Synthesis and properties of a Pr(III) complex with 2-acetylbenzimidazoledehyde-glycine Schiff-base ligand

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Abstract The 2-acetyl-benzimidazoledehyde-glycine Schiff-base ligand and the corresponding Pr(III) complex Pr₂L₃(NO₃)₃ • 2CH₃OH (L=C₁₁H₁₀N₃O₂) were synthesized in methanol and characterized by a series of methods, including chemical analysis, elemental analysis, TOF-MS, ¹H NMR, UV-, IR-, Raman spectra, thermal analysis, and the three-dimension fluorescence excitation and emission spectra. The Pr(III) complex exhibits extraordinary water-solubility and the Pr(III) hydroxide appears at pH≥13. The complex also possesses specific fluorescent properties. Thus, at the excitation wavelengths 200.0−280.0 and 260−350 nm the fluorescence bands were observed at 290.0 and 400.0 nm, respectively.

Keywords: 2-acetyl-benzimidazoledehyde-glycine Schiff-base, rare earth complex, three-dimension fluorescence excitation and emission spectra.

Exhibiting a broad spectrum of biological activities and outstanding optical properties, complexes of d- and rare-earth metals Schiff-base type ligands derived from amino acids attract a great interest of researchers in recent years[1-4]. The metal complexes comprizing benzimidazole moiety are of particular interest due to a range of important biological properties with antitumor and fungicide complexes among them. The metal complexes containing benzimidazolyl group were frequently used as models for metalloenzymes. As it is expected, a substituent at the 2-position of benzimidazole fragment can enhance useful biological activities of the benzimidazole ring[5,6]. At the same time, benzimidazoles possess an extended conjugate system. When this or another way coordinated to a rare-earth metal center, this conjugate system is capable to sensibilize the latter photochemically (i.e. to provide an efficient transfer of the energy of the absorbed photon to the metal) and this way gives rise to remarkable luminescent abilities[7]. Moreover, the study on the rare earth complexes with amino acids-derived Schiff-bases has not been reported yet. All this mentioned above forced us to undertake a research on the rare earth complexes with the 2-acetyl/benzimidazoledehyde amino acids and, especially, on their luminescent behavior. In this paper, we report preparation of 2-acetyl-benzimidazoledehyde-glycine Schiff-base and a Pr(III) complex derived from it. The composition, structure and optical properties of the Pr(III) complex are also discussed.

1 Experimental

1.1 Materials and methods

Commercially available glycine (biochemical reagent), Pr₆O₁₁, lactic acid, and Cr₂O₃ (analytical grades) were used. Elemental analyses were performed on Vario EL III CHNOS elemental analyzer; ¹H NMR spectra were recorded on Varian INOVA-400 spectrometer (400 MHz, CD₃OD); pH titration data were obtained on JB-3 isothermal magnetic stirring apparatus and Sartorius PB-20 standard pH-meter; mass spectra were recorded on Kratos AXIMA CFR plus MALDI-TOF mass spectrometer, with α-cyano-4-hydroxyacinnamic acid as a matrix; IR spectra were obtained using EQUINX 55 Fourier transform infrared spectrometer (KBr pellets); Raman spectra were recorded on HR 800 Laser Raman spectrometer (laser wavelength 632.81 nm, confocal hole 100 μm, slit 100 μm, scanning time 10 s); UV-Vis spectra were measured on LAMBDA 40P UV/Vis spectrophotometer; fluorescence spectra were gained on F-4500 fluorescence spectrophotometer (xenon lamp, slit EX/EM 5.0/5.0 nm, scanning range EX/EM 200-900 nm). All the measurements were made at room temperature..

1.2 Synthesis of the ligand

(i) Synthesis of the precursor 2-acetylbenzimidazole.

The starting 2-acetylbenzimidazole was prepared according to refs. [8, 9] and identified by its melting point.
(ii) Synthesis of the ligand (2-acetylbenzimidazole-dehyde-glycine Schiff-base (potassium salt KL)).

Glycine (0.1 mmol) and KOH (0.1 mmol) were dissolved in methanol, the mixture was refluxed at 50 °C for 15 min and then the methanol solution of 2-acetylbenzimidazole (0.1 mmol) was added to the mixture. After refluxing for 4 h, the color of the mixture changed from yellow to deep brownish-yellow. On partial removal of the solvent, filtering, washing with hot methanol and drying, the brownish-yellow powder was obtained. The ligand decomposes above 271 °C (color changes).

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\begin{align*}
\text{HNMR (400 MHz, CD}_3\text{OD): } & \delta 7.6 (q, 2H, a H-Ar coupling peak), \\
& \delta 7.3 (q, 2H, b H-Ar coupling peak), \\
& \delta 5.311 (d, 1H, H-N), \\
& \delta 2.582 (s, 2H, -CH}_2-), \\
& \delta 1.652 (s, 3H, CH}_3), \\
& \text{and IR (KBr) } \nu \text{C=N } 1643 \text{ cm}^{-1}.
\end{align*}
\]

1H NMR(400 MHz, CD3OD): \(\delta 7.6 (q, 2H, a \text{H-Ar coupling peak}), \delta 7.3 (q, 2H, b \text{H-Ar coupling peak}), \delta 5.311 (d, 1H, \text{H-N}), \delta 2.582 (s, 2H, -\text{CH}_2-), \delta 1.652 (s, 3H, \text{CH}_3), \text{and IR(KBr)} \nu \text{C-N } 1643 \text{ cm}^{-1}.

Found (calculated for C11H10N3O2·1/4CH3OH): C: 51.51% (51.31%), H: 4.55% (4.21%), N: 16.15% (15.96).

1.3 Synthesis of the complex

Methanol solution of Pr(NO3)3·6H2O was added slowly to the heated methanol solution of the ligand KL. A yellow precipitate started to form immediately. The mixture was stirred for 2 h at 50 °C till the reaction completed, and cooled down to room temperature, and the precipitate was filtered off, washed several times with hot methanol, and dried until constant weight appeared in a desiccator over H2SO4. Elemental analysis for Pr was performed as follows: the weighed sample of the complex was placed into a muffle oven (800 °C, 2.5 h), dissolved in known volume of HCl (1:1) and the concentration of the solution was determined by complexometric titration (EDTA). Found (calculated for C35H38N12O22Pr2): Pr 23.56%(23.87), C 35.77%(35.60), H 2.976%(3.221), N 14.00%(14.24). Elemental composition of the complex matches Pr2L3(NO3)2·2CH3OH (L = C11H10N3O2). Mass spectrometric data (aqueous solution): 1223.27 (theoretical value 1223.76) [Pr2L3NO3 + matrix + K]+; 934.13 (theoretical value 933.49) [Pr2L3NO3]+; 972.02 (theoretical value 972.59) [Pr2L3 + K]+; mixed solvent of the 1:1 water and methanol, 1344.96 (theoretical value 1344.85) [Pr2L3(NO3)2(CH3OH)+ K]+, (L’ = C11H11N3O2).

2 Results and discussion

2.1 Solubility

The Schiff-base ligand KL and its Pr(III) complex are both brownish-yellow air-stable powders with decomposition points around 280 °C. The solubilities of the salt KL and its Pr(III) complex differ from those of the rare-earth metal salt and 2-acetylbenzimidazole. Both ligand salt KL and Pr(III) complex derived from it are moderately soluble in water, methanol, ethanol, n-butyl alcohol, and pyridine, but not in acetonitrile, dimethylsulfoxide, benzene, and acetone. In addition, in water-alcohol mixtures the solubility is dramatically greater than in pure solvents, with significant exothermic heat effects observed. The ligand molecule comprises a non-polar benzene ring on one end and a polar carboxyl group on the other, and, thus, exhibits distinct detergent properties. The complex itself presents a weak acid in water medium. Under acidic conditions the ligand dissociates and compound dissolves in water. Meanwhile, when base pH \(\geq 7\), the complex starts to dissolve. The solubility of the complex increases with the increase of pH. Interaction with a base, likely, changes the structure of the complex that causes the solubility growth. Above pH 13, jelly precipitate of Pr(OH)3 forms.

2.2 UV spectra

We measured UV spectra of the \(1\times10^{-4} \text{ mol} \cdot \text{L}^{-1}\) solutions (water-ethanol) of 2-acetylbenzimidazole, ligand KL and Pr(III) complex. Wavelengths of their absorption maxima (nm) are listed below:

- 2-acetylbenzimidazole: 209.0 nm, 232.0 nm, 298.0 nm
- Schiff-base ligand: 213.0 nm, 233.7 nm, 305.0 nm
- Pr(III) complex: 217.5 nm, 233.0 nm, 305.0 nm