Synthesis, Characterization and Bioactivity of two Rare-Earth Complexes with Schiff base from Lysine-Salicylaldehyde

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***Abstract*—Two novel rare earth complexes with Schiff base from Lysine-Salicylaldehyde were synthesized by using the drop by drop reaction. On the basis of molar conductance and elemental analysis, a formula of the target complex was given. Moreover, the target complexes were also characterized by IR and UV-visible. The antibacterial experiments indicated that the target complexes have good antibacterial activities against *S. aureus, E. coli, B. subtillis* and *P. aeruginosa*.**

Keywords—Lysine-Salicylaldehyde ;Schiff base; Rare-Earth Complexes; Synthesis; Bioactivity.

Introduction

Schiff bases and their metal complexes have been widely Used in medicines, industrial catalysis, chemical analysis, metal corrosion and photochromism [1-4], due to their special biological functions. Early in the middle of the twentieth century, Rasenberg have found that amino acid-Schiff bases could inhibit cell division of E. coli. And then, a new field in the drug discovery research has been inaugurated since the antibacterial and anticancer activities of amino acid-Schiff bases were confirmed in 1969 [5-9].In recent years, with the development of functional complexes and bioinorganic chemistry, transition metal complexes of amino acid-Schiff bases also have made considerable progress. For example, they can be used as anticarcinogen, catalyzer of transamination of vitamin B_6, carrier of biotic ligand model, antioxidant, and so on. Therefore, to study the amino acid-Schiff base complex is very significant.

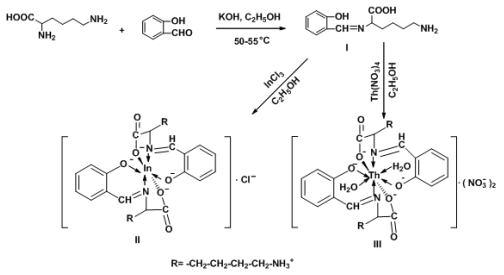
In this study, two novel of Rare-Earth (indium and thorium) Complexes with Schiff base from Lysine-Salicylaldehyde (Lys-Sal) were synthesized via the drop by drop reaction. The title complexes were confirmed by molar conductance, elemental analysis, IR and UV-visible. The bioassay revealed that the title complexes displayed good antibacterial activities. For example, they were effective in controlling *S. aureus*, *E. coli*, *B. subtillis* and *P. aeruginosa*. And to our knowledge, indium and thorium complexes with Lys-Sal Schiff base have not been reported.

I. EXPERIMENT

A. *Meterial and Instruent*

All the analytical grade reagents were purchased from commercial sources and used without further purification. Melting points were determined with an uncorrected X-4 digital melting point apparatus. UV spectra were measured on a ZF-6 ultraviolet analyzer at room temperature. IR spectra were recorded by using KBr pellets on a FTIR-8400S infrared spectrometer. Elemental analyses were determined with VarioEL type III elemental analyzer.

B. *Synthesis*



Scheme 1 The synthesis route of the title complexes **I, II**

B.1.Synthesis of Lys-Sal Schiff base (I)

Lysine (1.46 g, 10.0 mmol), KOH (0.56 g, 10.0mmol) and anhydrous ethanol (100 mL) were added into a dry three-neck flask. The mixture was heated to 50 °C until it was dissolved completely. Then, salicylaldehyde (1.22g, 10.0 mmol) which was dissolved in anhydrous ethanol (50 mL) was added slowly to the stirring mixture. The reaction was stirred at 55 °C for 0.5 h according to TLC analysis. After the pH adjusted to 6 ~ 8, the final mixture was filtered off by suction, and then washed with ether. The crude was recrystallized from anhydrous alcohol to yield the Lys-Sal Schiff base (I) as a yellow powder (1.56g, yield 62.3%, m.p. 228.1 ~ 229.6℃).

B.2. Synthesis of rare-earth metal complexes with Lys-Sal Schiff base (II)

To a stirred saturated solution of compd (I) (0.5g, 2.0 mmol) in anhydrous ethanol, another saturated solution of Indium chloride (0.22g, 1.0mmol) in anhydrous ethanol was added dropwise. The reaction was stirred at 55 °C until the finalization (appr 1.5 h) according to TLC analysis. Then, the mixture was concentrated *in vacuo*. Finally, the crude was recrystallized with anhydrous alcohol to obtain the title compd (II) as a yellow powder (0.35g, yield 54.1%, D.T. 255°C).

Complex（Ⅲ） was prepared by the same method as mentioned above and obtained as a yellow powder (0.59g, yield 67.2%, D.T. 283°C).

II. RESULTS AND DISCUSSION

A. Elemental analysis and molar conductance

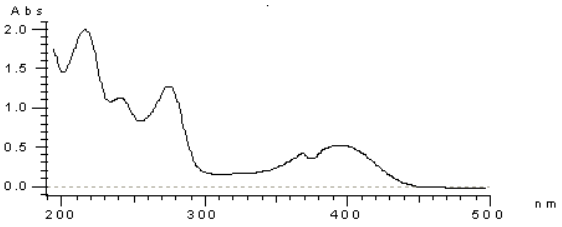
Elemental analysis and molar conductance values were listed in Tab. 1. The complexes were dissolved in DMF solution (1.0×10^{-3}mol•L^{-1}) and their molar conductances were determined at 25℃. It was obvious that molar conductivities of the target complexes I and II were greater than 60. So, it could be speculated that they were electrolyte.

Tab. 1 Elemental analysis and molar conductance of the compounds

Compds	Formula	Elemental analysis (calcd.)/ %				Λ_M ($S.c^2.mol^{-1}$)
		C%	H%	N%	RE%	
I	$C_{13}H_{18}N_2O_3$	62.23 (62.40)	7.12 (7.20)	11.25 (11.20)		
II	$InC_{26}H_{34}N_4O_6Cl$	48.26 (48.13)	5.33 (5.24)	8.86 (8.64)	17.57 (17.71)	62.43
III	$ThC_{26}H_{38}N_6O_{14}$	35.19 (35.04)	4.52 (4.26)	9.33 (9.43)	26.04 (26.10)	70.50

B. UV SPECTRA

Ultraviolet visible spectra of the free ligand (compd I) were given in Fig.2.1. The four absorption peaks of the ligand at ultraviolet region at 215, 241, 276, and 400 nm were assigned to the band of n - π* transitions of benzene ring and O atom in phenolic hydroxyl (E_2 band), π - π* transition of imidogen and benzene ring (K band), π - π* transition of benzene ring (B band), and of n-π* transition of benzene ring and N atom in imidogen (R band), respectively. And that, the weak absorption intensity of R band revealed that the electronics transition probability was low. Consequently, it was no doubt that Lys-Sal Schiff base (the free ligand, compd I) has been obtained successfully.

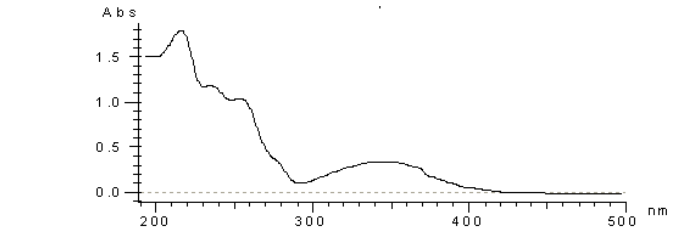


Peak #	Start (nm)	Apex (nm)	End (nm)	Height (Abs)	Area (Abs*nm)	Valley (nm)	Valley (Abs)
1	497.0	400.0	313.0	0.510	37.472	316.0	0.163
2	313.0	276.0	251.0	1.265	44.297	252.5	0.153
3	251.0	241.0	233.0	1.103	50.244	232.0	1.002
4	233.0	215.0	196.0	1.686	64.257	199.0	1.493

Fig.2.1 UV spectra of Lys-Sal Schiff base (compd I)

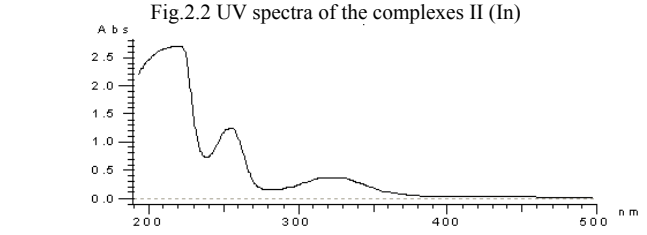
Ultraviolet visible spectra of the complexes II and III were shown in Fig.2.2 and Fig.2.3, respectively. At about 400nm, the original absorption peak disappeared, while a new absorption peak appeared at about 330nm. The reason could be that the increased electron delocalization has reduced the energy of π - π* transition due to the coordination between the

rare-earth metal and the O, N atoms in ligand. In other words, the complexes II and III were acquired smoothly.



Peak #	Start (nm)	Apex (nm)	End (nm)	Height (Abs)	Area (Abs*nm)	Valley(nm)	Valley(Abs)
1	497.0	348.5	295.5	0.333	23.115	298.5	0.123
2	295.5	220.0	196.0	1.691	98.527	199.0	1.496

Fig.2.2 UV spectra of the complexes II (In)



Peak #	Start (nm)	Apex (nm)	End (nm)	Height (Abs)	Area (Abs*nm)	Valley (nm)	Valley (Abs)
1	497.0	326.0	285.5	0.371	24.285	88.5	0.160
2	285.5	257.0	242.5	1.213	28.753	245.5	0.937
3	242.5	222.5	196.0	2.680	97.030	99.0	2.441

Fig.2.3 UV spectra of the complexes III (Th)

Tab. 2 UV spectra data of Lys – Sal Schiff base and its complexes

Compds	λ_1/nm	λ_2/nm
I / H_2L	276	400
II / InL_2Cl	220	348
III / $ThL_2(NO_3)_2 \cdot 2H_2O$	257	326

C. Ir Spectra

A strong absorption bands appeared at a low frequency 1616 cm^{-1} was attributed to the C=N group, which further illustrated the existence of the ligand (compd I). The original absorption peak of phenolic hydroxyl disappeared in the formed complexes. It indicated that the H atom of phenolic hydroxyl has been eliminated, while the O anion and metal ion have been cooperated. The absorption bands appeared at 762 ~ 745 cm^{-1} and 656 ~ 601 cm^{-1} were belonged to the RE-O bond and the RE-N bond, respectively.

In the complex III, an absorption band exhibited at 3413 cm^{-1} revealed the presence of water, which may be involved in the coordination. And, a strong absorption band appeared at about 1384 cm^{-1} was ascribed to the free NO_3^-. It revealed that the NO_3^- was outside of the complex, which was consistent with the results of molar conductance. Additionally, in the complexes II and III, the -COO^- frequency differences between the symmetric and antisymmetric stretching vibration were 94 cm^{-1} and 111cm^{-1}, respectively. Therefore, it could be speculated that the carboxyl group of lysine played a role of monodentate in the coordination reaction.

Tab.3 IR spectra data of the Schiff base and its complexes

Compds	IR,σ/cm^{-1}					
	ν-OH	νC＝N	COO^- vas	COO^- va	νRE-O	νRE-N
I / H_2L	3435	1616				
II / InL_2Cl		1608	1525	1431	745	656
III / $ThL_2(NO_3)_2 \cdot 2H_2O$		1622	1584	1473	762	601

D. Antibacterial activity

The bioassay of the free ligand (I) and the title complexes (II, III) was evaluated by filtering paper method against four bacterial species, such as *S. aureus*, *E. coli*, *B. subtillis* and *P. aeruginosa*. The used level of bactericide was 2 mg/mL. Compd I and II were dissolved in DMSO, while compd III was dissolved in anhydrous ethanol. A similar group was dosed with DMSO and anhydrous ethanol to serve as the control. Obviously, the antibacterial activities of the complexes (II, III) were enhanced in general after chelating (as shown in Tab. 4). It demonstrated that the rare earth metal ions have played a certain promotive role in bioactivity of the complexes.

Tab. 4 Antibacterial activity of the Schiff base and its complexes

Compds	*S. aureus*	*E. coli*	*B. subtillis*	*P. aeruginosa.*
I / H_2L	-	-	+	-
II / InL_2Cl	+	+	++	+
III/$ThL_2(NO_3)_2 \cdot 2H_2O$	+	+	+	++

"-"show weak，"+"show strong，"++"show very strong

III. CONCLUSION

To sum up, two new rare-earth metal complexes with Schiff base of lysine-salicylaldehyde [In(Lys -Sal), Th(Lys -Sal)] were synthesized and characterized. And their bioactivities were also evaluated. The bioassay showed that the target complexes have excellent antibacterial activities.

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