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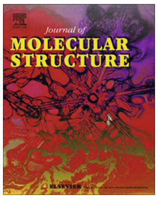

Polymer complexes. LVII. Supramolecular assemblies of novel polymer complexes of dioxouranium(VI) with some substituted allyl azo dye compounds

M.A. Diab, A.Z. El-Sonbati *, A.A. El-Bindary, M.Z. Balboula [1]

Chemistry Department, Faculty of Science, Damietta University, Damietta, Egypt

HIGHLIGHTS

- HL_{1-5} behaves as a chelating bidentate neutral ligand.
- HL_{1-5} were characterized by analytical and spectral methods.
- Ligands are suitable for building a supramolecular structure.
- Jones and El-Sonbati equations were used to calculate the U—O bond distances.
- The effect of Hammet constant is also discussed.

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ABSTRACT

A novel method to synthesize some dioxouranium(VI) polymer complexes of the general formula $[UO_2(L_n)_2(OAc)_2]$ (where HL_n = azo allyl rhodanine). The structure of the novel mononuclear dioxoutranium(VI) polymer complexes was characterized using elemental analysis, spectral (electronic, infrared, ^1H & ^{13}C NMR) studies, magnetic susceptibility measurements and thermal analysis. The molar conductivities show that all the polymer complexes are non-electrolytes. The IR showed that the ligand HL_n act as bidentate neutral through carbonyl group and imine group nitrogen atom forming thereby a six-membered chelating ring and concomitant formation of an intramolecular hydrogen bond. The υ_3 frequency of UO_2^{+2} has been shown to be an excellent molecular probe for studying the coordinating power of the ligands. The values of υ_3 of the prepared complexes containing UO_2^{+2} were successfully used to calculate the force constant, F_{UO} (10^{-8} N/Å) and the bond length R_{UO} (Å) of the U—O bond. A strategy based upon both theoretical and experimental investigations has been adopted. The theoretical aspects are described in terms of the well-known theory of 5d–4f transitions. Wilson's, matrix method, Badger's formula, and Jones and El-Sonbati equations were used to calculate the U—O bond distances from the values of the stretching and interaction force constants. The most probable correlation between U—O force constant to U—O bond distance were satisfactorily discussed in term of Badger's rule and the equations suggested by Jones and El-Sonbati. The effect of Hammet constant is also discussed.

1. Introduction

Substantial work has been done by El-Sonbati and coworkers [1–10] on heterocyclic azodyes derived from rhodanine and/or quinoline with various aromatic amines. However, there is no previous work on the complexes of allyl azo rhodanine. Azodyes 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.

Heterocyclic azo dye attract considerable interest and play an important role in development of the chemistry of chelates system due to their application as potential ligands for a large number of metals ions. Literature survey reveals an excellent work devoted to synthesis and characterization of azo dyes as well as their metal complexes [1–10]. It is well known that azo dyes and their metal complexes have been widely used in different fields such as high technology areas [11], biological studies [2].

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, υ_1, appearing between 800 and 900 cm^{-1}; an asymmetric stretching frequency, υ_3, appearing between 850 and 1000 cm^{-1}; and a bending frequency in the

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* Corresponding author. Tel.: +20 1060081581; fax: +20 572403867.
E-mail address: elsonbatisch@yahoo.com (A.Z. El-Sonbati).

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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] discuss 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 (υ_1) and (υ_3) O—U—O frequencies, which do not depend on the masses of oxygen and/or uranium atoms instead of the linear relation between υ_1 and υ_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 and Smith [13].

El-Sonbati [12,14–16] discuses 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.

Diab et al. [17–21] found out that the stability of multiple hydrogen bonded “dimmers” depends not only on the number of hydrogen bonds but also on the hydrogen bonding pattern. The importance of clarifying the structure and stability of hydrogen-bonded complexes has opened up an area of surface science that has attracted a considerable attention in the environmental chemistry.

Of late, a large number of complexes of rhodanine azodye have been prepared and characterized by magnetic and spectral studies [16–25]. In our laboratories the coordination behavior, 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.

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 [15–25], 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.

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 3-allyl-2-thioxo-1,3-thiazolidine-4,5-dione-5-[(4-derivatives phenyl) hydrazone]($HL_{1–5}$) and the properties of the first hydrazone uranyl supramolecular polymer complexes $[UO_2(HL_{1–5})_2(OAc)_2]_n$ were studied.

2. Experimental

All reagents used for the preparation of the ligand and polymer complexes were of analytical grade.

2.1. Reagents

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. 2,2′-Azobisisobutyronitrile (AIBN) was purified by fraction crystallization from EtOH [26]. The experimental technique has been described previously [1–10].

2.2. Preparation of 3-allyl-2-thioxo-1,3-thiazolidine-4,5-dione-5-[(4-derivatives phenyl) hydrazone]($HL_{1–5}$)

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 ml, 10.73 mmol) or a 4-derivatives aniline (**1**). 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 (**2**) was consecutively coupled with an alkaline solution of allyl rhodanine (10.73 mmol) (**3**) in 20 ml of pyridine. The orange precipitated, 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 desiccator over P_2O_5. The analytical data confirmed by expected composition (Table 1). The ligands were also characterized by ^1H NMR and IR spectroscopy. The reaction is shown in Scheme 1.

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

Compounds[c]	Λ_M[d]	Exp. (Calcd.) (%)				
		C	H	N	S	Metal
HL_1	–	50.70	4.24	13.44	20.20	–
		(50.82)	(4.12)	(13.68)	(19.8)	
$[(UO_2)_2(HL_1)_2(OAc)_2]_n$	9.90	36.10	3.3	8.66	12.93	24.15
1		(35.93)	(3.19)	(8.38)	(12.78)	(23.75)
HL_2	–	53.54	4.37	14.12	22.33	–
		(53.61)	(4.47)	(14.43)	(21.99)	
$[(UO_2)_2(HL_2)_2(OAc)_2]_n$	10.35	37.22	3.18	8.82	13.60	24.90
2		(37.11)	(3.30)	(8.66)	(13.20)	(24.54)
HL_3	–	52.11	4.09	15.31	23.51	
		(51.99)	(3.97)	(15.16)	(23.11)	
$[(UO_2)_2(HL_3)_2(OAc)_2]_n$	10.80	35.77	3.10	9.25	13.83	25.76
3		(35.67)	(2.97)	(8.92)	(13.59)	(25.27)
HL_4	–	46.10	3.11	13.77	20.86	–
		(46.23)	(3.21)	(13.48)	(20.55)	
$[(UO_2)_2(HL_4)_2(OAc)_2]_n$	11.48	34.26	2.82	8.90	13.40	24.77
4		(34.41)	(2.77)	(8.60)	(13.11)	(24.37)
HL_5	–	44.60	3.00	17.66	20.12	–
		(44.72)	(3.11)	(17.39)	(19.88)	
$[(UO_2)_2(HL_5)_2(OAc)_2]_n$	11.98	34.14	2.78	10.30	13.30	24.54
5		(34.04)	(2.74)	(9.93)	(12.97)	(24.11)

[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 as given in Fig. 1.

[d] Molar conductivity (Ω^{-1} cm^2 mol^{-1}) of 1.00×10^{-3} M DMF solutions at 25 ± °C.