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Xishi Tai^a; Huiqin Wang^a; Xiaozheng Sun^a; Minyu Tan^b

^a Department of Chemistry, Weifang University, Weifang, People's Republic of China ^b College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, People's Republic of China

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Synthesis and Spectral Characterization of Methyl-2-pyridyl Ketone Benzoyl Hydrazone and Its Complexes with Rare Earth Nitrates

Xishi Tai, Huiqin Wang, and Xiaozheng Sun

Department of Chemistry, Weifang University, Weifang,
People's Republic of China

Minyu Tan

College of Chemistry and Chemical Engineering, Lanzhou University,
Lanzhou, People's Republic of China

Abstract: The hydrazone ligand, methyl-2-pyridyl ketone benzoyl hydrazone (L), and its complexes with rare earth nitrates have been synthesized. These new complexes with the general formula of $\text{Ln}(\text{L})_2(\text{NO}_3)_3 \cdot \text{nH}_2\text{O}$ (where $\text{Ln} = \text{La}$, $n = 5.5$; Ce , Pr , $n = 5$; Nd , Eu , $n = 4$) were characterized by mass spectra, elemental analysis, IR spectra, thermal analysis, UV spectra, molar conductivity, and luminescent spectra. All the complexes are stable in air. The results show that the lanthanide ions in each complex are coordinated through oxygen and nitrogen atoms of the ligand, the oxygen atoms of the nitrate, and coordinated water molecules. The amide-oxygen atoms of L coordinate to the Ln ions in its keto-form. Tentative structures for the complexes have been proposed.

Keywords: Complex, methyl-2-pyridyl ketone benzoyl hydrazone, rare earth nitrates, spectral characterization, synthesis

INTRODUCTION

Metal complexes of hydrazone derived from 2-acetylpyridine have received considerable attention over the past two decades.^[1–6] This may be attributed

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Address correspondence to Xishi Tai, Department of Chemistry, Weifang University, Weifang 261061, People's Republic of China. E-mail: taixishi@lzu.edu.cn

to unusual structural features in the resultant metal complexes and their biological activities. Some of the metal complexes have antioxidative activities,^[4,5] and electronic and photophysical properties.^[6,7] Although a lot of research on that has been reported, the lanthanide complexes of these ligands are rare. In order to understand further the coordination and the spectral properties of rare earth complexes with hydrazone ligands derived from 2-acetylpyridine, we report herein the synthesis and spectroscopic studies of some rare earth nitrate complexes with a hydrazone ligand (L) derived from 2-acetylpyridine and benzoyl hydrazine.

EXPERIMENTAL

All the starting materials used in the synthesis were analytical grade and used without further purification. Rare earth nitrates were prepared according to a literature method.^[8]

Physical Measurements

Carbon, hydrogen, and nitrogen were analyzed on a Elementar Vario EL (Germany) elemental analyzer. Infrared spectra (4000–400 cm^{−1}) were determined with KBr optics on a Nicolet NEXUS 670 FTIR (USA) spectrophotometer. Ultraviolet spectra in the 190–700 nm region in DMF solution were recorded on a thermo UV-340 spectrophotometer. The thermal behavior was monitored on a WCT-2A (China) thermal analyzer. The molar conductance values were determined using a DDS-11A (China) conductivity meter with methanol as solvent (10^{−3} mol L^{−1} solution) at 25°C. Mass spectra (FAB) was measured using a MASPEC II (England) system analyzer. Luminescent spectra were recorded by means of RF-540 (Japan) spectrometer.

Preparation of the Ligand (L)

2-Acetylpyridine (10 mmol) was added to a solution of benzoyl hydrazine (10 mmol) in 20 mL ethanol and the contents were stirred continuously for 8 hr at room temperature. The light-yellow precipitate was obtained by filtration and purified by crystallization with anhydrous ethanol. Yield 86%. m.p. 149 ~ 150°C. Calculated for C₁₄H₁₃N₃O: 70.3% C, 5.5% H, 17.6% N. Found: 70.1% C, 5.2% H, 17.7% N. MS: M + H = 240 (found), M = 239 (calculated). IR (in KBr pellets) cm^{−1}: 1665 (−C=O), 1654 (−C=N−).

Preparation of the Complexes

La(NO₃)₃ · 6H₂O (1.0 mmol) in 10 mL ethanol was added to the solution of methyl-2-pyridyl ketone benzoyl hydrazone (2.0 mmol) in 10 mL chloroform.

The mixtures were stirred for 3 hr at room temperature, and the product formed was then collected by filtration, washed several times with ethanol and chloroform, and dried in a vacuum. The other complexes were also synthesized by this method.

RESULTS AND DISCUSSION

Composition of the Complexes

The results of elemental analyses (Table 1) indicated the composition of the complexes as $\text{Ln}(\text{L})_2(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ (where $\text{Ln} = \text{La}$, $n = 5.5$; Ce , Pr , $n = 5$; Nd , Eu , $n = 4$), indicating that all these complexes conform to 1:2 metal-to-ligand stoichiometry.

IR Spectra

The characteristic IR peaks of the ligand and the complexes are reported in Table 2. IR spectra of the five complexes are strikingly similar in relative positions and intensities of the peaks, which suggests a close structural relationship among the compounds. The ν ($\text{C}=\text{O}$) and ν ($\text{C}=\text{N}$) vibration of the free ligand are at 1665 cm^{-1} and 1654 cm^{-1} , for the complexes shift to $1620 \sim 1624\text{ cm}^{-1}$ and $1617 \sim 1621\text{ cm}^{-1}$, respectively, which strongly suggests the oxygen atom of $\text{C}=\text{O}$ and the nitrogen atom of $\text{C}=\text{N}$ coordinate to rare earth ions.^[9] The larger shift for $\nu_{\text{C}=\text{O}}$ indicates that the bond of $\text{Ln}-\text{O}$ ($\text{C}=\text{O}$) is stronger than that of $\text{La}-\text{N}$ ($\text{C}=\text{N}$) in the complexes and also shows that the coordination involves the keto-form of the ligand.^[10] The vibration ν

Table 1. Elemental analytical data and molar conductance values of complexes

Complexes	Elemental Analyses % Calc. (Found)			$\Lambda_m/$ ($\text{S cm}^2 \text{ mol}^{-1}$)
	C	H	N	
$\text{La}(\text{L})_2(\text{NO}_3)_3 \cdot 5.5\text{H}_2\text{O}$	37.3 (37.2)	4.1 (4.0)	14.0 (14.0)	170
$\text{C}_{28}\text{H}_{37}\text{N}_9\text{O}_{16.5}\text{La}$				
$\text{Ce}(\text{L})_2(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	37.6 (37.6)	4.0 (3.9)	14.1 (14.5)	168
$\text{C}_{28}\text{H}_{36}\text{N}_9\text{O}_{16}\text{Ce}$				
$\text{Pr}(\text{L})_2(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	37.6 (37.4)	4.1 (4.1)	14.1 (13.8)	180
$\text{C}_{28}\text{H}_{36}\text{N}_9\text{O}_{16}\text{Pr}$				
$\text{Nd}(\text{L})_2(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$	38.2 (38.0)	3.9 (4.1)	14.3 (14.1)	186
$\text{C}_{28}\text{H}_{34}\text{N}_9\text{O}_{15}\text{Nd}$				
$\text{Eu}(\text{L})_2(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$	37.9 (37.7)	3.9 (4.0)	14.2 (13.9)	178
$\text{C}_{28}\text{H}_{34}\text{N}_9\text{O}_{15}\text{Eu}$				

Table 2. Most important IR bands (cm⁻¹)

Compounds	ν (C=O)	ν (C=N)	ν_1 (NO ₃ ⁻)	ν_3 (NO ₃ ⁻)	ν_4 (NO ₃ ⁻)	ν (Ln-O)	ν (Ln-N)	ν (OH)
L	1665	1654						
La(L) ₂ (NO ₃) ₃ · 5.5H ₂ O	1624	1620	1480	817	1301	423	546	3391
Ce(L) ₂ (NO ₃) ₃ · 5H ₂ O	1622	1621	1475	815	1302	423	541	3358
Pr(L) ₂ (NO ₃) ₃ · 5H ₂ O	1624	1617	1476	814	1300	416	541	3339
Nd(L) ₂ (NO ₃) ₃ · 4H ₂ O	1620	1617	1476	815	1299	417	543	3355
Eu(L) ₂ (NO ₃) ₃ · 4H ₂ O	1621	1617	1475	817	1298	423	545	3391

(C=C + C=N) of the pyridine ring at 1544 cm^{-1} splits into two bands at ca. 1540 cm^{-1} and 1573 cm^{-1} for the complexes. This indicates that all the pyridyl nitrogen atoms take part in coordination to rare earth ions.^[11] The new bands at $416 \sim 423\text{ cm}^{-1}$ and $541 \sim 546\text{ cm}^{-1}$ are assigned to the $\nu(\text{Ln}-\text{O})$ and $\nu(\text{Ln}-\text{N})$ vibration. The band corresponding to the $\nu(\text{OH})$ at $3340 \sim 3390\text{ cm}^{-1}$ shows that the complexes contain a water molecule, which is in accordance with the results of elemental analyses. In addition, the band of the NO_3^- groups (C_{2v}) at ca. 1476 cm^{-1} (ν_1), 817 cm^{-1} (ν_3), and 1384 cm^{-1} (D_{3h}) suggest the presence of both coordinated and uncoordinated nitrates exist in the complexes,^[11] which is in accordance with the results of molar conductances of the complexes. The value $|\nu_1 - \nu_4| = 176\text{ cm}^{-1}$ shows that the coordinated NO_3^- groups in the complexes are didentate ligands.

Electronic Spectra

The spectrum of the free ligand exhibits three absorption bands at 209 nm, 301 nm, and 375 nm. The complexes yield peaks at approximately 295 nm and 370 nm, which may be attributed to the $\pi \rightarrow \pi^*$ transitions of the ligand according to their positions and molar absorption coefficient. The absorption and strength of UV spectral in the spectrum of the ligand and complexes are different, indicating that ligand coordinates to rare earth ions, which is in accordance with the results of IR spectra.

Thermal Analysis

All the complexes are stable in air. The thermal analysis of the Ce complex has been studied in air atmosphere using Al_2O_3 as reference. The DTA curve of the Ce complex shows two endothermic peaks at about 87°C and 184°C , losing weight about 6.45% at $79 \sim 100^\circ\text{C}$ and 2.08% at $176 \sim 200^\circ\text{C}$ in the TG curve, which correspond to the loss of $3\frac{1}{2}$ molecules (cacl., 7.04%) and $1\frac{1}{2}$ coordinated water molecules (cacl., 3.02%), respectively. The complex has no melting point. On heating to 800°C , the complex decomposes step by step, as there are two exothermic peaks at 297°C and 402°C . This indicates that both lattice water molecules and coordinated water molecules are in the complexes.

According to the aforementioned data, for the complexes prepared we propose the structure shown in Fig. 1.

Fluorescence Studies

Excited by the absorption band at 375 nm, the ligand in DMF solution exhibits broad emission bands ($\lambda_{\text{max}} = 418\text{ nm}$). The luminescence spectra of the

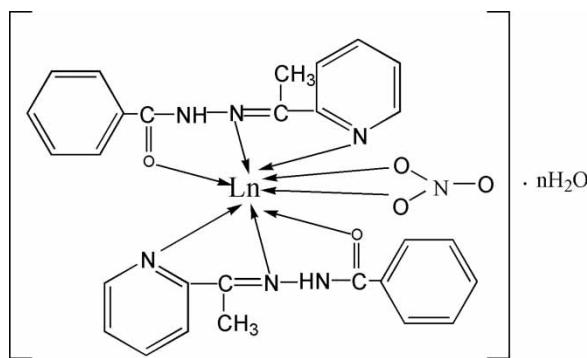


Figure 1. The proposed chemical structure for the rare earth complexes ($\text{Ln} = \text{La, Ce, Pr, Nd, Eu}$; $n = 4, 5$, or 5.5).

Eu(III) complex in solid was investigated. The emissions at 680 nm , 615 nm , and 590 nm resulting from excitation at 398 nm are all characteristic emissions of the Eu(III) ion. Which showing more efficient ligand-to-metal energy-transfer process (antenna effect) in the Eu(III) complex. The luminescence spectra data of the Eu(III) complex are shown in Table 3. The luminescence of Ln^{3+} chelates is related to the efficiency of the intramolecular energy transfer between the triplet level of ligand and the emitting level of the ions, which depends on the energy gap between the two levels.^[12] From Table 3, we can see that the fluorescence intensities of Eu(III) complex in solid are weak; this may be due to the energy gap between the ligand triplet levels, and the emitting level of europium does not favor the energy transfer process for europium. A detailed luminescence study is in progress.

Solubility and Molar Conductance

All complexes are easily soluble in DMSO, DMF, and methanol, slightly soluble in ethanol and acetone, and insoluble in benzene, diethyl ether, and tetrahydrofuran. The molar conductance values of the complexes measured

Table 3. Luminescence data of the Eu complex

Compounds	λ_{ex} (nm)	λ_{em} (nm)	Luminescence intensity	Assignment
$\text{Eu(L)}_2(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$	398	590	10.9	$^5\text{D}_0 - ^7\text{F}_1$
		615	28.6	$^5\text{D}_0 - ^7\text{F}_2$
		680	13.1	$^5\text{D}_0 - ^7\text{F}_4$

in methanol solution (1×10^{-3} mol dm $^{-3}$) at 25°C are in the range of 168~186 S cm 2 mol $^{-1}$ (Table 1). This shows that all the complexes are 2:1 electrolytic behavior in DMF.^[13]

CONCLUSIONS

According to the data and discussion above, the methyl-2-pyridyl ketone benzoyl hydrazone ligand has formed stable complex with rare earth nitrates. Obvious IR spectrum changes were observed after the ligand formed complexes with rare earth nitrates. In the complexes, rare earth ions were coordinated to the oxygen atoms of amide C=O and pyridine nitrogen atoms. The complex exhibited characteristic fluorescence of europium ion. Based on those results, a series of new hydrazone ligands could be designed and synthesized to investigate further the coordination and the spectral properties of rare earth complexes.

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