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

التركيب الكيميائى لبعض مشتقات صبغات الأليل أزو مع متراكبات بوليمرات اليورانيوم

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الملخص العربى

تم تحضير بعض المتراكبات البوليمارية لعنصر اليورانيوم. واثبات التراكيب الفراغى لهما باستخدام الأجهزة الطيفية المتنوعة. وقد تم تعيين كل من ($A°$) Rou و (10^{-8} N/ $A°$) Fou من خلال العديد من النظريات المتنوعة (Badger's, Jones and El-Sonbati equation) مع ايجاد العلاقة بينهما. وتم مناقشة Hammett constant

Abstract

Novel five polymeric dioxouranium(VI) of bidentate allyl azo homopolymer compounds derived from allyl rhodanine 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_3 of the prepared polymer complexes containing UO_2^{2+} were successfully used to calculate the force constant, F_{UO} (1n mdyn/$A°$) and the bond length R_{UO} (in $A°$) 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; 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 rhodanine. 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_3, 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_3) 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_3 with the slope corresponding to $(1 + 2M_O/M_U)^{1/2}$, where M_O and M_U 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.

Of late, a large number of complexes of rhodanine azodye 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 HL_1-HL_5 are prepared and studies. 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 allyl compound is a subject of current and growing interest and that may have numerous applications chemically azo rhodanine sulphadrug containing moieties are of great interest because of their great versatility as ligands [17-25], due to 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 amines, we report herein the synthesis, characterization and structure of HL_1-HL_5 and properties of the first example of hydrazone uranyl supramolecular polymer complexes $[UO_2(HLn)_2(OAc)_2]_n$ [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-thioxo-1,3-thiazolidine-4,5-dione-5-[(4-derivatives phenyl) hydrazone](HLn)

The standard chemical allyl rhodanine, aniline and 4-alkyl-anilines (alkyl: OCH_3, CH_3, Cl and NO_2; 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 allyl 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 P_2O_5. The analytical data confirmed by expected composition, are shown in (Table1). The ligands were also characterized by ^1HNMR and IR spectroscopy.

Synthesis of the polymer complexes

The uranyl salt, $UO_2(CH_3COO)_2.2H_2O$ (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.
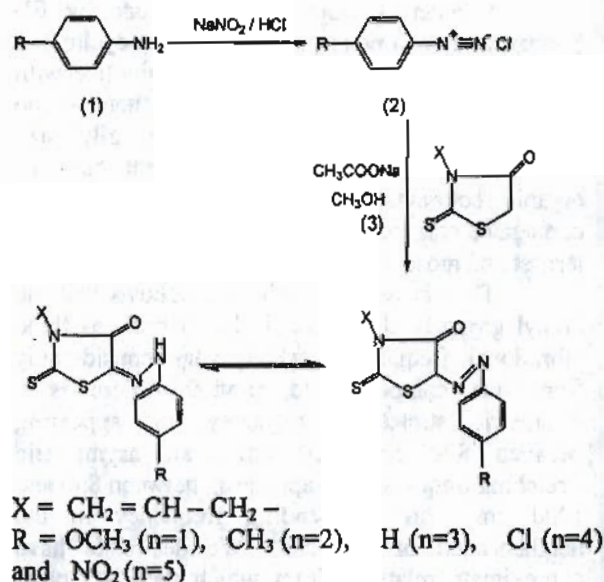

$X = CH_2 = CH - CH_2 -$
$R = OCH_3$ (n=1), CH_3 (n=2), H (n=3), Cl (n=4) and NO_2 (n=5)

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 $=1000^{0}C$ and weighing the residue as U_3O_8. The analytical data are given in Table 1. El-Sonbati equation has been manipulated by using a computer program developed in our laboratories using C Language

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.

Stoichiometeries of the new uranyl polymer complexes

The fact that HLn complexes with $UO_2(CH_3COO)_2.2H_2O$ 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 $[UO_2(HLn)_2.(OAc)_2]_n$ 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 U_3O_8 around 700 °C [5]. The molar conductivity in DMF indicates that the complexes are non-electrolytes [24].

$$UO_2(CH_3COO)_2.2H_2O + HLn \xrightarrow{DMF} [UO_2(HLn)_2(OAc)_2]_n \quad (n = 1\text{-}5)$$
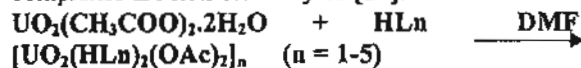
The magnetic measurements of the dioxouranium(VI) complexes are independent of field strength and temperature [5,8] and the ground states of dioxouranium(VI) compounds contain no unpaired electrons. The compounds are, therefore, weakly diamagnetic as observed by previous workers [5,8].

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-ph*, π-π*) and 29410–29250 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 ($\cong$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 $\cong$ 25000 cm^{-1}. These shifts or the disappearance of the bands are indicative of coordination of the ligands to UO_2(II). The dioxouranium complexes exhibits a new bands at 24390–24210 cm^{-1}, which is assigned to the $^1\Sigma_g^U \to$ $^3\pi_U$ transition, typical of OUO 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-d$_6$ using TMS as the internal standard. The broad signal exhibited by the ligands can be assigned to intramolecular hydrogen bonded proton of NH (hydrazone) at ~11.4 ppm and disappear in the presence of D$_2$O 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 the sequence: p-NO$_2$ > p-Cl > H > p-OMe > p-CH$_3$. 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 HL$_3$ monomer showed the expected peaks and pattern of the vinyl group (CH$_2$=CH), i.e. δ(DMSO-d$_6$) 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 CH$_2$ 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 HL$_3$ 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. [$\upsilon_3 = \upsilon_1(1 + 2M_O/M_U)$] is already small.

2) The possibility that use the variation in υ_3 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 = OCH$_3$, CH$_3$, H, NO$_2$, Cl). This of course

implies an understanding of the effects producing the change in υ_3 (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 υ_3 and/ or υ_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 U 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 1st and 2nd transition series. Now there exist 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 5f-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 - 270370 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 [5,8,12,15]. 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 [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 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 [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 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.

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 υC=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 NH_2 function. This confirms the formation of the azo compounds.

ii) The strong band observed at 1135-1140 cm^{-1} may be assigned to $\upsilon(N-N)$ 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 υC=O. However, the broad band located at 3420 cm^{-1} leads to characterize the υNH rather than hydrogen bonded-OH with N=N. This is rather confirmed from the observation of Karabatoser [30] and El-Sonbati 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 υC-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 H_2O in the complexes as is clear from the IR and thus the equatorial coordination number for UO_2^{2+} is 6.

x)   The ligand orbitals of hydrazo rhodanine 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 υ(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 υ(U – O).

Stereochemistry and the structure of the complexes

3-allyl-2-thioxo-1,3-thiazolidine-4,5-dione-5-[(4derivativesphenyl)hydrazon] (HLn) react with $UO_2(CH_3COO)_2.2H_2O$ (molar ratio 2:1) giving solid, dark brown or red complexes with expected show $[UO_2(HLn)_2.(OAc)_2]_n$ 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 UO_2^{2+} ion possessing $D_{\infty h}$ 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 UO_2^{2+} 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] $R_{U-O} = 1.08 F^{-1/3} + 1.17$. 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 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.

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 affect on uranyl ion spectra

Uranyl ion UO_2^{2+} is quit 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 $v(U=O)$ in all the complexes has been assigned in 940-910 cm^{-1} and 840-795 cm^{-1} region as v_3 and v_1 respectively (Table 2).The experimental results reveals an excellent linear relation between v_1 and v_3 with the slope corresponding to $(1 + 2\ M_O/M_U)^{1/2}$ (M_O and M_U are the masses of oxygen and uranium atoms respectively, Fig. 3-a). It is obvioused that good linearly 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_3 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-O} mdyn/Å), $(F^s_{U-O})_t$, $(F^s_{U-O})_o$ and $(F_{UO,UO})$ with neglect the interaction of the UO bands with the ligands and the U–O bond distance [r_{U-O} Å] were calculated [5,12] (Table 2). Another observation is that a plot of (v_1+v_3) and/or v_3 versus force constant for the U–O (F_{U-O} mdyn/Å) or $(F^*_{U-O}$ mdyn/Å) and the U–O bond distance (r_{U-O} Å or $r_{3\ U-O}$ Å) gives a straight line with increase the value of v_1+v_3 and/or v_3 , accompanied by decreasing r_{U-O} and increasing the force constant of the U–O bond (Figs. 4-6). There is also a straight line relationship between r_{U-O} 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. 7). Moreover, by plotting of r_1, r_2, r_3, and r_t (bond distance, r_{U-O}) versus v_3 give a straight line with increase the value of v_3 decrease r_{U-O} (Fig. 8).

The electron withdrawing p-substituent increases the positive charge on the UO_2^{2+} leading to an increase in v_3 and F_{U-O} and subsequently a decrease in r_{U-O}. Accordingly, r_{U-O} values can be arranged in the order: p-$OCH_3 > p$-$CH_3 < H < p$-$Cl < p$-NO_2, which are consistent with the values of their σ^R.

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

Force constant, F_{U-O} and bond lengths, R_{U-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 scantly. 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^*_1). The (v^*_1) data are in turn used to evaluate the (F_{U-O}) (force constant) and ($\overline{F}_{UO,UO}$) (bond-bond interaction) with neglect of the ligand (Table 2). There is also a straight line relationship between v^*_1 and v_3 (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 sulpher 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 reactvities. 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 containg 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 characterizion of further uranyl compounds of this family of ligands and towards the development of the materials they produce.

In our laboratory, Diab and El-Sonbati 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 presentatns and discussions explored many important points and still many questions remain.

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Table 1. Analytical data UO_2^{2+} complexes[a] of HL_n (for molecular structure see Fig.1)[b].

Compounds	Serial No.	Exp.(Calecd.)%					Compositions
		C	H	N	S	Metal	
HL_1		50.70 (50.82)	4.24 (4.12)	13.44 (13.68)	20.2 (19.8)	-	
	1	36.10 (35.93)	3.3 (3.19)	8.66 (8.38)	12.93 (12.78)	24.15 (23.75)	$[(UO_2)_2(HL_1)_2(OAc)_2]_n$
HL_2		53.54 (53.61)	4.37 (4.47)	14.12 (14.43)	22.33 (21.99)	-	
	2	37.22 (37.11)	3.18 (3.30)	8.82 (8.66)	13.60 (13.20)	24.90 (24.54)	$[(UO_2)_2(HL_2)_2(OAc)_2]_n$
HL_3		52.11 (51.99)	4.09 (3.97)	15.31 (15.16)	23.51 (23.11)		
	3	35.77 (35.67)	3.10 (2.97)	9.25 (8.92)	13.83 (13.59)	25.76 (25.27)	$[(UO_2)_2(HL_3)_2(OAc)_2]_n$
HL_4		46.10 (46.23)	3.11 (3.21)	13.77 (13.48)	20.86 (20.55)	-	
	4	34.26 (34.41)	2.82 (2.77)	8.90 (8.60)	13.40 (13.11)	24.77 (24.37)	$[(UO_2)_2(HL_4)_2(OAc)_2]_n$
HL_5		44.60 (44.72)	3.00 (3.11)	17.66 (17.39)	20.12 (19.88)	-	
	5	34.14 (34.04)	2.78 (2.74)	10.30 (9.93)	13.30 (12.97)	24.54 (24.11)	$[(UO_2)_2(HL_5)_2(OAc)_2]_n$

[a] Microanalytical 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] HL1 – HL5 are the ligands as given in Fig. 1..

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Table 2. Various force constants (mdynes/A°), U-O band distances (A°) and frequencies (cm⁻¹) ν_1 and ν_3 of the isolated UO_2^{2+} polymer complexes (for molecular structure see Fig. 1).

ν_i	ν_i'	ν_i	ν_i'	r_{ro}	r_1	r_2	$(F'_{U-O})_b$	r_3	$(F'_{U-O})_c$	r_{av}	%error	$(F_{U-O})_d$	$\omega\cdot\gamma$	r_3	ω_3	ω_4	$(r\times r)_e$	$(r\times r)_f$	$(r\times r)_g$
790	800	915	838	6.9105	1.3710	1.3123	6.0174	1.3638	5.7954	1.7714	1.5	-0.8974	825.2	6.2654	1.7558	800.2	64×10⁻⁴	7.1834×10⁻⁴	2.6523×10⁻⁵
800	883	918	846	6.959	1.7358	1.7301	5.9006	1.7613	5.0046	1.7574	0.8	-0.8626	825.6	6.5946	1.7549	811.2	4.106×10⁻³	6.5925×10⁻⁴	2.0214×10⁻³
805	926	856	67.0666	1.7325	1.7040	6.2141	1.7574	6.0481	1.3628	0.92	-0.8701	827	6.3661	1.7527	815.2	2.209×10⁻²	9.1809×10⁻⁴	2.8536×10⁻⁵
815	898	934	867	7.2106	1.7503	1.6981	6.2043	1.7577	6.2045	827.3	0.80	-0.8696	828.7	6.4376	1.7505	-0.7736	927.8	894.2	6.764×10⁻²	4.0656×10⁻⁴	3.1840×10⁻⁵
822	882	939	874	7.2633	1.7277	1.6952	6.4129	17.509	6.3052	1.7346	0.77	-0.3418	872.6	6.4738	1.7485	-0.7998	952.8	929.2	1.96×10⁻⁶	7.2361×10⁻⁴	3.1025×10⁻⁴

| | | | = -1.3559×10⁻⁴ | = -3.8165×10⁻⁵ | = -0.0142688 |
| | | | = 0.0519759 | = 0.1602746 | = 0.2429186 |

ᵃ The serial number corresponds to that used in Table 1 and Fig. 1.

ᵇ $\bar{r}$ = Interatomic distance U-O calculated by using Badger equation and Jones equation.

ᶜ U-O force constant and UO_2^{+0} interaction constant with neglect of the interaction of the U-O bonds with the ligands, (F'_{0-U-O} = bond-bond interaction).

ᵈ Symmetric stretching frequency evaluated by using El-Sonbati equation.

ᵉ (ν_1, ν_3) symmetric and symmetric stretching frequency with neglect of the ligands.

ᶠ (F'_{U-O}) is the true value of force constant.

ᵍ (F'_{U-O}) is the constant calculated with respect of the ligands.

ʰ F'_{U-O} is the bond force constant which evaluated by using El-Sonbati equation.

ⁱ r_1: Interatomic distance U-O calculated by using the true value of force constant.

ʲ r_2: Interatomic distance U-O calculated by using the symmetric stretching frequency with neglect of the ligands.

ᵏ r_3: Interatomic distance U-O calculated by using the symmetric stretching frequency evaluated by using El-Sonbati equation.
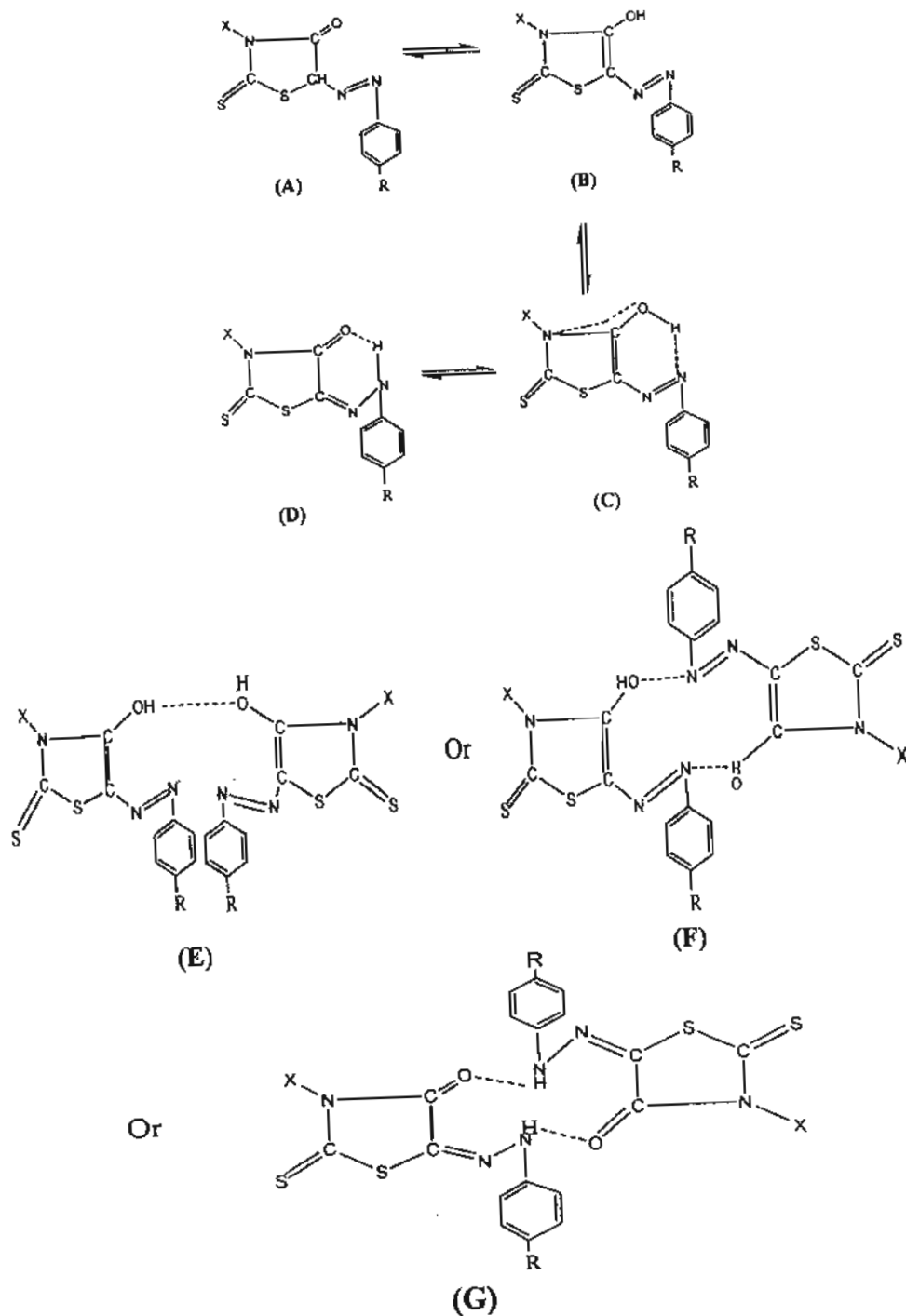
n=1   R=OCH₃   n=2   R=CH₃   n=3   R=H
n=4   R=Cl   n=5   R=NO₂   X=CH₂=CH-CH₂-

Fig.1. General formula and proton numbering of the 3-Allyl-2-thioxo-1,3-thiazolidine -4,5-dione-5-{(4-derivatives phenyl) hydrazone]
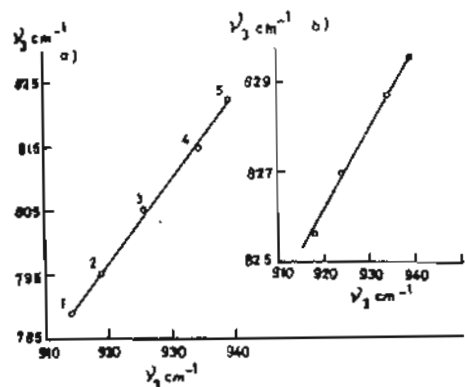
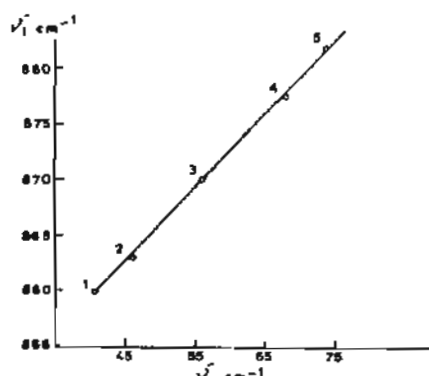**Fig. 3** The relation between a) v_1 *vs.* v_3 and b) v_1^* *vs.* v_3

Fig. 4 The relation between v_1^- *vs.* v_3^-
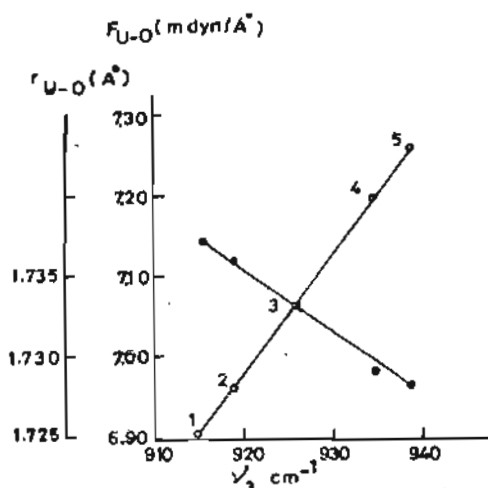
Fig. 5 The relation between r_{U-O} (Å) and F_{U-O} (mdyn Å^{-1}) *vs.* v_3
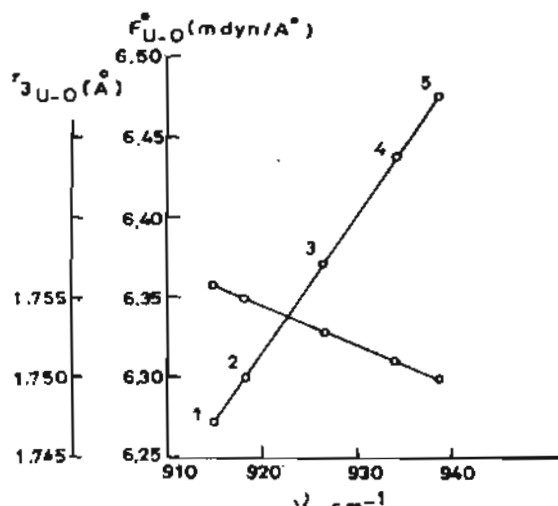
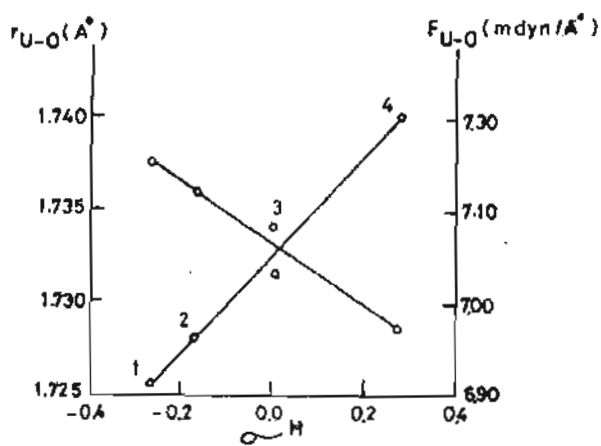**Fig. 6** The relation between $r_{3\,U-O}$ (Å) and F^*_{U-O} (mdyn Å^{-1}) *vs.* v_3

Fig. 7 The variation of *p*-substituted Hamett's with a) r_{U-O} (Å) and b) F_{U-O} (mdyn Å^{-1}).
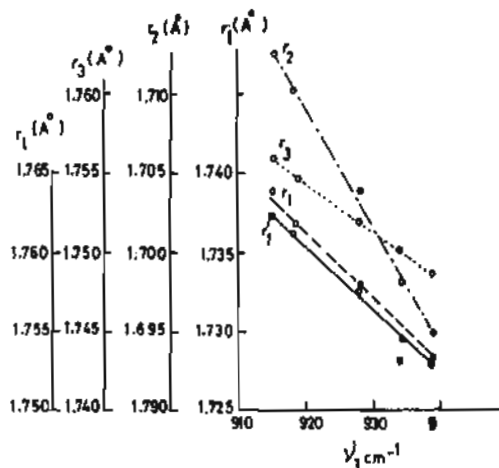
Fig. 8 The relation between:1) r_1 *vs.* v_3 ; 2) r_2 *vs.* v_3; 3) r_3 *vs.* v_3 and 4) r_t *vs.* v_3