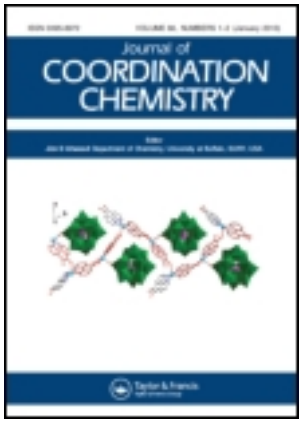

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Synthesis and characterization of uranyl(VI) chiral Schiff-base complexes derived from salicylaldehyde and L-aminoacids

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Complexes of uranyl(VI) (U(VI)) with tridentate ligands derived from salicylaldehyde and aminoacids are reported, bis 2-((2-hydroxybenzylidene)amino)acetic acid U(VI), $UO_2(SalGly)_2$ (**1**); tri aqua 2-((2-hydroxybenzylidene)amino)propanoic acid U(VI) nitrate, $[UO_2(SalAla)(H_2O)_3]NO_3$ (**2**); tri aqua 3-hydroxy-2-((2-hydroxybenzylidene)amino)propanoic acid U(VI) nitrate, $[UO_2(SalSer)(H_2O)_3]NO_3$ (**3**); tri aqua 2-((2-hydroxybenzylidene)amino)-3-methylbutanoic acid U(VI) nitrate, $[UO_2(SalVal)(H_2O)_3]NO_3$ (**4**), and tri aqua 2-((2-hydroxybenzylidene)amino)-4-(methylthio)butanoic acid U(VI) nitrate, $[UO_2(SalMet)(H_2O)_3]NO_3$ (**5**). The characterization of the complexes was performed by electrospray mass spectroscopy, ultraviolet-visible spectroscopy, Fourier transform infrared spectroscopy, nuclear magnetic resonance, fluorescence spectroscopy, and thermal analysis. The complexes are electrolytes (1 : 1) having a molar ratio M : L = 1 : 1, except **1**, which is a nonelectrolyte with a molar ratio M : L = 1 : 2. The fluorescence intensity of the complexes is more intense than uncomplexed uranyl, except **1** and **5**. High fluorescence of the uranyl SalAla complex (**2**) was used to assess complexes–DNA interaction based on fluorescence quenching assay. The interaction of **2** with DNA was assessed by measuring the relative fluorescence quenching of the complex when nucleic acids were added.

Keywords: Uranyl complexes; Aminoacid Schiff-base ligands; DNA Fluorescence

1. Introduction

Uranyl(VI) (U(VI)) ions exist in all parts of the environment, in various concentrations, present in certain types of rocks and artificial combinations [1]. The dioxouranium(VI) ions have a collinear shape, O–U–O. The U(VI) ion possesses luminescence and photochemical reactivity. These properties are attributed to the linear O = U=O group, which gives a long-lived and highly oxidizing $*UO_2^{2+}$ excited state as a result of uranium 5f ← oxygen 2p LMCT electronic transition [2]. The UO_2^{2+} group can coordinate 4–6 other donors in the equatorial plane with a strong tendency to make these ligating atoms coplanar [3].

U(VI) complexes with salen and salophens have numerous applications, ranging from catalysts to sensors [4]. Contrasting solvent and capping ligand effects direct the photochemistry of U(VI) Schiff-base complexes. The photochemistry of the U(VI)

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complexes coordinated by chromophoric or asymmetric ligands make them good candidates for contrast agents [5].

The luminescence of actinide complexes and their binding affinity to DNA indicate these complexes for application as spectroscopic probes for nucleic acids [6]. Understanding how metal complexes interact with DNA has become a research topic at the interface between chemistry, molecular biology, and medicine [7]. Metals play a very important role in organisms and their complexes can interact with nucleic acids. Many metal complexes were used to induce DNA conformational changes for mediation of duplex DNA strand scission or as chemotherapeutic agents [8, 9]. DNA-binding studies are very important for the development of new therapeutic agents and DNA detection. Generally, there are three kinds of binding models for small molecules with DNA, (i) intercalation, (ii) groove binding, and (iii) external electrostatic binding. In these interaction models, the binding is the strongest in intercalation, making a sandwich, between the aromatic heterocyclic pairs of DNA [10]. The luminescent lanthanides (europium, gadolinium, terbium) and actinides (uranium) are increasingly exploited in confocal cellular imaging using their visible emission [11, 12]. In comparison with metal ions, their complexes may have different binding properties and stronger binding affinity [13].

The most reported studies focus on U(VI) complexes with aminoacids based on L-glycine [14, 15], L-cysteine [16], histidine [17], tyrosine [18], and tryptophan [19]. Heteroditopic chiral uranyl-salen can be used as receptor for molecular recognition of amino acid ammonium salts [20]. Less attention has been given for uranyl complexes with Schiff bases derived from salicylaldehyde and aminoacids or peptides as ligands.

Here, we report the synthesis of tridentate amino acid Schiff-base complexes of dioxouranium. These amino acid Schiff-base complexes can be distinguished by the asymmetric center. The general structure of Schiff bases used as ligands is illustrated in figure 1.

The complexes prepared from salicylaldehyde, amino acids, and U(VI) ions are presented in table 1.

2. Experimental

2.1. *Chemicals and apparatus*

All chemicals and solvents used for the synthesis were commercially available reagents and used without purification. Herring sperm DNA was purchased from Boehringer Mannheim GmbH, Germany.

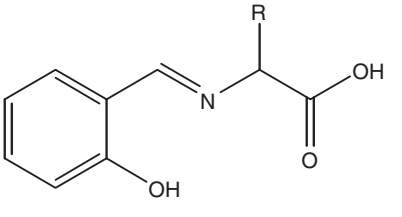

Figure 1. Schiff bases used as ligands.

Table 1. Schiff bases, amino acids, and corresponding U(VI) complexes.

Complexes	R	Amino acid	Schiff-base ligand	Nomenclature	Formula	M : L ratio
1	H	Glycine	SalGly	Bis 2-((2-hydroxybenzylidene)amino) acetic acid) U(VI)	$[UO_2(SalGly)_2]$	1 : 2
2	CH_3	L-alanine	SalAla	tri aqua 2-((2-hydroxybenzylidene)amino) propanoic acid U(VI) nitrate	$[UO_2(SalAla)\ (H_2O)_3]NO_3$	1 : 1
3	CH_2OH	L-serine	SalSer	tri aqua 3-hydroxy-2-((2-hydroxybenzylidene)amino) propanoic acid U(VI) nitrate	$[UO_2(SalSer)\ (H_2O)_3]NO_3$	1 : 1
4	$CH(CH_3)_2$	L-valine	SalVal	tri aqua 2-((2-hydroxybenzylidene)amino)-3-methylbutanoic acid U(VI) nitrate	$[UO_2(SalVal)\ (H_2O)_3]NO_3$	1 : 1
5	$CH_2CH_2SCH_3$	L-methionine	SalMet	tri aqua 2-((2-hydroxybenzylidene)amino)-4-(methylthio)butanoic acid U(VI) nitrate	$[UO_2(SalMet)\ (H_2O)_3]NO_3$	1 : 1

Electrospray mass spectroscopy (ESMS) spectra were recorded on an XCalibur device in $MeOH/CH_2Cl_2/H_2O$ solution at 3 kV. Ultraviolet-visible (UV-Vis) spectra were recorded with a Cintra 101 spectrophotometer using a capped quartz cuvette of light-pass length 10 mm. The optimal concentration of ligand and complexes solution was 10^{-4} mol L^{-1}. The fluorescence emission spectra of complexes (10^{-4} mol L^{-1}) and ligands (10^{-4} mol L^{-1}) were recorded with Perkin Elmer LS 50 B spectrofluorimeter in acetonitrile as solvent. Fourier transform infrared spectroscopy (FTIR) spectra were obtained on an FT/IR 660 Plus (Jasco) device, in KBr pellets. Conductance measurements were carried out at room temperature in alcoholic solutions (10^{-3} mol L^{-1} in methanol) with a Consort K 912 conductivity meter. The nuclear magnetic resonance (^{1}H NMR) spectra were recorded in DMSO-d_6 on a Bruker 400 MHz device. Thermogravimetric measurements, TG, and DTG were made with an MOM derivatograph (Budapest). The analyses were run with 30 mg sample placed in a platinum crucible at a heating rate of 10°C min^{-1} within the 30–750°C temperature range.

2.2. *Synthesis of the complexes*

The complexes were prepared according to Ando's method [21]. A salicylaldehyde (5 mmol) solution in ethanol (10 mL) was added to an aqueous amino acid solution (10 mL, 5 mmol), under stirring, followed by addition of an aqueous solution of sodium acetate (5 mL, 10 mmol). The color of solution changed to yellow. Then, 5 mL of uranyl nitrate (1.2 g, 3 mmol) solution was added dropwise. The solution color shifts to red and a precipitate appears immediately. The mixture was refluxed for 1 hour and then filtered and washed with water, acetone, and diethyl ether. The obtained complexes were purified by recrystallization from ethanol : water (1 : 2, v : v).

All experiments involving interaction of the complex with DNA were performed in a Tris-HCl buffer (0.01 mol L^{-1}, pH = 7.4).

3. Results and discussion

The tridentate Schiff bases are very good chelating agents with five- and six-membered rings prepared from glycine, β-alanine, serine, valine, and methionine. The ligands are good chelators for di-oxo ions (UO_2^{2+}). Analytical results for the synthesized complexes, summarized in table 2, support the formation of complex in 1 : 2 molar ratio for **1** and

Table 2. Analytical results of the uranium complexes.

Complexes	*m/z*	Conductivity (S cm^{-1})	Yield	Color	m.p.
1	644.27	11.79	67.06%	Orange	Decomposition
2	579.32	116.3	92.73%	Orange	217°C
3	609.21	86.98	77.64%	Light orange	196°C
4	607.30	75.4	78.54%	Orange	221°C
5	657.62	83.5	73.41%	Dark orange	219°C

1 : 1 for **2**, **3**, **4**, and **5**. Attempts to prepare single crystals suitable for X-ray diffraction measurements were unsuccessful.

3.1. *ESMS spectra*

The ESMS spectra of complexes provide useful information about the composition and coordination [22]. Complex **4** has a molecular peak m/z: 607.30 corresponding to $\{H[UO_2SalVal]NO_3\}^+$, see figure 2(a). The peak at 544.24 corresponds to $\{H[UO_2SalVal]\}^+$, from removal of nitrate, the peak at 239.09 corresponds to $[HU]^+$, and the peaks at 221.10 and 120.15 correspond to residues $[HC_{12}H_{14}NO_3]^+$ and $[HC_7H_5NO]^+$, respectively.

ESMS spectrum for **5** shows a molar ratio $m/z = 657.62$ corresponding to the $\{H[UO_2SalMet]NO_3H_2O\}^+$, figure 2(b). The peak at 577.22 corresponds to $\{H[UO_2SalMet]\}^+$ and clearly shows that water and nitrate ion were removed from outer coordination sphere. Moreover, removal of water from the coordination sphere corresponds to the peak at 523.19. The peak at 239.07 corresponds to $[HU]^+$ and the peaks at 135.99 and 120.12 were attributed to $[HC_5H_9O_2S]$ and $[HC_7H_5NO]^+$ fragments. Fragmentation pattern of $UO_2SalMet$ complex is shown in "Supplementary material."

3.2. *Infrared spectra*

The FTIR spectra of complexes show the characteristic absorptions $\nu(H_2O)$ at 3430 cm^{-1} and carboxylic $\nu(C=O)$ at 1724–1625 cm^{-1}. The band positions and

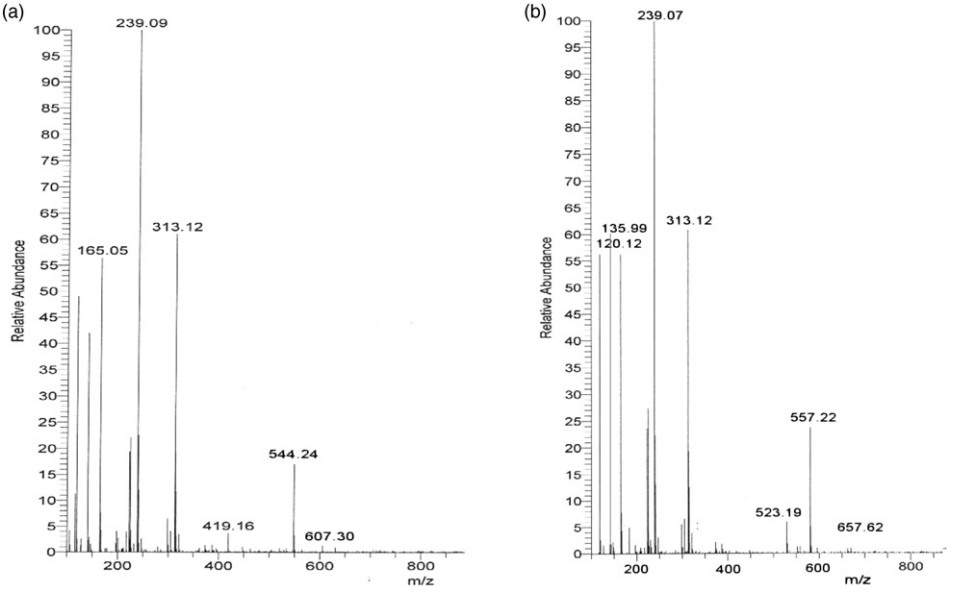

Figure 2. Mass spectra for **4** (a) and **5** (b).

intensities were changed as compared to free aminoacids, indicating coordination of the amino acids carboxylic oxygen to uranyl. The characteristic of azomethine ν(C=N) is the strong absorption at 1633–1601 cm^{-1} for the complexes. These bands are characteristic for Schiff bases [23]. The carboxyl groups $\nu(COO^-)$ show two normal vibrations between 1594–1537 and 1393–1352 cm^{-1}. The FTIR bands due to the UO_2^{2+} group are observed at 901–933 cm^{-1} and 800–842 cm^{-1} being attributed to the asymmetric stretching frequency ν_{as}(O=U=O) and the symmetric stretching frequency ν_s(O=U=O), respectively [24]. The main FTIR frequencies are presented in table 3.

The ν(C–O) at 1137–1153 cm^{-1} indicates coordination of oxygen. The FTIR spectra of **2**, **3**, **4**, and **5** show one absorption near 1380 cm^{-1} attributed to free nitrate. The mono-coordinated nitrate shows bands at 1290, 1030, and 745 cm^{-1} corresponding to ν_1, ν_2, and ν_3 [25]. Thus, nitrate is not directly involved in coordination with the uranyl ions. However, in **1** the nitrate bands are not present. In the 600–400 cm^{-1} region a series of bands assignable to U–O and U–N bonds can be distinguished.

3.3. *UV-Vis spectra*

The UV-Vis spectra of the complexes, recorded in DMF, reveal four absorptions in the region 226–471 nm, as shown in table 4.

Equatorial ligation has only a minor influence on the spectra [23, 26]. The uranyl complexes show two absorptions, λ_1 and λ_2, between 374 and 471 nm, assigned to charge transfer (LMCT) transitions. In all complexes bands at 226–273 nm (λ_4) correspond to π–π^* transitions related to aromatic ring. The band (λ_3) from the near UV region (338–341 nm) is due to the π–π^* or n–π^* transition related to azomethine [27].

Table 3. The main FTIR frequencies of U(VI) Schiff-base complexes.

ν \ Complexes	**1**	**2**	**3**	**4**	**5**
$\nu(OH_2)$	3444	3434	3422	3433	3436
ν(C=O)	1630	1625	1642	1657	1724
ν(C=N)	1604	1601	1623	1633	1614
$\nu_{as}(COO^-)$	1594	1593	1537	1586	1547
$\nu_s(COO^-)$	1393	1356	1352	1395	1387
δ(C–OH)	1209	1238	1247	1192	1204
ν(C–O)	1153	1149	1150	1137	1150
ν(C–N)	1066	1054	1030	1065	1073
$\nu_{as}(UO_2)$	901	933	932	932	905
$\nu_s(UO_2)$	806	841	835	800	803

Table 4. UV-Vis data of U(VI) Schiff-base complexes.

Complexes	λ_1 (nm)	$\log \varepsilon_1$	λ_2 (nm)	$\log \varepsilon_2$	λ_3 (nm)	$\log \varepsilon_3$	λ_4 (nm)	$\log \varepsilon_4$
1	471	4.3471	388	5.0305	338	5.3671	273	5.7295
2	446	3.4471	375	4.5888	339	4.7929	226	5.2958
3	445	3.5314	375	4.5579	341	4.7548	266	5.2689
4	445	3.9722	374	4.806	339	4.9617	268	5.4676
5	459	4.4055	388	5.112	339	5.3938	269	5.8187

3.4. *^{1}H NMR spectra*

The signals of different protons of the uranyl complexes are provided in "Supplementary material" and their chemical shifts (^{1}H, ppm) are listed in table 5. ^{1}H NMR spectra of the complexes are in line with the proposed structures. The methyl protons of alanine, valine, and methionine have signals between 1.52 and 1.96 ppm. The signals can be distinguished between 2.36 and 4.01 ppm. The proton from CHR groups of the aminoacids was found around 5 ppm. The aromatic protons appear as multiplets at 6.66–7.81 ppm. The imine proton (HC=N) is a singlet at 9.10–9.27 ppm.

3.5. *Fluorescence spectra*

Fluorescence properties of the complexes refer to modification of the fluorescence intensity or shift the emission maximum of the parent ion. A variety of molecular interactions can modify fluorescence properties, including excited state reaction, molecular rearrangement, energy transfer, ground-state complex formation, etc. [28]. U(VI) has a characteristic long-living luminescence, a feature that is strongly influenced by ligand coordination and thus providing additional information on complex formation.

Fluorescence emission spectra of the U(VI) complexes in DMSO, at room temperature, show an increase in fluorescence intensity and significant bathochromic shift of the emission maxima. Emission spectra of the complexes were recorded upon excitation at 350 nm, see figure 3.

The emission spectrum of **1** shows a maximum at 442 nm. The fluorescence spectrum of **2** shows two emission maxima at 386 and 420 (sh) nm. For **5,** the emission maximum was at 440 nm, while **3** and **4** show weak emission maxima at 390 and 440 (sh) nm and 386 and 425 (sh) nm, respectively. The emission intensities of the complexes are more pronounced than the emission intensity of free UO_2^{2+}, which shows three weak peaks at 488, 509, and 533 nm [29].

3.6. *Thermal studies*

The TG and DTG studies for all the complexes were carried out from 35 to 750°C. Thermal decompositions of the uranyl complexes reveal pathways, depending on the nature of ligands. All complexes decomposed in four steps with the first step related to water release; then organic molecules are eliminated and finally only U_3O_8 residue remains. The TG and DTG curves of **2** are provided in "Supplementary material."

Table 5. ^{1}H NMR data (ppm) of U(VI) Schiff-base complexes.

Complexes	(m, H, CH_3)	(m, H, CH_2)	(s, H, CHR)	(m, 4H, Har)	(s, 1H, HC=N)
1	–	–	5.01	6.69–7.55	9.26
2	1.96	–	4.94	6.67–7.58	9.23
3	–	3.50–4.01	5.11	6.69–7.57	9.10
4	1.74	–	4.98	6.68–7.56	9.18
5	1.52	2.36	4.96	6.69–7.55	9.27

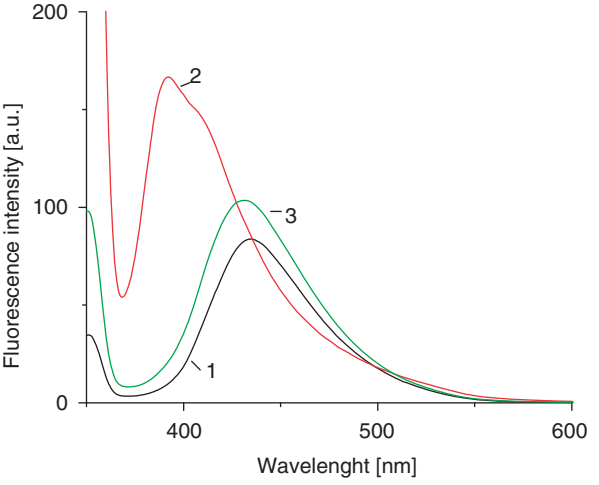

Figure 3. Fluorescence emission spectra of **1** (curve 1), **2** (curve 2), and **5** (curve 3).

Thermograms of **2** in the first stage of thermal analysis show removal of water held physically (experimental 1.55% and calculated 1.53%). The second stage marks the removal of NO_3^- from outside of the coordination sphere, and the removal of three bound water molecules. In the third stage, the thermal decomposition of ligand takes place with the removal of the salicylic aldehyde and the aminoacid ($C_9H_{10}O$) residue. The next step consists of the removal of N and CO from the ligand molecule. Finally, over 650°C there remains a residue of U_3O_8 [17, 20] (resulting from elimination of one oxygen atom from three molecules UO_3).

Except **5** and **1**, the thermal decomposition steps for the other complexes are basically the same. For **5** the physically retained water is initially removed, and then NO_3+3H_2O+C_2H_5S, C_2H_4O, and C_8H_5NO are eliminated. Perhaps due to the presence of S in the final structure of the ligand, the decomposition occurs at higher temperatures. Due to the symmetry of **1**, a slightly different thermal decomposition takes place. First two water molecules, then one of two molecules of C_3H_2NO and two molecules of C_6H_4O are removed. The stages of thermal decomposition for all complexes are summarized in table 6.

On the basis of these results we can assess the coordination of ligands to uranyl. Uranyl as well as other actinide ions has strong affinity for oxygen donors, including water, nitrate, etc. [30]. These Schiff-base ligands contain two oxygen and one nitrogen donors, and as a result of the carbon-chain linkages, possess sufficient steric freedom to allow metal ions to easily approach binding sites. With these ligands, uranyl forms eight-coordinate complexes, containing six equatorial donors of ligands and two axial oxygen atoms of the uranyl group. Therefore, the ligands are coordinated to uranyl by nitrogen from azomethine group, oxygen of the aromatic ring and carboxylate oxygen from aminoacids [31]. Complex **1** is a nonelectrolyte and contains two molecules of ligand in the coordination sphere, figure 4(a). The other complexes contain one molecule of ligand and three water molecules in the coordination sphere and one nitrate outside the coordination sphere, figure 4(b).

The differences between these structures could be attributed to the amino acid side chain and steric hindrances. Thus, in the absence of the side chain (R=H), the flexibility

Table 6. Thermogravimetric data of U(IV) Schiff-base complexes.

Complexes	T (°C)		Mass lost experimental (%)	Mass lost calculated (%)	Assignment
	T_i	T_f			
1	25	125	2.63	2.53	H_2O
	125	300	2.72	2.53	H_2O
	300	362	20.95	21.38	$2C_3H_2NO$
	362	558	28.84	29.06	$2C_6H_4O$
Residue			44.94	44.49	U_3O_8
2	25	120	1.49	1.54	$½H_2O$
	120	277	19.36	19.94	$NO_3^- + 3H_2O$
	277	431	23.14	23.21	$C_9H_{10}O$
	431	551	7.72	7.34	CNO
Residue			48.19	47.97	U_3O_8
3	25	121	1.37	1.52	$½H_2O$
	121	307	19.32	19.42	$NO_3^- + 3H_2O$
	307	438	25.5	25.14	$C_9H_{10}O_2$
	438	641	7.82	7.29	CNO
Residue			45.98	46.64	U_3O_8
4	25	107	2.94	3.06	H_2O
	107	344	18.42	18.75	$NO_3^- + 3H_2O$
	344	496	25.75	26.13	$C_{11}H_{14}O$
	496	660	7.55	6.91	CNO
Residue			45.33	45.15	U_3O_8
5	25	126	2.31	2.90	H_2O
	126	392	27.07	27.15	$NO_3 + 3H_2O + C_2H_5S$
	392	555	5.32	6.87	C_2H_4O
	555	750	21.29	20.13	C_8H_5NO
Residue			44.00	42.96	U_3O_8

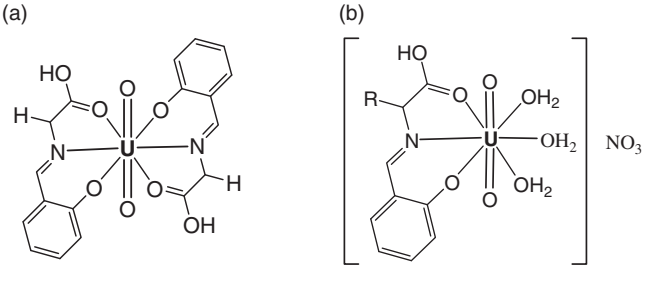

Figure 4. Proposed structure for the uranyl complexes: (a) **1**; (b) **2**, **3** **4,** and **5**.

of glycine-based ligand is enhanced. When this side chain is larger, the complex could adopt a slightly distorted octahedral coordination [24]. The counterion environment should not be neglected. The salen ligands have an advantage over other polydentate cyclic ligands due to free rotation between aromatic groups giving freedom to orientate the two donor oxygen atoms for favorable U–O(salen) interactions, hence alleviating excess steric repulsions around the uranyl center. The steric freedom can be influenced also by the solvent [30].

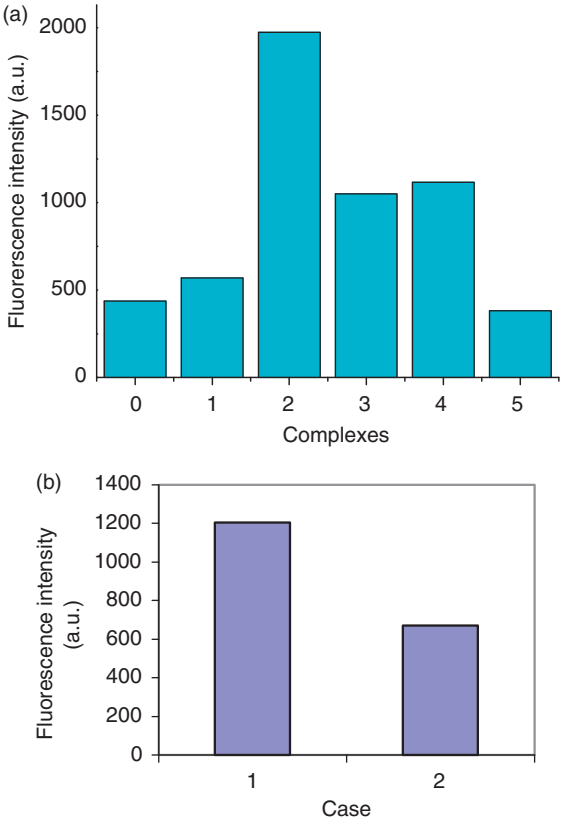

Figure 5. (a) The relative fluorescence of uranyl nitrate (0) and Schiff-base complexes **1** (1), **2** (2), **3** (3), **4** (4), and **5** (5); and (b) the fluorescence quenching of **1** (1) in the presence of DNA (2).

3.7. *The interaction of uranyl Schiff-base complexes with DNA*

Exploration of the complexes binding with DNA was carried out by studying the variation of the fluorescence when DNA is added [32]. Coordination of a ligand often changes the luminescence quantum yield, resulting in quenching or enhancement of the luminescence intensity. For instance, in some U(VI) complexes with organic ligands, the quantum yields are close to zero [33].

Since all the complexes display an intrinsic fluorescence, we studied the interaction of those assemblies with DNA. Uranyl nitrate was used as a standard fluorescence compound possessing lower fluorescence than the obtained complexes, see figure 5(a). No significant interaction of DNA with glycine and methionine complexes was observed. Thus, the fluorescence of glycine complex is slightly higher than uranyl nitrate. In contrast, the fluorescence of methionine complex is reduced by 10–15%, which is expected since the sulfur of the ligand induces a quenching phenomenon. The fluorescence intensity increases more than double when Ala, Ser, and Val were used as ligands. The fluorescence intensity for these complexes varies in the order: **2** > **3** > **4**.

Therefore, we chose **2** for further investigations. The quenching studies show that addition of DNA decreases the fluorescence. The uranyl cations partially neutralize the

negative charges of the DNA phosphate backbone. Thus, we cannot exclude the presence of electrostatic interactions.

The addition of the complexes caused quenching florescence of the DNA system, indicating that the complex was intercalated within the groove of DNA system, which leads to the sodium ions leaving the DNA system; the ligand is less exposed to the light and the complexes emission intensity is decreased, figure 5(b).

This behavior shows there is moderate binding and a considerable affinity between the complex and DNA [11, 23, 34]. Probably the water molecules from the complex were expelled during this binding process.

4. Conclusion

Tridentate Schiff bases obtained from salicylaldehyde and amino acids form complexes with uranyl ions. Complex **1** has a molar ratio M : L = 1 : 2, while **2**–**5** are nonelectrolytes having an M : L = 1 : 1 ratio. In these complexes, oxygen of a phenolate, carboxylic oxygen from aminoacids, and imine nitrogen are involved in coordination in the equatorial position. Fluorescence quenching studies show that **2** displays maximum fluorescence intensity and can be easily intercalated into a double strand of DNA.

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