Synthesis, Characterization and Antibacterial Activity of New Ln(III) Complexes with an Unsymmetrical Schiff Base Ligand

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Abstract A new unsymmetrical Schiff base ligand (H2LLi) was synthesized using L-lysine, salicylaldehyde and 2-hydroxy-1-naphthaldehyde. Three solid metal complexes of this ligand [Ln(H2L)(NO3)] NO3·2H2O (Ln = La, Sm, Ho) have been prepared and characterized by elemental analyses, IR spectra, UV spectra, TG-DTG and molar conductance. The antibacterial activities of the ligand and its complexes are also studied. The antibacterial experiments indicate that the ligand and its complexes possess antibacterial activity against Escherichia coli, Staphylococcus aureus and Bacillus subtilis and that the complexes have higher activity than those of the ligand.

Key words unsymmetrical Schiff base; Ln(III) complex; synthesis; characterization; antibacterial action

1 Introduction

Some Schiff base complexes derived from amino acids are particularly active in biology catalysis and material. The study of them is focus of the study of coordination chemistry. Recently, studies of such metal complexes of mono-Schiff bases have been reported (Fan et al., 2003a, b; Liu et al., 2003; Sigh and Agrawal, 1985). To continue the investigation in this area, a new unsymmetrical Schiff base ligand has been synthesized starting from L-lysine, salicylaldehyde and 2-hydroxy-1-naphthaldehyde. Since this ligand has not been reported in the literature, this paper deals with the preparation and characterization of the complexes formed from this Schiff base ligand (See Fig.1) with La(III), Sm(III) and Ho(III). The antibacterial activities of the ligand and its complexes are also studied. This paper offers a new method for preparing this kind of unsymmetrical Schiff base and its complexes, which is of significance in many fields of biology.

Fig.1 Structure of the ligand.

2 Experiment

2.1 Physical Measurement and Reagents

Elemental analyses were carried out with a model 2400 Perkin-Elmer analyzer. The metal content was determined gravimetrically. The ultraviolet spectra were recorded on a Shimadzu UV-3000 spectrophotometer in DMSO. The molar conductance was measured with a Shanghai DDS-11A conductivity meter. The infrared spectra of the ligand and its complexes were recorded in KBr pellets using a Bio-Rad FTS 165 spectrophotometer. Thermogravimetric measurements were made using a Perkin-Elmer TGA7 instrument. The heating rate was programmed to be 10°C min⁻¹ with a protecting stream of N₂ flowing at a rate of 40 mL min⁻¹. The mass spectrogram of the ligand was recorded on a Finnegan MAT-212 mass spectrometer.

All reagents used in this work were of analytical grade. Hydrated Ln(III) nitrate was prepared by reaction of Ln(III) oxide with nitric acid.

2.2 Preparation of Ligand

Mono-Schiff Base (HR); L-lysine (2.193 g, 15 mmol) was dissolved in 230 mL anhydrous ethanol and methanol in the ratio of 1:1, heated for 1.5 h at 50–55°C, and filtered. Salicylaldehyde (1.7 mL, 15 mmol) was added dropwise to the above filtered solution and stirred for 2 h at 50–55°C to give a yellow precipitate. The precipitate was collected by filtration, washed with ethanol, and dried in vacuum. Yield: 2.929 g (78%); mp: 223 – 224°C.
Unsymmetrical Schiff base (H₂Li): HR (1.251 g, 5 mmol) and lithium hydroxide (0.120 g, 5 mmol) were dissolved in 60 mL anhydrous methanol and isopropanol in the ratio of 1:5 and stirred for 1 h at 50 – 55 °C. 2-Hydroxy-1-naphthaldehyde (0.861 g, 5 mmol) dissolved in 15 mL isopropanol was added dropwise to the above solution and stirred for 4 h at 50 – 55 °C to give a brown precipitate. The precipitate was collected by filtration, washed with ethanol and dried in vacuum. Yield: 1.457 g (76%)

2.3 Preparation of Complexes

The unsymmetrical Schiff base (1.231 g, 3 mmol) dissolved in 65 mL anhydrous methanol and isopropanol in the ratio of 1:5 was mixed with the lanthanide nitrate hexahydrate (3.0 mol) dissolved in 15 mL anhydrous ethanol and stirred for 3 h at 50 – 55 °C to give a light-brown precipitate. The precipitate was filtered, recrystallized with anhydrous methanol and isopropanol in the ratio of 1:5 and dried in vacuum. The purity of the complexes was higher than 99%.

3 Results and Discussion

The synthesis reactions of the ligand are shown in Fig. 2.

Table 1 Analytical and physical data of the ligand and its complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Empirical formula</th>
<th>Formula weight</th>
<th>Yield (%)</th>
<th>Color</th>
<th>D.P. (°C)</th>
<th>Anal. found (Calcd.) (%)</th>
<th>Molar conductance (S cm² mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂Li</td>
<td>C₂H₂LiN₂O₄</td>
<td>410.4</td>
<td>76</td>
<td>Brown</td>
<td>308</td>
<td>69.95 (70.23) 5.64 (5.65) 6.30 (6.83)</td>
<td>55.4</td>
</tr>
<tr>
<td>La(H₂Li)(NO₃)₂(H₂O)₂</td>
<td>C₆H₁₂LaN₄O₁₂</td>
<td>702.4</td>
<td>68</td>
<td>Light</td>
<td>249</td>
<td>41.80 (41.04) 3.84 (3.87) 7.94 (7.98) 20.55 (19.78)</td>
<td>60.1</td>
</tr>
<tr>
<td>Sm(H₂Li)(NO₃)₂(H₂O)₂</td>
<td>C₆H₁₂SmN₄O₁₂</td>
<td>713.9</td>
<td>62</td>
<td>Light</td>
<td>216</td>
<td>40.78 (40.38) 3.79 (3.81) 7.82 (7.85) 20.51 (21.07)</td>
<td>60.1</td>
</tr>
<tr>
<td>Ho(H₂Li)(NO₃)₂(H₂O)₂</td>
<td>C₆H₁₂HoN₄O₁₂</td>
<td>728.4</td>
<td>71</td>
<td>Light</td>
<td>232</td>
<td>39.77 (39.58) 3.76 (3.74) 7.63 (7.69) 22.92 (22.64)</td>
<td>60.2</td>
</tr>
</tbody>
</table>

Note: D. P. stands for decomposition temperature.

The synthesis reaction of the complexes may be represented as shown below.

\[ \text{Ln(NO}_3\text{)}_3 \cdot x\text{H}_2\text{O} + \text{H}_2\text{Li} \rightarrow [\text{Ln(H}_2\text{Li)(NO}_3\text{)}_2\text{H}_2\text{O} + \text{Li(NO}_3\text{)}_2 + (x \text{-} 2)\text{H}_2\text{O}] \]

The results of the elemental analyses and molar conductance data are shown in Table 1. The molar conductance values of the complexes measured in DMSO in 1.00 \times 10⁻³ mol L⁻¹ solution fall in the range 55.4 – 60.1 S cm² mol⁻¹, which is expected for 1:1 electrolytes (Geary, 1971). This suggests that one nitrate ion be within the coordination sphere and the second nitrate ion be ionic and not coordinated. The complexes are stable in air and soluble in DMSO and DMF; however they are insoluble in diethyl ether, benzene and acetone.

3.1 Mass Spectrum

The mass spectrum of H₂Li is shown in Fig. 3. The molecular weight of H₂Li is 410, which indi-