Rev. Téc. Ing. Univ. Zulia, Vol. 16, No. 1, 21 - 26 , 1993

Fluorescence studies of Pr^{3+}, Sm^{3+}, and Ho^{3+}, amino acid ternary complexes in aqueous solution

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Abstract

Pr^{3+} and Ho^{3+} ternary complexes using glycine (G) and leucine (L) as primary ligands and 2,3 - butandiol (BD) as secondary ligand exhibit only one fluorescence band. However, in the case of similar complexes of Sm^{3+}, three fluorescence bands have been observed. The assignments of the fluorescence bands have been given.

Key words: Fluorescence spectra, Pr^{3+}, Sm^{3+}, and Ho^{3+} ternary amino acid complexes.

Estudios de fluorescencia de complejos amino ácidos ternarios de Pr^{3+}, Sm^{3+}, y Ho^{3+}, en solución acuosa.

Resumen

Complejos ternarios Pr^{3+} y Ho^{3+} usando glicina (G) y leucina (L) como ligandos primarios y 2,3 - butanodiol (BD) como ligando secundario, exhiben solo una banda de fluorescencia. Sin embargo, en el caso de complejos similares de Sm^{3+}, tres bandas de fluorescencia han sido observadas. La asignación de las bandas de fluorescencia ha sido realizada.

Palabras claves: Espectros de fluorescencia, complejos ámino ácidos ternarios Pr^{3+}, Sm^{3+}, y Ho^{3+}

Introduction

The absorption spectra of lanthanide binary and ternary amino acid complexes have been a subject of recent study in this laboratory [1-7]. The fluorescence spectra using optimum excitation wavelength in the case of Pr^{3+}, Sm^{3+}, and Ho^{3+} ternary complexes, using glycine and leucine as primary ligands and 2,3- butandiol as secondary ligands are reported in the present paper.

Experimental

The complexes of Pr^{3+}, Sm^{3+}, and Ho^{3+} with amino acid glycine or leucine as primary ligand 2,3 butandiol as secondary ligand in the molar ratio 1:1:1, 1:2:1 and 1:1:2 have been synthesized by the usual method [8]. The reagents used were of AR grade. $PrCl_3$. $6H_2O$, $SmCl_3$, and $HoCl_3.6H_2O$ (99.99% pure) were supplied by Indian Rare - Earths limited. The complexes were crystallized under vaccum. The composition of the complexes was verified by carrying out their elemental analysis. The fluorescence spectra were recorded on "Hitachi F-3000"

fluorescence spectrophotometer in the region 450 nm - 700 nm in triple distilled water with an accuracy of ± 0.1 nm. The optimum excitation wavelength was determined by carrying out prescan of the excitation wavelength.

Results and Discussion:

The fluorescence spectra of all the complexes of Pr^{3+} under study have been given in Figs. 1 and 2. The variation of ligands and their molar ratios has little effect on their spectra. Consequently, for Sm^{3+} and Ho^{3+} only representative spectra for their similar complexes with Glycine and 2,3 - butandiol in the molar ratio 1:1:1 have been given in figs. 3 and 4 respectively.

Pr^{3+} Complexes: Fluorescence of Pr^{3+} ternary amino acid complexes under study in aqueous solution were studied using excitation wavelengths (λ_{ex})= 444, 469, 482 and 590 nm, which correspond to absorption peaks of these complexes. It is interesting to note that only one fluorescence peak at 482 nm is obtained irrespective of excitation wavelength (table 1, figs. 1 and 2). However, the maximum fluorescence was obtained when λ_{ex} is kept at 444 nm. This excitation corresponds to the transition $^3H_4 \rightarrow {}^3P_2$. The most intense emission band centered at 482 nm indicates that the non-radiative transitions from higher levels $^3P_2$ and $^3P_0$ are more pronounced, resulting in the increased population of $^3P_0$ level, which in turn results in a strong emission band through the radiative transition to the ground level $^3H_4$. It is further observed that fluorescence quenching increases with the increase in concentration of the ion which has been tested for 0.01 M, 0.05 M and 0.1 M concentrations. Our results agree with the fluorescence of Pr^{3+}chelates [9] and Pr^{3+} in different environments [10]. The band at 525 nm may be attributed to the solvent water used.

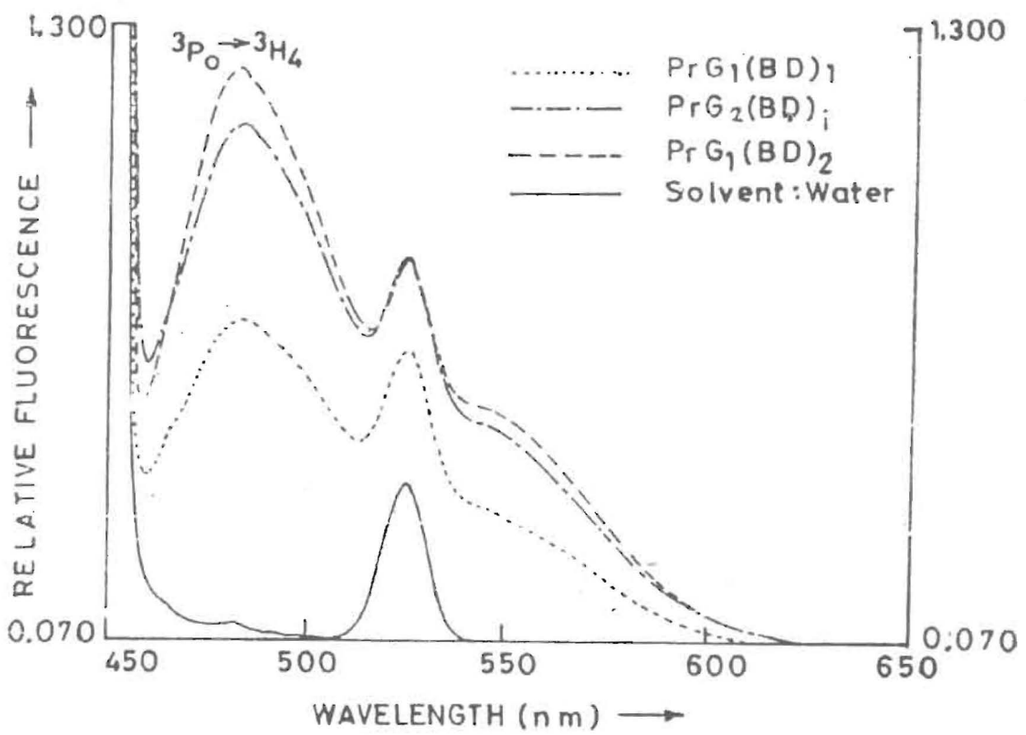

Fig. 1. Fluorescence Spectra of Pr^{3+} in ternary amino acid complexes.

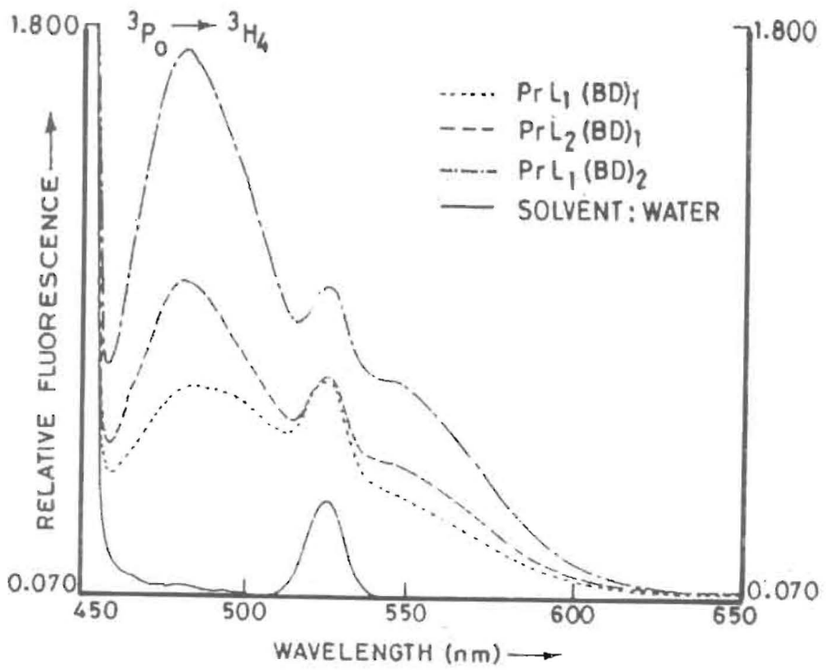

Fig. 2 Fluorescence Spectra of Pr^{3+} in ternary amino acid complexes.

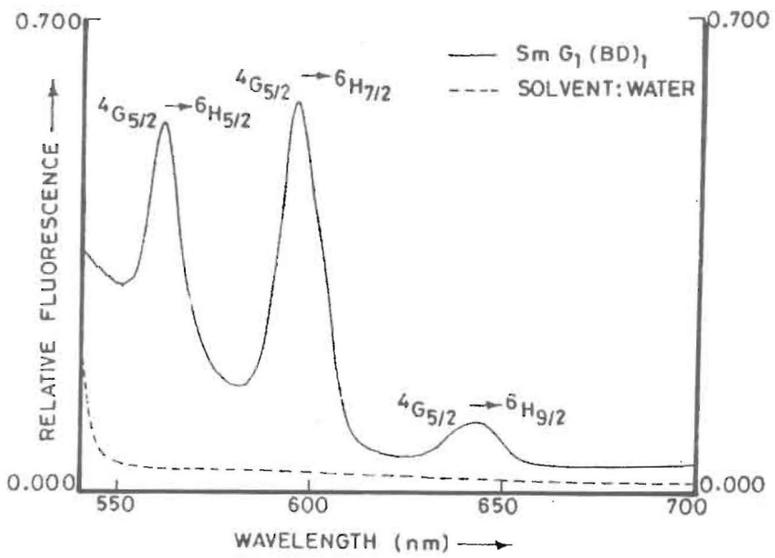

Fig. 3 Fluorescence Spectra of Sm^{3+} in ternary amino acid complex.

Table 1. Observed values of wavelength (λ) and energy (ν) of various fluorescence peaks for lanthanide amino acid complexes in aqueous solution.

Complex[a]	Excitation λ (nm)	Emission λ (nm)	Emission ν (cm^{-1})	Assignment
Pr G_1 $(BD)_1$	444.0	482.6	20721	$^3P_0 \rightarrow {}^3H_4$
Pr G_2 $(BD)_1$	444.0	481.6	20764	$^3P_0 \rightarrow {}^3H_4$
Pr G_1 $(BD)_2$	444.0	482.4	20729	$^3P_0 \rightarrow {}^3H_4$
Pr L_1 $(BD)_1$	444.0	484.0	20661	$^3P_0 \rightarrow {}^3H_4$
Pr L_2 $(BD)_1$	444.0	481.6	20764	$^3P_0 \rightarrow {}^3H_4$
Pr L_1 $(BD)_2$	444.0	482.0	20746	$^3P_0 \rightarrow {}^3H_4$
Sm G_1 $(BD)_1$	401.0	642.8	15556	$^4G_{5/2} \rightarrow {}^6H_{9/2}$
		595.6	16789	$^4G_{5/2} \rightarrow {}^6H_{7/2}$
		560.4	17844	$^4G_{5/2} \rightarrow {}^6H_{5/2}$
Sm G_2 $(BD)_1$	401.0	643.0	15552	$^4G_{5/2} \rightarrow {}^6H_{9/2}$
		595.8	16784	$^4G_{5/2} \rightarrow {}^6H_{7/2}$
		560.6	17838	$^4G_{5/2} \rightarrow {}^6H_{5/2}$
Sm G_1 $(BD)_2$	401.0	643.2	15547	$^4G_{5/2} \rightarrow {}^6H_{9/2}$
		596.0	16778	$^4G_{5/2} \rightarrow {}^6H_{7/2}$
		560.4	17844	$^4G_{5/2} \rightarrow {}^6H_{5/2}$
Sm L_1 $(BD)_1$	401.0	643.2	15547	$^4G_{5/2} \rightarrow {}^6H_{9/2}$
		595.4	16795	$^4G_{5/2} \rightarrow {}^6H_{7/2}$
		560.6	17838	$^4G_{5/2} \rightarrow {}^6H_{5/2}$
Sm L_2 $(BD)_1$	401.0	642.2	15571	$^4G_{5/2} \rightarrow {}^6H_{9/2}$
		595.6	16789	$^4G_{5/2} \rightarrow {}^6H_{7/2}$
		560.4	17844	$^4G_{5/2} \rightarrow {}^6H_{5/2}$
Sm L_1 $(BD)_2$	401.0	642.6	15562	$^4G_{5/2} \rightarrow {}^6H_{9/2}$
		595.4	16795	$^4G_{5/2} \rightarrow {}^6H_{7/2}$
		560.6	17838	$^4G_{5/2} \rightarrow {}^6H_{5/2}$
Ho G_1 $(BD)_1$	451.0	556.2	17979	$^5F_4, {}^5S_2 \rightarrow {}^5I_8$
Ho G_2 $(BD)_1$	451.0	551.8	18122	$^5F_4, {}^5S_2 \rightarrow {}^5I_8$
Ho G_1 $(BD)_2$	451.0	551.6	18129	$^5F_4, {}^5S_2 \rightarrow {}^5I_8$
Ho L_1 $(BD)_1$	451.0	555.8	17992	$^5F_4, {}^5S_2 \rightarrow {}^5I_8$
Ho L_2 $(BD)_1$	451.0	556.6	17966	$^5F_4, {}^5S_2 \rightarrow {}^5I_8$
Ho L_1 $(BD)_2$	451.0	551.2	18142	$^5F_4, {}^5S_2 \rightarrow {}^5I_8$

a:
G = Glycine
L = Leucine
BD = 2, 3- butandiol

Sm^{3+} Complexes: The maximum fluorescence was observed by excitation with wavelength (λ_{ex})= 401 nm, which is the most intense peak in absorption in the visible region. Three fluorescence peaks at 642, 595 and 560 nm have been recorded for all sm^{3+} ternary amino acid complexes (Fig. 3 and Table 1) which on energy

consideration may be assigned to $^4G_{5/2} \rightarrow {}^6H_{9/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$, and $^4G_{5/2} \rightarrow {}^6H_{5/2}$ transitions respectively. With the change of ligands, a very small change in fluorescence intensity is observed. The fluorescence peak at 561.8 nm was also reported in the case of Sm^{3+} thenoyltrifluoroacetonate chelate at 77°K [11].

Our results for peaks at 560 nm and 595 nm also agree with those for nitrogen donor ligand complexes [11,12]. However, they differ from those of Sm^{3+} complexes of benzoic acid and its derivative in methanol [13], where no fluorescence was observed, which my be due to the possibility of the transfer of an electron from the organic part to the Sm^{3+} ion with its reduction to Sm^{2+} [14].

Ho^{3+} Complexes: Aqueous solution of Ho^{3+} amino acid complexes under study were excited by λ_{ex} = 361($^5I_8 \rightarrow {}^3H_6$), 451($^5I_8 \rightarrow {}^5G_6$), 538($^5I_8 \rightarrow {}^5F_4$) and 642 nm ($^5I_8 \rightarrow {}^5F_5$). Weak fluorescence was observed when excited with 451 nm. In other cases fluorescence could not be recorded. Change of ligands and their molar ratios did not produce much change in fluorescence intensity. The fluorescence peak may be assigned to $^5F_4$, $^5S_2 \rightarrow {}^5I_8$ (Fig. 4 and Table 1).

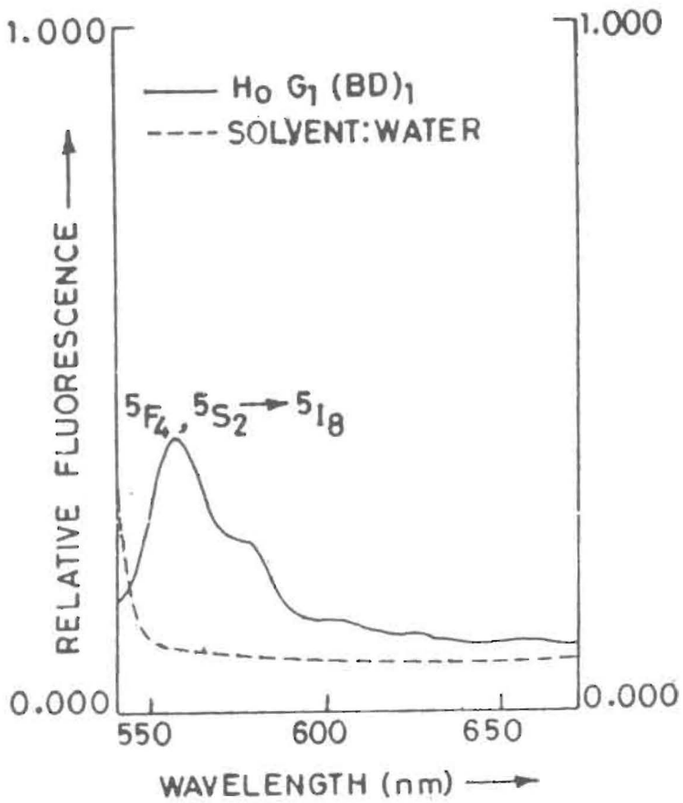

Fig. 4 Fluorescence Spectra of Ho^{3+} in ternary amino acid complex.

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Recibido el 05 de Noviembre de 1991.
En forma revisada el 23 de Junio de 1992