



Synthesis and Spectral Studies of Lanthanum(III) and Neodimium(III)-2.9 Dimethyl-1.10 Phenantroline Complexes with Piperidine Dithiocarbamate

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ABSTRACT

Synthesis and spectral analysis of Lanthanide complexes with piperidine dithiocarbamate ligand have been synthesized. Complex compound were prepared by "in situ method" and characterized using fourier transform infrared and UV-vis analysis. The result of the studies reveals that complex compound the both of La(III) and Nd(III)-piperidine dithiocarbamate-2,9 dimethyl-1,10 phenantroline successfully synthesized. The infra-red spectral studies reveals that dithiocarbamate behaves as bidentat ligand and coordinates to La(III) and Nd(III) via the two sulphur of dithio group. The UV-vis spectral studies reveal that electronic transition of complex compound i.e $\pi-\pi^*$.

Keywords: Lanthanum; Neodimium; Piperidine dithiocabamate; Dimethyl phenantroline; Spectral; FT-IR; UV-vis

INTRODUCTION

Dithiocarbamate are chelating ligand which form stable complexes with all the transition elements and also the majority of main group, lanthanide and actinide elements [1]. The lanthanides present various unique chemical properties that are favorable for both biological and materials research, and interest in their applications is increasing [2,3]. Lanthanide complexes have received attention due to a wide field of applications [4-6].

Metal or ligands can be varied in an easily controlled way to facilitate individual applications [7] and the study of lanthanide complexes with organic ligands has received considerable attention [8,9].

They have diverse applications such as additives to commercial pavement asphalt, [10] in analytical determinations, [11] and as potent biological pesticides and/or pharmaceuticals [12] and recently their use in catalysis [13] and materials science [14] is receiving considerable attention.

Two structures La(Pipdte)₃(Dmphen) and Nd(Pipdte)₃(Dmphen) have been synthesized. In the present study, complex Ln(C₆H₁₀NS₂)₃ (C₁₄H₁₄N₂) has been synthesized by reaction of lanthanide chloride with potassium piperidine-dithiocarbamate (abbreviated as pip-dtc) and 2,9 dimethyl-1,10 phenantroline (abbreviation as Dmphen) in absolute methanol, and characterized by UV-vis and FT-IR spectroscopy.

We are interested in characterization of 'spectroscopies' in the process of the preparations for dithiocarbamate and lanthanide complexes, which would help further understanding of these complexes and provide a numeric basis for the computer-aided molecular designs of new materials.

EXPERIMENTAL SECTIONS

Synthesis of the ligand

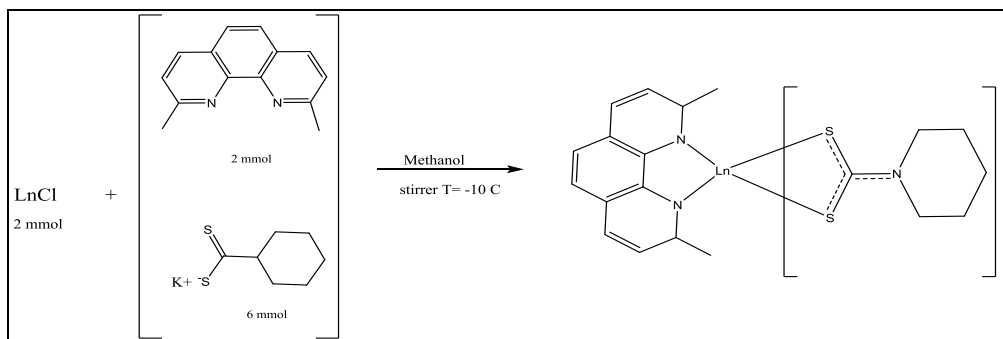
The ligand piperidine dithiocarbamate potassium salt (pip-dtc) has been synthesized using reported method with slight modification [15]. In a typical experiment potassium hydroxide (6 mmol) was dissolved 2 mL of water in ice bath and 15 mL of methanol was added to it.

The solution was stirred with the addition of carbon disulfide (6 mmol), followed by drop by drop of pipridine (6 mmol) which yield yellow solution. The yellow solution was collection and slow evaporated and the pure white product was precipitated by adding required volume of methanol-chloroform (2:3). FT-IR (KBr pellet, cm^{-1}): $\nu_{\text{C-N}}$, 1479; $\nu_{\text{C-S}}$, 1001.06. UV-vis (nm): 2,62 and 305.

Synthesis of Ln(III) complexes

The method adopted for synthesis of these complexes is shown in scheme 1. In a typical experiment, a solution of pip-dtc (6 mmol) and DmPhen (2 mmol) in 15 mL methanol was added to solution of corresponding lanthanide chloride (2 mmol) in 5 mL methanol.

The reaction was stirred for 2 hours in ice bath temperature (minus 10°C) and solid complex gets precipitated. Then the solid complex was isolated through filtration and washed several times with methanol. The Ln(III) complexes were characterized using UV-vis and FT-IR techniques.



Scheme 1: Preparation of the $[\text{Ln}(\text{pip-dtc})_3(\text{Dmphen})]$, where Ln = La(III) and Nd(III)

RESULTS AND DISCUSSION

The $[\text{Ln}(\text{pip-dtc})_3(\text{Dmphen})]$ complexes (where Ln = La(III) and Nd(III)) were synthesized and characterized using spectroscopic techniques as UV-vis and FT-IR.

Electronic absorption studies

The electronic absorption spectrum the both of $[\text{La}(\text{pip-dtc})_3(\text{Dmphen})]$ and $[\text{Nd}(\text{pip-dtc})_3(\text{Dmphen})]$ were recorded in mix chloroform-methanol solvent and are shown in figures 1 and 2, respectively. For the mix ligand complexes, there are three absorption bands in UV region at 266, 307 and 329 nm.

The first band (shorter wavelength band) in the spectrum attributed to the $\pi-\pi^*$ transition of the bidentate aromatic Dmphen ligand. The very intense band at 266 nm is a result overlapping absorption peaks of the aromatic Dmphen ligands and the NCS_2 chromophore of the dithiocarbamate [16].

In the visible region, weak and narrow peaks characteristic of the Laporte-forbidden f-f transitions of the lanthanide ions are observed figure 2.

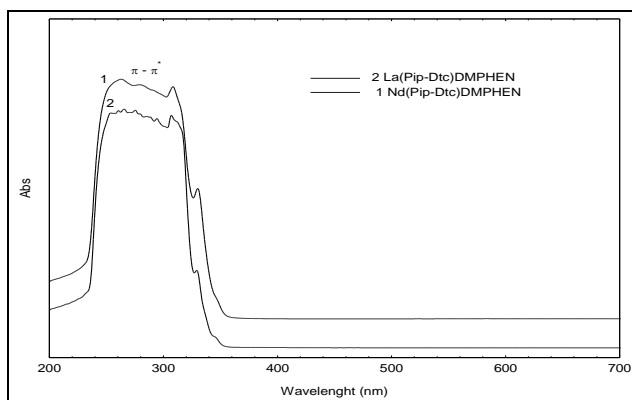


Figure 1: Electronic absorption spectrum of [Nd(pip-dtc)₃Dmphen (1) and [La(pip-dtc)₃Dmphen(2)

The observed f-f transition for [La(pip-dtc)₃(Dmphen)] and [Nd(pip-dtc)₃(Dmphen)] are given in figure 2.1 and 2.2, respectively. For the [La(pip-dtc)₃(Dmphen)], the absorbed f-f transition (figure 2) corresponds to transitions from the ground state ³H₄ to the excited state ³P₂, ³P₁, ³P₀ and ¹D₂.

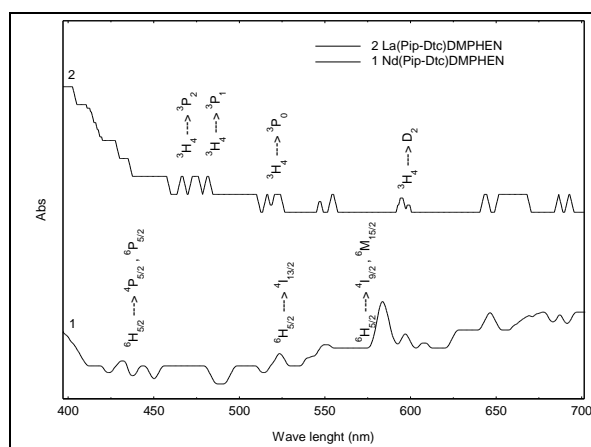


Figure 2: The inset shows the f-f transitions of complexes, [Nd(pip-dtc)₃Dmphen (1) and [La(pip-dtc)₃Dmphen (2)

From optical properties (transmittance) measurements (400-700 nm) of selected complex [Nd(pip-dtc)₃Dmphen] in figure 3, it was obtained the maximum optical transmittance of complex compound is 99% (599 nm).

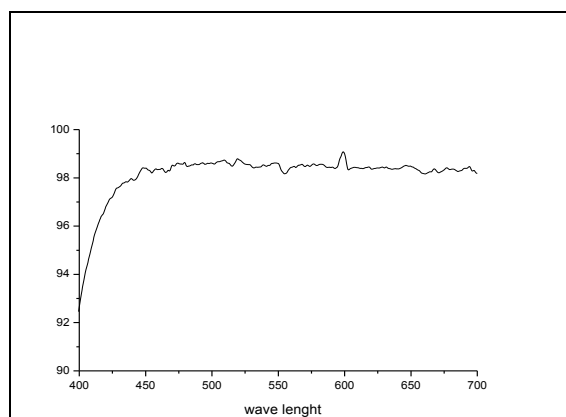


Figure 3: Optical properties of complex [Nd(pip-dtc)₃Dmphen

FT-IR study

Comparison of infrared spectra of the complexes are depicted in Figure 3 and table 1. The important infrared peaks of the complexes are shown in table 1. The $\nu(\text{C}=\text{N})$ modes appeared in the region of thioureide band ($1450\text{--}1550\text{ cm}^{-1}$), while $\nu(\text{C}=\text{S})$ modes appeared in the region $950\text{--}1002\text{ cm}^{-1}$ [17-18]. The FT-IR spectrum of the free dithiocarbamate ligand exhibited a doublet at 1002 and 967 cm^{-1} corresponds to $\nu\text{C-S}$ stretching [19]. The FT-IR spectra both of the the $[\text{Nd}(\text{pip-dtc})_3\text{Dmphen}]$ and $[\text{La}(\text{pip-dtc})_3\text{Dmphen}]$ complexes are similar, it appeared as a singlet peak at 1003.9 and 1000.29 cm^{-1} indicating coordination of the ligand in a bidentat manner with lanthanide ion. The peak corresponds to C-N stretching appeared at 1502.05 and 1520.1 cm^{-1} in the $[\text{Nd}(\text{pip-dtc})_3\text{Dmphen}]$ and $[\text{La}(\text{pip-dtc})_3\text{Dmphen}]$, respectively.

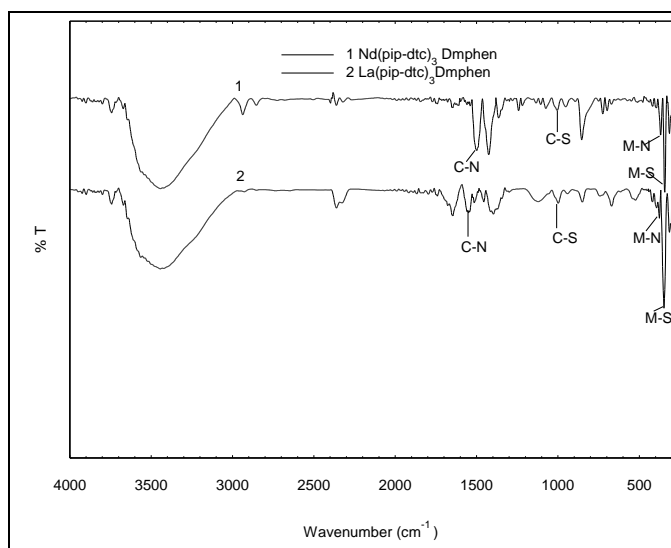


Figure 4: Infrared spectrum of $[\text{Nd}(\text{pip-dtc})_3\text{Dmphen}]$ (1) and $[\text{La}(\text{pip-dtc})_3\text{Dmphen}]$ (2)

Table 1: Infrared data for $\text{Ln}(\text{Pip-dtc})_3\text{Dmphen}$

Complexes	Frequency (cm^{-1})			
	C-N	C=S	Ln-N	Ln-S
$\text{La}(\text{pip-dtc})_3$ (Dmphen)	1502.05	1003.9	368.585	346.927
$\text{Nd}(\text{pip-dtc})_3$ (Dmphen)	1520.1	1000.29	379.415	350.537

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