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Synthesis and Characterization of Lanthanon Chelates of Thiohydroxamic Acids: Studies on Lanthanon Chelates of N-Thioacetyl-N-phenylhydroxylamine

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ABSTRACT

New chelates of lanthanon with N-thioacetyl-N-phenylhydroxylamine have been prepared. The available data and physical properties of the chelates indicate the attachment of each rare earth ion to three molecules of ligand and four molecules of water. This is supported by elemental analysis and UV and IR absorption spectra.

INTRODUCTION

In continuation to our studies on the chelating behavior of thiohydroxamic acids [1-4], the present communication describes the preparation and spectral characteristics of La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, and Gd^{3+} N-thioacetyl-N-phenylhydroxylamine complexes. Physicochemical studies

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enhanced the chelation of each lanthanon ion to three molecules of the ligand under investigation and four molecules of water. Elemental analysis and UV and IR absorption spectra support the chelation.

EXPERIMENTAL

All chemicals used were of AnalaR grade. The metal content in all the chelates was estimated by standard methods [5, 6].

N-thioacetyl-N-phenylhydroxylamine was prepared by a slight modification of the method of Egwa et al. [7]. N-acetyl-N-phenylhydroxylamine [8] was prepared, and its thionation with phosphorous pentasulfide in dioxane yielded N-thioacetyl-N-phenylhydroxylamine. It was crystallized from ethanol. The purity of the compound was checked by elemental analysis, thin-layer chromatography, and IR spectra.

A weighed quantity of the lanthanon oxide was dissolved in hydrochloric acid (AR), and the solution was evaporated to dryness to remove excess acid. The residue was extracted with 25 mL of ethanol to which a calculated amount of N-thioacetyl-N-phenylhydroxylamine (mole ratio of 1:3) in 30 mL of absolute alcohol was added. The pH was adjusted to 5.5. The resulting mixture was concentrated on a steam bath to separate the solid lanthanon complex. Crystals of the complex so obtained were washed several times with acetonitrile to remove the undesired impurities of ligand and metal, and dried in a vacuum desiccator. These complexes were found to be soluble in dimethylformamide and chloroform.

The physicochemical properties of N-thioacetyl-N-phenylhydroxylamine-lanthanon chelates are summarized in Table 1.

RESULTS AND DISCUSSION

IR Spectra

The 3170-3160 cm^{-1} region enhances the lowering of νOH in the complexes.

The peaks observed around 1180-1165 cm^{-1} of the complexes correspond to the characteristic group νC=S.

The 930-800 cm^{-1} region is very important because it contains the C–N and N–O stretching vibrations which provide interesting information on the strength of the bond formed by the metal to the ligand. The C–N stretching vibrations observed are of low intensity and are found in the 860-825 cm^{-1} region (Table 2).

TABLE 1. Physicochemical Properties of Rare-Earth Complexes of N-Thioacetyl-N-phenylhydroxylamine

Compound	mp (°C)	Elemental analysis (%)				Molecular weight	
		Calculated		Found			
		N	S	N	S	Calculated	Found
$(C_8H_8NOS)_3La4H_2O$	196	5.92	13.54	5.73	13.72	708.91	712.82
$(C_8H_8NOS)_3Pr.4H_2O$	203	5.91	13.50	5.82	13.62	710.99	718.22
$(C_8H_8NOS)_3Nd.4H_2O$	184	5.88	13.44	5.84	13.36	714.24	721.35
$(C_8H_8NOS)_3Sm.4H_2O$	227	5.83	13.33	5.94	13.24	720.35	730.40
$(C_8H_8NOS)_3Gd.4H_2O$	219	5.77	13.20	5.65	13.36	727.25	732.10

TABLE 2. IR Spectra of Rare-Earth Complex of N-Thioacetyl-N-phenylhydroxylamine

Compound	IR Nujol maximum (cm^{-1})			
$(C_8H_8NOS)_3La.4H_2O$	3165	1170	930	851
$(C_8H_8NOS)_3Pr.4H_2O$	3170	1165	925	834
$(C_8H_8NOS)_3Nd.4H_2O$	3165	1178	928	842
$(C_8H_8NOS)_3Sm.4H_2O$	3160	1174	920	825
$(C_8H_8NOS)_3Gd.4H_2O$	3168	1169	924	858

TABLE 3. UV Spectra and Molecular Conductance of Rare-Earth Complexes of N-thioacetyl-N-phenylhydroxylamine

Compound	UV λ_{max} ($CHCl_3$) (nm)	Molecular conductivity (mhos)
$(C_8H_8NOS)_3La.4H_2O$	287	14
$(C_8H_8NOS)_3Pr.4H_2O$	278	10
$(C_8H_8NOS)_3Nd.4H_2O$	289	8
$(C_8H_8NOS)_3Sm.4H_2O$	294	11
$(C_8H_8NOS)_3Gd.4H_2O$	285	17

Molecular Conductance

The molecular conductivities of the lanthanon chelates was determined in dimethylformamide (M/1000 solution) solvent, and they are indicative of the nonelectrolyte nature of the chelates (Table 3).

Electronic Spectra

Electronic spectra of these chelates in chloroform were also observed and the results are given in Table 3.

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