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Structural model of dioxouranium(VI) with hydrazono ligands

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Abstract

Synthesis and characterization of several new coordination compounds of dioxouranium(VI) heterochelates with bidentate hydrazono compounds derived from 1-phenyl-3-methyl-5-pyrazolone are described. The ligands and uranayl complexes have been characterized by various physico-chemical techniques. The bond lengths and the force constant have been calculated from asymmetric stretching frequency of O-U-O groups. The infrared spectral studies showed a monobasic bidentate behaviour with the oxygen and hydrazo nitrogen donor system. The effect of Hammett's constant on the bond distances and the force constants were also discussed and drawn. Wilson's matrix method, Badger's formula, Jones and El-Sonbati equations were used to determine the stretching and interaction force constant from which the U-O bond distances were calculated. The bond distances of these complexes were also investigated. © 2004 Elsevier B.V. All rights reserved.

Keywords: Force constant; U-O bond distance; McGlynn and Badger's formula; Hammett's constant

1. Introduction

The azo compounds have gained much attention because of their use as models for biological systems [1]. In our laboratory, the coordination behaviour and chemical equilibria of some azo compounds have been investigated in depth. Heterocyclic nitrogen-containing hydrazones and their metal complexes have shown very important biological effects [2–4]. Some of these compounds are used in analytical separation of many metal ions in a mixture and as analytical reagents [4], the coordination chemistry, new structural features and biological activity [5]. A literature survey indicates, however, the lacking of research on the synthesis and properties of azodyes. These molecules are capable of possessing azo-hydrazo tautomers (Scheme 1).

El-Sonbati and co-workers [5–8] found that the bisbidentate azodyes ligands play a key role in our understanding of coordination chemistry of transition metal ions. In this paper the coordination compounds of these ligands with UO_2^{2+} nitrate are presented. The major interest of this paper are: (i) the synthesis of new substituted 1-phenyl-3-methyl-(4-derivatives phenylhyrazo)-5-pyrazolone (HL_n) ligand (Scheme 1), (ii) the synthesis of UO_2^{2+} complexes derived from this ligand, (iii) assigning the stereochemistry of the complexes based on the infrared and (iv) knowing the mode of bonding of these complexes from the infrared (IR) spectral data, and (v) The nature of binding of nitrate group.

2. Experimental

All the chemical used were of BDH quality. 1-Phenyl-3methyl-(4-dervitives phenylhydrazo)-5-pyrazolone was prepared by the methods outlined by El-sonbati and coworkers [5–8], and the experimental techniques have been described therein.

2.1. Preparation of the azo compounds

New azodyes prepared from aniline or its p-substituted derivatives (10 mmol) was dissolved in hydrochloric acid (20 mmol/25 ml distilled H₂O). The hydrochloric compound was diazotized below -5 °C with a solution of sodium nitrate (0.8 g, 10 mmol; 30 ml distilled H₂O). The diazonium chloride was coupled with an alkaline solution of start in 20 ml of

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Scheme 1. General formula and proton numbering of the 1-phenyl-3-methyl-(4-derivatives phenylhydrazo)-5-pyrazolone.

ethanol. The crude dye was collected by filtration and crystallized from dimethylformamide; then dried in a vacuum desiccator over P_2O_5 .

2.2. Synthesis of the complexes

A hot solution of $UO_2(NO_3)_2 \cdot 6H_2O(0.01 \text{ mol})$ in ethanol (30 cm^3) was added to the appropriate ligands (0.012 mol) in ethanol (30 cm^3) . Polycrystalline solid complexes were immediately formed in each case. The reaction mixture was then maintained at reflux temperature for 1/2 h to ensure complete reaction. The solid complexes were filtered off while hot and washed several times with EtOH, followed by Et₂O, and dried in vacuo over P₂O₅.

2.3. Physical measurements

C, H and N microanalyses were carried out at King Khalid University, Analytical Center, Saudi Arabia, using a Perkin-Elmer 2400 Series II Analyzer. The uranium content of each complex was determined by igniting a definite mass of the complex at ~1000 °C and weighing the residue as U_3O_8 . The ¹H NMR spectra was obtained with a Jeol FX 900 Q Fourier Transform spectrometer with DMSO-d₆ as the solvent and tetramethylsilane (TMS) as an internal reference. Infrared spectra (IR) were recorded using Perkin-Elmer 1340 spectrophotometer. UV spectra of the compounds were recorded in Nujol using a Unicam SP 8800 Spectrophotometer. TG measurements were made using a DuPont 950 thermobalance. Ten milligrams samples were heated at 10 °C min⁻¹ in a dynamic nitrogen atmosphere (70 ml min⁻¹); the sam-



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

ple holder was boat-shaped, $10 \text{ mm} \times 5 \text{ mm} \times 2.5 \text{ mm}$ deep; the temperature measuring thermocouple was placed within 1 mm of the holder.

3. Results and discussion

3.1. Stoichiometries of the new uranyl complexes

The fact that the complexes with $UO_2(NO_3)_2 \cdot 6H_2O$ involving 1:1 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 $[UO_2(L_n)NO_3] \cdot nH_2O$ complexes, but its steric features and arrangement in space can also favorably influence the stabilization of 1:1 complexes. All complexes are diamagnetic and sparingly soluble in most common organic

solvents, and it is thus difficult to determine the molecular weight.

3.2. ¹H NMR Spectra

The ¹H data are in agreement with the proposed structures. The ¹H spectrum of the ligand (HL₃) and uranyl complex (Table 1) supports the occurrence of the form depicted in Scheme 1. A broad signal in HL₃ observed at δ 11.3 ppm is attributed to the NH proton. The latter proton disappears in the presence of D₂O. Further, the CH signal vanish and a new NH and C=N signal appears, i.e., change from azo to hydrazo form (Scheme 1). The protons of the aromatic ring resonate downfield in the δ 7.3–8.4 ppm range [5].

3.3. Thermal analysis measurements

The thermogravimetric analysis of the free ligand and their corresponding complexes were carried out to get information as to whether decomposition occurs and on the relative volatility of the complexes. It was found that the ligands are stable up to about 150 °C and then start losing weight very rapidly and volatilize completely at about 450-550 °C. In most cases, U₃O₈ is obtained as the final product beyond \sim 500 °C. The volatilization of the ligands proceeds simultaneously. It is clear from the thermograms that the complexes containing the bidentate ligands have no H₂O molecule which is coordinate. Coordinated NO3 could be removed within the range of 210–315 °C. $[UO_2L_nNO_3]H_2O$ (*n* = 4, 5) loses the H₂O molecule at ~115 °C to give [UO₂L_nNO₃], which decomposes to give U_3O_8 ; whereas the $[UO_2L_nNO_3]2H_2O(n =$ 1–3) loses the two H₂O molecules in two steps at \sim 100 and \sim 125 °C and then decompose further to give finally U₃O₈ at \sim 500 °C. The oxide U₃O₈ is formed around 650 °C via the formation of UO₃, following which there is no measurable change in weight. In brief, these changes can be shown as:

Table 1

Elemental analysis data for UO₂²⁺ complexes^a with hydrazono ligands derived from 1-phenyl-3-methyl-5-pyrazolone (for molecular structures see Scheme 1)^b

Complex ^c	Code	Experimental (ca	lculated) (%)			Composition
		C	Н	Ν	Metal	
HL ₁	1	66.1 (66.2)	5.1 (5.2)	18.5 (18.2)	35.3 (35.3)	[UO ₂ L ₁ NO ₃]2H ₂ O
		30.2 (30.2)	2.2 (2.2)	10.4 (10.7)		
HL ₂	2	69.8 (69.9)	5.6 (5.5)	19.4 (19.2)	36.5 (36.1)	[UO ₂ L ₂ NO ₃]2H ₂ O
		30.9 (31.0)	2.3 (2.3)	10.9 (10.6)		
HL ₃	3	69.0 (20.1)	5.1 (5.0)	20.3 (20.1)	37.1 (36.9)	[UO ₂ L ₃ NO ₃]2H ₂ O
		29.7 (29.8)	1.9 (2.0)	11.1 (10.9)		
HL_4	4	59.0 (59.4)	3.9 (4.0)	21.9 (21.7)	35.7 (35.4)	[UO ₂ L ₄ NO ₃]2H ₂ O
		28.5 (28.6)	1.9 (1.8)	12.6 (12.5)		
HL ₅	5	61.5 (61.4)	4.1 (4.2)	20.1 (20.3)	36.3 (36.0)	[UO2L5NO3]2H2O
		28.9 (29.0)	1.7 (1.8)	10.5 (10.6)		

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

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

 $^{c}\,$ HL_1–HL_5 are the ligand as given in Scheme 1 and L_1–L_5 are anions.

Table 2

 $Thermogravimetric analysis of uranyl complexes of 1-phenyl-3-methyl-(4-derivatives phenyl hydrazo)-5-pyrazolone ligands (for molecular structures see Scheme 1)^a$

Complexes ^b	Temperature	Mass loss	s (%)	Effect type	Assignment
•	range (°C)	(found)		••	-
1	60-110	5.33	5.63	Endo	Loss of 2H ₂ O molecules
	215-255	14.92	15.34	Exo	Loss of NO ₃ group
	275-455	54.35	60.09	Exo	Decomposition of complex and formation of metal oxide (UO_3)
2	90-110	5.46	5.78	Endo	Loss of 2H ₂ O molecules
	235-300	15.32	15.73	Exo	Loss of NO ₃ group
	460	61.24	61.64	Exo	Decomposition of complex and formation of metal oxide (UO_3)
3	70-120	5.57	5.72	Endo	Loss of 2H ₂ O molecules
	250-290	15.92	16.12	Exo	Loss of NO ₃ group
	420–530	62.81	63.16	Exo	Decomposition of complex and formation of metal oxide (UO_3)
4	105-125	2.68	2.79	Endo	Loss of 1H ₂ O molecule
	210-250	12.32	11.94	Exo	Loss of NO ₃ group
	380-460	52.91	52.24	Exo	Decomposition of complex and formation of metal oxide (UO_3)
5	100-120	2.72	2.96	Endo	Loss of 1H ₂ O molecule
	225-252	12.05	12.43	Exo	Loss of NO ₃ group
	350-500	56.05	56.88	Exo	Decomposition of complex and formation of metal oxide (UO ₃)

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

^b See Table 1 and Scheme 1.

$$[\mathrm{UO}_{2}(\mathrm{L}_{n})\mathrm{NO}_{3}]2\mathrm{H}_{2}\mathrm{O} \overset{60-120\,^{\circ}\mathrm{C}}{\longrightarrow} [\mathrm{UO}_{2}(\mathrm{L}_{n})\mathrm{NO}_{3}]$$

$$\overset{215-300\,^{\circ}\mathrm{C}}{\longrightarrow} \mathrm{UO}_{2}\mathrm{L} \overset{275-530\,^{\circ}\mathrm{C}}{\longrightarrow} \mathrm{UO}_{3} \overset{550\,^{\circ}\mathrm{C}}{\longrightarrow} \mathrm{U}_{3}\mathrm{O}_{8}$$

$$[\mathrm{UO}_{2}(\mathrm{L}_{n})\mathrm{NO}_{3}]\mathrm{H}_{2}\mathrm{O} \xrightarrow{100-130^{\circ}\mathrm{C}} [\mathrm{UO}_{2}(\mathrm{L}_{n})\mathrm{NO}_{3}]$$

$$\xrightarrow{210-250^{\circ}\mathrm{C}} \mathrm{UO}_{2}\mathrm{L} \xrightarrow{380-500^{\circ}\mathrm{C}} \mathrm{UO}_{3} \xrightarrow{550^{\circ}\mathrm{C}} \mathrm{U}_{3}\mathrm{O}_{8}$$

The determined temperature ranges, % losses in mass and thermal effects accompanying the changes in the solid complexes on heating are given in Table 2. The results of the metal contents [%M], calculated from the masses of the residual oxides, support the stoichiometry obtained from the elemental analyses.

3.4. Electronic spectra

The UV spectra of the uranyl complexes exhibit a band in the 20,800–22,600 cm⁻¹ region assigned to ${}^{1}E_{g}^{+} \rightarrow {}^{3}\pi_{u}$ transition. This band is similar to the O–U–O symmetric stretching frequency for the first excited state [8]. Also, the bands observed in the spectra of the ligands as well as the uranyl complexes in the 47,200–47,840, 43,100–43,500 and 34,400–36,400 cm⁻¹ regions are assigned to π – π * and n– π * transitions, respectively. Another band at ~34,900 cm⁻¹ in the spectra of the HL_n is assigned to complex formation with UO₂²⁺ and to the disappearing of hydrogen bonding and association [9].

3.5. Mode of bonding

The bonding of the ligands to different metal ion was investigated by comparing the IR spectra of the free ligands with those of their solid complexes (Table 3). The following conclusions can be drawn:

The infrared spectra of ligands exhibit a strong band at $1650-1625 \text{ cm}^{-1}$. This is due to ν (CO of the pyrazolone ring) [10]. The discussed infrared features beside the band appeared at $1595-1575 \text{ cm}^{-1}$, can guide to assume the presence of ν C=N (attached to the hydrazo group) structure through resonating phenomena [11]. In general, the presence of electron attracting group minimizes the charge transfer from the phenyl ring and this leads to increase the CO band modes. The

Table 3

Solid state infrared frequencies (cm⁻¹) of uranyl complexes of 1-phenyl-3-methyl-(4-derivatives phenyl hydrazo)-5-pyrazolone ligands (for molecular structures see Scheme 1)^a

Complex ^a	νOH	νCO	vNO ₃ (coordinated)	ν Μ —Ο	vM—N
1	3500-3400	1667	1505, 1270, 1030	612, 452	560,370
2	3500-3400	1655	1500, 1280, 1040	604, 466	572,360
3	3500-3400	1650	1495, 1283, 1043	602, 470	575,358
4	3500-3400	1645	1493, 1285, 1045	600, 475	577,355
5	3500-3400	1642	1490, 1288, 1048	595, 478	580,350

^a See Table 1 and Scheme 1.

 β C–H, δ C–H and γ C–H modes of vibrations are identified by the presence of strong bands in the 1180–1110, 1030–930 and 840–780 cm⁻¹ regions, respectively. The C–C vibrations are also identified by the presence of several bands at frequencies lower than 755 cm⁻¹. Generally, the electron donor methoxy group enhances the change transfer from the phenyl ring to the heterocyclic moiety. This leads to increase both polarizability of the carbonyl group. Such class of compounds, as illustrated in Scheme 1, have different types of hydrogen bonding [12–14], as follows:

- 1. H-bonding of the type $O-H \cdots N$ between the -OH group and -N=N- group (1B).
- 2. H-bonding of the type $N-H \cdots O$ between the --NH group and C=O group (1C).
- 3. Intermolecular hydrogen bonding of the O–H···N (1D) or N–H···O (1E) type of one molecule to another. The (2) case is more favored than (1). This is due to the presence of a broad band located at 875-975 cm⁻¹, which could be taken as a good evidence for the intermolecular hydrogen bonding [5]. This is illustrated in Scheme 1.

The following features for some of the prepared complexes are observed.

- 1. The infrared spectra of the free ligands show no characteristic absorption assignable to NH_2 function. This confirms the formation of the azo compounds.
- 2. The strong band observed at $1130-1140 \text{ cm}^{-1}$, which may be assigned to $\nu(N-N)$ vibration modes [14] is affected on complexation. It is blue shifted and appeared as a weak band.
- 3. In all complexes, 3480–3150 cm⁻¹ is observed. Such a 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 presence of water molecules.
- 4. 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 1595–1575 cm⁻¹ for ligands.
- 5. The spectra exhibit a strong band at 1650 cm^{-1} , which is indicative to ν CO. However, the broad band located at 3430 cm^{-1} leads to characterize the ν NH rather than hydrogen bonded –OH with N=N. This is rather confirmed from the observation of Karabatoses et al. [15] where the hydrazone formed is more than the azo structure for similar compounds. This is also proved by the appearance of N=N in splitted strong spectra bands at $1435-1535 \text{ cm}^{-1}$ combined with observing a strong bands at 1230 cm^{-1} characteristic to NH stretching vibration. All these data with lack of the ν C–O of enol in the IR spectrum lead us to assume the structure (1C) for this compounds.
- 6. Introduction of a hydrazo group instead of N=N leads to a change in the coordination mode of the azo group from the azo-nitrogen to the amine nitrogen (NH) (Scheme 1).

Variation of 1	orce con	istant (mdy	yn Å−1) 1	U—O bond	l distances (,	Å) and frequ	encies (cm ⁻	$^{-1}$) ν_1 and ν_3	of the isolate	ed UO ₂ ²⁺ cor	nplexes					
Serial no. ^a	٧1	$\bar{\nu}_1$	V3	$\overline{\nu}_3$	$F_{\rm UO}$	r_1	r_2	$(F^{\rm s}_{\rm U-O})_{\rm t}$	r _t	$(F^{\rm s}_{\rm U-O})_{\rm o}$	r_0	$(F_{\rm UO-U0}^{-})^{\rm b}$	$(\nu_1{}^2)^{c}$	$F^*{\rm U-0}$	r3	(Fuo-uo ⁻) ^t
1	792	829.1	908	842.6	6.8052	1.7399	1.7177	6.0001	1.7643	5.8602	1.7690	-0.9450	824.4	6.2160	1.75774	-0.6001
2	798	833.6	913	848.9	6.8803	1.7378	1.7139	6.0711	1.7620	5.9481	1.7661	-0.9322	824.94	6.2511	1.7563	-0.6345
3	805	838.0	918	856.4	7.1851	1.7297	1.7101	6.2676	1.7558	6.0537	1.7626	-1.1314	825.9	6.4092	1.7514	-0.7821
4	830	743.2	933	880.0	7.2159	1.7298	1.6974	6.4409	1.7505	6.4050	1.7516	-0.7817	828.64	6.3137	1.7543	-0.6479
5	835	857.6	940	888.3	7.2933	1.7269	1.6937	6.5298	1.7478	6.5131	1.7483	-0.7802	830.096	6.4938	1.7489	-0.8061
$\overline{\nu}_1, \overline{\nu}_3$: symm force constar	eyric and it which	asymmet evaluated	by using	hing frequ El-Sonbat	iency with n ti equation;	leglect of the r_t : internucle	e ligands; (<i>l</i> ear distance	⁷⁵ U-O)t: the t U-O calcula	rue value of ted by using	force constar	It; $(F^{s}_{U-O)a}$ force consta	the constant cal nt; r_0 : internucle	culated with r ar distance U-	eglect of th O calculat	e ligands; F ed by using	[*] U-0: the bond the asymmetric
calculated by	using B.	adger equi	ation and	Jones equ	ation.	al uistallee e	O Calcula	ginten de non	nominitée om	ic succuming i	reducited ev	anarea ouy usua		quauon, 1,2		n uisiaille u-c

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^a The serial number corresponds to that used in the Table 1 and Scheme 1.

interaction constant with neglect the interaction of the UO bonds with the ligands ($F_{\rm UO-UO}^{-}$ = bond-bond interactions) F^*_{U-O} : force constant and UO-UO⁻ interaction constant with neglect the Symmetric stretching frequencies evaluated by using El-Sonbati equation. Ą

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- 7. 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 (Table 3).
- 8. The infrared spectrum of the nitrate complex shows bands corresponding to coordinated nitrate group. These should show absorptions [16] at 1505–1475 cm⁻¹ (ν_1), 1325–1275 cm⁻¹ (ν_5), 1045–1020 cm⁻¹ (ν_2) and 803 cm⁻¹ (ν_6). The complexes under study show IR bands at ~1430 cm⁻¹ (ν_1), 1384 cm⁻¹ (ν_3), 1274 cm⁻¹ (ν_5), 1010 cm⁻¹ (ν_2) and 839 cm⁻¹ (ν_6). The separation of ~200 cm⁻¹ between ν_1 and ν_5 indicates the bidentate nature of the nitrate group [16].
- 9. There is no coordinated H_2O in the complexes as is clear from the IR and TGA curves and thus the equatorial coordination number for UO_2^{2+} is 4.
- The ligand orbitals of hydrazo pyrazolones are group theoretically, energetically and occupationally suitable for participation in both donor (U → L) and acceptor (L → U) π-interactions with the uranyl ion [17]. Convincing evidence [17] has been adduced that U → L π-bonding makes a significant contribution to the bonding in uranyl complexes.
- Electron-withdrawing substituents appear to decrease the donor capacity of the carbonyl groups. This is evident from the ν(C−O) values of these complexes and is a general feature of all transition and non-transition metal β-ketoenolates with electron-withdrawing substituents [18]. In the mean time, U → O π-bonding will be facilitated by such substituents, leading to a positive contribution to ν(U−O).

3.6. Complexation effect on uranyl ion spectra

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, electronwithdrawing 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 chelates.

Uranyl ion UO_2^{2+} is quite peculiar in its own structure and in its coordination compounds [5–8,11]. The ion retains its identities over a wide range of vibrations in experimental conditions and can be considered from the geometrical point of view as a single particle. In the present investigation, the $\nu(U-O)$ in all the complexes has been assigned in 938–910 and 840–792 cm⁻¹ regions as ν_3 and ν_1 , respectively (Table 4). The ν_3 values decrease as the donor characteristic increase as is observed for π -electron substituents, when the basicity of the donating atom increases. The experimental results reveal an excellent linear relation between v_1 and v_3 with the slope corresponding to $(1 + 2M_0/M_u)^{1/2}$ (M_0 and M_u are the masses of oxygen and uranium respectively, Fig. 1a), and the data satisfy the equations: (i) $v_s = -115 + 1.0v_{as}$ for compounds (1), (2), and (4) and (ii) $v_s = -100 + 1.0v_{as}$ for compounds (3) and (5). Similar results have been reported by McGlenn et al. [19]. It is obvious that good linearity obtained in the case of \bar{v}_1 and \bar{v}_2 .

Instead of the linear reaction between v_1 and v_3 frequencies, El-Sonbati equation [20] has focused attention on their normalized differences with a slope A (0.000192) and constant B (1.835) 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 serve as fairly an accurate measure for U-O bond distance in given compounds. The force constant for the U–O (F_{U-O} mdyn Å⁻¹), (F^{s}_{U-O})_t, (F^{s}_{U-O})_o and ($F_{UO UO^{-}}$), when neglecting the interaction of the U-O bonds with the ligands and the U–O bond distance $[r_{U-O} Å]$, were calculated [19,21] (Table 4). Another observation is that a plot of $(v_1 + v_3)$ and/or v_3 versus force constant for the U–O $(F_{U=0} \operatorname{mdyn} \overset{\circ}{A}^{-1})$ or $(F^*_{U=0} \operatorname{mdyn} \overset{\circ}{A}^{-1})$ and the U–O bond distance $(r_{U-Q} \text{ Å or } r_{3U-Q} \text{ Å})$ gives a straight line with increasing 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. 2-4). There is also a straight line relationship between $r_{\rm U-O}$ and the p-substituents, when Hammett's constant ($\sigma^{\rm R}$) was applied, giving a negative slope, i.e. the higher the value of σ^{R} , the lower r_{U-Q} and the higher the force constant of the U–O bond (Fig. 5). Moreover, plotting of r_1 , r_2 , r_3 , and r_t (bond distance, r_{U-O}) versus v_3 gives a straight lines with an increase in the values of v_3 and a decrease in r_{U-O} (Fig. 6).

The electron withdrawing p-substituents 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} value can be arranged in the order p-OCH₃ > p-CH₃ > p-CH₃



Fig. 2. The relation between v_1 and $v_1 + v_3$.



Fig. 3. The relation between r_{U-O} (Å) and F_{U-O} (mdyn Å⁻¹) vs. ν_3 .

El-Sonbati equation [20], which has been used to determined the symmetric stretching frequency (ν_1^*) data should eventually serve as a fairly accurate evaluation for (F_{U-O}), (r_{U-O}) and ($F_{uo,uo}^-$) [Table 4]. There is also a straight line relationship between (ν_1^*) and ν_3 (O=U=O) (Fig. 1b).

3.7. Stereochemistry and structure of the complexes

1-Phenyl-3-methyl-(4-dervitives phenylhdrazo)-5-pyrazolone reacts with $UO_2(NO_3)_2 \cdot 6H_2O$ (molar ratio 1:1) giving solid complexes. The proposed structure of uranyl complexes are given in Scheme 1. The spectra of all complexes show two bands attributed to the asymmetric and symmetric stretching frequency. A group theoretical consideration [22] shows that a linear and symmetrical triatomic UO_2^{2+} ion possessing $D_{\alpha h}$ symmetry gives rise to three fundamental modes of vibrations. Wilson's matrix method [23] has been also used to determine the stretching and interaction force constants.



Fig. 4. The relation between $r_{3 \text{ UO}}$ and $F^*_{\text{ UO}}$ vs. v_3 .



Fig. 5. The variation of p-substituted Hammett's with (a) r_{U-O} (Å) and (b) F_{U-O} (mdyn Å⁻¹).

The results are in turn used to evaluate U–O bond distances following Badger's formula [24].

In the equatorial bonding, the more effective overlap of O–U–O group orbital by nitrogen than by oxygen in the ligands leading to lowering v_3 values for UO₂²⁺ complexes with the former. The force constant of U–O bond in the present investigation has been calculated following McGlenn et al. [19], and the U–O bond distance for corresponding complexes are evaluated using the Jones equation [21] $R_{u-o} = 1.08 F^{-1/3} + 1.17$. The evaluated values are given in Table 4, and such a report is also found for other uranyl complexes, which is due to the presence of electron donating or electron withdrawing substituents in the equatorial position.



Fig. 6. The relation between (1) r_1 vs. ν_3 , (2) r_2 vs. ν_3 , (3) r_3 vs. ν_3 and (4) r_1 vs. ν_3 .

In the present investigation, it is well established that uranyl ion possesses planar hexagonal structure with nitrogen and oxygen atoms in the axial position. HL_n behaves as a chelating bidentate monobasic ligand, bonding through oxygen and amine nitrogen.

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