Asian Journal of Chemistry Vol. 19, No. 4 (2007), 2873-2876

Synthesis and Characterization of Macrocyclic Zinc(II) Complexes Containing Schiff Base

HASSAN KEYPOUR* and FARZANEH AZIZZADEH ARAEY
Department of Chemistry, Bu-Ali Sina University, Hamadan, Iran
Fax: (98)(811)8257407; Tel: (98)(811)8257019; E-mail: keypour@basu.ac.ir

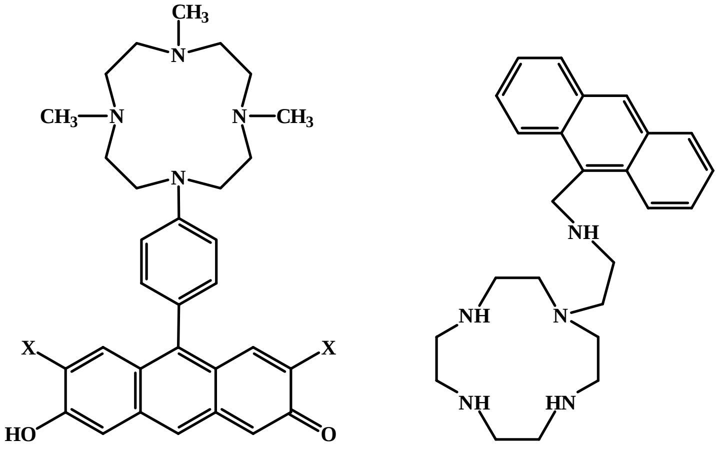
An anthracene fragment was appended through a methylene group to the scorpionands ethylamine side chain to give macrocyclic systems L^1 and L^2 with a flexible pendant-arm as a potentially versatile fluoresecent system. Zn(II) complexes of $[ZnL^1Cl]^{2+}$ and $[ZnL^2Cl]^{2+}$ have been prepared by the direct reaction of performed ligand (L^1 and L^2) with Zn^{2+} ion.

Key Words: Macrocyclic complexes, Side chain, Schiff base, Zinc(II).

INTRODUCTION

The synthesis of macrocyclic polyamine ligands bearing functional pendant donor group and their coordination to metal ions has been an active area of research for many years[1]. Zinc is the second most abundant trace metal in human body[2] and is particularly important since it is an essential component of many biological substrates, as enzymes and transcription factors and significance in several biomedical field. Zn(II) macrocyclic systems provided with a flexible pendant arm containing (anthracenyl methyl)amino (**II**) group acts as a fluorophores[3]. Nagano *et al.*[4] developed a new Zn^{2+}-sensor (**I**) based on fluorescein, linked to a macrocyclic system (polyamine receptor) allowing direct visible light excitation increased 14-fold. Previously, macrocyclic polyamine Zn^{2+} acceptors were developed by Czarink an co-workers[5], in which at pH = 10, the fluorescence intensity increased by 14-fold upon coordination. Concerning macrocyclic systems provided with a flexible pendant arm, Kimora *et al.*[6,7] have reported the synthesis and studies of Zn^{2+}-sensor, using (anthracenyl methyl)amino (**II**) (Fig. 1) as fluorophors. In those cases, upon Zn^{2+}complexation, the fluorescence intensity increased by 8-fold at pH around 7.4-7.8 and 25°C.

Herein, the synthesis and characterization of two new Zn(II) macrocyclic complexes with a Schiff base side chain containing anthracene fragment and its reduced form is reported (Fig. 2).



I

(X = H or Cl)

II

Fig. 1

EXPERIMENTAL

All solvents were of reagent grade quality and purchased commercially. *tris*(2-aminoethyl)amine, 1,2-dibromo ethane, salicylaldehyde and anthraldehyde were obtained from Aldrich and used without further purification. 1,4-*Bis*(2'-formyl phenyl)-1,4-dioxabutane was prepared by the literature method[8,9]. IR spectra were measured on Shimadzu IR-435 spectrometer.

Synthesis of ligands L^1 and L^2

To a stirred solution of 1,4-*bis*(2'-formyl phenyl)-1,4-dioxabutane 0.207 g (0.77 mmol) in 200 mL hot methanol was added *tris*(2-aminoethyl)amine 0.1137 g (0.77 mmol) in 50 mL hot methanol. The mixture was refluxed for 2 d. The solution was then allowed to cool to room temperature after which sodium borohydride was added in small portions to the stirred solution over 5 min. The volume was then reduced to 20 mL by rotary evaporation, exess water was added to the mixture and the pH was adjusted to 12 with sodium hydroxide. The solution was extracted with CH_2Cl_2 (×3). The CH_2Cl_2 extracts were combined and dried over anhydrous sodium sulfate. The dried extracts were then evaporated on a rotary evaporator to obtain an oily product[10] (Fig. 2). The resulting product was dissolved in hot methanol (20 mL) and was added to a stirred solution of anthraldehyde (0.3 mmol) in same solvent. The mixture was refluxed for 2 d to obtain ligand L^1. Then sodium borohydride was added in small portions to the stirred solution over 5 min. The volume was then reduced to (20 cm^3) by rotary evaporation. Excess water was added to the mixture and the pH was adjusted to 12 with sodium hydroxide. The solution was extracted with CH_2Cl_2 (×3). The CH_2Cl_2 extracts were combined and dried over anhydrous sodium sulfate. The dried extracts were then reduced to a small volume on a rotary evaporator to obtain ligand L^2 (Fig. 2).

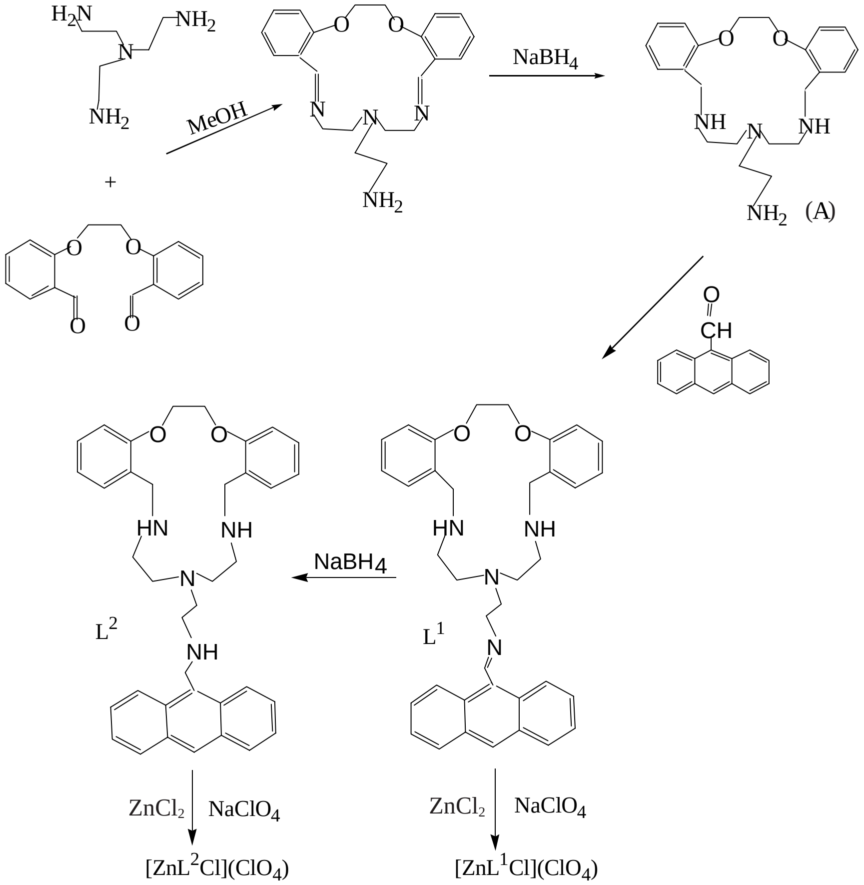


Fig. 2

General synthesis of complexes: Both complexes were readily prepared by the following method. The metal salt $ZnCl_2$ (0.3 mmol) was dissolved in absolute ethanol (10 cm^3) and slowly added to a stirred boiling solution of the ligands L^1 or L^2 (0.3 mmol) in same solvent. The resulting mixture was refluxed for 15 h. The solvent was evaporated to a small bulk and after addition of a warm solution (10 mL) of $NaClO_4$ (0.6 mmol), crystalline products were obtained.

Safe note: Perchlorate complexes are potentially explosive. But no problem has been experienced with the compounds described in this work, but it should be treated with caution and handled in small quantities.

$[ZnL^1Cl](ClO_4)\cdot 3H_2O$: IR (Nujol mull, ν_{max}, cm^{-1}): 3519, 3252, 1638, 1602, 1092, 662. Anal. Found (calcd.) % for $ZnC_{37}H_{46}N_4O_9Cl_2$: C, 54.8 (53.7); H, 5.4 (5.5); N, 5.6 (6.7) %. ^1H NMR δ_H (CD_3CN, ppm): 2.7-4.40 (24H, m), 7.12-8.18 (17H, m), 8.72 (1H, s). ^{13}C NMR δ_C (CD_3CN, p.p.m): 51.68, 49.72, 47.88, 124.04, 125.49, 126.08, 126.26, 127.55, 127.92, 130.02, 130.91, 131.30, 157.25.

$[ZnL^2Cl](ClO_4)\cdot 1.5H_2O$: IR (Nujol mull, ν_{max}, cm^{-1}): 3530, 3240, 1623, 1602, 1085, 622. Anal., Found (Calcd.) % for $ZnC_{37}H_{45}N_4O_{5.5}Cl_2$: C, 56.6 (55.4); H, 5.4 (5.61); N, 5.8 (6.98) %. ^1H NMR (CD_3CN, ppm): 1.079-5.05 (26H, m), 7.058-8.6 (17H, m), 8.6 (2H, s), 8.10 (1H, s).

RESULTS AND DISCUSSION

Scorpionate complexes are novel fluorescence switches whose control has a mechanical nature and such as a three-position switch (high/low/off)[11]. Ligand L^1 was prepared by direct cyclocondensation between **A** and anthraldehyde in methanol. Ligand L^2 also was prepared by an *in situ* reduction of ligand L^1 with $NaBH_4$. The synthesis of Zn(II) complexes of these ligands was confirmed with elemental analysis as well as IR and ^1H NMR spectra. The analytical data are consistent with existence of one chloride ion in the structure of both complexes. The chloride ion probably is coordinated to Zinc(II) metal ion as it confirmed by X-ray crystal structure for a similar Zinc(II) macrocyclic complex[3]. One strong peak at 3252 cm^{-1} in $[ZnL^1Cl](ClO_4)$ can be attributed to the vibration of the secondary amine. Amine stretch of $-NH_2$ group in L^1 is unassignable. One strong peak at 3244 cm^{-1} in $[ZnL^2Cl](ClO_4)$ can be attributed to the vibration of the secondary amine in ring and side chain. The strong (C=N) stretching band for $[ZnL^1Cl](ClO_4)$ complex is occurred at about 1638 cm^{-1} in the IR spectrum. The spectra also show single bands at about 1080 cm^{-1} with no splitting attributable to uncoordinated ClO_4^- anion.

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(*Received*: 28 April 2006; *Accepted*: 23 January 2007) AJC-5336