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Supramolecular structure and substituents effect on the spectral studies of dioxouranium(VI) azodyes complexes

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ABSTRACT

The synthesis of several coordination azo compounds of dioxouranium(VI) heterochelates with bidentate azo compounds derived from 4-alkylphenylazo-5-sulfo-8-hydroxyquinoline (HL_n) ligands, are described. The ligands and structural composition of azo complexes were confirmed and characterized by various physico-chemical techniques. The bonding sites of the azo compounds are deduced from IR and ¹H NMR spectra and the ligands were found to bond to the UO_2^{2+} ion in a bidentate fashion. The ligands obtained contain N=N and phenolic functional groups in different positions with respect to the quinoline group. IR spectra show that the azo compounds (HL_n) acts as a monobasic bidentate ligand by coordinating via the azo nitrogen atom of azodye (-N=N-) and oxygen atom of the phenolic group forming thereby a six-membered chelating ring and concomitant formation of an intramolecular hydrogen bond. The v_3 frequency of UO₂²⁺ has been shown to be an excellent molecular probe for studying the coordinating power of the ligands. The values of v_3 of the prepared complexes containing UO_2^{2+} were successfully used to calculate the force constant, F_{UO} (1n 10⁻⁸ N/Å) and the bond length R_{UO} (in Å) of the U–O bond. A strategy based upon both theoretical and experimental investigations has been adopted. The theoretical aspects are described in terms of the well-known theory of 5d-4f transitions. Wilson's, matrix method, Badger's formula, and Jones and El-Sonbati equations were used to calculate the U-O bond distances from the values of the stretching and interaction force constants. The most probable correlation between U-O force constant to U-O bond distance were satisfactorily discussed in term of Badger's rule and the equations suggested by Jones and El-Sonbati. The effect of Hamette's constant is also discussed. © 2011 Elsevier B.V. All rights reserved.

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1. Introduction

The chemical properties of quinoline complexes and their derivatives are of interest due to their biological relevance [1], coordination capacity [2,3] and their use as metal extracting agent [4]. A number of recent papers from the laboratory of El-Sonbati and co-workers [5–12] have described the preparation and isolation of novel solid complexes of several quinoline derivatives. It was reported that hydrogen bonded supramolecular quinoline azodyes and/or hydrozone ligands moiety can be viewed as hydride structure, composed of a carbonyl/azomethine function and OH/=N–NH group, which has mutual electronic and steric influence on the hydrogen bonding formation dependent on the conformation of the molecules, determined by the two competitive conjugated π - π * and n- π systems and steric effect [11–16].

In this paper, we investigate the supramolecular chemistry of azo 8-hydroxyquinoline derivatives namely 4-alkylphenylazo-5-

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¹ Abstracted from her M.Sc.

sulfo-8-hydroxyquinoline (HL_n). These are achieved by reporting the studies of (i) the synthesis of novel 4-alkylphenylazo-5sulfo-8-hydroxyquinoline (HL_n) ligands, (ii) the synthesis of UO₂(II) complexes derived from these ligands, (iii) investigating the stereochemistry of the complexes based on the electronic spectra and other measurements, (iv) determining the vibrational mode of bonding, stability and structures of the hydrogen-bonding complexes, (v) deduced the correlation between U—O force constant to U—O bond distance using Badger's rule and the equation suggested by Jones and El-Sonbati [17,18], and also, the effect of Hamett's constant is also discussed.

2. Experimental

All the chemicals used were of BDH quality.

2.1. Synthesis of 4-alkylphenylazo-5-sulfo-8-hydroxyquinoline (HL_n) ligands

4-Alkylphenylazo-5-sulfo-8-hydroxyquinolines (HL_n) were typically prepared by adding a 25 mL of distilled water containing hydrochloric acid (12 M, 2.68 mL, 32.19 mmol) were added to





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aniline (10.73 mmol) or *p*-derivatives. To the resulting mixture, stirred and cooled to 0 °C, a solution of sodium nitrite (10.73 mmol, in 20 mL of water) was added drop wise. The so-formed diazonium chloride was consecutively coupled with an alkaline solution of sulfooxine (10.73 mmol) in 20 mL of ethanol containing 602 mg (10.73 mmol) of potassium hydroxide. The red precipitate, which formed immediately was filtered and washed several times with water. The crude product obtained was purified by crystallization from hot ethanol (yield ~60–80%).

The resulting formed ligands are: 4-methoxyphenylazo-5-sulfo-8-hydroxyquinoline (HL₁), 4-methyphenylazo-5-sulfo-8-hydroxyquinoline (HL₂), 4-phenylazo-5-sulfo-8-hydroxyquinoline (HL₃), 4-chlorophenylazo-5-sulfo-8-hydroxy quinoline (HL₄) and 4-nitrophenylazo-5-sulfo-8-hydroxyquinoline (HL₅) were characterized by microanalyses, IR and ¹H NMR spectroscopy.

2.3. Measurements

Microanalysis of all samples was carried out at Microanalytical unit at Cairo University, Cairo, Egypt. Infrared spectra were recorded as KBr pellets using a Pye Unicam SP 2000 spectrophotometer. ¹H NMR spectra were obtained on a JEOL FX 900Q Fourier transform spectrometer with deutrated dimethylsulfoxide (DMSO-d₆) as solvent and TMS as internal reference. The equation suggested by El-Sonbati has been manipulated by using a computer program developed in our laboratories using C Language.

3. Results and discussion

The analytical data of the ligands and their uranyl complexes (1–5) are summarized in Table 1. The stoichiometry of the



n=1, R = OCH₃ (HL₁); n=2, CH₃ (HL₂); n=3, H (HL₃); n=4, Cl (HL₄); and n=5, NO₂ (HL₅) The formation mechanism of azodye ligands (HL_n)

2.2. Synthesis of the uranyl complexes

A hot solution of UO₂(NO₃)₂·5H₂O, (0.01 mol) in EtOH (30 cm³) was added to the appropriate ligands (0.022 mol) in EtOH (30 cm³). The reaction mixtures were maintained under reflux temperature for 1.5 h to ensure complete reaction. Polycrystalline solid complexes were immediately formed. The solid complexes were filtered off while hot, washed several times with EtOH, followed by Et₂O, and finally dried in a vacuum over P₂O₅. The uranium content of the complexes was determined by ignition of a definite mass of each complex at ~1000 °C and weighing the residue as U_3O_8 .

prepared uranyl(II) complexes are consistent with the proposed structure $[UO_2(L_n)_2]$.

The fact that HL_n complexes with $UO_2(NO_3)_2 \cdot 5H_2O$ involving 2:1 ligand to UO_2^{2+} ratio (Table 1), have been isolated, clearly illustrates that the ligands under study does not introduce sufficiently severe steric hindrance as to preclude the formation of $[UO_2(L_n)_2]$ complexes, but its steric feature and arrangement in space can also favorably influence the stabilization of 2:1 complexes. The complexes are microcrystalline or powder-like, stable under ambient conditions, and partially soluble in warm DMF and DMSO to varying extents. The complexes do not melt but decompose on heating and are converted to U_3O_8 around 700 °C [16].

Table 1							
Analytical	data of HL ₂	ligand	and	their	UO_{2}^{2+}	comple	exes.

Compounds ^b /Serial No.	Color	Yield (%)	Exp.(Calecd.)%			Compositions		
			С	Н	Ν	S	Metal	
HL ₁	Black	60.4	53.88 (53.48)	3.82 (3.62)	12.21 (11.70)	9.35 (8.91)	-	
1	Brown	69.3	39.21 (38.95)	2.45 (2.43)	8.81 (8.32)	6.83 (6.49)	24.60 (24.19)	$[(UO_2)_2(L_1)_2]$
HL ₂	Red	62.0	56.12 (55.98)	3.90 (3.79)	12.72 (12.25)	9.71 (9.33)	-	
2	Dark red	70.3	40.33 (40.25)	2.55 (2.52)	8.99 (8.81)	6.90 (6.71)	25.40 (24.95)	$[(UO_2)_2(L_2)_2]$
HL ₃	Pale red	64.7	54.87 (54.71)	3.45 (3.34)	13.22 (12.77)	10.10 (9.73)	-	
3	Orange	72.0	39.02 (38.88)	2.22 (2.16)	9.42 (9.07)	7.32 (6.91)	26.25 (25.70)	$[(UO_2)_2(L_3)_2]$
HL ₄	Red	68.8	49.64 (49.52)	2.84 (2.75)	11.93 (11.55)	9.21 (8.80)	-	
4	Dark orange	74.3	36.30 (36.18)	2.01 (1.81)	8.75 (8.44)	6.74 (6.43)	24.50 (23.92)	$[(UO_2)_2(L_4)_2]$
HL ₅	Dark red	78.0	48.30 (48.13)	2.72 (2.67)	15.30 (14.97)	8.83 (8.56)	-	
5	Reddish brown	80.0	35.66 (35.43)	2.15 (1.97)	11.44 (11.02)	6.71 (6.30)	23.80 (23.43)	$[(UO_2)_2(L_5)_2]$

^a Microanalytical data as well as metal estimations are in good agreement with the stoichiometry of the proposed complexes.

^b L_1-L_5 are the anions.



Fig. 1. The relation between Hamette's *t* substitution coefficient (σ^{R}) and yield %.

 $UO_2(NO_3)_2 \cdot 5H_2O + HL_n \xrightarrow{DMF} [UO_2(L_n)_2](n = 1-5)$

As shown in Table 1, the values of yield % is related to the nature of the *p*-substituent as they increase according to the following order *p*-(NO₂ > Cl > H > CH₃ > OCH₃). This can be attributed to the fact that the effective charge experienced by the d-electrons increased due to the electron withdrawing *p*-substituent (HL₄ and HL₅) while it decreased by the electrons donating character of (HL₁ and HL₂). This is in accordance with that expected from Hamett's constant (σ^R) as in Fig. 1 correlate the yield % values with (σ^R), it is clear that all these values increase with increasing σ^R . The above results show clearly the effect of substitution in the *para* position of the benzene ring on the stereochemistry of UO₂(II) complexes. It is important to note that the existence of a methyl and/or methoxy group enhances the electron density on the coordination sites and simultaneously decreases the values of yield %.

The molar conductance of 10^{-3} M of solutions of the complexes in DMSO is calculated as 25 ± 2 °C. It is concluded from the results that UO₂(II) chelates with HL_n ligand under investigation were found to have molar conductance values in the range from 0.8 to 4.6 ohm⁻¹ cm² mole⁻¹ which indicates that the complexes have molar ratio of metal:ligand as 1:2. The lesser molar conductance values



n=1, R = OCH₃ (HL₁); n=2, R = CH₃ (HL₂); n=3, R = H (HL₃); n=4, R = Cl (HL₄);

n=5, R = NO₂ (HL₅); The structure of UO₂(II) complexes indicate that they are all non-electrolytic in nature. This is in accordance with the fact that conductivity values for a non-electrolytes are below 50 ohm⁻¹ cm² mole⁻¹ in DMSO [19]. The elemental analyses data concern well with the planned formulae for the ligands and also recognized the $[M(L_n)_2]$ composition of the UO₂(II) chelates.

3.1. Electronic spectra

HL_n exhibited bands at 32,500–32,150 cm⁻¹ (CN) (π – π^*), 33,450– 33,340 cm⁻¹ (H-bonding and association), 40,038–39,460 cm⁻¹ (phenyl) (Ph–Ph*, π – π^*) [13,14] and 29,340–29,230 cm⁻¹ transition of phenyl rings overlapped by composite broad (π – π^*) of azo structure. The band due to the $n \rightarrow \pi^*$ transition obtained in the visible region is associated mainly with the color of the respective compound [14]. The band due to $\pi \rightarrow \pi^*$ transition moves to lower energy. These shifts or the disappearance of the bands are indicative of coordination of the ligands to UO₂(II). The position of their bands is varied from one dye to the other which may be due attributed to the *p*-phenylazo substituent variable donating power. The dioxouranium complexes exhibits a new bands at 24,390–24,210 cm⁻¹, which is assigned to the ${}^{1}\Sigma_{g}^{U} \rightarrow {}^{3}\pi_{U}$ transition, typical of OUO for the symmetric stretching frequency for the first excited state [16].

In general, most of the azo compounds give spectral localized bands in the wavelength range 46,620-34,480 and 31,250- $270,370 \text{ cm}^{-1}$. The first region is due to the absorption of the aromatic ring compared to ¹B_b and ¹L_b of mono substituted benzene and the second region is due to the conjugation between the azo group and the aromatic nuclei with intermolecular charge transfer resulting from π -electron migration to the diazo group from electron donating substituents. The *p*-substituents increase the conjugation with a shift to a longer wavelength. Most of the simple *p*-substituted compounds are in the azoid form in cyclohexane and alcohols. The substituted effect is related to the Hamett's constant values [8,14,16]. The position of the π - π ^{*} transition of the azo groups remains as one of the more interesting unanswerable questions of molecular spectroscopy. For azo benzenes, as the possibilities of the mesomerism became greater, the stabilization of the excited state is increased relative to that of the ground state and a bathochromic shift of the absorption bands follow [16]. Based on MO theory [20] the energy terms of the molecular orbital



Fig. 2. Representation of the dimeric structure and intramolecular hydrogen bond.

became more closely spaced as the size of the conjugated system increases. Therefore, with every additional conjugated double bond the energy difference between the highest occupied and the lowest vacant π -electron level became smaller and the wavelength of the first absorption band corresponds to this transition is increased. The azo group can act as a proton acceptor in hydrogen bonds [14,16]. The role of hydrogen bonding in azo aggregation has been accepted for some time.

3.2. IR spectra

The IR spectroscopy is known to be a powerful tool for structural determinations of the ligand and metal chelates. The assignments of fundamental functional groups are basic for such purposes.

By tracing the IR spectra of the azo compounds, no NH₂ stretching vibrations are apparent. This supports the formation of azodye ligands. The mode of bonding of the HL_n to the metal ions was elucidated by investigating the IR spectra of the complexes on the basis of a comparative analysis of the results with respect to literature data of related systems. The positions of the most relevant and characteristic bands are due to: (i) azo nitrogen, (ii) OH group and (iii) CNpy group. Due to the 1, 2-position of these donor groups in the molecule, six-and/or five membered chelate ring formation is possible on complexing. Much has been discussed about the —OH stretching frequency and intensity of phenol derivatives depending on many factors (*e.g.*, constituents, medium, *etc.*). Hoyer [21] reviewed the relationship between the hydrogen bond band and the —OH stretching frequency. In addition to that, there have been many other research workers who examined the problem in finer and more quantitative data. This has attracted our attention to acquire the IR technique to explain and justify the bonding in this study.

The free ligands exhibit broad and weak absorption bands in the region 3310–3320 cm⁻¹ due to v(OH) and strong bands at 1285– 1295 cm⁻¹ due to δ (OH). This latter band is replaced by at a higher frequency $(1345-1350 \text{ cm}^{-1})$ in complexes indicating that the ligands coordinate to the metal ion as deprotonated species. The disappearance of the bands due to v(OH) the complexes confirms that the C₈–OH group takes part in the complex formation through O⁻ owing to strong hydrogen bonding both intramolecular $[O-H \cdots N(Fig, 3B), O-H \cdots N(Fig, 3C)]$ and intermolecular hydrogen bonding of the O-H···N type between N=N of one molecule and OH group of another one (Fig. 4E), the frequency of the hydrogen bonded OH is probably lowered to considerable extent and overlaps with the OH vibrations, thus appearing as a broad band in the region 3310-3320 cm⁻¹. All the complexes exhibit v(C=C) in $\simeq 1498$ cm⁻¹. The presence of an *p*-disubstituted benzene ring in the ligands as well as in the complexes is indicated by strong and sharp bands around 720-740 cm⁻¹. Bands at 2950-3040 cm⁻¹ for the ligands and at ~2960–3040 cm⁻¹ for the complexes are assigned to v(C-H)



Fig. 3. Intermolecular hydrogen bond.



Fig. 4. The relation between (a) v_1 vs. v_3 and (b) (v_1^*) vs. v_3 (cm⁻¹).

vibrations of the aromatic system. This is also in agreement with the data reported by El-Sonbati and co-workers [6–14,16].

The assignment of the 1570 cm^{-1} (N=N) and 1585 cm^{-1} (CN) (non-bonded groups) stretching modes is based on our previous work [6–14,16], El-Sonbati [18] and Henry et al. [22]. Comparing the position of these bands for the different ligands, it is obvious that ring substitution results in a shift to lower frequencies. This behavior can probably be explained by the lowering in the electronic density caused by electronegative groups.

1570 cm⁻¹ (N=N) occurs at higher frequency in the ligands than in the respective complexes by 25–40 cm⁻¹, revealing its involvement in complexation [11–14]. In this case, the decrease of the electronic density of the ring may be correlated with the donor character of the oxygen and/or N atoms in the M–O and M–N bond. These is also another correlation, observed when comparing the position of the v(N=N) band in the free ligand and in the corresponding complexes. In these cases, the higher shift corresponds to higher electronegativity. Evidently, the presence of electronegative groups in the ring affects the donor capacity of the O and N atoms.

These comparisons show that the electronegativity of the ring substituents produces not only a decrease of the electronic density over the ring, generating a dimination in the v(N=N) stretching frequency, but also causes a lowering of the donor character of the N atom.

The interaction of azo compounds, R—N—R, with some transition metal salts produced complexes of at least four different types:

- (a) Containing the azo compound attached via nitrogen α -donor bonds.
- (b) Containing the azo compound bonded via π -bonds involving the π -electrons of the -N=N- system.
- (c) In case of aromatic derivatives, containing a metallated ligand attached via one nitrogen and a metal–carbon σ -bond to the ortho carbon of the ring.
- (d) Containing rearranged nitrogen-donor, e.g. *o*-semidine azobenzene acts as a fairly strong π -acid.

The presence of a sulfonate group in the quinoline ring confers special characteristics to the ligand, introducing changes in spectroscopic and structural properties of the metallic complexes. A charge density redistribution trough the ring, due to this negatively charged group, reinforces the ligand bonds counteracting, in some cases, the weakening effect generated after the coordination of the metal.

It has been known [7–9,15] that 8-hudroxyquinoline exists, in solution, in a monomer dimmer equilibrium. The results of this

paper suggest that in the monomeric form a strong intramolecular hydrogen bond is present. This is in agreement with a previous result [7–9,23]. The two such monomers lead to the dimmer by forming an additional hydrogen bonding yielding the bifureated hydrogen bonds and H—N—H nitrogen bridges (Fig. 2A).

In addition to the two bifureated intra/intermolecular $OH \cdots N$ hydrogen bonds (Figs. 2 and 3), two more intermolecular hydrogen bonding interactions are observed between nitrogen atom of azo/azomethine group and phenolic hydroxyl hydrogen oxygen atom. This additional H-bonding does not influence the intramolecular distance which shows a band at a lower frequency than the intermolecular interaction. Reason for this behavior might be due to the additional H-bond which influences the hydrogen bonding ability of the sulfonyl group by electronic and/or steric factors. The overall structure of the dimmer is close to planar with a slight shift of the two quinoline units from the plane. The dimmer is able to dissociate, while the intermolecular interaction can only be broken if appropriate hydrogen bond acceptors are attached then acting as competitors to the quinoline nitrogen atoms.

The two hydroxyquinoline units of the dimmer (Fig. $2B' \& 2C_2$) are in one plane. The intermolecular (I) as well as intramolecular (II) hydrogen bonding occur between the hydroxyl group and the quinoline nitrogen atom. The intermolecular hydrogen bond distance is shorter than the intramolecular one. This observation was also reported for other 8-hydroxyquinoline dimmers and might be due to an unfavored small O—H—N angle for the intramolecular interaction [24].

Hydrogen bonding represents one of the most versatile interactions that could be used for molecular recognition. Several attempts to modulate the strengths of hydrogen bonds in synthetic host–guest systems [23] and in biological approach. In view of the large differences in the substituent effects (*e.g.*, the Hamettetype substituent constants for *p*.positions and sulfonyl group); it might be possible to tune the strength of the hydrogen bond effectively by linking the hydrogen-bonding site to a reaction center through a conjugated spacer, and by altering the charge state of the reaction center in the solution. At the hydrogen-bonding end, azo/azomethine is used as a proton acceptor to form a hydrogen bond with OH group of ligand. The effects of protonation of the OH on the strength of the hydrogen bond of the ligand are simulated as a function of the length of the π -conjugated.

An electron-withdrawing bridge would be expected to increase the acidity of the proton donor and hence increase its binding ability. As the electron-withdrawing character of an azo group is relevant to the interesting signal-amplifying behavior [25]. The results indicate that in the HL_n, the effects of the bridges are electronwithdrawing and electron-donating, respectively. Accordingly, the efficiency of sp²-hybridized bridges is N=N > C=N.

Coggeshell [26], El-Sonbati et al. [7–13] found three kinds of bonded –OH structures on the basis of the frequencies: (i) only the oxygen is in the bridge while the hydrogen is free, (ii) a polymer chain is formed in which both hydrogen and oxygen atoms participate in the hydrogen bond, (iii) dimmer associates are formed.

Intramolecular hydrogen bond between the nitrogen atom of $C=N(CN_{Py})/N=N_{-}$ (five/six-membered) system and hydrogen atom of the phenolic hydroxyl hydrogen atom and hydrogen (C_8 —OH) are illustrated in (Fig. 2B, C and C'). Intermolecular hydrogen bonding can form cyclic dimmer through the O—H···OH type between C₈—OH/N=N of one molecule and C₈—OH/N=N group of another one (Fig. 3H, G and F) and/or ···N type between C₈—OH of one molecule and CNpy/—N=N— of another (Fig. 3D).

In general, hydrogen bonding involving OH groups are proton donors and their O atoms are proton acceptors. Both intra and intermolecular OH—N may form a number of structures in a simultaneous equilibrium.

Table 2				
¹³ C NMR and ¹ H NMR	spectrum	for HL ₅ (ppm	vs.	TMS). ^a

ΗL ₅ ^b	¹³ C NMR δ, ppm (C atoms, peak assignment)	¹ H NMR δ , ppm (H atoms, peak assignment)
14	157.68	-
11	157.68	_
07	147.15	9.87
02	147.04	8.44
10	146.45	_
08	136.87	_
04	135.88	8.77
05	129.37	_
06	128.22	_
13	124.89	8.26
15	124.89	8.26
09	123.58	8.26
12	121.12	7.77
16	121.12	7.77
03	116.89	7.38

^a The excellent agreement experimental data supports the assignment suggested in the present work.



3.3. ¹H NMR spectra

The ¹H NMR spectra of all the ligands were recorded in DMSO d_6 at room temperature (Table 2) supports the occurrence of the form depicted in Figs. 2 and 3. The signal due to methyl/methoxy proton appeared as singlet in 1.55/3.9 ppm. In the aromatic region, a few doublets and in few cases some overlapping doublets/multiplets are observed in the range δ 6.78–8.40 ppm. These doublets/ multiplets are due to aryl protons of three benzene rings. Another singlet corresponding to one proton for all compounds is observed in the range $\delta \sim 9.2$ –10.40 ppm. This signal disappeared when a D₂O exchange experiment was carried out. It can be assigned either to OH or NH, in either case it is strongly deshielded because of hydrogen bonding with the other atom (N/O) (Figs. 2 and 3). It may be noted that the integration of this signal perfectly matches with one proton and there is no other fragment(s) of this signal, which suggests that only one tautomeric form of the ligand exist in solution under the experimental conditions. Comparing with the solid state study, we prefer to assign this signal to OH, however, assignment of this peak to NH cannot be ruled out provided solid state structural evidence is not considered [27]. The main proton chemical shifts of dyes (1-5 except 3) appeared at different values depending upon the donating power effect of *p*-substituent of *p*-phenylazo groups. As reported in a previous study [28,29], this hydrogen bonding leads to a large deshielding of these protons. The shifts are in the sequence: $p-NO_2 > p-Cl > H > p-OMe > p-CH_3$. The ¹H NMR spectral data are reported along with the possible assignments was found as to be in their expected region [30]. The conclusion drawn from these studies lend further support to the mode of bonding discussed in their IR spectra. In the spectra of diamagnetic UO₂(II) complexes, the resonance arising from OH proton disappears, indicating the chelation of the ligands through the deprotonated phenolic OH group. The appearance of signals due to HC=N [~8.94 ppm (1H)] protons of the same positions in the ligand and its diamagnetic complexes shows the non-involvement of this group in coordination.

The assignments made from 13 C NMR spectrum of the ligand (HL₅) are shown in Table 2.

Therefore, it is clear from these results that the data obtained from the elemental analyses, IR and ¹H NMR spectral measurements are in agreement with each other.

4-Derivatives phenylazo-5-sulfo-8-hydroxyquinoline (HL_n) react with UO₂(NO₃)₂.5H₂O (molar ratio 2:1 in ethanol) giving solid, color complexes with expected show [UO₂(L_n)₂] stoichiometry. The IR spectra of all complexes show two bands attributable to the asymmetric and symmetric cm⁻¹ stretching frequency. A group theoretical consideration [31] shows that a linear and symmetrical triatomic UO₂²⁺ ion possessing D_{αh} symmetry gives rise to three fundamental modes of vibrations.

In the equatorial bonding the more effective overlap of O–U–O group orbital by nitrogen than by oxygen in the ligands leads to lower v_3 values for UO₂²⁺ complexes with the former. The force constant of U–O bond in the present investigation has been calculated following McGlynn et al. [32], and the U–O bond distance for the corresponding complexes are evaluated using the Jones equation [17] $R_{U-O} = 1.08 \ F^{-1/3} + 1.17$. The variation of bond length in the complexes is due to presence of electron releasing or electron



Fig. 5. The relation between v'_1 vs. v'_3 (cm⁻¹).



Fig. 6. The relation r_{U-O} (Å) and F_{U-O} (10⁻⁸ N/Å) with v_3 (cm⁻¹).



Fig. 7. The relation between r_3 (Å) and $F_{U=0}^{x} \times (10^{-8} \text{ N/Å})$ with v_3 (cm⁻¹).

withdrawing substitutents in the equatorial position. The v_3 values decrease as the donor characteristic increase as is observed for π -electron substituents, where the basicity of the donating atom increases.

Uranyl ion UO_2^{2+} is quite peculiar in its own structure and in its identity over wide ranges of vibrations in experimental conditions. Also, it can be considered from the geometric point of view, as a single particle. In the present investigation, the v(U=0) in all the complexes has been assigned in 940–910 cm⁻¹ and 840–795 cm⁻¹ cm⁻¹ region as v_3 and v_1 , respectively. The v_3 values decreased as the donor characteristics increases as is observed for π -electron substituents, where is the basicity of the donating atom increases. The experimental results revealed an excellent linear relation between v_1 and v_3 with the slope corresponding to $(1 + 2 M_0/M_U)^{1/2}$ (M_O and M_U are the masses of oxygen and uranium atoms respectively, Fig. 4a). It is obvioused that good linearly obtains also in case of v'_1 and v'_3 (Fig. 5).

Instead of the linear relation between v_1 and v_3 frequencies, the El-Sonbati equation [18] has focused attention on their normalized differences, in which such differences does not depend on the masses of oxygen and/or uranium atoms.

In the present investigation, El-Sonbati equation for the calculation of the U—O bond force constant of the prepared uranyl(II) complexes should be eventually serve as a fairly accurate measure



Fig. 8. The variation of *p*-substituted Hamette's with; (1) r_{U-O} (Å) and (2) F_{U-O} (10⁻⁸ N/Å).



Fig. 9. The relation between: (1) v_3 vs. r_1 ; (2) v_3 vs. r_2 and (3) v_3 vs. r_3 .

of the bond length of the U–O bond. Assuming no interaction in the spectral data, the force constant for the U–O bond $[F_{U-O}]$ 10^{-8} N/Å], $(F_{U-0}^{S})_{t}$, and $F_{UO,UO}$ are calculated. The plots of $v_{1} + v_{3}$ and/or v_3 vs. force constant for the U–O ($F_{U-O} 10^{-8}$ N/ Å), $(F_{U-O}^x \times 10^{-8} \text{ N/Å})$ and the U–O bond distance $(r_{U-O} \text{ Å}), (r_{3U-O} \text{ Å})$ are linear (Figs. 6 and 7). An increase in the value of the force constant of the U–O bond vs. $v_1 + v_3$ and/or v_3 (Fig. 6) and decrease on $r_{\rm II-0}$ with increasing $v_1 + v_3$ and/or v_3 were observed. The force constant of the U-O bond (Fig. 7). There is also a straight line relationship between r_{U-Q} and the *p*-substituent, Hamett's constant (σ^{R}) with negative slope, i.e. the higher the value of σ^{R} , the lower r_{U-O} and the higher the force constant of the U–O bond (Fig. 8). Also plotting the values of r_1 , r_2 , r_3 and r_t (bond distance, $r_{\rm II-0}$) vs. v_3 gave straight lines on increasing the value of v_3 . Our results also showed inversed relationship between v_3 and r_{U-0} (Fig. 9). The electron withdrawing increases the positive charge on the UO₂²⁺ leading to an increase in v_3 and F_{U-O} and subsequently a decrease in r_{U-O} . Accordingly to the r_{U-O} the following order:

$$HL_1 > HL_3 > HL_2 > HL_4 > HL_5$$

was achieved in consistent with the positive charge on the UO_2^{2+} . These data can be explained by El-Sonbati equation [18] by using the spectral data of complexes for calculating the symmetric stretching frequency (v_1^*) . The (v_1^*) data served as a an accurate evaluation to the (F_{U-O}) , (r_{U-O}) and $(F_{UO,UO})$. There is also a straight line relationship between (v_1^*) and (v_3) (O=U=O) (Fig. 4b). Perhaps a new light can be shed on the problem by looking at the values of r_1 , r_2 and r_3 from a different point of view. It might be worthwhile to focus attention on their normalized differences. Thus a new relationship between them with respect to r_t was determined by Global error which shows that the excellent validity is in the sequence:

$$\sqrt{(r_3 - r_t)^2} > \sqrt{(r_1 - r_t)^2} > \sqrt{(r_2 - r_t)^2}$$

for the force constant, F_{U-O} and bond lengths, R_{U-O} of the uranyl complexes.

Due to small scattering power of the oxygen atom, report of the determination of U—O bond length of some uranyl complexes by X-ray study is scantly. From the IR spectra, the stretching and interaction force constants of the complexes have been calculated [33–35]. The data were used to evaluate the U—O bond distances using Badger's formula, Jones equation [17,36] and El-Sonbati equation [18]. The data are quite close to results reported earlier for other uranyl complexes [18,17,36,32]. The variation of bond

length in the complexes is due to presence of electron releasing or electron withdrawing substituents in the equatorial position.

4. Concluding remarks

 HL_n behaves as a chelating bidentate monobasic ligand, bonding through the azo nitrogen atom of azodye (-N=N-) and oxygen atom of the phenolic group. HL_n was characterized by analytical and spectral methods before using it for the preparation of complexes.

Substituent effects on reactivities depend mainly on the rate controlling step and the nature of the transient species. Hamett's related the reactivity trends in ligands and complexes with the stability, i.e., the lower the stability the higher the reactivities. Based on Hamett's relationship, electron withdrawing substituents to ligands in their complexes enhance the stabilities of these complexes owing to the decrease of electron density at the metal central atom and thus the increase of the positive charge on the metal. Therefore, this effect results in decreasing reactivity. In contrast, the electron donating substituents increase the electron density at the metal and leading to decrease the stability of the metal chelates.

The results arising from the present investigations confirm that the selected 4-alkylphenylazo-5-sulfo-8-hydroxyquinolines (HL_n) ligands are suitable for building a supramolecular structure. Moreover, since the azo compounds experience photochemical isomerization and are therefore of interest for applicative purposes, uranyl complexes containing the 4-alkylphenylazo-5sulfo-8-hydroxyquinolines (HL_n) moiety combine features which could be useful in molecular materials. Work is underway on the synthesis and characterization of further uranyl compounds of this family of ligands and towards the development of the materials they produce.

The satisfactory analytical data coupled with the studies presented above indicate that the complexes under this investigation are of the general composition, $[UO_2(L_n)_2]$, where $HL_n = 4$ -alkylphenylazo-5-sulfo-8-hydroxyquinoline. In view of the well characterized of bis[(4-alkylphenylazo)-5-sulfo-8-hydroxyquinoline]uranyl (II) (involving a monoprotic bidentate (O, N-donor) azo ligand, octahedral structures with axial oxo group) and O, N-donor at the equatorial positions in *cis*-arrangement have been proposed for these complexes.

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