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Spectroscopic Study of DHDA Complex Formation of d- and f-Electron Metal Ions in Methanol Solution

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Synthesis and spectral characterization of *N*,*N*′-Bis(2,4-dihydroxobenzylidene)1,2-diaminobenzene (DHDA) complexes with chosen f- and d-metal ions are described. Physico-chemical properties of a series of complexes: DHDA–$La(NO_3)_3$, DHDA–$Eu(NO_3)_3$. DHDA–$Yb(NO_3)_3$, DHDA–$Cu(NO_3)_2$, DHDA–$Zn(NO_3)_2$, DHDA–$Co(NO_3)_2$, were studied in methanol solution using UV-VIS, IR and fluorescence spectroscopy. Based on the absorption spectra the conditional stability constants of the metal complexes were determined.

KEY WORDS: Lanthanide complexes; spectrophotometric study; stability constants; fluorescence spectra.

INTRODUCTION

A large number of Schiff bases and their complexes have been studied for their interesting and important properties and applications, e.g. photochromic properties [1], use as shift reagents [2,3] and contrast agents for magnetic resonance imaging [4]. Among the metal ions—Schiff base complexes, the best known is *N*,*N*′-bis(salicylaldehyde)-ethylenediimino type complexes [5,6].

In this communication we present the synthesis and spectral characterization of series complexes: DHDA–$La(NO_3)_3$, DHDA–$Eu(NO_3)_3$. DHDA–$Yb(NO_3)_3$, DHDA–$Cu(NO_3)_2$, DHDA–$Zn(NO_3)_2$, DHDA–$Co(NO_3)_2$, where DHDA stands for *N*,*N*′-Bis(2,4 dihydroxobenzylidene)1,2-diaminobenzene (DHDA), together with their physico-chemical properties. The conditional stability constants of the metal—DHDA complexes were calculated using the previously described procedure [7,8].

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EXPERIMENTAL

All chemicals were used of AR grade. The lanthanide oxides 99.9% (La_2O_3, Eu_2O_3, and Yb_2O_3) were dissolved in a slight excess of HNO_3. The nitrates of lanthanides and d-electron metals ($Cu(NO_3)_2 \cdot 3H_2O$, $Co(NO_3)_2 \cdot 3H_2O$ and $Zn(NO_3)_2 \cdot 3H_2O$) were dried and dissolved in methanol (spectroscopic grade) to give concentrations of 4×10^{-4} mol dm^{-3} which were standardized by EDTA titration. Tetraethylammonium perchlorate and sodium perchlorate were used to control the ionic strength in stability constants determination.

For the stability constants determination, the metal solution was added in small steps, using a microliter pipette to 40 cm^3 of a methanol solution containing DHDA (10^{-5} mol dm^{-3}) at a constant ionic strength (0.005) and stable temperature of 295 K. After each addition of metal cation solution the absorbance due to the M-DHDA complex was measured using a Shimadzu UV-VIS 2401/PC spectrophotometer. IR spectra were recorded on a spectrophotometer in the range of 4000–400 cm^{-1} (KBr pellets). Fluorescence and excitation spectra were performed on a MPF–3 spectrofluorimeter in methanol at 295 K. Methanol used as a solvent in spectroscopic studies was doubly distilled with the addition of metallic sodium.

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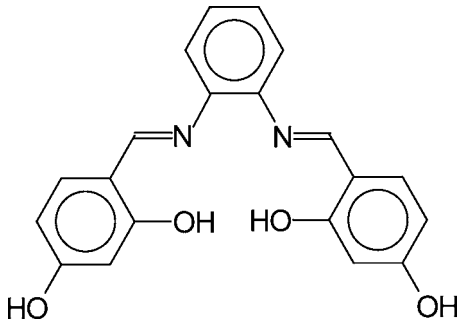

Fig. 1. Structure of DHDA.

Synthesis of the Ligand

1,2-Diaminobenzene (0.1 mol) was dissolved in 100 ml of ethanol, heated to reflux, and 2,4-dihydroxybenzaldehyde (0.1 mol) was added at once. Deep-yellow precipitate was formed in 5 min. Reflux was maintained for 30 min. After cooling, the product was filtered off, washed with ethanol and vacuum dried. Yield was 76%.

The ligand composition (Fig. 1) was identified with the use of elemental analysis (automatic Perkin–Elmer elemental analyser, type 240, USA) and mass spectrometry (Mariner Biospectrometer Workstation mass spectra), obtaining the following results:

Elemental analysis	Calculated: C 68.96 H 4.63 N 8.04 Found: C 69.05 H 4.56 N 7.98
MS (EI, *m*/*z*): 348 (M^+)	

Preparation of the Solid-State Complexes

A solution of metal nitrate (0.2 mmol) in methanol was added to a stirred solution of DHDA (0.2 mmol) over 1 h. The mixtures were stirred and refluxed for 4 h. After cooling to $-10°C$, the precipitates obtained were filtered and recrystallized from methanol to give yellow powder of complexes.

RESULTS AND DISCUSSION

IR Spectra

The IR spectra of the prepared complexes in solid state (KBr) show a band at 1640–1670 cm^{-1} assigned to ν(C═N) of the azomethine group. The band shifts to lower energy region by about 50–70 cm^{-1}, in the case of all complexes, suggest the co-ordination through N atom of the azomethine group. Medium peaks in the range 1540–1570 cm^{-1} are characteristic of the phenolic═C—O groups acquiring partial double bond character through conjugation. The metal complexes show new band in the range 480–450 cm^{-1} that are due to the formation of M—N and M—O bonds, respectively. The ligand has no absorption in the 1700 cm^{-1}, which indicates that free carbonyl groups are absent and so the ketimine structure is ruled out.

Absorption UV-VIS and Emission Spectra

The absorption spectra of solutions containing DHDA and metal ions, at different molar ratios, have been recorded. New absorption peaks have been formed and the peak of the ligand was shifted to lower frequencies (Figs. 2 and 3) with increasing concentration of metal ions (lanthanides and d-electron metals) at a constant concentration of DHDA, conforming the coordination of the metal ions to the ligand.

The complexes studied also exhibit similar absorption spectra in the UV-VIS region in methanol solution. Their absorption properties are summarized in Table I. The absorption spectrum of the ligand exhibits several bands in the region 240–300 and 300–430 nm. The band at lower energy involves a $\pi \rightarrow \pi^*$ transition, which includes the π orbital functions of the azometine chromophore. The other band (300–430 nm) arises from $\pi \rightarrow \pi^*$ transitions involving the phenyl rings.

Stability Constants Determination

The absorbance appearing in the range of 255–265 nm due to the metal—DHDA complex formation was used to determine the conditional stability constant at given ionic strength. The constant defined as $K_{ML} = [M - \text{DHDA}]/[M]\,[\text{DHDA}]$ was determined by the use of the following equation [7,8]:

$$\frac{M_T L_T}{A_{ML}} = \left(M_T + L_T - \frac{A_{ML}}{\varepsilon_{ML}}\right)\frac{1}{\varepsilon_{ML}} + \frac{1}{K_{ML}\varepsilon_{ML}}$$

where: M_T and L_T are the total concentrations of metal ion and DHDA, ε_{ML} is the molar absorptivity of ML complex (for the first approximation used $\varepsilon_{ML} = \varepsilon_L$), A_{ML} is the maximum absorbance at 255–265 region, and $A_{ML} = A_T - A_L$. (A_T—total absorbance in the studied spectral range). Plots of $M_T L_T/A_{ML}$ versus $M_T + L_T - (A_{ML}/\varepsilon_{ML})$ were almost linear only for $3 > \text{M:L} > 1$, what shows that the 1:1 complexes are only formed in these conditions. In the case of different investigation conditions (DHDA excess) probably other, more complicated structures are formed. The reciprocal of the slope of the line yielded the

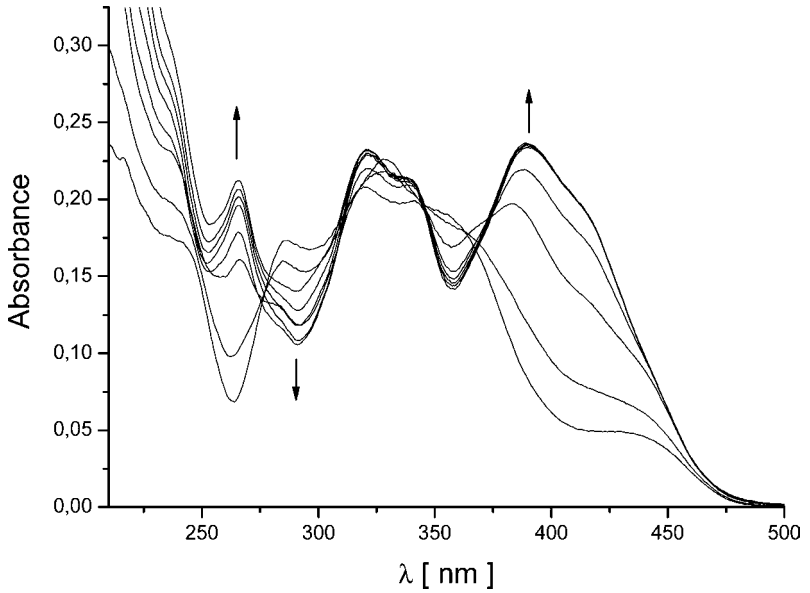

Fig. 2. Spectral changes of DHDA in 10^{-5} M methanol solution with increase of concentration of $Yb(NO_3)_3$.

correction value of ε_{ML}, which was utilized to replot the above relation. The slope/intercept ratio of the resulting plot gave the K_{ML} value. The results obtained for different metal ions are listed in Table I.

The characteristic changes in excitation and emission spectra of lanthanide complexes are shown in Fig. 4. The intensity of the excitation and emission peak at 360 nm decreases and increases, respectively, with increase of the density of electronic charges of lanthanide ions. The most interesting are the fluorescence proprieties of complex Co-DHDA (Fig. 5). The intensity of emission is about two orders of magnitude higher than for the remaining

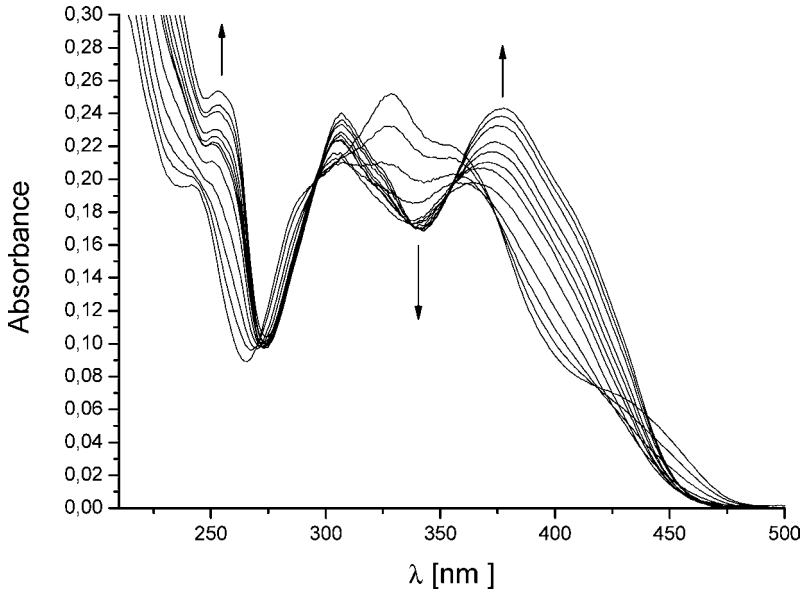

Fig. 3. Spectral changes of DHDA in 10^{-5} M methanol solution with increase of concentration of $Cu(NO_3)_2$.

Table I. Photophysical Data and Stability Constants of the Complexes Studied

Compound (the electric charge was omitted for simplicity)	Absorption λ_{max} [nm] ($\varepsilon \times 10^4$ [dm^3 mol^{-1} cm^{-1}])	Excitation λ_{exc} [nm]	Emission λ_{em} [nm]	Log K_{ML} M:L 1:1
DHDA	207(4.7), 242(0.30), 290(0.57) 325(2.1), 360(1.4), 430(0.40)	320	440	—
Cu-DHDA	207(4.5), 240(1.2), 265(0.85) 320(1.56), 345(1.2), 385(1.8), 425(1.0)	365	470	4.6 ± 0.2
Zn-DHDA	207(7.3), 228(5.8), 262(0.40) 280(0.5), 317(1.2), 287(0.19)	325	350, 465	4.5 ± 0.2
Co-DHDA	207(4.7), 245(1.85), 268(1.2) 321(1.3), 358(1.0), 389(1.0), 430(0.79), 455(0.48)	320	370	4.7 ± 0.2
La-DHDA	207(4.2), 227(1,7), 255(1.1), 300(1.3), 225(0.91), 372(1.7), 420(0.85)	330	360, 450	5.7 ± 0.15
Eu-DHDA	207(5.1), 228(2.1), 260(1.0), 300(1.3), 329(0.89), 372(1.6), 412(0.83)	335	360, 345	5.9 ± 0.2
Yb-DHDA	207(4.3), 228(1.5), 260(1.0), 300(1.3), 329(0.92), 373(1.7), 410(0.84)	340	360, 345	6.8 ± 0.15

complex compounds and the maximum efficiency of fluorescence took place at the molar ratio M:L < 0.1. Because the stability constants of all complexes are similar, it has been possible to conclude that the high emission intensity is a result of an increased degree of the cobalt ion oxidation by dissolved oxygen [9,10].

It was also found that the excitation and fluorescence spectra of DHDA and their metal complexes in water and methanol, after being exposed to ultraviolet radiation, show a very obvious photochromism, however observed only in the case of free ligand solutions. The spectra changes can be explained as a result of the change of enol-imine into the keto-amine form after UV irradiation, i.e., the hydrogen atom that originally bonded to the phenol hydroxyl group is transferred onto the nitrogen atom. In the case of metal complexes this situation cannot

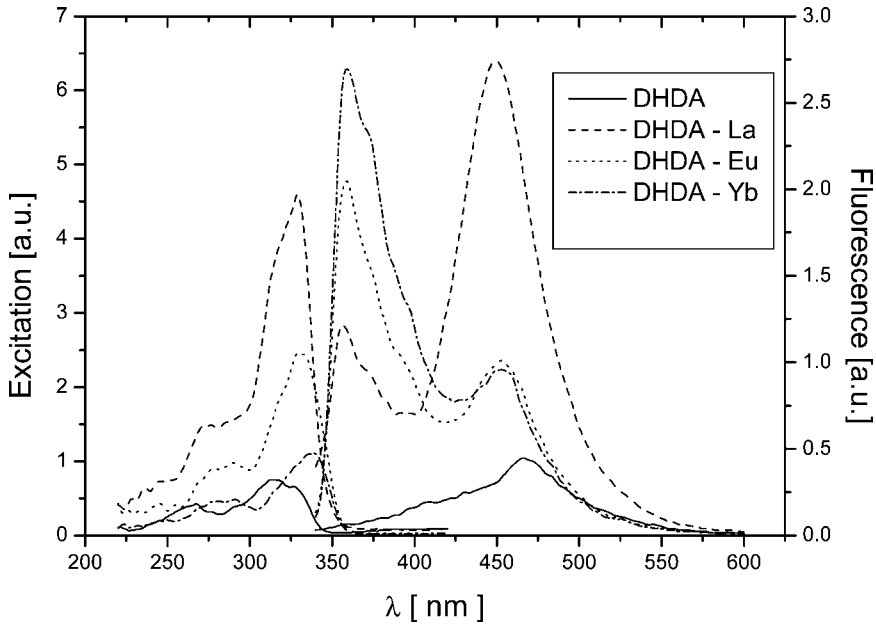

Fig. 4. The excitation and emission spectra of DHDA and their complexes with lanthanide ions in methanol.

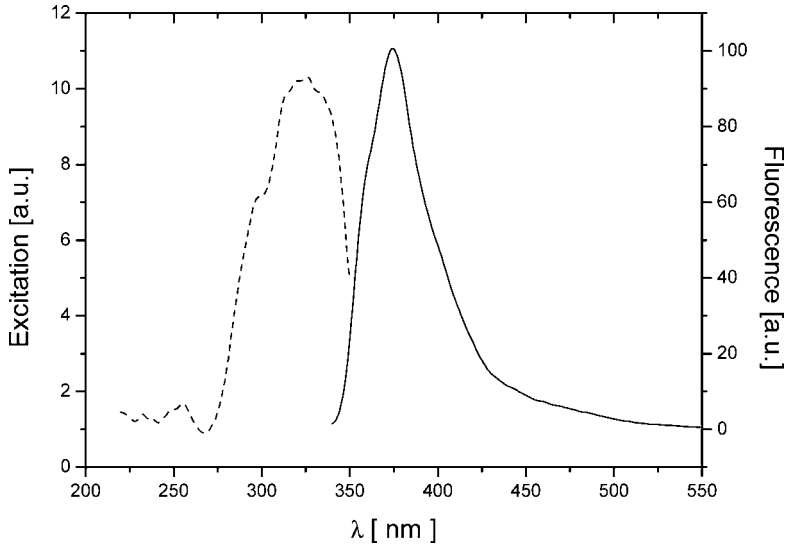

Fig. 5. The excitation and emission spectra of Co-DHDA complex (the ratio of metal:ligand = 1:1) in methanol, concentration of DHDA = 10^{-5} M.

take place, because the metal ions are complexed within the N_2O_2 cavity.

The addition of lanthanide ions to the Co-DHDA complex causes the increase of the luminescence intensity due to the formation of the polynuclear complex: Co-DHDA-Eu. It has been found that the absorption spectra of DHDA, after being exposed to ultraviolet irradiation, show a very obvious photochromism both in methanolic and water solutions [11].

The f,d-complexes can be used in electroluminescence study, mainly in systems containing oxide covered metal electrodes (Al, Tl or Mg) [12]. Due to changes of the redox properties of the metal ions and highly reducing or oxidizing conditions near the electrodes, the ECL of these compounds can be observed.

Investigations concerning luminescent and electroluminescent properties of this composition are under way.

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