

A Fluorescence Emission, FT-IR and UV-VIS Absorption Study of the Some Uranium (VI) Schiff Bases Complexes

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Abstract The capacity of metallic ions to form complexes depends on the electric charge and its mass and on the ligands nature. In this study we followed the coordination capacity of the uranyl ion (UO_2^{2+}) with a series of Schiff bases. The Schiff bases have been obtained through the condensation of some salicylic aldehyde derivates with a series of diamines. As a result of the reaction between these substances and the uranyl ions the mono-, bi-, or polynuclear complexes, depend on the nature of the ligands. The forming of the complexes is highlighted through ultraviolet-visible, Fourier transform infrared (IR), and fluorescence spectroscopy. In the IR studies the forming of the complexes is highlighted by the apparition of a new band at approximately 920 cm^{-1} , characteristic to the $\text{O}=\text{U}=\text{O}$ group. Also modifications of valence vibrations appear characteristic to the azomethinic groups, $\nu_{\text{C}=\text{N}}$, and the apparition of some new bands in the $300\text{--}500\text{ cm}^{-1}$ domain, characteristic to forming of some new bonds $\text{U}-\text{O}$ and $\text{U}-\text{N}$. The formed complexes represent tetragonal bipyramidal geometry. The study of the capacity coordination of uranyl ions is important in determining, dosing and precipitin of the ions in diverse used waters.

Keywords Fluorescence, FTIR · UV-VIS spectroscopy · Schiff bases · Uranium (VI) complexes

Introduction

In the last years the metallic compounds of Schiff bases have been demanding a special attention, through their antifungal, antibacterial and antimicrobiological properties [1–3], and through their antitumoral [4] and anticancer activities [5] present in some compounds. The books from this area of expertise is reminding of metallic complex with some Schiff bases that have the properties of some liquid crystals [6], which can be used in fine quantities in analytic chemistry [7], or in the purification of used water [8,9].

For determination of uranium speciation in biosystems such as plants, water, the investigation of the complexation behaviour of uranium (VI) with organic ligands is necessary [10–11]. As it is known, the capacity of metallic ions to form complexes depends on its size, and its ligand type [12–15]. The complexes with Schiff bases have been studied for their interesting and important properties and applications, e.g. photochromic properties (Fluor 1), contrast agents for magnetic resonance (Fluor 4) etc.

In this study we are following the fluorescence emission, Fourier transform infrared (FT-IR) and ultraviolet-visible (UV-VIS) absorptions of the some Schiff bases uranyl (UO_2^{2+}) complexes. The Schiff bases have been obtained through the condensation of the salicylic and β -hydroxy- α -naphthyl aldehydes with a series of diamines. In the reaction between the Schiff bases and the uranyl ions, the metallic complexes are formed in diverse combinations ratios.

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Table 1 The characteristics of Schiff bases

Schiff bases	Yield, η , %		Melting point, $^{\circ}\text{C}$		Color
	Catalyst CH_3COOH	Catalyst AcPTS	Catalyst CH_3COOH	Catalyst AcPTS	
(L1)	94	–	49	–	Yellow bright
(L2)	88	88	96	96	Yellow dark
(L3)	69	53	221	221	Yellow orange
(L4)	74	56	274	273	Yellow
(L5)	65	44	233	235	Yellow mustard
(L6)	43	40	224	224	Yellow bright
(L7)	87	89	309	308	Red
(L8)	88	78	326	329	Orange

Experimental part

The Schiff bases were obtained by the condensation reaction of the diamine and various primary aldehydes, in an organic solvent medium, in acid catalysis:

Method 1—acetic glacial acid as catalyst (CH_3COOH)

Method 2—*p*-toluene sulphonic acid as catalyst (*p*- $\text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_3\text{H}$; AcPTS)

Method 1 (Acetic glacial acid as catalyst (CH_3COOH)) In a glass balloon there were introduced 0.04 mol of aldehyde, 0.02 mol of diamine, dissolved in ethanol and four to five drops of glacial CH_3COOH , as catalyst. The reaction mixture was magnetic stirring under reflux 3 h. The bis Schiff base is removed from the system as a precipitate, when was filtered in vacuum, washed with water, then with ethanol and then purified.

Method 2 (p-toluene sulphonic acid as catalyst, p- $\text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_3\text{H}$ (AcPTS)). In a round bottom glass balloon, there are introduced 50 mL of benzene, 0.02 mol of diamine, 0.04 mol of aldehyde and *p*-toluene sulphonic acid as catalyst. The reaction mixture was heated, magnetic stirring, distilling a water–benzene azeotrope, with the introduction of fresh benzene in the balloon. The distillation, is continued until all the reaction's water was eliminated. Through the cooling of the reaction mixture, the azomethine has crystallized, which is filtered, dried and purified.

As the Table 1 shows us we can say that through both methods of condensation we've obtained the same products, the yields being close. It is recommended the first method as its toxicity levels are lower.

The purification has been made through column chromatography with Al_2O_3 , using as eluent acetone for L5 and L6 samples, dichloromethane (CH_2Cl_2) for L1, L2, L7 complexes, chloroform (CHCl_3) for L8 sample. The L3 and L4 samples were recrystallized from *N,N*-dimethylformamide–water system.

Results and discussion

The structure and general reactions of the synthesis of the Schiff bases are presented in Fig. 1. For the study to be as complete as it can be, we've considered the Schiff monobases with aniline of considered aldehyde also.

The names of the synthesized Schiff bases are:

- (L1): *N*-salicylidene-aminobenzene;
- (L2): *N*-(2-hydroxynaphtyl)-aminobenzene;
- (L3): bis-(salicylidene)-1,4-diaminobenzene;
- (L4): bis-(salicylidene)-4,4'-diaminodiphenyl;
- (L5): bis-(salicylidene)-1,5-naphtylenediamine;
- (L6): bis-(salicylidene)-1,4-hydrazine;
- (L7): bis-(2-hydroxynaphtylidene)-1,4-diaminobenzene;
- (L8): bis-(2-hydroxynaphtylidene)-4,4'-diaminodiphenyl.

The characterization of the earlier synthesized Schiff bases is systematized in Table 1. On the information in Table 1 we can appreciate the yields which are situated at a high level in both situations, the only exception being L6.

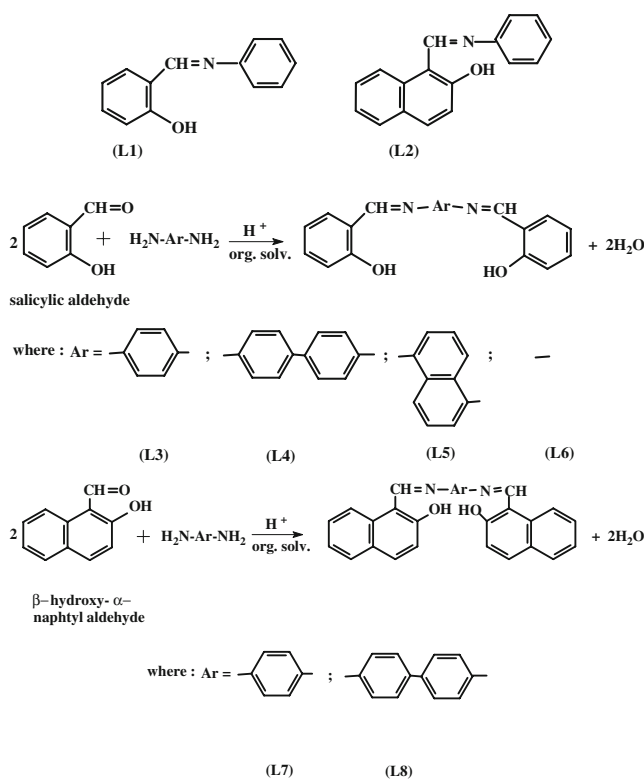


Fig. 1 The structures of the Schiff bases prepared

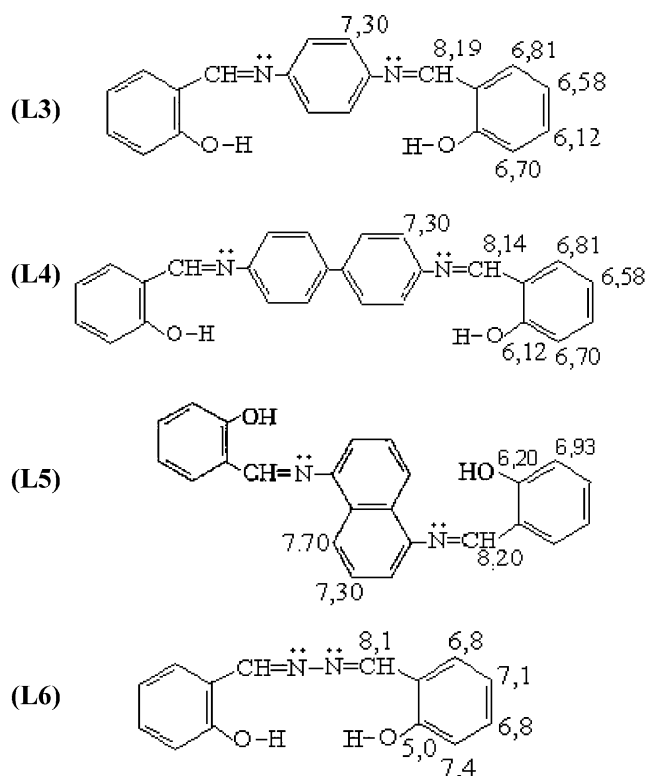


Fig. 2 Spectral shifts of Schiff bases from $^1\text{H-NMR}$ spectra (DMSO)

The chemical structures of the azomethines have been confirmed through spectroscopic methods (FT-IR, UV-VIS, $^1\text{H-NMR}$ nuclear magnetic resonance (NMR)). The $^1\text{H-NMR}$ spectra are confirming the proposed structures for the Schiff bases used as ligands. In Fig. 2 are represented the $^1\text{H-NMR}$ spectral shifts for the considered ligands.

The FT-IR spectra of the Schiff bases showed major bands around of $3,400\text{ cm}^{-1}$ attributed to δ_{OH} vibration, around $1,615\text{ cm}^{-1}$ that can be assigned to $\nu_{\text{C=N}}$, and around $1,560\text{ cm}^{-1}$ and $1,500\text{ cm}^{-1}$ that can be assigned to aromatic rings vibrations. The band around $1,280\text{ cm}^{-1}$ was assigned to the deformation of the Ar–OH outside the plane of the Ar–OH moiety, δ_{OH} , and the bands around $1,230\text{ cm}^{-1}$ and $1,050\text{ cm}^{-1}$ were assigned to $\nu_{\text{C-N}}$, and $\nu_{\text{C-O}}$, respectively, Table 2 [16–18].

The electronic spectra of the Schiff bases in acetonitrile showed two strong absorption bands in the UV-VIS region (200–432 nm), that could be attributed respectively to the $\sigma\text{-}\sigma^*$, $\pi\text{-}\pi^*$ or $n\text{-}\pi^*$ transitions [19, 20]. In the spectra of the corresponding U(VI) complexes, the position and intensity of the bands characteristic of the ligand appeared to be modified with respect to those of the free ligand.

The main valence vibrations of the studied ligands are represented in Table 2.

Table 2 FTIR and UV-VIS characteristics of Schiff bases

Schiff bases	IR characteristic absorptions (cm^{-1})	UV-VIS characteristics ^a λ (nm), $\log \epsilon$ ($\text{l}\cdot\text{mol}^{-1}\text{ cm}^{-1}$)	$\ln \beta_n$ for ULI ($i=1\text{--}8$)
(L1)	–OH _{phenolic} (3,441) –HC=N– (1,616) Ar (1,590; 1,571; 1,485)	$\lambda_1=330$ (3.94) $\lambda_2=249.5$ (4.26) $\lambda_3=219.2$ (4.55)	13.32
(L2)	–OH _{phenolic} (3,416) –HC=N– (1,616) Ar (1,589; 1,570; 1,483; 1,452)	$\lambda_1=354$ (4.06) $\lambda_2=292.5$ (4.12) $\lambda_3=219$ (4.04)	7.17
(L3)	–OH _{phenolic} (3,433) –HC=N– (1,610) Ar (1,568; 1,493; 1,456)	$\lambda_1=367$ (2.94) $\lambda_2=250.5$ (2.76) $\lambda_3=211$ (3.36)	10.08
(L4)	–OH _{phenolic} (3,441) –HC=N– (1,618) 4,4'-diphenyl (1,570; 1,485; 1,454)	$\lambda_1=275.5$ (3.42) $\lambda_2=264.5$ (3.54) $\lambda_3=209.5$ (3.96)	10.00
(L5)	–OH _{phenolic} (3,441) –HC=N– (1,614) 1,5-naphtalene (1,578; 1,506; 1,491; 1,458; 933; 889)	$\lambda_1=367$ (3.32) $\lambda_2=267$ (3.58) $\lambda_3=213$ (3.88)	13.04
(L6)	–OH _{phenolic} 3,464 –HC=N– (1,624) Ar (1,574; 1,485; 1,450)	$\lambda_1=366.5$ (3.06) $\lambda_2=316$ (3.19) $\lambda_3=220$ (3.99)	13.32
(L7)	–OH _{phenolic} (3,422) –HC=N– (1,622) Aromatic rings	$\lambda_1=274$ (3.31) $\lambda_2=209.5$ (4.00)	7.28
(L8)	–OH _{phenolic} (3,420) –HC=N– (1,622) Aromatic rings	$\lambda_1=399$ (3.01) $\lambda_2=272.5$ (3.39) $\lambda_3=209.5$ (3.86)	7.84

^a Solvent is acetonitrile

The second direction, followed in the here present case, has been the determination of the coordinate capacity of the uranyl ion (UO_2^{2+}) with the synthesized Schiff bases.

The obtained metallic complexes have been obtained through a co-bonding reaction, in an organic solvent medium ($\text{C}_2\text{H}_5\text{OH}$), of organic ligands (synthesized azomethines) with the uranyl ion, provide by the corresponding acetate, at

different molar ratios. The reaction time varies from 45 min to 8 h, depending of the nature of the ligand.

The forming of complexes has been monitorized through UV-VIS, FT-IR, and fluorescence spectra. Regarding to the IR, UV-VIS and fluorescence spectra, we can appreciate the coordination of the uranyl ion at the studied ligands. Thus, the modification of the positions and intensity of the

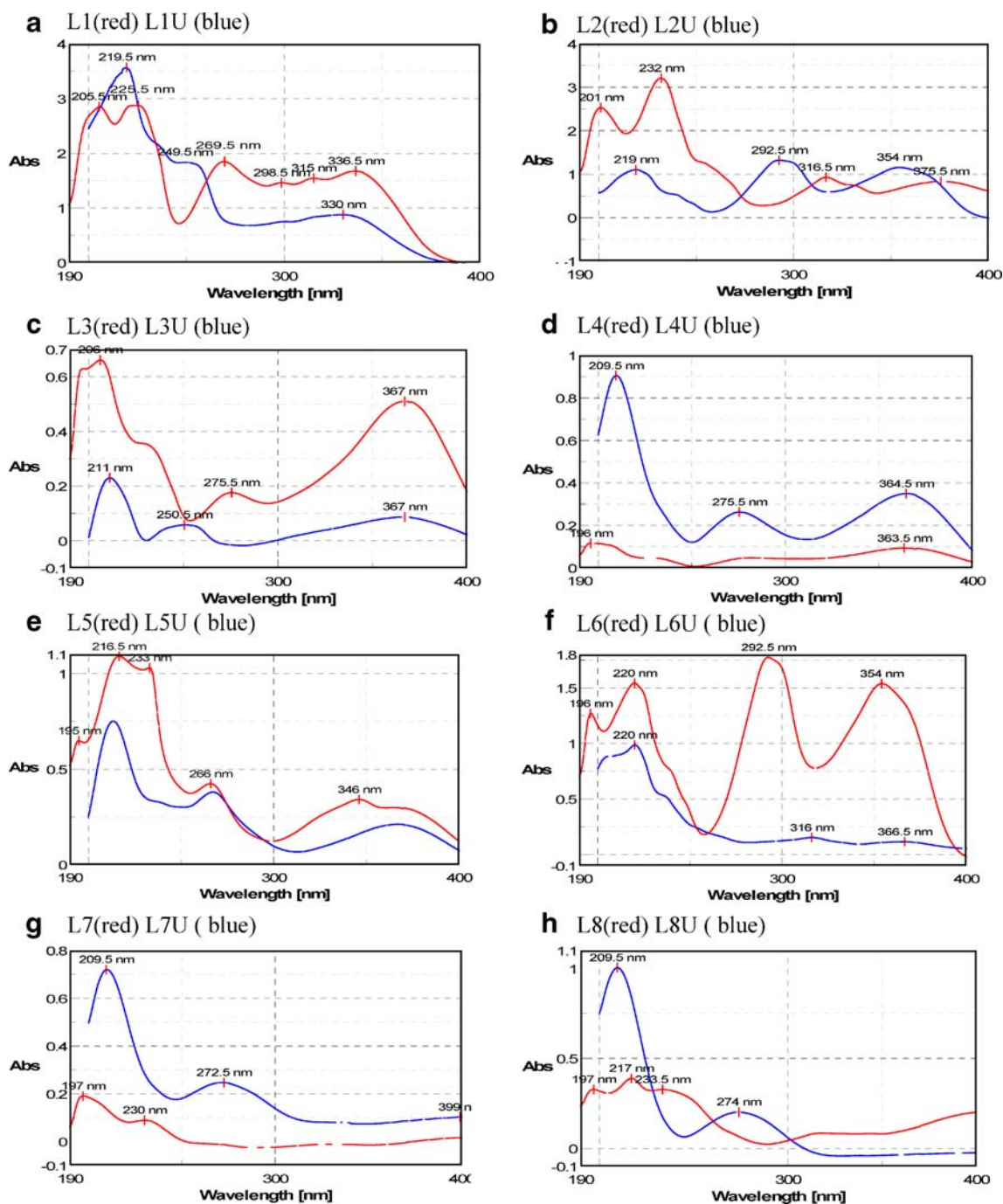


Fig. 3 UV-VIS spectra for complexes and ligands, comparatively: Li–ligand (red), LiU–uranyl ion complexes ($i=1\dots 8$; blue); **a** L1 (red) L1U (blue), **b** L2 (red) L2U (blue), **c** L3 (red) L3U (blue), **d** L4 (red)

L4U (blue), **e** L5 (red) L5U (blue), **f** L6 (red) L6U (blue), **g** L7 (red) L7U (blue), **h** L8 (red) L8U (blue)

Table 3 Fluorescence properties of different U(VI) complexes and free ligands ($\lambda_{\text{excitation}}=350$ nm)

Species	Fluorescence emission bands (nm)		
(L1)	390.5	410	–
(L1U)	–	–	531
(L2)	300	–	–
(L2U)	390	410	497
(L3)	389.5	420.5	529
(L3U)	–	422.5	529
(L4)	390.5	–	–
(L4U)	–	443.5	520
(L5)	379	–	500.5
(L5U)	–	425	532
(L6)	390	416	526.5
(L6U)	–	423.5	528
(L7)	390.5	–	528.5
(L7U)	390.5	–	528.5
(L8)	390	–	506.5
(L8U)	–	–	508

spectral lines from UV-VIS and fluorescence spectra indicates the presence of the uranyl ion in the newly formed compounds.

This is confirmed by the presence in the FTIR spectra of a new band, situated around 920 cm^{-1} , characteristic to the uranyl ion. In the $3,600\text{--}3,500\text{ cm}^{-1}$ domain the values of the water molecules vibrations become visible, existing in the complexes.

The modification of the valence vibrations from ligands, corresponding to the azomethine bond $\text{C}=\text{N}$ from $1,620\text{ cm}^{-1}$, of vibrations of the $\text{C}-\text{O}$, $\text{C}-\text{N}$ bonds, and the appearance of new bands in the $600\text{--}400\text{ cm}^{-1}$, indicates the bonding of the uranyl ion with the Schiff bases through the N atoms, through the azomethine group and phenolic oxygen [17, 18].

The UV-VIS spectra for the uranyl ion complexes, comparative with those of ligands (used solvent acetonitrile), has a series of modifications (Fig. 3).

As shown, the UV-VIS spectra of the new structures have significant modifications compared with those of ligands. The detected significant increase in the absorption and a bathochromic shift of the absorption maxima compared to the free uranyl cation and Schiff bases indicate complex formation between the uranyl cation and Schiff bases. New band formed can be attributed to the U(5f)–Schiff bases (O), ligand to metal charge transfer band [13, 20, 21].

In βn -stability constant for complexes

The information provided by the fluorescence spectra (Table 3, Fig. 4), for the complexes with the uranyl ion, comparing it with the ones of ligands, are capable to show

exactly which of the studied ligands have managed to coordinate with the uranyl ion. The used wavelength for excitation was 350 nm, and the used solvent was the same as the UV-VIS determinations (acetonitrile), used to remove some supplemental variables. As shown in Table 3, the wavelength consists in a move of the peaks, less or more, depending of type of ligand, and of the nature of the obtained complexes.

The fluorescence emission spectra of the U(VI) complexes solutions showed an increase in the fluorescence intensity and a significant bathochromic shift of the emission maxima by complexation of some ligands, in comparison with fluorescence of free ligands. For the other, by complexation some ligands the fluorescence bands disappear, Fig. 4.

It is noticeable that the L1, L2, L3, L4 ligands have formed well individualized complexes through significant wavelength movement. (L1 $390.5\text{ nm} \rightarrow$ L1U 531 nm ; L2 $300\text{ nm} \rightarrow$ L2U 497 nm ; L3 $389\text{ nm} \rightarrow$ L3U 422 nm , respectively L3 $529\text{ nm} \rightarrow$ L3U 529 nm ; L4 $390\text{ nm} \rightarrow$ L4U 520 nm). In the case of ligand L5 it is noticeable the remove of the peak from 379 nm and the apparition of a new peak at 425 nm for L5U, but the absorption being smaller.

This behavior can evidenciate a special complexation mode, justified through the geometry of the ligand, with a big space maker (naphthalene) between the two asymmetrical groups. For the behavior of the ligand L6 at complexation we can appreciate the low co-bonding tendencies, the movement of the wavelength being reduced: L6 $416\text{ nm} \rightarrow$ L6U 423 nm , L6 $526\text{ nm} \rightarrow$ L6U 528 nm . The L7 and L8 ligands do not show significant red/blue shift, fact that shows us that no co-bonding had place between the ligand and the uranyl ion. This thing was predictable thus the forming structures would be extremely packed, and the developed steroidal repulsions are very high [21]. The molar fluorescence yield of the uranyl complexes species is clearly higher than the molar fluorescence yield of the free Schiff bases.

The formed coordinative compounds represent a bipyramidal pentagonal geometry, and depending by the combination rapport, and conforming to the information available in the literature [18, 22].

Conclusions

We've synthesized and characterized a series of Schiff bases, starting from the salicylic aldehyde and the β -hydroxy- α -naphthyl aldehydes and different aromatic diamines. We've followed the coordinating capacity of the uranyl ion (UO_2^{2+}) with the synthesized azomethines, after the co-bonding, compounds mono-, bi- or polynuclear being formed, depending of the ligands nature. The study

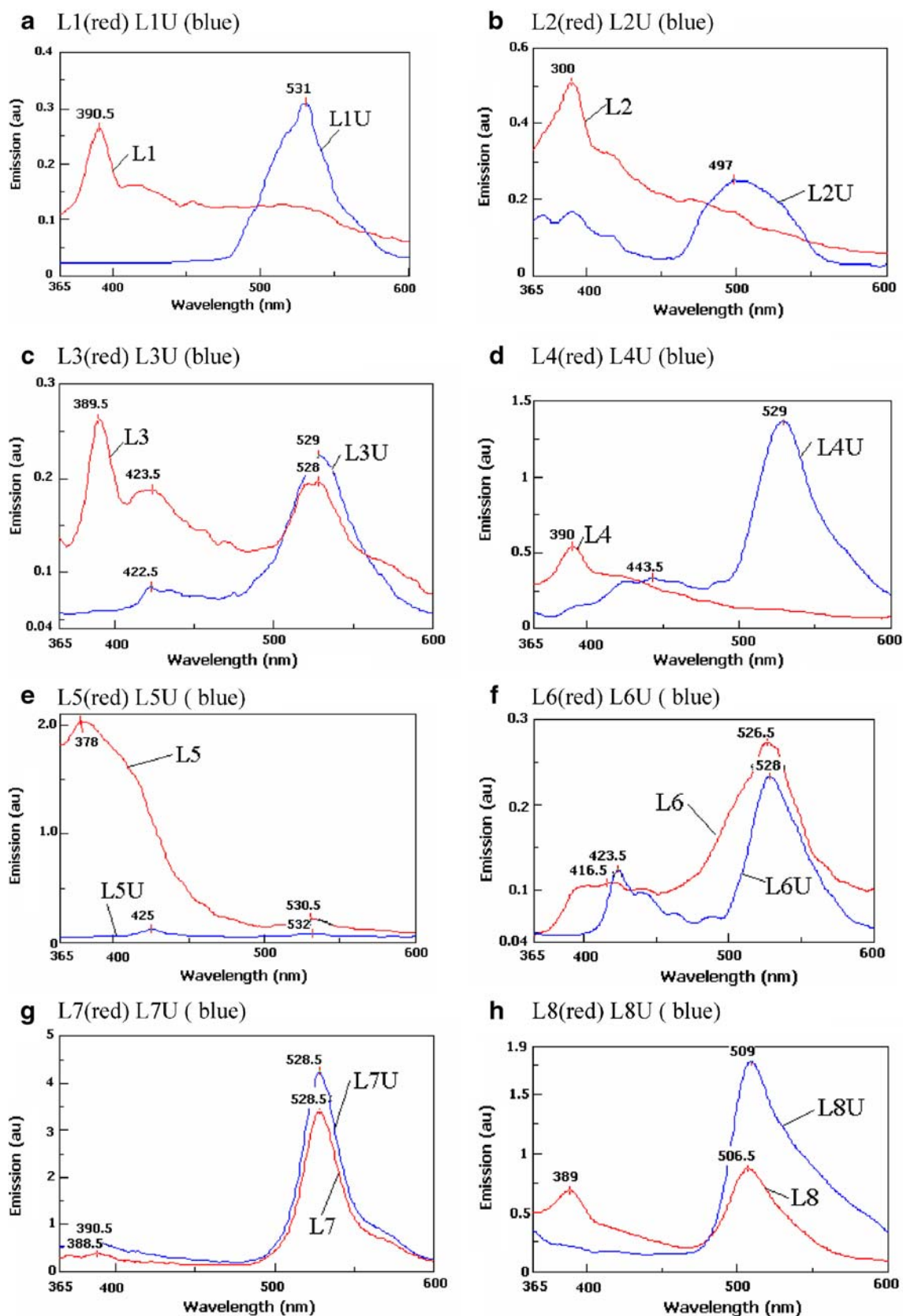


Fig. 4 Fluorescence emissions for complexes and ligands, comparatively: Li–ligand (red), LiU–uranyl ion complexes ($i=1\dots 8$; blue); **a** L1 (red) L1U (blue), **b** L2 (red) L2U (blue), **c** L3 (red) L3U (blue), **d**

L4 (red) L4U (blue), **e** L5 (red) L5U (blue), **f** L6 (red) L6U (blue), **g** L7 (red) L7U (blue), **h** L8 (red) L8U (blue)

of the coordinating capacity of uranyl ions represents a great importance in the determination, dozation and precipitation of these ions in various medium (residual mixtures, used waters, etc.).

The forming of the complexes can be highlighted, except through the usual standard methods, also through fluorescence spectroscopy, the obtained data gives us sure information regarding the co-bonding process between the uranyl ion and considered ligands. The interpretation of the obtained results through fluorescence tests is relatively easy and extremely eloquent.

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