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Stereochemistry of new nitrogen containing heterocyclic compound XII. Polymeric uranyl complexes of hydrazone compounds

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Abstract

Several dioxouranium(VI) heterochelates with tetradentate monobasic hydrazone compounds (HL_n) have been synthesized. The heterochelates of the type $[(UO_2)_2(HL_n)(L_n)_2(OAc)_2(OH_2)_2]_n$ have been characterized on the basis of elemental analyses, IR and electronic spectra, conductance and magnetic susceptibility measurements. The complexes are polymeric, non-electrolytes, diamagnetic and eight-coordinated.

Wilson, G.F. matrix method, Badger's formula, Jones and El-Sonbati equations were used to determine the stretching and interaction force constants from which the U–O bond distances were calculated. The bond distances of these complexes were also investigated. © 2004 Published by Elsevier B.V.

Keywords: Polymeric complexes; Force constant; U-O bond distance

1. Introduction

Hydrazone compounds of rhodanine usually react as chelating ligands with transition metal ions by bonding through the oxygen and hydrazinic nitrogen atoms [1,2], as they form a stable six-membered characterization of 5-(4'-alkylphenylazo)-3-phenylamino-2-thioxothiazolidin-4-one (HL_n) and their complexes with dioxouranium(VI). The ligands act as tetradentate monobasic reacting with UO₂(II) through the CO (rhodanine moiety), hydrazinic N with displacement of hydrogen atom, CS (rhodanine moiety) and amidic N.

2. Experimental

3-Phenylamino-2-thioxthiazolidin-4-one was prepared according to El-Sonbati et al. [1].

The standard chemical aniline and 4-alkylanilines (alkyl: CH₃, OCH₃, Cl and NO₂; Aldrich Chemical Co.) were used

without any further purification. The experimental technique has been described previously [1–3].

2.1. Preparation of 5-(4'-alkylphenylazo)-3phenylamino-2-thioxothiazolidin-4-one (HL_n)

In typical preparation, 25 ml of distilled water containing hydrochloric acid (12 M, 2.68 ml, 32.19 mmol) was added to aniline (0.979, 10.73 mmol) or a 4-alkyl-aniline. To the resulting mixture stirred and cooled to 0° C, a solution of sodium nitrite (740 mg, 10.73 mmol, in 20 ml of water) was added dropwise. The so-formed diazonium chloride was consecutively coupled with an alkaline solution of 3-phenylamino-2-thioxothiazolidin-4-one (10.73 mmol) in 20 ml of pyridine. The brown precipitate, which formed immediately, was filtered, washed several times with water. The crude product was purified by recrystallization from hot ethanol, yielding 70%. The analytical data confirmed the expected compositions (Table 1). The ligands were also characterized by ¹H NMR and IR spectroscopy (Fig. 1).

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Fig. 1. 5(-4'-alkylphenylazo)-3-phenylamino-2-thioxothiazolidin-4-one (HL_n); R=OCH₃ (n = 1), CH₃ (n = 2), H (n = 3), Cl (n = 4) and NO₂ (n = 5).

2.2. Synthesis of the complexes

A hot solution of $UO_2(OAc)_2 \cdot 2H_2O$ (0.01 mol) in EtOH (30 cm³) was added to the appropriate ligands (0.022 mol) in EtOH (30 cm³). Polycrystalline solid complexes were immediately formed in each case. The reaction mixture was then maintained at the reflux temperature for 1.5 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. Elemental analysis

The uranium content of each complex was determined by igniting a definite mass of the complex at ~ 800 °C and weighing the residue as U₃O₈. Carbon, hydrogen and nitrogen contents were determined at the Microanalytical unit at Cairo University, Cairo, Egypt. The analytical data are given in Table 1.

Table 1		
Analytical data UO2 ²	+ complexes ^{a,b,c}	of HL _n

3. Results and discussion

The reaction of UO_2^{2+} in ethanol with 5(-4'alkylphenylazo)-3-phenylamino-2-thioxothiazolidin-4-one resulted in the formation of the complexes of the general composition $[(UO_2)_2(HL_n)(L_n)_2(OA_c)_2(OH_2)_2]_n$. Analytical results and some physical properties of the complexes are listed in Table 1. All the complexes are powder-like, stable in air and slightly soluble in methanol and ethanol. Also, the complexes are soluble in DMF and dimethylsulphoxide (DMSO). The isolated uranyl complexes have a general formula $[(UO_2)_2(HL_n)(L_n)_2(OA_c)_2(OH_2)_2]_n$ (where L: tetradentate monobasic hydrazone). The molar conductivities of complexes in DMF at 25 °C are in the $2-11 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ range, indicating a non-electrolytic nature [4]. The magnetic susceptibility measurements at room temperature indicate that the complexes are diamagnetic as expected for a fo system.

3.1. Stoichiometries of the new uranyl complexes

The fact that HL_n complexes with $UO_2(CH_3COO)_2 \cdot 2H_2O$ involving 2:1 ligand to UO_2^{2+} (Table 1) have been isolated clearly illustrates that the ligand under study does not introduce sufficiently severe steric hindrance as to preclude the formation of $[(UO_2)_2(HL_n)(L_n)_2(OA_c)_2(OH_2)_2]_n$ complexes, but its steric feature and arrangement in space can also favorably influence the stabilization of 2:3 complexes. The ligands present three donor sites: azo nitrogen, the

Complex (colour)	Code	mp (°C)	Experime	ntal (calculate	ed) (%)		Composition
			С	Н	Ν	Metal	
HL ₁ (brown)			53.6	3.9	15.6	_	
		131	(53.6)	(4.0)	(15.6)		
	1		35.3	2.8	9.6	26.7	$[(UO_2)_2(HL_1)(L_1)_2(OAc)_2(OH_2)_2]_m$
			(35.3)	(2.8)	(9.5)	(27.0)	
HL ₂ (brown)			55.8	4.1	16.4	-	
		161	(56.0)	(4.1)	(16.4)		
	2		36.2	3.0	10.1	27.3	$[(UO_2)_2(HL_2)(L_2)_2(OAc)_2(OH_2)_2]_n$
			(36.3)	(2.9)	(9.8)	(27.7)	
HL ₃ (brown)			54.8	3.6	16.9	_	
		164	(54.9)	(3.7)	(17.1)		
	3		35.0	2.7	10.3	28.0	$[(UO_2)_2(HL_3)(L_3)_2(OAc)_2(OH_2)_2]_m$
			(35.1)	(2.6)	(10.0)	(28.4)	-
HL ₄ (brown)			49.6	3.0	15.4	_	
		164	(49.7)	(3.1)	(15.5)		
	4		32.9	2.4	9.1	26.4	$[(UO_2)_2(HL_4)(L_4)_2(OAc)_2(OH_2)_2]_m$
			(33.0)	(2.3)	(9.4)	(26.8)	
HL ₅ (brown)			48.2	2.9	18.7	_	
		178	(48.3)	(3.0)	(18.8)		
	5		32.4	2.1	11.8	25.9	$[(UO_2)_2(HL_5)(L_5)_2(OAc)_2(OH_2)_2]_n$
			(32.5)	(2.3)	(11.6)	(26.3)	

^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.

 $^{c}\,$ HL_1–HL_5 are the ligands and L_1–L_5 are the anions.

carbonyl oxygen and thionyl sulphur of rhodanine moiety and the NH group of 3-phenylamino. However, it is clear that the utilization of all the four bonding sites would introduce certain steric restrictions and hence either both the azo nitrogen and the carbonyl group would coordinate or the NH group and the carbonyl group would coordinate. The coordination of NH group and the carbonyl group seems unlikely in view of the large size of the chelated ring.

3.2. Infrared spectra and nature of coordination

The mode of bonding of the azodyes to the uranyl ions was elucidated by investigating the IR spectra of the chelates 2M:3L as compared to those of the free ligands.

The infrared spectra of ligands exhibit strong to medium broad bands in the frequency range $3295-2950 \text{ cm}^{-1}$. These bands can be attributed to intramolecular hydrogen-bonded –NH group [5]. Furthermore, all ligands exhibit a strong band at $1730-1710 \text{ cm}^{-1}$. This is due to ν C=O [2]. The discussed infrared features beside the band appearing at $1640-1600 \text{ cm}^{-1}$ can guide to assume the presence of C=N structure through resonating phenomena [6]. Such class of compounds is with different types of hydrogen bonding [7–9]:

- 1. H-bonding of the type N−H···O between the −NH (hydrazone) group and C=O group;
- 2. intermolecular hydrogen bonding of the N–H \cdots O type of one molecule to another one;
- 3. the case is more favored. This is due to the presence of a broad band located at $870-965 \text{ cm}^{-1}$ which could be taken as a good evidence for the intermolecular hydrogen bonding.

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 NH₂ function. This confirms the formation of the azo compounds.
- The strong band observed at ~1110-1120 cm⁻¹ may be assigned to ν(N-N) vibration modes [9] and is affected on complexation. It is blue shifted and appeared as a weak band.
- 3. 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 ~1625–1610 cm⁻¹ for ligands. This is rather confirmed from the observation of Karabatores et al. [10] 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 1435 and 1520 cm⁻¹ combined with the tracing of a strong band at 1230 cm⁻¹ characteristic of NH stretching vibration. All these data with lack of the νC-O of enol in the IR spectrum lead us to assume the structure for this compound.

- 4. The spectra exhibit a very strong band at $\sim 1720 \text{ cm}^{-1}$. This is a powerful indicative to ν C=O.
- 5. In all complexes, 3480–3130 cm⁻¹ is observed. Such region is attributed to –NH group (3-phenylamine).
- 6. The absence of any peak attributable to the =N–NH $(3180 \text{ and } 3220 \text{ cm}^{-1})$ moiety implies that in solution, the ligands change to form. However, in solution and in the presence of uranyl ion, these compounds exist in equilibrium. The main change is observed in the azo stretching vibration, thus suggesting that the form prevails. The form reacts with uranyl ion by loss of proton (of hydrazone) (C=N–NH) as mononegative chelating agents producing (N₂)/(NH) mode of the free ligands.
- 7. New bands assigned to ν (NH) (hydrazone) in the free ligands are absent, suggesting the cleavage of intramolecular hydrogen-bonded ν NH [11] with subsequent deprotonation of NH group and coordination of nitrogen to the metal ion.
- 8. Introduction of a hydrazo group instead of N=N leads a change in the coordination mode of the azo group from the azo-nitrogen to the amine nitrogen (NH) (hydrazone).
- Coordination of the carbonyl oxygen and the hydrazone nitrogen in the chelate ring is supported by the appearance of new bands at 625–685 and 580–580 cm⁻¹, which are assigned to M–N and M–O, respectively.
- 10. The phenyl ring vibration appears at $1480-1510 \text{ cm}^{-1}$. The presence of a *p*-substituted benzene ring in the ligands as well as in the complexes is indicated by strong and sharp bands around $610-635 \text{ cm}^{-1}$. Bands at 2930-3030 cm⁻¹ for the ligands and at ~2970 cm⁻¹ for the complexes are assigned to ν (C–H) vibration of the aromatic system.
- 11. The strong bands around 3160 and 1615 cm⁻¹ in the free ligands are due to ν N–H and δ N–H. Practically, no affect on these frequencies after complexation precludes the possibility of complexation at (3-phenylamine) group.
- 12. An intensive strong band at 845 cm^{-1} in the free ligand spectrum is due to ν (C=S) which has been found to shift to lower frequency by \sim 50 cm⁻¹ in the complexes, pointing to the coordination of the sulphur to uranyl(II) atom.

3.3. ¹H NMR spectra

The proton magnetic resonance of the ligands and complexes has been recorded in DMSO–d₆ 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 NH(3-phenylamine) at ~9.0 ppm were not affected by dilution and disappear in the presence of D₂O and the first band also disappears in uranyl complex and the second shifted to ~8.8 ppm indicating the coordination of the nitrogen atoms with the metal ion. The shifts are in the sequence: p-NO₂ > p-Cl > H > p-OMe > p-CH₃.

3.4. Spectral studies

HL_n exhibits bands at 26,350–26,150 cm⁻¹ (CS) ($n \rightarrow$ π^*), 30,460–30,250 cm⁻¹ (CO) ($n \rightarrow \pi^*$), 32,980– $33.100 \,\mathrm{cm}^{-1}$ (h-bonding and association), 40,240- $39.890 \,\mathrm{cm}^{-1}$ (phenyl) (ph-ph*, $\pi - \pi^*$) [12] and 29,610-29,350 cm⁻¹ transition of phenyl rings overlapped by composite broad $\pi - \pi^*$ of azo structure. In the dioxouranioum(VI) complexes, the (CS and CO) $(n-\pi^*)$ transition shifts to lower energy. These shifts or the disappearance of the bands are indicative of coordination of the ligands to UO_2^{2+} . The dioxouranium complexes exhibit a new band at 24,490-24,310 cm⁻¹, which is assigned to the $^1\sum_g^u \rightarrow \,^3\pi_u$ transition, typical of OUO for the symmetric stretching frequency for the first excited state.

3.5. Complexation on uranyl ion spectra

Uranyl ion $UO_2^{2^+}$ is quite peculiar in its own structure and in 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 920–890 and 845–815 cm⁻¹ region as ν_3 and ν_1 , respectively (Table 2). The ν_3 values decrease as the donor characteristic increase as is observed for π -electron substituents, where the basicity of the donating atom increases.

The experimental results reveal an excellent linear relation between ν_1 and ν_3 with the slope corresponding to $(1 + 2M_{\rm O}/M_{\rm U})^{1/2}$ ($M_{\rm O}$ and $M_{\rm U}$ are the masses of oxygen and uranium atoms, respectively).

Instead of the linear relation between v_1 and v_3 frequencies, the El-Sonbati equation [13] has focused attention on their normalized differences, which do not depend on the masses of oxygen and/or uranium atoms.



Fig. 2. The variation of *p*-substituted Hammet's with (1) r_{U-O} (Å); and (2) F_{U-O} (mdyn Å⁻¹).

various lorce	constan	urs (mayne	es/A), U	-O distar	ices (A) and	. irrequencie	s (cm) v	and v3 of u	le isolated (U2 ⁻ polym	er complex	es					
Serial no. ^a	۳ı	ν'_1	ν3	ν'_3	$F_{\rm U-O}$	r_1	r_2	$(F_{U=0}^{S})_{t}$	$r_{\rm t}$	$(F_{\mathrm{U-O}}^{\mathrm{S}})_{\mathrm{o}}$	$r_{ m o}$	Error (%)	F _{UO} -UO ^{, b}	$\nu_1^{\ *c}$	$(F_{U=0}^{x})_{o}$	r_3	F _{UO} -UO ^{,b}
_	815	813.1	890	867.0	6.5381	1.7318	1.7476	6.0158	1.7638	6.2045	1.7577	3.14	-0.5278	824.3	6.0798	1.7617	-0.4660
5	820	817.6	895	872.3	6.6117	1.7279	1.7454	6.0847	1.7616	6.2806	1.7554	3.22	-0.5327	824.0	6.1087	1.7608	-0.5087
~	830	826.5	905	883.0	6.7603	1.7200	1.7412	6.2230	1.7572	6.4356	1.7506	3.42	-0.5430	824.2	6.1830	1.7584	-0.5869
4	840	835.4	915	893.6	6.9105	1.7123	1.7370	6.3702	1.7526	6.5910	1.7460	3.47	-0.5462	825.2	6.2662	1.7558	-0.6494
10	845	839.8	920	898.9	6.9862	1.7085	1.7350	6.4401	1.7505	6.6695	1.7438	3.56	-0.5521	826.0	6.3121	1.7544	-0.6838
(ν'_1, ν'_3) : sym	metric a	nd asymm	tric str	retching fr	equency wi	th neglect o	of the liganc	ls; $(F_{\rm U-0}^{\rm S})_{\rm f}$ j	s the true v	alue of force	constant; (1	$r_{\rm U-0}^{\rm rS}$ is the	constant calcula	ated with n	eglect of the	ligands; $(F_{\rm l})$	$(-0)_{0}$ is the
pand force cc	instant v	which is e	valuated	l by using	El-Sonbati	equation; r_1	t: internucle	ear distance	J-O calcul	ated by using	g the true va	alue of force c	onstant; r _o : inte	rnuclear d	istance U-O	calculated l	by using the
asymmetric s	tretchin	g frequenc	:y with I	neglect of i	the ligands;	r3: internuc	clear distanc	ce U-O calc	ulated by us	sing the symn	netric stretc	hing frequenc:	<i>r</i> ; <i>r</i> ₁ , <i>r</i> ₂ : internu	clear dista	nce U-O cal	culated by u	sing Badger

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Table 2

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

equation and Jones equation.

^b U-O force constant and UO, UO' interaction constant with neglecting the interaction of the UO bonds with the ligands, (F_{UO-UO}': bond-bond interaction)

Symmetric stretching frequency evaluated by using El-Sonbati equation.



Fig. 3. The relation between (1) ν_3 vs. r_n ; (2) ν_3 vs. r_2 ; and (3) ν_3 vs. r_3 .

Our objective is to get El-Sonbati equation from which the U-O bond force constant should be eventually served as a fairly accurate measure of the U-O bond distance in given compounds. The force constant for the U–O bond $[F_{U-O}]$ $(\text{mdyn } \text{\AA}^{-1})], (F_{U-O}^{S})_{t}, (F_{U-O}^{S})_{o} \text{ and } F_{UO,UO'} \text{ with neglecting}$ the interaction of the spectral data used herein are presented in Table 2; a plot of $v_1 + v_3$ and/or v_3 versus force constant for the U–O ($F_{\rm U-O}$ (mdyn Å⁻¹)) and the U–O bond distance ($r_{\rm U-O}$ (Å)) gives a straight line with the increase in the value of v_1 + v_3 and/or v_3 decreases $r_{\rm U-O}$ and increases the force constant of the U–O bond. There is also a straight line relationship between r_{U-O} and the *p*-substituent, Hammett's constant (σ^R) with negative slope, i.e. the higher the value of σ^R , the lower the r_{U-O} and the higher the force constant of the U-O bond (Fig. 2). Also, plotting of the r_1 , r_2 and r_3 (bond distance, $r_{\rm U-O}$) versus v_3 gives straight line with increase in the value of v_3 and decrease in r_{U-O} (Fig. 3). Our results also showed an inverse relationship between v_3 and $r_{\rm U-O}$. This can be explained. 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, $r_{\rm U-O}$ values can be arranged in the order, p-OCH₃ > p-CH₃ < H < p-Cl < p-NO₂, which are consistent with the values of their σ^R .

3.6. Force constant, F_{U-O} , and bond lengths, r_{U-O} , of the uranyl complexes

Due to small scattering power of the oxygen atom, report of the determination of U–O bond length of some uranyl complexes by X-ray study is scanty. From infrared spectra, the stretching and interaction force constants in the present complexes have been calculated [14–16]. The results are in turn used to evaluate U–O bond distances using Badger's formula, Jones equation [17,18] and El-Sonbati equation [13]. The values are given in Table 2 and such report is also found for other uranyl complexes [13,14,18,19]. The variation of bond length in the complexes is due to presence of electron-releasing or electron-withdrawing substituents in the equatorial position.

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