(II) dimer along with two chloroform molecules as a solvent of crystallization. Zn(II) was bounded with ligands forming helical like structure. All N-Zn-N bond angles were deviate from octahedral geometry and formed distorted octahedral structure. The most important structural data of both complexes are presented in Tables 1–3.

**Fluorescence.** Fluorescence characteristics of complexes and ligands were studied in dichloromethane because of low solubility of these compounds in other solvents at room temperature. The spectra demonstrated fluorescence in the range between 350 and 800 nm (Fig. 3). The complexes exhibited more intense fluorescence than their corresponding ligands. Among those compound, complex **4** was characterized by the maximum fluorescence at 549 nm.



**Fig. 3.** Steady-state fluorescence (SSF) spectra of the synthesized compounds (*1*–4) **1**–4.

**Table 3.** Selected bond lengths in  $[Zn(L^1)_2]$  and  $[Zn_2(L^2)_2]$ 

Bond	d, Å	Bond	<i>d</i> , Å		
$[Zn(L^1)_2]$					
Zn <sup>1</sup> –N <sup>6</sup>	2.064(4)	Zn <sup>1</sup> –N <sup>3</sup>	2.157(5)		
$Zn^1-N^1$	2.198(4)	Zn <sup>1</sup> –N <sup>4</sup>	2.174(4)		
$Zn^1-N^2$	2.063(5)	Zn <sup>1</sup> –N <sup>5</sup>	2.197(4)		
$[Zn_2(L^2)_2]$					
$Zn^1-N^1$	2.014(8)	Zn <sup>2</sup> –N <sup>0L</sup>	2.549(7)		
Zn <sup>1</sup> –N0L	2.480(1)	Zn <sup>2</sup> –N <sup>0M</sup>	2.480(1)		
Zn <sup>1</sup> –N0M	2.552(7)	Zn <sup>2</sup> –N <sup>5</sup>	2.011(8)		

**Transesterification.** Transesterification ability of various esters in the presence of zinc complexes **3** and **4** was tested with methanol in chloroform medium (Table 4). The best results were achieved for 4-nitrophenyl acetate that reacted with methanol completely in the presence of catalysts **3** and **4**, respectively. This could be attributed to the presence of the electron withdrawing group in the substrate ester. Similar results were observed with vinyl acetate and phenyl acetate. According to the data presented in Table 4, electron donating groups on a substrate could slow down the transesterification reaction, for example, the methyl group prolonged the reaction time from 5 to 10 h. Similar trends were observed with

Table 4. Transesterification of esters by methanol in the presence of catalysts 3 and  $4^{a,b}$ 

	Substrate	Homogeneous catalyst	
Entry		$Zn(L^1)_2$	$Zn_2(L^2)_2$
		time, h	
1	Vinyl acetate	4	5
2	4-Nitrophenyl acetate	3	4
3	Phenyl acetate	5	6
4	4-Methyl phenyl acetate	10	28
5	4-Chlorophenyl benzoate	7	8
6	Phenyl benzoate	9	11
7	4-methyl phenyl benzoate	20	32

<sup>a</sup> All esters were completely converted into the corresponding products.

<sup>b</sup> Reaction conditions: esters, 0.05 mmol, catalyst 2 μmol, solvent CH<sub>3</sub>OH/CHCl<sub>3</sub> (1:1) (1 mL) at 50°C.

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benzoate series that were comparable with those reported in literature [24, 25].

# CONCLUSIONS

Two new complexes,  $[Zn(L^1)_2]$  and  $[Zn_2(L^2)_2]$ , have been prepared by deprotonation of *N*-(quinolin-8-yl)picolinamide (HL<sup>1</sup>) and *N*<sup>2</sup>, *N*<sup>6</sup>-di(quinolin-8-yl)pyridine-2,6-dicarboxamide (H<sub>2</sub>L<sup>2</sup>), respectively. FT-IR, <sup>1</sup>H NMR and single crystal XRD studies confirm formation of the complexes. The crystal structures of  $[Zn(L^1)_2]$  and  $[Zn_2(L^2)_2]$  are characterized by the distorted octahedral geometry around Zn(II). Both complexes are fluorescent with the higher quantum yield determined for  $[Zn_2(L^2)_2]$ . Both complexes act as active catalysts in transestrification reactions.  $[Zn(L^1)_2]$  Demonstrates the superior catalytic activity.

### ACKNOWLEDGMENTS

The authors are thankful to Higher Education Commission of Pakistan (HEC) for providing funds to carry out this research work.

## CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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