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New complexes of lanthanide Ln(III), (Ln = La, Sm, Gd, Er) with Schiff bases derived from 2-furaldehyde and phenylenediamines

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ABSTRACT

Some new Schiff bases derivates from 2-furaldehyde and phenylenediamines (L^{1-3}) and their complexes with lanthanum (La), samarium (Sm), gadolinium (Gd) and erbium (Er) have been synthesized. These complexes with general formula $[Ln(L^{1-3})_2(NO_3)_2]NO_3 \cdot nH_2O$ (Ln = La, Sm, Gd, Er) were characterized by elemental analysis, UV–Vis, FT-IR and fluorescence spectroscopy, molar conductivity and thermal analysis. The metallic ions were found to be eight coordinated. The emission spectra of these complexes indicate the typical luminescence characteristics of the Sm(III), La(III), Er(III) and Gd(III) ions.

1. Introduction

Luminescent lanthanide complexes have attracted a lot of attentions due to their applications in fluorescence materials, electroluminescent devices and medicinal diagnostics. The luminescent properties of lanthanides complexes are dependent of the f-configuration of the metal and organic ligands [1]. The Schiff bases are considered a very important class of ligands, which form complexes with many metals. These complexes have wide applications in some biological aspects [2], analytical fields [3,4], organic catalysis [5,6], oxygen carriers [7,8].

The coordinative chemistry of lanthanides has received intense interest because of its intriguing variety of architecture and potential applications in various areas such as magnetism, optics, electronics and catalysis, sensors in biomedical field area [9,10]. The ability to detect analytes such as DNA, proteins or other biological active molecules at small concentration and in the presence of a complicated matrix or even *in vivo* remains a challenging task. Many of these bioassays often rely on lanthanide fluorescence, which can furnish detection limits in the nano and picomolar region [11]. Specifically, large shift and their long-living fluorescence make trivalent cations as very attractive reporters for these assays. Lanthanide complexes with Schiff bases can be used as fluorescent indicators for neutral sugars and cancer biomarkers [12].

Coordination numbers of lanthanide complexes are in range from six to twelve, eight and nine being the most common coordination numbers. Lanthanides are weak Lewis acids and preferably coordinate to hard Lewis bases like oxygen.

In this paper, we report synthesis of some new complexes of La(III) and Sm(III), Er(III) and Gd(III) with Schiff bases derived from 2-furaldehyde and aromatic diamines. The complexes were analyzed by elemental analysis, UV–Vis, FT-IR and fluorescence spectroscopy, thermal analysis and molar conductance.

2. Experimental

2.1. Materials and methods

All reagents used in this work were of analytical grade. Elemental analysis (C, H, N) was performed by Perkin–Elmer analyser model 240. ^1H NMR of the ligand was performed using a Bruker AM 350 spectrometer. Spectra were obtained in $CDCl_3$ and chemical shifts calculated in ppm with respect to TMS ($\delta = 0$). The mass spectra were recorded on a GCMS-QP 2010 Shimadzu mass spectrometer with DI (direct inlet) and CI (chemical ionization). The system was equipped with a 25 m × 0.25 mm × 0.25 μm DB-5 ms capillary column. The ion source, the quadrupole and interface temperatures were 330 °C. Helium was used as carrier gas at constant flow (1.54 mL min^{-1}), with an initial pressure of 90.7 kPa, while methane was used as reagent gas in the mass spectrometer. The electron multiplier voltage was set at 1250 V. Two microliters of diluted solution were injected in cold pulsed splitless mode (initial injector

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temperature at 250 °C). Temperature of the AT-5 column was programmed from 50 °C, stay 2 min, then to 320 °C at a rate of 15 °C min^{-1}, stay 5 min then to 320 °C. The electronic UV–Vis spectra of the ligands and complexes solution were determined with UV–Vis Jasco 550 spectrophotometer in acetonitrile solutions. The fluorescence emissions of complexes and ligands were recorded with Perkin–Elmer LS 50 B spectrometer in acetonitrile solutions (1 mM). The infrared spectra of the ligand and complexes in the region 400–4000 cm^{-1} were recorded using a Digilab BioRad FTS 2000 FT-IR spectrophotometer, using KBr pellets, 24 scans, resolution 4 cm^{-1}. The molar conductance was measured with Consort K 912 conductivity meter. Thermal studies were made with Perkin–Elmer Diamond device, between 35 and 950 °C, in an atmosphere of nitrogen, with a heating rate of 10 °C min^{-1}, and the debit of nitrogen of 110 mL min^{-1}.

2.2. Preparation of ligand

The ligands were obtained from the condensation of 1-furfurylaldehyde and corresponding diamine in 2:1 M ratio, in an organic solvent medium; the acetic acid was used as catalyst. The yellow-orange precipitates obtained were filtered, washed with ethanol and dried in vacuum. The yield of the Schiff bases was between 61% and 89%.

L^1: Yield 61%; melting point (M.p.) 169–170 °C; MS-EI(+): *m/z* 264. ^1H NMR ($CDCl_3$) δ(ppm): 8.35 (s, 2H, –CH=N), 7.65 (d, 2H, fur., *J* = 2.56 Hz), 7.35 (s, 4H, arm., *J* = 2.85 Hz), 7.05 (d, 2H, fur., *J* = 2.65 Hz), 6.55 (t, 2H, fur., *J* = 2.69 Hz).

L^2: Yield 89%; melting point (M.p.) 240–242 °C; MS-EI(+): *m/z* 340. ^1H NMR ($CDCl_3$) δ(ppm): 8.35 (s, 2H, –CH=N), 7.60 (d, 2H, fur., *J* = 8.33 Hz), 7.45 (s, 4H, arm., *J* = 7.91 Hz), 7.25 (d, 4H, ar., *J* = 6.64 Hz), 7.00 (d, 2H, fur., *J* = 2.76 Hz), 6.50 (t, 2H, fur., *J* = 2.55 Hz).

L^3: Yield 67%; melting point (M.p.) 173 °C; MS-EI(+): *m/z* 314. ^1H NMR ($CDCl_3$) δ(ppm): 7.75 (s, 2H, –CH=N), 7.55 (d, 2H, fur., *J* = 2.21 Hz), 7.35 (d, 4H, arm., *J* = 5.79 Hz), 7.28 (t, 2H, arm., *J* = 5.92 Hz), 7.05 (d, 2H, fur., *J* = 2.35 Hz), 6.60 (t, 2H, fur., *J* = 2.46 Hz).

2.3. Synthesis of complexes

The Ln(III) (Ln = La, Sm, Gd and Er) complexes were synthesized by reactions of $Ln(NO_3)_3{\cdot}nH_2O$ (n = 4, 6) and corresponding ligands. To a solution of 1 equiv. of ligand, dissolved in 25 mL of EtOH at 40 °C, was added by dropping 0.5 equiv. of $Ln(NO_3)_3$ water solution (10 mL). The solution was stirred (at 40–50 °C) for 2 h. After cooling at the room temperature, the solid was filtered and washed with water, ethanol–water and absolute ethanol. After drying in vacuum the complexes were analyzed.

3. Results and discussion

The general structures of the ligand are presented in Fig. 1

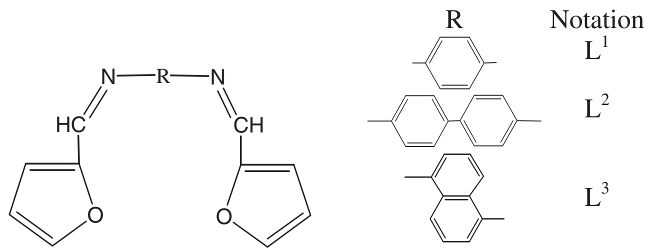

Fig. 1. The structures of the ligands.

The ligands were characterized by elemental analysis, ^1H NMR, FT-IR, UV–Vis spectroscopy and mass spectrometry. The results of these analyses confirm the structure of the ligands.

The formations of the complexes were monitorized through elemental analyses, UV–Vis, FT-IR and fluorescence spectroscopy, conductometry, thermal analysis and mass spectrometry. These complexes are stable in air and soluble in DMF, DMSO, acetonitrile and slightly soluble in methanol, ethanol and poorly soluble in chloroform. The elemental analysis presented in Table 1 indicates that the obtained complexes have a good purity.

Mass spectrometry is an effective method for investigation of molar weight and structure of the ligands and complexes. Mass spectrometry chemical ionization (MS CI) of the ligands show abundant molecular ions $[M]^{\cdot+}$ at m/z = 340, and important fragments at 270 $[C_{18}H_{13}N_2O]^+$ (obtained by loss a furfural molecule $[C_4H_3O]$), 170 $[C_{12}H_{13}N]^+$ and 152 $[C_{12}H_8]^+$, Fig. 2. The mass spectra of the complexes exhibited a peak at a m/z value corresponding to their molecular weight, Table 1. Around this value, some other peaks were present that could be assigned to the molecular weight of the compounds with the various isotopes [13].

The molar conductance value of the complexes measured in DMF solution (10^{-3} mol L^{-1}) at 25 °C are in range 78–89 S cm^2 mol^{-1}, indicating 1:1 electrolytes [14]. These data suggest that two nitrate ions are present inside of the coordination sphere and another is outside sphere. The results of elemental analysis indicate that the composition of the complexes is $[Ln(L^{1-3})_2(NO_3)_2]{\cdot}NO_3{\cdot}nH_2O$ (Ln = La, Sm, Gd, Er) and the ratio of Ln/L in all complexes are 1:2.

The electronic spectra of the free ligands in acetonitrile showed strong absorption bands in UV–Vis region (264–370 nm) attributed to the π–π^* and n–π^* transitions [15,16]. The complexes spectra generally show the characteristic bands of the free ligands with some changes both in frequencies and intensity, Fig. 3.

All modifications in the UV–Vis spectra are presented in Table 2.

These modifications of the shifts and intensity of the absorption bands confirmed the coordination of the ligand to the metallic ion. The Ln(III) ions have a d^0 configuration and they have not d–d transition bands.

3.1. Infrared spectra

The IR spectra of the ligands and complexes all showed major bands around 1625 cm^{-1} that can be assigned to $\nu_{C=N}$ and around 1586, 1490, 1285, 1151, 1070 cm^{-1} corresponding to furfural ring and 1556, 1109 and 821 cm^{-1} assigned to vibrations rings of phenyl groups. The $\nu_{C–O}$, $\nu_{C–C}$ and $\nu_{C–O}$ stretching vibration in the complexes are observed as a number of bands lying in the region 1285–1145 cm^{-1} [17].

FT-IR spectra of the complexes present modification of the ligands' bands and there appear some new bands. The strong and relatively broad band around 1625 cm^{-1} in the spectra of free ligands is observed at nearly the same frequency in the Ln(III) complexes. This observation indicate at once that nitrogen atoms are not the binding sites and oxygen atoms should be the most probable sites to coordinate with the Ln(III) ions [15]. The absorption bands assigned to the coordinate nitrate groups were observed around of 1315, 1031, 1420 cm^{-1} in these complexes, respectively. The majority of the structurally characterized lanthanide nitrate complexes the nitrate ligands are bidentated [18]. And the noteworthy band at 1385 in the spectra of the complexes indicates that the free nitrate group is present [19]. There are new bands around 3400 cm^{-1} which are characteristically for H_2O non-coordinated to metal ions, in the complexes, which is in accordance with the results of TG–DTA. Furthermore, two additional new bands are observed around of 1650 and 850 cm^{-1} due to the bending and rocking motion of H_2O [20].