Polymer Complexes. LVII. Structures of Supramolecular Assemblies of Polymer Complexes of Dioxouranium(VI) with some Substituted Allyl Azoxydes

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Abstract

Novel five polymeric dioxouranium(VI) of bidentate allyl azo heteropolymer compounds derived from allyl rhodamine were prepared for the first time. The infrared spectra of the samples were recorded and their fundamental vibrational wave number was obtained. The resulting polymeric uranyl complexes have been characterized on the basis of elemental analyses, conductance and spectral (IR, NMR, and electronic spectra) data. The nature of bonding has been further discussed based on IR spectral data. The theoretical aspects are described in terms of the well-known theory of 5d-4f transitions. The coordination geometries and electronic structures are determined from a framework for the modeling of novel polymer complexes. The values of $v_1$ of the prepared polymer complexes containing $\text{UO}_2^{2+}$ were successfully used to calculate the force constant, $F_{UO}$ (in mdy/nm$^2$) and the bond length $R_{UO}$ (in A$^\circ$) of the U-O bond. 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", "Jones" and "El-Sonbati equations". The Hammett constant is also discussed.

Keywords: Supramolecular structures; $\text{UO}_2^{2+}$ azo. polymeric complexes; McGlynn, Badger's models, Jones and El-Sonbati equations

1. Introduction

Substantial work has been done by El-Sonbati and coworkers [1-10] on heterocyclic azo dyes derived from rhodanine and/or quinoline with various aromatic amines. However, there is no previous work on the complexes of allyl azo rhodamine. Azo dyes are an important class of organic colorants which consist of at least a conjugated chromophore azo (N=N-) group and the largest and most versatile class of dyes.

The above mentioned work shows that the uranyl group is almost surely linear and has three vibrational frequencies which vary considerably from one compound to another. There is a symmetric stretching frequency, $v_1$, appearing between 800 and 900 cm$^{-1}$; an asymmetric stretching frequency, $v_2$, appearing between 850 and 1000 cm$^{-1}$; and a bending frequency in the neighborhood of 200 cm$^{-1}$. We desire to have approximate relations from which the U-O bond force constant can be calculated for a given compound with reasonable accuracy. The U-O bond force constant should eventually serve as a fairly accurate measure of the U-O bond distance in a given compound. Zachariasen [11] discusses the crystal structures of many uranyl compounds and points out that in all cases known the uranyl group is collinear.

El-Sonbati [12] has focused attention on the perfect normalized differences between ($v_1$) and ($v_2$) O-U-O frequencies, which do not depend on the masses of oxygen and/or uranium atoms instead of the linear relation between $v_1$ and $v_2$ with the slope corresponding to $(1+2M_0/M_1)^{1/2}$, where $M_0$ and $M_1$ are the masses of oxygen and uranium atoms respectively) according to McGlynn et al [13].

El-Sonbati [12, 14-16] discussed the force constant of many uranyl complexes of a bond is related to the vibrational frequencies and to a first approximation is a measure of the strength of a bond. Stronger equatorial bonding will lead to larger L-M charge transfer (in general) giving a higher negative contribution towards the effective charge on the uranium atom.

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Of late, a large number of complexes of rhodanine azodyes have been prepared and characterized by magnetic and spectral studies [17-24]. In our laboratories the coordination behaviour, chemical equilibria, nuclear and electron paramagnetic resonance and the solution chemistry of transition and inner transition metal of HL₂HL₄ are prepared and studied. However, no structural and coordinating studies in solid and solution have been reported for azodyes containing both rhodanine and aliphatic/aromatic amines functional groups [18,20,23,24]. The existing literatures on the coordination chemistry of these ligands are obscure.

Rhodanine azo alky1 compound is a subject of current and growing interest and that may have numerous applications chemically azo rhodanine sulphadiazine containing moieties are of great interest because of their great versatility as ligands [17-25]. In the presence of several potential donor atoms, their flexibility and ability to coordinate in either neutral or deprotonated form [17]. They also contain C=N-NH structure unit, which forms a strong chelate ring giving possible electron delocalization associated with extended conjugation that may affect the nature of the complex formed. They can yield polymeric complexes some of which are biologically relevant [26].

As part of our ongoing work [17-24] in the area of supramolecular assembly of polymer complexes based on aromatic and/or aliphatic animes, we report herein the synthesis, characterization and structure of HL₂HL₄ and properties of the first example of hydrazone uranyl supramolecular polymer complexes [UO₂(HL)₂(OAc)₂]ₜₐₐ [Fig.1] based on coordination, semicoordination and hydrogen bonds, which are of current interest due to their potential application related to inclusion phenomena, guest exchange and molecular based uranium. Further studies are in progress involving other d- and/or f-metals and different stoichiometries in order to obtain a reasonable explanation and a better insight into this field of magnetic interactions.

2. Experimental
Preparation of 3-allyl-2-thiocco-1,3-thiazolidin-4,5-dione-5-(4-derivatives phenyl) hydrazone(HL₄a)

The standard chemical alky1 rhodanine, aniline and 4-alkyl-anilines (alkyl: OCH₃, CH₃, Cl and NO₂, Aldrich Chemical Co.) were used without any further purification. The experimental technique has been described previously [1-10].

In a typical preparation, 25 ml of distilled water containing hydrochloric acid (12 M, 2.68 ml, 32.19 mmol) were added to aniline (0.979, 10.73 mmol) (1) or a 4-alkyl-aniline. The resulting mixture stirred and cooled to 0 °C, then a solution of sodium nitrite (740 mg, 10.73 mmol, in 20 ml of water) was added dropwise. The formed diazonium chloride (2) was consecutively coupled with an alkaline solution of alky1 rhodanine (10.73 mmol) (3) in 20 ml of pyridine. The orange precipitate, which formed immediately was filtered through sintered glass crucible, washed several times with water and ether. The crude product was purified by recrystallization from hot ethanol, yield 65% then dried in vacuum desicator over P₂O₅.

The analytical data confirmed by expected composition, are shown in (Table1). The ligands were also characterized by £HNMR and IR spectroscopy.

Synthesis of the polymer complexes

The uranyl salt, UO₄(CH₃COO)₂·2H₂O (Aldrich Chemical Co.), was used as supplied. A 50 ml portion of a 0.5 M solution of the metal salt in N,N-dimethylformamide (DMF) was mixed with 50 ml of the monomer solution (0.1 M) in the same solvent and 0.1% w/v azobisisobutyronitrile (AIBN) as an initiator. The mixture was stirred under reflux for 6 h and the resulting polymer complexes were precipitated by addition to a large excess of distilled water containing hydrochloric acid to remove the excess metal salt. The precipitate was filtered, washed with water and dried in a vacuum oven at 40 °C for several days.

X = CH₃ = CH – CH₃ –
R = OCH₃ (n=1), CH₃ (n=2), H (n=3), Cl (n=4) and NO₂ (n=5)

Fig. 2. Molecular structures of the ligand
Elemental analyses

The uranium content of each complex was determined by igniting a definite mass of the complex at 1000°C and weighing the residue as UO₂. The analytical data are given in Table 1. El-Sonbati et al. has been manipulated by using a computer program developed in our laboratories using C program.

3. Results and Discussion

Elemental Analysis

The polymer complexes under investigation were subjected to elemental (C, H, N, and M) analysis, the results of which are given in Table 1. Stoichiometries of the new uranyl polymer complexes

The fact that HLₙ complexes with UO₃(OHCOCH₃)₂H₂O involving 2:1 ligand to UO₂⁺ ratio (Table 1), have been isolated, clearly illustrates that the ligands under study do not introduce sufficiently severe steric hindrance as to preclude the formation of [UO₂(HLₙ)(OAc)₃] complexes, but its steric feature and arrangement in space can also favorably influence the stabilization of 2:1 complexes. The polymer complexes are microcrystalline or powder-like, stable under ambient conditions, and partially soluble in warm DMF and DMSO to varying extents. The polymer complexes do not melt but decompose on heating and are converted to U₂O₈ around 700 °C [5]. The molar conductivity in DMF indicates that the complexes are non-electrolytes [24].

\[ \text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} + \text{HL}_n \xrightarrow{\text{DMF}} \text{[UO}_2(\text{HL}_n)_2(\text{OAc})_3]} \quad (n = 1-5) \]

The magnetic measurements of the dioxouranium(VI) complexes are independent of field strength and temperature [5,8] and the ground states of dioxouranium(VI) compounds contain no unpaired electrons. The compounds are, therefore, weakly diamagnetic as observed by previous workers [5,8].

Electronic spectra

HLₙ exhibits bands at 26415 – 26250 cm⁻¹ (CS) (n→π⁺), 30674 – 30540 cm⁻¹ (CO) (n→π⁺), 33550 – 33444 cm⁻¹ (H-bonding and association), 40480 – 39470 cm⁻¹ (phenyl) (ph-π⁺, π→π⁺) and 29410–29230 cm⁻¹ transition of phenyl rings overlapped by composite broad π→π⁺ of azo structure. In the dioxouranium(VI) complexes, the (CS) (n→π⁺) transition shifts slightly to lower energy and remain almost constant. The (CO) (n→π⁺) transition disappears with the simultaneous appearance of a new bands (≈29500 cm⁻¹), being attributed to π→π⁺ (C≡C) as a sequences of enolization. The band due to π→π⁺ transition moves to lower energy at ≈ 25000 cm⁻¹. These shifts or the disappearance of the bands are indicative of coordination of the ligands to UO₂⁺(II). The dioxouranium complexes exhibits a new bands at 24390–24210 cm⁻¹, which is assigned to the \( \frac{1}{2} \Sigma^+ \rightarrow \frac{3}{2} \Sigma^+ \) transition, typical of UO₂ for the symmetric stretching frequency for the first excited state [18,20].

\(^1\)H NMR spectra

The \(^1\)H data are in agreement with the proposed structures. The \(^1\)H spectra of the ligands and uranyl complex (3) (see Table 1) supports the occurrence of the form depicted in Figure 1. The proton magnetic resonance of the ligands and complexes have been recorded in DMSO-d₆ using TMS as the internal standard. The broad signal exhibited by the ligands can be assigned to intramolecular H-bonded proton of NH (hydrazide) at ~1.14 ppm and disappear in the presence of D₂O and not affected by uranyl ion indicating the coordination of the nitrogen atoms of NH group with the metal ion.

Further, the CH signal vanish and a new NH and C=N signal appears i.e., change from azo to hydrazo form (Fig. 1). The shifts are in sequence: p-NO₂ > p-Cl > H > p-OCH₃ > p-CH₃. The protons of the aromatic ring resonate downfield in the δ 7.3 – 8.4 ppm range [5,20]. This may be due to the decrease of electron density after forming the polymer complex.

The NMR spectrum of HLₙ monomer showed the expected peaks and pattern of the vinyl group (CH₃=CH), i.e. δ(DMSO-d₆) 6.25 (dd, J = 17, 11 Hz) for the vinyl CH proton and proton δ 5.12 ppm (AM part of AMX system dd, J = 17, 1 Hz) for the vinyl CH₃ protons, respectively. These peaks disappeared on polymerization while a triplet at δ 1.86 (t, J = 7 Hz) and a doublet at 1.80 ppm (d, J = 7 Hz) appeared. This indicates that the polymerization of HLₙ monomer occurs on the vinyl group [8,10]. It is worth noting that the rest of the proton spectrum of the monomer and polymer remain almost without change.

General

Before proceeding to what is considered the main result of this work it is appropriate to make the following points:

1) It is seen from Fig. 1, that ligand masses important in determining frequency. This is due to be in Eq. \( \nu = \nu_0 (1 + 2M_0/M_1) \) is already small.

2) The possibility that use the variation in \( \nu_0 \) as a very sensitive probe to measure indicative and conjugative effects of various groups attached to common ligating species as for example Ph-p-x (x = OCH₃, CH₃, H, NO₂, Cl). This of course
implies an understanding of the effects producing the change in \( v_1 \) (vide infra).

3) Linearity of the data of (Fig. 3a), might be constructed as good substantiating evidence of linearity of the uranyl ion in good agreement with the data reported elsewhere [5, 27].

4) In Table 2 it is evident that the value of \( v_1 \) and/or \( v_1 \) decreased as one proceeds along the spectrochemical series and/or the effect of electron withdrawing or electron donating in the \( p \)-position of the benzene ring of the ligand in the equatorial position. In any case the correlation is almost as good as the agreement between the individual of various groups.

5) The strength of the uranium-ligand bond varies inversely as the strength of the uranium-axial oxygen bonds, thus, the ligands are placed closer to O than O’s as shown in Figs. 1 & 5.

Such agreement is indeed remarkable and can be attributed only with a very small probability to coincidence. It is the more remarkable when one considers that the various spectrochemical series and/or electron withdrawing or electron donating in the \( p \)-position of the benzene ring have been established from considerations of electronic transitions of intra-d-shell type in ligated elements primarily of the 1\(^{st}\) and 2\(^{nd}\) transition series. Now there exists a rather excellent inverse correlation of the energies of these intra-d-shell transitions with infrared vibrational transitions in the uranyl ion, the ligation of which involves primarily the overlap of ligand orbital with 5\( f \)-orbitals of the uranium.

**The solid state structures**

In general, most of the azo compounds give spectral localized bands in the wavelength range 46620 - 34480 and 31250 - 270379 cm\(^{-1}\). The first region is due to the absorption of the aromatic ring compared to 1.48 and 1.60 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 \( \pi \)-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 alcohol. The substituted effect is related to the Hammett constant values [5, 8, 12, 15]. The position of the \( \pi-\pi^* \) transition of the azo groups remains as one of the more interesting unanswered 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 [8]. Based on MO theory [28] the energy terms of the molecular orbital 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 \( \pi \)-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 [8]. The role of hydrogen bonding in azo aggregation has been accepted for some time.

**Infrared spectra and nature of coordination**

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

a) Containing the azo compound attached via nitrogen \( \alpha \)-donor bonds.

b) Containing the azo compound bonded via \( \pi \)-bonds involving the \( \pi \)-electrons of the \(-N=N-\) system.

c) In case of aromatic derivatives, containing a \( \text{metal(I)} \)ated ligand attached via one nitrogen and a metal-carbon \( \alpha \)-bond to the ortho carbon of the ring.

d) Containing rearranged nitrogen-donor, e.g. o-semidine azobenzene acts as a fairly strong \( \pi \)-acid.

**Mode of bonding**

The infrared spectra of ligands exhibit strong to medium broad bands in the frequency range 3240 – 2900 cm\(^{-1}\). These bands can be attributed to intramolecular hydrogen bonded-OH group [14, 18-20]. Furthermore, all ligands exhibit a strong band at 1735-1720 cm\(^{-1}\). This is due to \( \nu_{C=O} \) [14, 18-20]. The discussed infrared features beside the band appeared at 1610-1595 cm\(^{-1}\) can guide to assume the presence of C=N structure through resonating phenomena [1-8]. Such class of compounds is with different types of hydrogen bonding [1-10, 18-20].

i) H-bonding of the type O-H...N between the OH group and –N=N- group (Fig. 1C).

ii) H-bonding of the type N-H...O between the –NH group and C=O group (Fig. 1D).

iii) Intermolecular hydrogen bonding of the O-H...O (E) or O-H...N (F) or N-H...O (Fig. 1G) type of one molecule to another one. The (ii) case is more favoured than (i). This is due to the presence of a broad band located at 870 – 970 cm\(^{-1}\) which could be taken as a good evidence for the intermolecular hydrogen bonding (Fig. 1).
The following features for some of the prepared complexes are observed:

i) The infrared spectra of the free ligands show no characteristic absorption assignable to NH₂ function. This confirms the formation of the azo compounds.

ii) The strong band observed at 1135-1140 cm⁻¹ may be assigned to ν(N-N) vibration modes [29] is affected on complexation. It is blue shifted and appeared as a weak band.

iii) In all complexes 3490-3150 cm⁻¹ is observed. Such region is attributed to different probabilities: (a) it is due to either free OH or NH (b) bonded OH group or NH group or (c) due to the presence of coordinated water molecules.

iv) The spectra of ligands do not show absorption characteristic of the N=N function owing to the formation of the hydrazone. The sharp, medium intensity band of C=N (hydrazone) appears at 1610-1595 cm⁻¹ for ligands.

v) The spectra exhibits a very strong band at 1720 cm⁻¹. This is a powerful indicative to ν(C=O). However, the broad band located at 3420 cm⁻¹ leads to characterize the ν(NH) rather than hydrogen bonded OH with N=N. This is rather confirmed from the observation of Karabatose [30] and El-Sobati et al [18,20] where the hydrazone form is more than the azo structure for similar compounds.

This is also proved by the appearance of N=N in splitted strong spectral bands at 1440 and 1530 cm⁻¹ combined with the tracing of a strong bands at 1225 cm⁻¹ characteristic to NH stretching vibration. All these data with lack of the ν(C=O) of enol in the i.r. spectrum leads us to assume the structure (1D) for this compounds.

vi) Introduction of a hydrazo group instead of N=N leads to (i) a change in the coordination mode of the azo group from the azo-nitrogen to the amine nitrogen (NH); (ii) stabilization of the chelate ring by intermolecular hydrogen bonding between hydrogen of water of this chelate ring and the basic oxygen of the six-membered chelate ring and the basic oxygen of the six-membered chelate ring of an carbonyl group (see Fig. 1).

This hydrogen bonding interaction will prevent the hydrazone group from rearranging to the energetically more favorable N-coordination mode. This behaviour has been observed with other metal azo compounds that contained the substituent C=N-NH instead of C=O in the vicinity of the azo group.

vii) The broad, medium intensity band at ~2900 cm⁻¹ in the free ligand is shifted to ~2400 cm⁻¹ on complex formation, a behaviour attributed to the OH of the hydrogen bond [31].

viii) Coordination of the carbonyl oxygen and the amine nitrogen in the chelate ring is supported by the appearance of new bands, which are assigned to U-N and U-O, respectively.

ix) There is no coordinated H₂O in the complexes as it is clear from the IR and thus the equatorial coordination number for UO₂⁺ is 6.

x) The ligand orbitals of hydrazo rhodamine are group theoretically, energetically and occupationally suitable for participation in both donor (U→L) and acceptor (L→U) π-interactions with the uranyl ion [32]. Convincing evidence [32] has been adduced that U→L π-bonding makes a significant contribution to the bonding in uranyl complexes.

xi) Electron-withdrawing substituents appear to be decrease the donor capacity of the carbonyl groups. This is evident from the ν(C=O) values of our complexes and is a general feature of all transition and non-transition metal β-Ketoenolates, with electron-withdrawing substituents [33]. In the mean time, U→O π-bonding will be facilitated by such substituents, leading to a positive contribution to ν(U=O).

Stereocchemistry and the structure of the complexes

3-allyl-2-thioxo-1,3-thiazolidine-4,5-dione-5-[(4derivativesphosphinyl)hydrazone] (HLn) react with UO₂(CH₃COO)₂·2H₂O (molar ratio 2:1) giving solid, dark brown or red complexes with expected show [UO₂(HLN)₃·(OAe)₃]ₙ stoichiometry. The IR spectra of all complexes show two bands attributable to the asymmetric and symmetric cm⁻¹ stretching frequency. A group theoretical consideration [34] shows that a linear and symmetrical triatomic UO₂⁺ ion possessing D₃₅₉ 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 ν₃ values for UO₂⁺ complexes with the former. The force constant of U-O bond in the present investigation has been calculated following McGlynn et al. [35], and the U-O bond distance for the corresponding complexes are evaluated using the Jones equation [28] Rₐ = 1.08 F - 1.71. The evaluated values are given in Table 2 and such report is also found for other uranyl complexes. The variation of bond length in the complexes is due to presence of electron releasing or
electron withdrawing substituents in the equatorial position. The $v_3$ values decrease as the donor characteristic increase as it is observed for $\pi$-electron substituents, where the basicity of the donating atom increases.

In the present investigation, it is well established that uranyl ion possesses planar hexagonal structure with nitrogen and oxygen atoms in the axial position. Two ligands units and two acetate molecules remain in the equatorial plane. It is also suggested that the two acetate molecules remain in the trans-position. In these cases, all the complexes are eight coordinated. HLN behaves as a chelating bidentate neutral ligand.

Complexation effect on uranyl ion spectra

Uranyl ion UO$_2^{2+}$ is quite peculiar both in its own structure and in its coordination compounds [5,8,11-15,18-20]. The ions reactions its identity over a wide range of vibrations in experimental conditions and can be considered from the geometric point of view, as a single particle. In the present investigation, the $\nu$(U=O) in all the complexes has been assigned in 940-910 cm$^{-1}$ and 840-795 cm$^{-1}$ region as $v_1$ and $v_2$ respectively (Table 2). The experimental results reveal an excellent linear relation between $v_1$ and $v_2$ with the slope corresponding to $(1+2M_0/M_2)^{1/2}$ (M$_0$ and M$_2$ are the masses of oxygen and uranium atoms respectively, Fig. 3-a). It is obvious that good linearity obtains also in case of $v_1$ and $v_3$ (Table 2 and Fig. 4).

Instead of the linear relation between $v_1$ and $v_2$ frequencies, El-Sonbati equation [12] has been focus attention on their normalized differences, which do not depend on the masses of oxygen and/or uranium atoms. The objective in using El-Sonbati equation, from which the U=O bond force constant is calculated, should be eventually serve as fairly accurate measure of U=O bond distance in given compounds. The force constant for the U=O (F$_{(U\ldots O)}$ Mdyn/Å), (F$^{a}_{(U\ldots O)}$, F$^{b}_{(U\ldots O)}$, and (F$^{c}_{(U\ldots O)}$) with neglect the interaction of the UO bonds with the ligands and the U=O bond distance [$r_{(U\ldots O)}$ Å] were calculated [5,12] (Table 2). Another observation is that a plot of $(v_1+v_2)$ and/or $v_1$ versus force constant for the U=O (F$_{(U\ldots O)}$ Mdyn/Å) or (F$^{a}_{(U\ldots O)}$ Mdyn/Å) and the U=O bond distance ($r_{(U\ldots O)}$ Å or $r_{(U\ldots O)}$ Å) gives a straight line with increase the value of $v_1+v_2$ and/or $v_1$, accompanied by decreasing $r_{(U\ldots O)}$ and increasing the force constant of the U=O bond (Figs. 4-6). There is also a straight line relationship between $r_{(U\ldots O)}$ and the $p$-substituent, Hammett's constant ($\sigma_p$) with negative slope, i.e. the higher the value of $\sigma_p$, the lower $r_{(U\ldots O)}$ and the higher the force constant of the U=O bond (Fig. 7). Moreover, by plotting of $r_1$, $r_2$, $r_3$ and $r_4$ (bond distance, $r_{(U\ldots O)}$) versus $v_3$ give a straight line with increase the value of $v_3$ decrease $r_{(U\ldots O)}$ (Fig. 8).

The electron withdrawing $p$-substituent increases the positive charge on the UO$_2^{2+}$ leading to an increase in $v_1$ and $F_{(U\ldots O)}$ and subsequently a decrease in $r_{(U\ldots O)}$. Accordingly, $r_{(U\ldots O)}$ values can be arranged in the order: $p$-OCH$_3$ > $p$-CH$_3$ < $p$-Cl < $p$-NO$_2$, which are consistent with the values of their $\sigma_p$.

Perhaps 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 $r_1$ (Table 2) were determined by Global error which shows that the excellent validity is in the sequence: $\sqrt{(r_3-r_1)^2} < \sqrt{(r_3-r_2)^2} < \sqrt{(r_1-r_2)^2}$.

Force constant, $F_{(U\ldots O)}$ and bond lengths, $r_{(U\ldots O)}$ of the uranyl polymer 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 scanty. From infrared spectra, the stretching and interaction force constants in the present complexes have been calculated [5,12,15]. The results are in turn used to evaluated U=O bond distances using Badger's formula, Jones equation [28] and El-Sonbati equation [12]. The values are given in Table 2 and such report is also found for other uranyl complexes [8,11-15,18-20]. The variation of bond length in the complexes is due to presence of electron releasing or electron withdrawing substituents in the equatorial position. El-Sonbati equation [12] has been used to determine the symmetric stretching frequency ($v^s$). The ($v^s$) data are in turn used to evaluate the $F_{(U\ldots O)}$ (force constant) and ($F_{(U\ldots O)}$) (bond-bond interaction) with neglect of the ligand (Table 2). There is also a straight line relationship between $v^s$ and $r_{(U\ldots O)}$ (O=U=O) (Fig. 3-b).

4. Concluding Remarks

From the overall studies presented, it is concluded that in the uranyl complexes, HLN behaves as a chelating bidentate neutral ligand, bonding through carbonyl group and imine group nitrogen atom. The CS breathing mode of the ligand is observed . It remains unaltered in the polymer complexes commensurate with absence of coordinations through the sulphur atom of the CS group.
Hln 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. Hammett's related the reactivity trends in ligands and complexes with the stability, i.e., the lower the stability the higher the reactivities. Based on Hammett'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 3-allyl-2-thioxo-1,3-thiazolidine-4,5-dione-5-[(4-derivatives phenyl) hydrazon](Hln) ligands are suitable for building a supramolecular structure. Moreover, since the azo polymer compounds experience photochemical isomerization and are therefore of interest for applicative purposes, uranyl polymer complexes containing the 3-allyl-2-thioxo-1,3-thiazolidine-4,5-dione-5-[(4-derivatives phenyl) hydrazon](Hln) 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.

In our laboratory, Diab and El-Sonbat et al [5,12,15,18-20] published a series of papers to give spot lights on the chemistry, structural models and the chemical equilibria of azo compounds and their complexes. The presentations and discussions explored many important points and still many questions remain.

References


Table 1. Analytical data UO$_2^{2+}$ complexes$^a$ of HL$_n$ (for molecular structure see Fig.1)$^b$.

<table>
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<td>52.11</td>
<td>4.09</td>
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<td>(51.99)</td>
<td>(3.97)</td>
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<td>(35.67)</td>
<td>(2.97)</td>
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<td>HL$_4$</td>
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<td>46.10</td>
<td>3.11</td>
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<td>(3.21)</td>
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<td>(2.77)</td>
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<td>(34.04)</td>
<td>(2.74)</td>
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$^a$ Micrometrical data as well as metal estimations are in good agreement with the stoichiometry of the proposed complexes.

$^b$ The excellent agreement between calculated and experimental data supports the assignment suggested in the present work.

$^c$ HL$_1$ – HL$_5$ are the ligands as given in Fig. 1.
Fig.1. General formula and proton numbering of the 3-Allyl-2-thioxo-1,3-thiazolidine-4,5-dione-5-[(4-derivatives phenyl) hydrazone]
Fig. 3 The relation between a) $v_1$ vs. $v_3$ and b) $v_1'$ vs. $v_3$

Fig. 4 The relation between $v_1$ vs. $v_3'$

Fig. 5 The relation between $r_{U-O}$ (Å) and $F_{U-O}$ (mdyn A$^{-1}$) vs. $v_3$

Fig. 6 The relation between $r_{3U-O}$ (Å) and $F'_{U-O}$ (mdyn A$^{-1}$) vs. $v_3$

Fig. 7 The variation of $p$-substituted Hammet's with a) $r_{U-O}$ (Å) and b) $F_{U-O}$ (mdyn A$^{-1}$).

Fig. 8 The relation between: 1) $r_1$ vs. $v_3$; 2) $r_2$ vs. $v_3$; 3) $r_3$ vs. $v_3$ and 4) $r$ vs. $v_3$