Potentiometric determination of novel complexes of selected lanthanide ions with *N,N'*-bis(5-methylsalicylidene)-4-methyl-1,3-phenylenediamine

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Abstract

The stability constants of the complexes formed in the *N,N'*-bis(5-methylsalicylidene)-4-methyl-1,3-phenylenediamine (H_2L) and La(III), Eu(III), Gd(III), Ho(III), and Lu(III) ion systems were determined in solution with the potentiometric method. The pH-metric titrations were performed in dimethyl sulfoxide/water (v:v, 30:70) mixture at 25.0 °C in 0.1 M $LiNO_3$ ionic strength. The tests were performed for systems with Ln(III) to H_2L 1:2 and 1:3 molar ratio but only data of the systems with the metal/ligand ratio 1:2 were taken into calculation. The molar ratio 1:1 was not studied because of the high coordination numbers of the lanthanide ions, and inadequate donor atoms of the ligand. Computer analysis (HYPERQUAD software) of potentiometric data indicated that in solution the lanthanide (Ln) complexes exist as LnL_2 , $Ln(HL)_2$, and $Ln(H_2L)_2$ forms, depending on pH unlike to the solid state where only one form of $Ln(H_2L)_2$ occurs. Formation constants increase with decreasing size of the Ln(III) ions. Moreover, complex formation in the Ln^{3+}/H_2L systems in solution was performed using UV–Vis spectrophotometric titration.

Keywords Potentiometry · Schiff-base complexes · Lanthanides · UV–Vis Spectrophotometric titration

Introduction

Schiff-base ligands attract the attention of researchers because of their antitumor, antibacterial, antiviral, and antifungal activity which is improved by coordinating ligands to a metal ion [1–3]. Moreover, transition metal complexes with salen-type ligands have applications in heterogeneous and homogeneous catalysis [4–7], diagnostic pharmaceuticals and laser technology [8]. An additional reason for the current interest in Schiff-base complexes derives from their magnetic and optical properties [9]. The unique properties of lanthanide complexes qualify them for use as magnetic materials, e.g., lanthanide ions are particularly suitable for the synthesis of 4f single-molecule magnets (SMM)

[10–17]. Aza-containing Schiff's base can be used as a neutral ion carrier of a highly selective Ln^{3+} -PVC membrane electrode [18]. Lanthanide ions indicate high coordination numbers, variable, and flexible coordination environments [19, 20]. Schiff-base salen-type ligands are very flexible compounds, and the combination of these species has great potential in the synthesis of novel and unusual coordination compounds of mononuclear [21, 22], polynuclear [23] or polymer [24–27]—type complexes.

The potential applications of Schiff-base lanthanide complexes, especially the unique biological [28] and diagnostic [29] activities associated with them, encouraged us to continue our studies of these compounds.

In this paper by using potentiometry, we determined the stability constants of the complexes formed in the systems *N,N'*-bis(5-methylsalicylidene)-4-methyl-1,3-phenylenediamine (H_2L , Fig. 1) with the lanthanide (La^{3+} , Eu^{3+} , Gd^{3+} , Ho^{3+} and Lu^{3+}) ions in dimethyl sulfoxide/water (v:v, 30:70) mixture at 25.0 °C and $I = 0.1 \text{ mol.dm}^{-3} LiNO_3$.

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Fig. 1 Formula of *N,N'*-bis(5-methylsalicylidene)-4-methyl-1,3-phenylenediamine (H_2L)

Experimental

Lanthanum(III), europium(III), gadolinium(III), holmium(III), and lutetium(III) nitrates,

5-methylsalicylaldehyde and 4-methyl-1,3-phenylenediamine were obtained from the Aldrich Chemical Company. Dimethyl sulfoxide (DMSO) was obtained from the Avantor Performance Materials Poland S.A. (formerly POCH S.A.). The reagents were used without further purification

IR spectra were recorded using KBr pellets in the range of 4000–400 cm^{-1} on a Bruker IFS 66v/S spectrophotometer. Mass spectra were performed using electrospray ionization (ESI) techniques. Electrospray mass spectra were determined in methanol using a Waters Micromass ZQ spectrometer. The concentrations of the compounds were approximately 10^{-4} M. Sample solutions were introduced into the mass spectrometer source with a syringe pump with a flow rate of 40 $\mu L min^{-1}$, a capillary voltage of + 3 kV and a desolvation temperature of 300.0 °C. The source temperature was 120.0 °C. The cone voltage (V_c) was set to 30 V to allow transmission of ions without fragmentation processes. Scanning was performed from $m/z = 200$ –1000 in 6 s, and 10 scans were summed to obtain the final spectrum. ^{13}C NMR and 1H NMR spectra were recorded in CD_2Cl_2 on a Varian Gemini 300 spectrometer with chemical shift (ppm) reported relative to TMS as an internal reference. Electronic absorption spectra were measured on a JASCO V-550 spectrophotometer in ethanol and dimethyl sulfoxide. Microanalyses (CHN) were obtained using a PerkinElmer 2400 CHN microanalyzer.

All experiments were prepared using dimethyl sulfoxide/water 30:70 (v/v) solution (demineralised CO_2 -free water was used). The concentration of metal ions was determined by inductively coupled plasma optical emission spectrometry (ICP OES). Potentiometric titrations were carried out using a Titrimo 702 Metrohm equipped with an autoburette with a Metrohm Solvotrode combination pH glass electrode specially designed for use with nonaqueous acid–base titrations, calibrated prior to each titration [30].

A correction of the pH-meter reading was made prior to each measurement series, and two standard buffers were used (pH 4.002 and pH 9.225). All potentiometric titrations were made in an atmosphere of neutral gas (helium 5.0) at a constant ionic strength (0.1 M $LiNO_3$), at 25.0 °C using CO_2 -free NaOH as a titrant at a concentration of 0.1823 M, the concentration of solution of NaOH was determined by inductively coupled plasma optical emission spectrometry (ICP OES). The concentration of the ligand was 1×10^{-3} M, and HCl was added to the systems (1.5 ml; 0.1 M). The metal to ligand ratios was 1:2 and 1:3, but only data of the systems with the metal/ligand ratio 1:2 were taken into calculation because at a molar ratio higher than 1:2 a precipitate of complexes were obtained. The molar ratio 1:1 was not studied due to the tendency of lanthanide ions to achieve high coordination numbers, and inadequate number of donor atoms of the ligand. Determined pK_w for dimethyl sulfoxide/water (30:70) was 14.501 [31]. The protonation constants of the *N,N'*-bis(5-methylsalicylidene)-4-methyl-1,3-phenylenediamine, the selection of the models as well as the stability constants of the complexes were determined with HYPERQUAD software which uses the nonlinear method of least squares [32]. Distribution of respective forms was obtained by applying the HySS (Hyperquad Simulation and Speciation) program [33]. The calculations were performed using 150–350 points for each job taking into account only the part of the titration where no precipitate occurred. In all cases, the testing began with the simplest hypothesis, and then in the following steps, the models were expanded to include progressively more species. The results were scrutinized to eliminate the species that were rejected in the refinement procedures. The criteria used for verification of results are given in an earlier paper [34, 35].

Samples for electronic spectra were prepared in dimethyl sulfoxide/ H_2O (30:70 v/v) solution, acidified with HCl (1.5 ml; 0.1 M) at $Ln^{3+}:H_2L$ 1:2 ratio. Concentration of ligand H_2L was 1×10^{-4} M. The spectra were recorded at 20.0 °C in a quartz cell with a 1 cm path length on an Evolution 300 UV–Vis ThermoFisher Scientific spectrometer equipped with a xenon lamp (range 250–500 nm, accuracy 0.2 nm, sweep rate 120 $nm min^{-1}$). UV–Vis spectra were measured in pH intervals, from 3 to 10.

Synthesis of *N,N'*-bis(5-methylsalicylidene)-4-methyl-1,3-phenylenediamine (H_2L)

The *N,N'*-bis(5-methylsalicylidene)-4-methyl-1,3-phenylenediamine (H_2L) was prepared according to reported procedure [36] and was obtained from the condensation reaction of 5-methylsalicylaldehyde (27 mg, 0.2 mmol) and 4-methyl-1,3-phenylenediamine (12 mg, 0.1 mmol) in a 2:1 molar ratio of substrates. The mixture was stirred in ethanol (30 mL) at room temperature for 24 h. The yellow solution was concentrated to half of its initial volume and allowed to crystallize. The crystals formed were collected, washed with

cold ethanol and dried in air. Yield: 31.6 mg (89.0%). Anal. Calcd for $C_{23}H_{22}N_2O_2 \cdot C$, 77.07; H, 6.16; N, 7.82%. Found: C, 76.92; H, 6.10; N, 7.74. ESI-MS: m/z 359 (M^+ , 100%). M.p.: 144.0 °C. 1H NMR and COSY NMR (300 Hz; CD_2Cl_2 ; Me_4Si , δ_H) 12.97, 12.92 (two s, H-1, H-18, 2OH), 8.66, 8.61 (two s, H-8, H-16, 2HC=N), 7.32 (*d*, $J = 8.3$ Hz, H-10, Ar-H), 7.25 (*dd*, $J = 11.3$ Hz, H-3, H-20, Ar-H), 7.20 (*dd*, $J = 8.0$ Hz, H-2, H-19, Ar-H), 7.14 (*dd*, $J = 8.0$ Hz, H-15, Ar-H), 7.08 (*d*, $J = 2.1$ Hz, H-11, Ar-H), 6.91 (*t*, $J = 7.6$ Hz, H-6, H-23, Ar-H), 2.40 (*s*, 3 H-13, Ar-CH₃), 2.33, 2.32 (two *s*, 3H-5, 3H-22, two Ar-CH₃). ^{13}C NMR (300 Hz; CD_2Cl_2 ; Me_4Si , δ_C) 162.83, 162.32, 158.99, 158.89, 148.44, 147.58, 134.30, 134.11, 132.32, 132.22, 131.44, 131.01, 128.25, 118.83, 118.75, 118.67, 116.99, 116.97, 111.05, 20.34, 17.88. FT-IR (KBr, cm^{-1}): $\nu(O-H)$ 3379, $\nu(O-H \cdots N)$ 2701, $\nu(C=N)$ 1621, $\nu(C-O)$ 1283, $\nu(C=C)$ 1488, 781, 671.

Results and discussion

N,N'-bis(5-methylsalicylidene)-4-methyl-1,3-phenylenediamine ligand (H_2L) (Fig. 1) was obtained in a condensation reaction, and single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent [36]. Due to the insolubility of that type of ligand in water, the potentiometry studies were performed in mixtures of organic solvents, e.g., dimethyl sulfoxide [37], methanol [38], ethanol [39] or dioxane [40] with water. Our research led to the selection of a mixture of the dimethyl sulfoxide water 30:70 (v/v) [41].

Potentiometric measurements

The formation of complexes between *N,N'*-bis(5-methylsalicylidene)-4-methyl-1,3-phenylenediamine ligand (H_2L) and La^{3+} , Eu^{3+} , Gd^{3+} , Ho^{3+} , and Lu^{3+} ions (Ln^{3+}) was studied by pH-metry titration. Potentiometric titration was performed in dimethyl sulfoxide/water 30:70 (v/v) mixture ($pK_w = 14.501$). As it is shown in Fig. 2, three protonation constants were determined from computer analysis of the titration data: $\log K_1 = 10.05$, $\log K_2 = 8.49$ and $\log K_3 = 5.45$ for *N,N'*-bis(5-methylsalicylidene)-4-methyl-1,3-phenylenediamine.

The values received for the ionization constants were in consistent with those obtained previously for similar compounds such as *N,N'*-bis(salicylidene)-4-methyl-1,3-phenylenediamine ($\log K_1 = 8.54$, $\log K_2 = 6.36$ and $\log K_3 = 5.54$) [41]. The increase in the value of ionization constants as compared with our earlier investigation is due to the inductive electron-donor effect of the next methyl substituent on the aromatic ring [37, 41]. *N,N'*-bis(5-methylsalicylidene)-4-methyl-1,3-phenylenediamine ligand (H_2L) occurs in solution in three forms: unionized (neutral, H_2L), partially (HL^-), and fully (L^{2-}) deprotonated

Fig. 2 Species distribution diagrams of the *N,N'*-bis(5-methylsalicylidene)-4-methyl-1,3-phenylenediamine (H_2L), solvent DMSO/ H_2O (30/70, v/v)

depending on pH. The species distribution diagram of H_2L ligand shows that in the pH range 5–8 the form H_2L dominated but in the pH range 9–11 the three forms H_2L , HL^- , and L^{2-} coexist. Values $\log K_1 = 10.05$, and $\log K_2 = 8.49$ correspond to protonation of the phenolic groups, whereas $\log K_3 = 5.45$ corresponds to protonation of an imine nitrogen [1, 37, 41].

The stability constants ($\log \beta$) and equilibrium constants ($\log K$) of the complexes formed in the Ln^{3+}/H_2L systems are listed in Table 1. The model assumed was verified by analysis of the standard deviations and the convergence of the experimental data with a theoretical curve obtained for the chosen model (evaluated by the Hamiltonian test and Chi-squared tests). For the sake of simplicity, ion charges in potentiometric description of the complexes were omitted.

The complexes of $Ln(H_2L)_2$, $Ln(HL)_2$, and LnL_2 type are observed for all systems (Fig. 3). All these species exist in solution up to pH 8. Precipitation occurs above this pH value.

Complex formation in solution starts at pH 4.5 for the La^{3+} , Eu^{3+} systems and pH 4.0 for the Gd^{3+} , Ho^{3+} , and Lu^{3+} system formation of $Ln(H_2L)_2$ complexes with two unionized (neutral) ligands. The equilibrium constants of $Ln(H_2L)_2$ formation were calculated according to the reaction and formula:

$$\log K_{Ln(H_2L)_2} = \log \beta_{Ln(H_2L)_2} - 2 \log \beta$$

and are 5.70, 5.66, 6.43, 6.59, and 6.81 for La^{3+} , Eu^{3+} , Gd^{3+} , Ho^{3+} and Lu^{3+} , respectively (Table 1). The stability constants of $Ln(H_2L)_2$ are 42.78, 42.74, 43.51, 43.67, and 43.89 for La^{3+} , Eu^{3+} , Gd^{3+} , Ho^{3+} , and Lu^{3+} , respectively.

Table 1 Stability constants ($\log \beta$) and equilibrium constants ($\log K_e$) of complexes formed in the $\text{Ln}^{3+}/\text{H}_2\text{L}$ systems (standard deviations of stability constants are given in brackets)

	$\text{La}^{3+}/\text{H}_2\text{L}$		$\text{Eu}^{3+}/\text{H}_2\text{L}$		$\text{Gd}^{3+}/\text{H}_2\text{L}$		$\text{Ho}^{3+}/\text{H}_2\text{L}$		$\text{Lu}^{3+}/\text{H}_2\text{L}$	
	$\log \beta$	$\log K_e$	$\log \beta$	$\log K_e$	$\log \beta$	$\log K_e$	$\log \beta$	$\log K_e$	$\log \beta$	$\log K_e$
$\text{M}(\text{H}_2\text{L})_2$	42.78(8)	5.70	42.74(8)	5.66	43.51(5)	6.43	43.67(7)	6.59	43.89(5)	6.81
$\text{M}(\text{HL})_2$	28.79(7)	8.69	28.77(4)	8.67	29.71(4)	9.61	30.28(8)	10.18	30.68(4)	10.58
ML_2	12.28(6)	12.28	12.29(6)	12.29	13.51(6)	13.51	13.42(8)	13.42	15.12(5)	15.12

Fig. 3 Distribution diagrams of the studied systems: **a** $\text{La}^{3+}/\text{H}_2\text{L}$, **b** $\text{Eu}^{3+}/\text{H}_2\text{L}$, **c** $\text{Gd}^{3+}/\text{H}_2\text{L}$, **d** $\text{Ho}^{3+}/\text{H}_2\text{L}$ and **e** $\text{Lu}^{3+}/\text{H}_2\text{L}$. $C_{\text{Ln}} = 0.001 \text{ M}$ and $C_{\text{H}_2\text{L}} = 0.002 \text{ M}$

$\text{Ln}(\text{HL})_2$ species with two monoprotonated ligands are formed at a pH in which the ligand H_2L is partly deprotonated, and the lanthanide(III) ion is connected to this form. The equilibrium constants of $\text{Ln}(\text{HL})_2$ formation were calculated according to the reaction $\text{H}_2\text{L} \rightleftharpoons \text{HL} + \text{H}$ and $2\text{HL} + \text{Ln} \rightleftharpoons \text{Ln}(\text{HL})_2$. Coordination of these types of complex begins at pH 6.0 for La^{3+} and Eu^{3+} during for Gd^{3+} , Ho^{3+} , and Lu^{3+} at pH 5.5. The equilibrium constants of formation of $\text{Ln}(\text{HL})_2$ were calculated according to the formula:

$$\log K_{\text{Ln}(\text{HL})_2} = \log \beta_{\text{Ln}(\text{HL})_2} - 2 \log \beta_{\text{HL}}$$

and are 8.69, 8.67, 9.61, 10.18, and 10.58 for La^{3+} , Eu^{3+} , Gd^{3+} , Ho^{3+} , and Lu^{3+} , respectively, indicating the similar stability of these complex species for all lanthanides complexes (Table 1). The stability constants of $\text{Ln}(\text{HL})_2$ are 28.79, 28.77, 29.71, 30.28, and 30.68 for La^{3+} , Eu^{3+} , Gd^{3+} , Ho^{3+} and Lu^{3+} , respectively (Table 1).

Finally, LnL_2 complexes are formed as the result of total ligand deprotonation according to $\text{HL} \rightleftharpoons \text{L} + \text{H}$ and $2\text{L} + \text{Ln} \rightleftharpoons \text{LnL}_2$ equilibria. These complexes start to form at pH 7.5 for La^{3+} , Eu^{3+} , and Ho^{3+} ions and at pH 7.0 for Gd^{3+} and Lu^{3+} ions. The stability constants of LnL_2 are 12.28, 12.29, 13.51, 13.42, and 15.12 for La^{3+} , Eu^{3+} , Gd^{3+} , Ho^{3+} , and Lu^{3+} , respectively (Table 1). The excellent agreement between the experimental and theoretical curves (Fig. S1) indicates the presence of only the 1:2 molar ratio complexes such as $\text{Ln}(\text{H}_2\text{L})_2$, $\text{Ln}(\text{HL})_2$, and the LnL_2 type.

The stability constants of the $\text{Ln}(\text{H}_2\text{L})_2$, $\text{Ln}(\text{HL})_2$, and LnL_2 complexes fall into the following order: $\text{La} \approx \text{Eu} < \text{Gd} < \text{Ho} < \text{Lu}$ which reflect the size of the lanthanide ions. This can be attributed to the change of properties of lanthanide ions, not only for stabilities but also for structural changes of lanthanide compounds. These properties are associated with the systematic decrease of an ionic radius with an increasing atomic number of lanthanides which is correlated with the lanthanide contraction [42]. As a result, the coordination number of the lanthanide ions decreases along a series: For the light lanthanides (La–Dy), this is preferably 10 or 9, while for the heavy lanthanides (Ho–Lu) it is 9 or 8 (sometimes even 7) [43–47]. Comparison of stability constants determined for the all systems studied: $\text{Ln}(\text{H}_2\text{L})_2$, $\text{Ln}(\text{HL})_2$, and LnL_2 reveals that the highest values are for $\text{Ln}(\text{H}_2\text{L})_2$ complexes. Our previous investigations showed that only complexes with a unionized (neutral) ligand formed well-defined crystals [45, 46]. In the solid state, two types of complexes of general formulae $[\text{Ln}(\text{H}_2\text{L})_3(\text{NO}_3)_3]$ ($\text{Ln} = \text{La}, \text{Eu}, \text{Tb}$) and $[\text{Ln}(\text{H}_2\text{L})_2(\text{NO}_3)_3\text{EtOH}]\text{MeOH}$ ($\text{Ln} = \text{Er}, \text{Tm}$) were obtained. In the complexes formed in solution, it is likely that coordination spheres of light lanthanide ions are complemented by a solvent and not by a ligand molecule as in solid state. The lower stability constants of the $\text{Ln}(\text{HL})_2$, and LnL_2 complexes (lower volume of stability constants) cause these species to form only in solution.

Comparison of the equilibrium constants determined for the presented systems with those obtained previously for similar systems $\text{Ln}/N,N'$ -bis(salicylidene)-4-methyl-1,3-phenylenediamine shows that additional methyl substituent on the ligands affects the volume of the stability constants of the complexes [41]. The presence of third methyl groups significantly decreases the equilibrium constants of the studied complexes (Fig. 4).

Electronic spectroscopy

The sensing behavior of the N,N' -bis(5-methylsalicylidene)-4-methyl-1,3-phenylenediamine ligand (H_2L) toward Ln^{3+} was monitored by UV–Vis spectrophotometric titration. The titration was carried out in a dimethyl sulfoxide/water 30:70 (v/v) mixture at a concentration of H_2L 1×10^{-4} M. Spectrophotometric titration spectra were collected from pH 3 to 10 covering a wavelength range of 250–500 nm. Figure 5 presents the absorption spectra for one chosen studied system ($\text{Gd}^{3+}/\text{H}_2\text{L}$).

Because of pH domination, the absorption spectra of the complexes for all systems were taken at pH 6 and pH 8 and are presented in Fig. 6. Table 2 summarizes absorption parameters for the studied systems. $\text{Ln}(\text{H}_2\text{L})_2$ and $\text{Ln}(\text{HL})_2$ complexes are the dominant systems at pH 6 and 8, respectively. Spectra of $\text{Ln}(\text{H}_2\text{L})_2$ and $\text{Ln}(\text{HL})_2$ complexes for all systems studied are characterized by three main absorption bands which are assigned to the $\pi-\pi^*$ and $n-\pi^*$ transitions of the Schiff-base ligand. The 210–300 nm bands are due to the $\pi-\pi^*$ transitions of the aromatic rings. The bands at the 300–350 nm range are assigned to the $\pi-\pi^*$ transitions of the $\text{C}=\text{N}$ group. Maximum absorption of about 380–400 nm can be assigned to the intramolecular charge transfer interaction.

Fig. 4 Comparison of equilibrium constants of $\text{Ln}^{3+}/N,N'$ -bis(salicylidene)-4-methyl-1,3-phenylenediamine systems (previous investigations)—red line, and $\text{Ln}^{3+}/\text{H}_2\text{L}$ systems—black line

Fig. 5 3D representing absorption spectrum of $\text{Gd}^{3+}/\text{H}_2\text{L}$ system

Fig. 6 UV-Vis absorption spectra of: **a** $\text{Ln}^{3+}/\text{H}_2\text{L}$ system at pH = 6.0, **b** $\text{Ln}^{3+}/\text{H}_2\text{L}$ system at pH = 8.0, **c** $\text{Ln}(\text{H}_2\text{L})_2$ complexes at pH = 6.0, **d** $\text{Ln}(\text{HL})_2$ complexes at pH = 8.0 (spectra of complexes were obtained by subtracting the ligand spectrum of $\text{Ln}^{3+}/\text{H}_2\text{L}$ system spectra)

Table 2 Absorption data for the studied systems at pH 6 and pH 8; $\lambda_{\max}$ [nm]; ϵ [$10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$]

	H_2L		$\text{La}^{3+}/\text{H}_2\text{L}$		$\text{Eu}^{3+}/\text{H}_2\text{L}$		$\text{Gd}^{3+}/\text{H}_2\text{L}$		$\text{Ho}^{3+}/\text{H}_2\text{L}$		$\text{Lu}^{3+}/\text{H}_2\text{L}$	
	$\lambda_{\max}$	ϵ	$\lambda_{\max}$	ϵ	$\lambda_{\max}$	ϵ	$\lambda_{\max}$	ϵ	$\lambda_{\max}$	ϵ	$\lambda_{\max}$	ϵ
pH = 6	258	12.73	259	18.05	258	15.67	258	16.98	258	13.94	258	32.34
	298	2.46	296	3.72	299	5.03	300	5.33	299	4.60	299	8.32
	338	3.67	338	6.65	338	4.41	338	4.83	339	3.75	337	8.96
pH = 8	259	10.99	258	14.72	258	14.32	257	15.60	258	12.90	258	29.47
	296	2.50	294	3.24	299	5.08	300	5.38	298	4.62	298	8.44
	340	3.02	341	4.38	342	2.85	340	4.26	344	3.30	340	7.95
	394	1.50	396	2.10	388	2.39	398	1.59	394	1.42	391	3.46

The maximum absorption of the band ($\lambda_{\max}$) in the $\text{Ln}^{3+}/\text{H}_2\text{L}$ systems showed only slight changes but absorption increases compared to the free ligand [48–50]. Furthermore, at pH 8, a new absorption band appears, at $\lambda_{\max} = 394 \text{ nm}$ for ligand and about 388–398 nm for all systems. The new absorption band is formed due to the deprotonation of the phenolic OH groups of the ligand (H_2L) [51].

The changes described above mainly depended on the type of complexes formed. Moreover, the coordination of the Ln^{3+} does not significantly influence the singlet-state energy of the ligand. The change of pH does not cause any significant shift in the spectra of the studied systems because some chromophores were only slightly affected by a pH change [52].

Conclusions

The complex formation processes, and the values of stability and equilibrium constants of the complexes of N,N' -bis(5-methylsalicylidene)-4-methyl-1,3-phenylenediamine (H_2L) with lanthanide ions (La^{3+} , Eu^{3+} , Gd^{3+} , Ho^{3+} and Lu^{3+}) were determined by potentiometric and spectrophotometric titration. The studied complexes are formed in solution only with lanthanide ions/ligand 1:2 ratio, and three types of complexes LnL_2 , $\text{Ln}(\text{HL})_2$, and $\text{Ln}(\text{H}_2\text{L})_2$ are created inversely to the solid state where only one form of $\text{Ln}(\text{H}_2\text{L})_2$ occurs. The diversity of the complexes in the solution is due to the fact that ligand (H_2L) occurs in solution in three forms: neutral (H_2L ; undepronated), monodepronated (HL^-), and fully depronated (L^{2-}), depending on pH. UV–Vis spectra of $\text{Ln}(\text{H}_2\text{L})_2$ and $\text{Ln}(\text{HL})_2$ complexes for all the studied systems are characterized by three main absorption bands which are assigned to the $\pi-\pi^*$ and $n-\pi^*$ transitions of the Schiff-base ligand. The maximum absorption of the band in the $\text{Ln}^{3+}/\text{H}_2\text{L}$ systems revealed only slight changes but absorption increases compared to the free ligand, and at pH 8 the new absorption band appears for the ligand and for the studied systems. The new absorption band is formed due to the deprotonation of the phenolic OH groups of the ligand (H_2L). These complexes could be

applied as potential antibacterial, antitumor or antifungal agents, and as catalysts.

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