



# Synthesis and Characterization of Dioxo-uranium(VI) Complexes of Some Aroylhydrazines and Their Schiff Bases With Acetone

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Received: 15 March 2008

Accepted: 11 September 2008.

## ABSTRACT

Some dioxouranium(VI) bis-complexes of ligands (LH); benzoylhydrazine (BH), salicyloylhydrazine (SalH), nicotinoylhydrazine (NH) and their Schiff bases with acetone ( $L'H$ ); isopropylenebenzoylhydrazine (IPBH), isopropylenesalicyloylhydrazine (IPSalH), isopropylenenicotinoylhydrazine (IPNH) in their both keto and enol forms have been prepared. Magnetic moment, electronic and infra-red spectral data, conductance and elemental analyses help describing the possible stereochemistry of the prepared complexes.

**Keywords:** aroylhydrazines, dioxouranium(VI), octahedral, schiff base.

## 1. INTRODUCTION

The Schiff base ligands obtained by condensation of diamines and triamines with various aldehyde/ketones are a class of ligands widely studied. Most studies are focused on complexes of the d-block elements, especially those of the first series. Dioxouranium(VI) complexes of mono/dibasic bi-, tri- or tetradentate Schiff base compounds have been reported. Complexes of the uranyl ion  $UO_2^{2+}$ , are of interest as they show flexible coordination geometries. Due to the spectral properties (absorption and luminescence) and excited-state electron-transfer properties of the  $UO_2^{2+}$  ion, dioxouranium(VI) complexes have possible applications in solar energy conversion systems [1].

Dioxouranium(VI) Schiff base complexes  $[UO_2(\text{Sal-OAP})(H_2O)]$ ,  $[UO_2(\text{Sal-OAP})(py)]$ ,

$[UO_2(\text{Sal-OAP})DMF]$ ,  $[UO_2(\text{Sal-OAP})(Et_3N)]$  (sal-OAP = orthoaminophenolsalicylideneiminato) [2] and  $[(UO_2(\text{sal-p-phdn}))]$  (sal-p-phdn = N, N'-p-phenylene-bis (salicylideneiminato) [3] have been prepared. Metal complexes of the Schiff base 2,5-dihydroxyacetophenone isonicotinoylhydrazone ( $LH_2$ ) synthesized by condensation of 2,5-dihydroxyacetophenone with isonicotinoylhydrazide in ethanol were prepared from salts of Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and  $UO_2^{4+}$  [4]. A novel series of  $UO_2^{2+}$  complexes showing two isomeric solid forms with 5-(4-derivatives phenyldiazo)-8-hydroxy-7-quinolinecarboxaldehyde, have been prepared [5].

Binary and ternary complexes of dioxouranium(VI) with 5-vinylsalicylaldehyde [6] and 8-hydroxy-7-quinolinecarboxaldehyde

behaving as bi-(O,O) and tetradentate ( $N_2O_2$ ) donors [7] have been prepared and characterized. New polymeric complexes of Cu(II), Co(II), Ni(II) and  $UO_2^{2+}$  with 5-(2' carboxyphenylazo)-8-hydroxyquinoline acting as a dibasic (bis-bidentate) chelating agent coordinating through CN, N=N, COOH and OH groups have been prepared and characterized [8]. 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 [9]. Dioxouranium(VI) Complexes with some other Schiff Bases derived from 4-Acetyl-2,3-Dimethyl-1-(4-Methylphenyl)-3-Pyrazoline-5-One and aromatic amines were reported as octacoordinated [10].

The synthesis, spectra and structure of  $[UO_2(3-EtOsalen)(H_2O)]H_2O$  [where (3-EtOsalen) is the Schiff base N,N'-ethylenebis(3-ethoxysalicylideneiminato)] are reported where  $UO_2^{2+}$  ion is coordinated to two nitrogen and two oxygen atoms of the ligand, with a water molecule completing the characteristic seven coordinate, pentagonal-bipyramidal geometry [1].

Some complexes of thorium(IV) and dioxouranium(VI) with the Schiff base of 2-hydroxy-1-naphthaldehyde condensed with 4-aminoantipyrine (HNAAP) with the general composition  $[ThX_4(HNAAP)_2]$  ( $X = Cl, Br, NO_3$  or  $NCS$ ),  $[ThX_4(HNAAP)_3]$  ( $X = I$  or  $ClO_4$ ),  $[UO_2X_2(HNAAP)_3]$  ( $X = Cl, Br, I, NO_3, NCS$  or  $CH_3COO$ ) or  $[UO_2(ClO_4)_2(HNAAP)_2]$  have been synthesized and characterized where neutral bidentate ligand coordinates through the azomethine nitrogen and the carbonyl oxygen [11].

The reactions of the Schiff base ligand 2,3-dimethyl-1-phenyl-4-salicylidene-3-pyrazolin-5-one (HL) with Co(II), Ce(III), and  $UO_2^{4+}$  in the presence of LiOH as a deprotonating agent yielded different types of

mononuclear complexes where HL is coordinated to the central metal atom as monoanionic tridentate ONO and/or monoanionic tetradentate ONON ligand. Also, the mixed ligand complexes of 2-aminopyridine, 8-hydroxy-quinoline, and oxalic acid were isolated [12]. Benzoylhydrazones and semicarbazones derived from 2,6-diacetylpyridine react with common dioxouranium(VI) compounds such as uranyl nitrate or  $[NBu_4]_2[UO_2Cl_4]$  to form air-stable complexes. 2,6-Diacetylpyridinebis(benzoylhydrazone), 2,6-diacetylpyridinebis(N4-phenylsemicarbazone) and the asymmetric proligand 2,6-diacetylpyridine(benzoylhydrazone)-(N4-phenylsemicarbazone) give yellow products of the neutral composition  $[UO_2(L)]$  possessing uranium atoms with distorted pentagonal-bipyramidal coordination spheres [13]. The complex  $[UO_2(L)(dmf)_2](NO_3)$  is formed by refluxing a suspension of HL [2-acetylpyridine-(2-aminobenzoylhydrazone)] with uranyl nitrate in methanol in the presence of a small quantity of triethylamine showing distorted pentagonal-bipyramidal geometry [14].

The complexes of the type  $UO_2(AAA)$ . MeOH where  $AAAH_2$  is a tridentate dibasic Schiff bases derived from salicylaldehyde, 5-chloro-, 5-bromo-, 5-nitro-, 3,5-dichloro-, 4-methoxy-, 5-methoxy- and 3-ethoxysalicylaldehyde and 2-hydroxy-1-naphthaldehyde and o-aminobenzyl alcohol, have been synthesized from uranylacetate and the Schiff base in methanol [15]. Again a series of dioxouranium(VI) complexes of the type  $[UO_2L_2X_2]$ , where L = bidentate Schiff base, derived from *p*-chloroaniline, *o*-anisidine, *o*-toluidine and *p*-phenitidine with 2-hydroxy-1-naphthaldehyde and  $X = Cl-, Br-, I-, NCS-, NO_3-, OAc-$  or  $0.5 SO_4^{2-}$  have been synthesized and characterized [16].

It is established that N-acylhydrazines can undergo enolization. In keto form ligands act

as neutral bidentate one. The secondary amido hydrogen can be removed during complex formation through enolization when ligands act as monobasic bidentate one. The enolization was enhanced by alkali. The Schiff base of these hydrazines with various aldehydes and ketones also obviously can undergo enolization. Attempts have been made to use benzoylhydrazine(BH), salicyloylhydrazine(SalH), nicotinoylhydrazine(NH) and their Schiff bases with acetone in both keto and enol form to prepare some complexes of dioxouranium(VI) ions.

## 2. METHODS AND MATERIALS

Uranyl nitrate hexahydrate was obtained from BDH Chemicals Ltd. Nicotinoylhydrazine and other chemicals used were obtained from the M/S Aldrich Chemicals Co. Inc. Ltd.

### 2.1 Preparation of Ligand LH

Ethylbenzoate or methylsalicylate (500 mmol) was added to hydrazine (500 mmol) for benzoylhydrazine (BH) and salicyloylhydrazine (SalH), respectively in a round bottomed flask fitted with a reflux condenser and a silica gel guard tube. It was heated to 130-140 °C under refluxed for several hours (21 hrs for BH, 5 hrs for SalH) with continuous stirring using magnetic stirrer where upon a white crystalline precipitate of SalH was formed whereas that of BH was formed when it was left to stand for 5 hrs. The product was filtered off and washed with ethanol and was recrystallized from same solvent (ethanol or water).

### 2.2 Preparation of Ligands L'H

Salicyloylhydrazine or benzoylhydrazine or nicotinoylhydrazine (100 mmol) was dissolved in acetone, stirred for about 20 minutes for isopropylsalicyloylhydrazine (IPSalH), isopropylbenzoylhydrazine (IPBH), isopropylene nicotinoylhydrazine

(IPNH), respectively and allowed to stand for crystallization. The white crystal obtained was filtered and washed with acetone and dried under vacuum over silica gel.

Prepared ligands are: Benzoylhydrazine, yield-80%, M.P.-110-112 °C; Salicyloylhydrazine, yield-80%, M.P.-142-144 °C; isopropylbenzoylhydrazine (IPBH), yield-70%, M.P.-139 °C; isopropylsalicyloylhydrazine (IPSalH), yield-70%, M.P.-230 °C; isopropylene nicotinoylhydrazine (IPNH), yield-70%, M.P.-157 °C.

### 2.3 Preparation of $[\text{UO}_2(\text{LH})_2](\text{NO}_3)_2$ and $[\text{UO}_2\text{L}_2]$

To the water (30 cm<sup>3</sup>) solution of ligands (LH) (4 mmol) dioxouranium(VI) nitrate hexahydrate,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (2 mmol) was added with continuous stirring. It was heated on a water bath for half an hour if necessary. This was then allowed to stand for crystallization. Product was filtered, washed with water and then with ethanol, finally dried under vacuum over silica gel. An aqueous solution of NaOAc was also added when  $[\text{UO}_2\text{L}_2]$  type complexes was prepared.

### 2.4 Preparation of $[\text{UO}_2(\text{L}'\text{H})_2](\text{NO}_3)_2$ and $[\text{UO}_2\text{L}'_2]$

Ligands (LH) (4 mmol) was taken in acetone (30 cm<sup>3</sup>). To this  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (2mmol) was added with continuous stirring. This was heated for half an hour on water bath if necessary. When coloured precipitate came out almost immediately. The precipitate was filtered, washed with distilled water and then with ethanol and was dried over silica gel under vacuum. An aqueous solution of Na-acetate was also added to prepare  $[\text{UO}_2\text{L}'_2]$  type complexes.

### 2.5 Physical Measurements

Melting point of the ligands and complexes were determined on an electrothermal melting

point apparatus. UV-absorption spectra were run of a Shimadzu UV-visible recording spectrophotometer (model-160). Infrared spectra were recorded on KBr pellets with Perkin-Elmer infrared spectrophotometer (Model-883). Magnetic moments were determined by the Gouy method. Conductivity measurements were performed on Philips conductivity meter (model-WPA CM-25) made by WPA, Saffron Walden, England.

## 2.6 Elemental Analyses

Elemental analyses of some of the

complexes were performed from Central Drug Research Institute (C.D.R.I), Lucnow, India. The analyses of the metal contents of the prepared complexes were done gravimetrically by the oxime [17].

The analytical data of the prepared complexes are given in Table 1.

## 3. RESULTS AND DISCUSSIONS

$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  reacts with the ligands in slight warm conditions, complete deprotonation of both ligand types is observed with the mandatorily addition of alkali, Na-acetate,

**Table 1.** Analytical and some physical data of complexes.

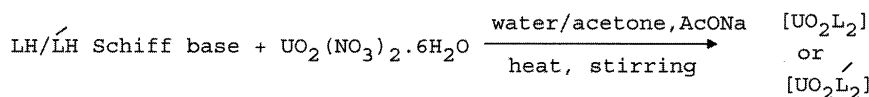
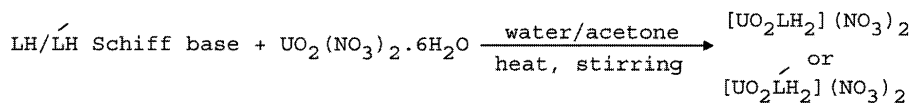
Sl. No.	Complexes	Color	% of Yield	M. P. °C	% MCH*	$\mu_{\text{eff}}$ B.M.	$\Lambda_m$ Ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>
1	$\text{UO}_2(\text{BH})_2(\text{NO}_3)_2$	Lt. yellow	80	210	M-35.1(35.7) C- 25.8(25.22 ) H- 3.49(2.42)	-	172.6
2	$\text{UO}_2(\text{BH})_2$	Yellow	70	>260	M-43.2(44.0) C-30.12(31.10) H-2.91(2.61)	-	14.3
3	$\text{UO}_2(\text{IPBH})_2(\text{NO}_3)_2$	Lt. yellow	80	225	M- 29.9(31.8) C-31.82(32.16) H-3.47(3.24)	Dia	180.5
4	$\text{UO}_2(\text{IPBH})_2$	Yellow	70	>260	-	Dia	18.3
5	$\text{UO}_2(\text{SalH})_2(\text{NO}_3)_2$	Lt. brown	90	205	M-33.5(34.0)	-	165.4
6	$\text{UO}_2(\text{SalH})_2$	Brick-red	80	>260	M-40.6(41.6)	Dia	19.3
7	$\text{UO}_2(\text{IPSalH})_2(\text{NO}_3)_2$	Lt. brown	85	200	M-30.3(30.5)	-	170.1
8	$\text{UO}_2(\text{IPSalH})_2$	Lt. yellow	80	>260	M-35.2(36.4)	Dia	20.5
9	$\text{UO}_2(\text{NH})_2(\text{NO}_3)_2$	Brownish	85	>260	M-35.1(35.6)	-	186.1
10	$\text{UO}_2(\text{NH})_2$	Yellow	75	>260	M-42.7(43.9)	-	18.8
11	$\text{UO}_2(\text{IPNH})_2(\text{NO}_3)_2$	Lt. yellow	80	200	M-30.4(31.8)	-	179.6
12	$\text{UO}_2(\text{IPNH})_2$	Lt. yellow	70	>260	M-38.2(38.3)	Dia	20.7

M.P. = melting point, Lt. = light, MCH= metal-carbon-hydrogen, dia=diamagnetic

\* Values in parentheses indicate calculated values.

and neutral dioxouranium complexes are formed. As the ligand dissolved completely in general solvents, reaction proceed is shown by the color change of the reaction mixture. Yellow precipitates are formed upon cooling,

which have been isolated and characterized by elemental analysis, IR and other conventional methods. Dioxouranium(VI) complexes of Schiff base ligands were synthesized by the general procedure according to:



Microanalytical data as well as metal and nitrate estimations are in good agreement with stoichiometry proposed for complexes (Table 1). All complexes exhibited high melting points, indicating a strong bonding between the ligands and metal ion. All complexes are stable at room temperature. The yields of the purified dioxouranium(VI) complexes for this general procedure are in the range 70-85%. The complexes are sparingly soluble in methanol, ethanol, acetone and chloroform, moderately soluble in hot acetonitrile and soluble in dimethylformamide and dimethylsulfoxide.

### 3.1 Spectroscopy

#### 3.1.1 Characterization of Ligand

In the ligand under investigation, three functional groups namely CO, OH and CN are of great interest in the infrared spectra. Infrared spectra of the ligands show broad, medium intensity bands at 3400, 2940 and 860  $\text{cm}^{-1}$  due to the stretching frequency of the OH and stretching vibration of hydrogen-bonding. Shoaib *et al.* [5], Mubarak *et al.* [7,9] and El-Sonbati *et al.* [8] have reported in detail studies the different types of hydrogen under investigation.

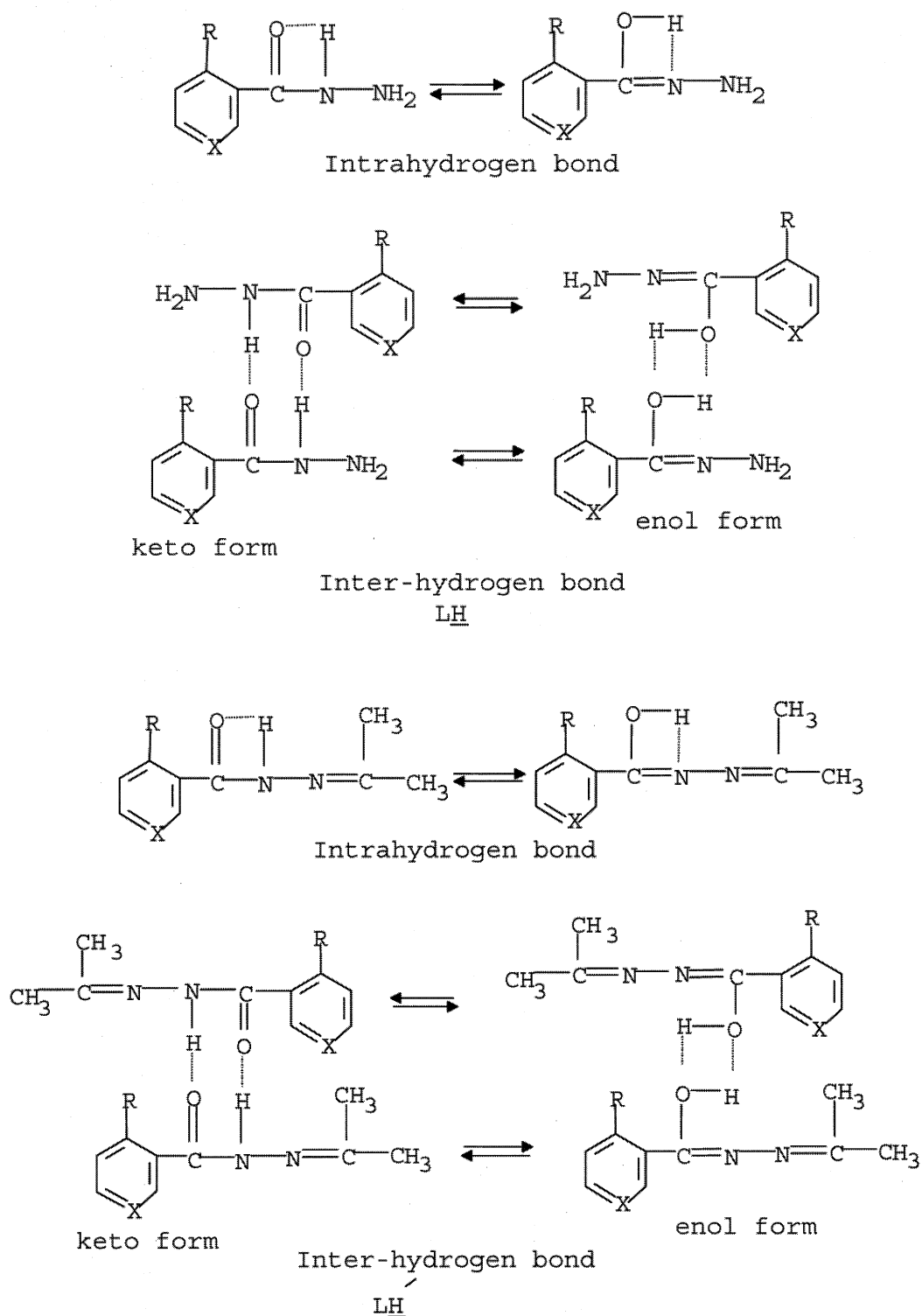
(a) Intra-molecular hydrogen bonding, ( $\text{N}-\text{H} \cdots \text{O}$ ,  $\text{O}-\text{H} \cdots \text{N}$ ) (Figure 1) exists

between hydrogen (enolic OH) and ketonic (CO) or nitrogen of azomethine group (CN) in a same molecule.

(b) Intermolecular hydrogen bonding results from two enolic OH groups, ( $\text{O}-\text{H} \cdots \text{O}-\text{H}$ ) and N-H of CN with CO, ( $\text{N}-\text{H} \cdots \text{O}$ ) between two molecules (Figure 1). The strong band at 860  $\text{cm}^{-1}$  is an indication of the existence of the ligand in a diametric skeleton. The ligands exist in an associated structure through intermolecular hydrogen bond. Data observed in the IR spectrum of ligands suggest the structures shown in Figure 1 [5,7,8]. This could be confirmed by the appearance of the high-frequency band (approx. 3500  $\text{cm}^{-1}$ ) as a result of intermolecular hydrogen bonding and that at lower frequency (approx. 2900  $\text{cm}^{-1}$ ) due to the intra-molecular hydrogen bonding [18].

#### 3.1.2 Characterization of Complexes

On the basis of literature evidences assignments of selected characteristic IR bands (4000–200  $\text{cm}^{-1}$ ) for the free ligands and its uranyl complexes have been given in Table 2 which indicate the bonding site of the primary ligand molecule when complexed with uranyl ion  $\text{UO}_2^{2+}$ . It also assumes the structural properties of the complexes.



**Figure 1.** Hydrogen bonding of ligand molecules.

**Table 2.** Infrared spectral and electronic spectral data of prepared complexes.

Cationic Complexes	Assignments (cm <sup>-1</sup> )						Electronic spectral data (nm)
	$\nu$ N-H	$\nu$ C=O	$\nu$ C-N	$\nu$ U=O=U	$\nu$ U-O	$\nu$ U-N	
1. $\text{UO}_2(\text{BH})_2(\text{NO}_3)_2$	3215w	1647s	1364vs	932vs	534s	378m 337m	390flsh, 320sh, 276, 249
2. $\text{UO}_2(\text{NH})_2(\text{NO}_3)_2$	3218w	1633s	1356m	921vs	544m 521m	433m 398m	470flsh, 388, 364, 284, 223
3. $\text{UO}_2(\text{SalH})_2(\text{NO}_3)_2$	3219s	1648s	1319m 1379w	927vs	567m 484m	414m	350flsh, 300, 279, 271, 255
4. $\text{UO}_2(\text{IPBH})_2(\text{NO}_3)_2$	3183m	1654s	1385vs 1380vs	933vs	531s	424w 376m	320sh, 270, 253
5. $\text{UO}_2(\text{IPNH})_2(\text{NO}_3)_2$	3220w	1653vs	1380vs	941s	528s	447w 398w	470, 388, 364, 284, 223
6. $\text{O}_2(\text{IPSalH})_2(\text{NO}_3)_2$	3292w 3221m	1647m	1383ms 1327m	926vs	566m 482w	416m	388, 364, 284, 223
Neutral Complexes	$\nu$ N-H	$\nu$ C=N	$\nu$ C-O	$\nu$ U=O=U	$\nu$ U-N	$\nu$ U-O	Electronic spectral data
7. $\text{UO}_2(\text{BH})_2$	3250w	1632s	1344w 1296w	926vs	490w	451vs	308sh, 270, 245
8. $\text{UO}_2(\text{NH})_2$	3187m	1602s	1336s 1284vs	898vs	523s	425m 385m	370, 271, 256
9. $\text{UO}_2(\text{SalH})_2$	3280w	1635m	1324m 1253m	933vs	579m 527w	375m	350, 302, 285, 268, 258
10. $\text{UO}_2(\text{IPBH})_2$	-	1645m	1240w	933vs	484w	409w	320flsh, 270, 256
11. $\text{UO}_2(\text{IPNH})_2$	-	1651m	1288w	939vs	531w	399m	300sh, 273, 241
12. $\text{UO}_2(\text{IPSalH})_2$	-	1633s	1224w	933vs	485w	444w	398, 392, 273, 241

W = weak, s = strong, vs = very strong, m = medium, flsh = flat shoulder, sh = shoulder

The O—H stretching of the free ligand (enol form) is expected in the region 3500-3300 cm<sup>-1</sup> [5]. However, the O-H stretching frequency is dislocated to around 2583 cm<sup>-1</sup> due to the hydrogen bridge OH...N=C [1]. A sharp band appearing in the region 3200-3292 cm<sup>-1</sup> for both ligands and complexes is

corresponding to NH stretching in bidentate neutral and monobasic forms [6,19]. Upon complexation, the band in this region disappears in case of enol form of L'H ligand indicating the enolization of the ligand [20]. A medium absorption band at ~3400 cm<sup>-1</sup> presents both in the ligands and complexes

assigned to the phenolic OH of the ligand in SalH or IPSalH. The complex and ligands show bands for C=O (keto form) and C=N (enol form) groups. The stretching frequency of carbonyl group  $\nu(\text{C=O})$  ( $1670\text{ cm}^{-1}$ ) disappears and a new band appears at  $\sim 1650\text{ cm}^{-1}$  due to the formation of C=N bond [6,7,14,20]. A negative shift of the band assigned to  $\nu(\text{C=O})$  of the free ligand ( $1670\text{ cm}^{-1}$ ) to a lower value ( $1633\text{--}1654\text{ cm}^{-1}$ ) by about  $15\text{--}20\text{ cm}^{-1}$  in its complexes, is consistent with coordination of the carbonyl oxygen to the central uranyl ion [5,7,18,21]. The azomethine stretch  $\nu(\text{C=N})$  is observed at lower frequency ( $1602\text{--}1651\text{ cm}^{-1}$ ) to complexes of enolic form of the corresponding ligands indicating the nitrogen coordination of the azomethine group of the Schiff bases [1,2,10,22]. This lowering is due to the reduction of the electron density in the azomethine link due to coordination of the nitrogen atom to the uranyl ion. The intensity of the band in this region is very high compared to those in the IR spectra of the ligands, which appears to be due to its origin in the stretching vibration mode of the conjugate C=N-N=C grouping analogues to those of azine ( $\text{L}'\text{H}$ ), showing the participation of the enolic oxygen in coordination [20].

Bands appearing at  $1319\text{--}1385\text{ cm}^{-1}$  have been assigned to  $\nu\text{C-N}$  (for keto) and that for  $\nu\text{C-O}$  are assigned to  $1224\text{--}1296\text{ cm}^{-1}$  (for enol) complexes [1,8]. The  $\nu(\text{C-O})$  of the ligand is shifted positively with a split band at in each of the complexes; this is because, while coordinating to the uranyl, ( $\text{UO}_2^{2+}$ ) ion, the ligand molecule undergoes deprotonation, generating a U-O linkage. These changes in IR spectra of the ligand on bonding to the metal ions occur through a covalent linkage with the oxygen atom of the enolic group [6,7]. The bands at  $455\text{--}445\text{ cm}^{-1}$  in the complexes are then assignable to  $\nu(\text{U-O})$ , while  $\nu(\text{U-N})$  is assigned to the medium band

at  $\sim 315\text{ cm}^{-1}$  [1,2, 7,12]. On the basis of the above studies bands appearing in the region  $468\text{--}584\text{ cm}^{-1}$  have been assigned to  $\nu\text{U-O}$  and  $\nu\text{U-N}$  bands for have been assigned to  $389\text{--}462\text{ cm}^{-1}$ .

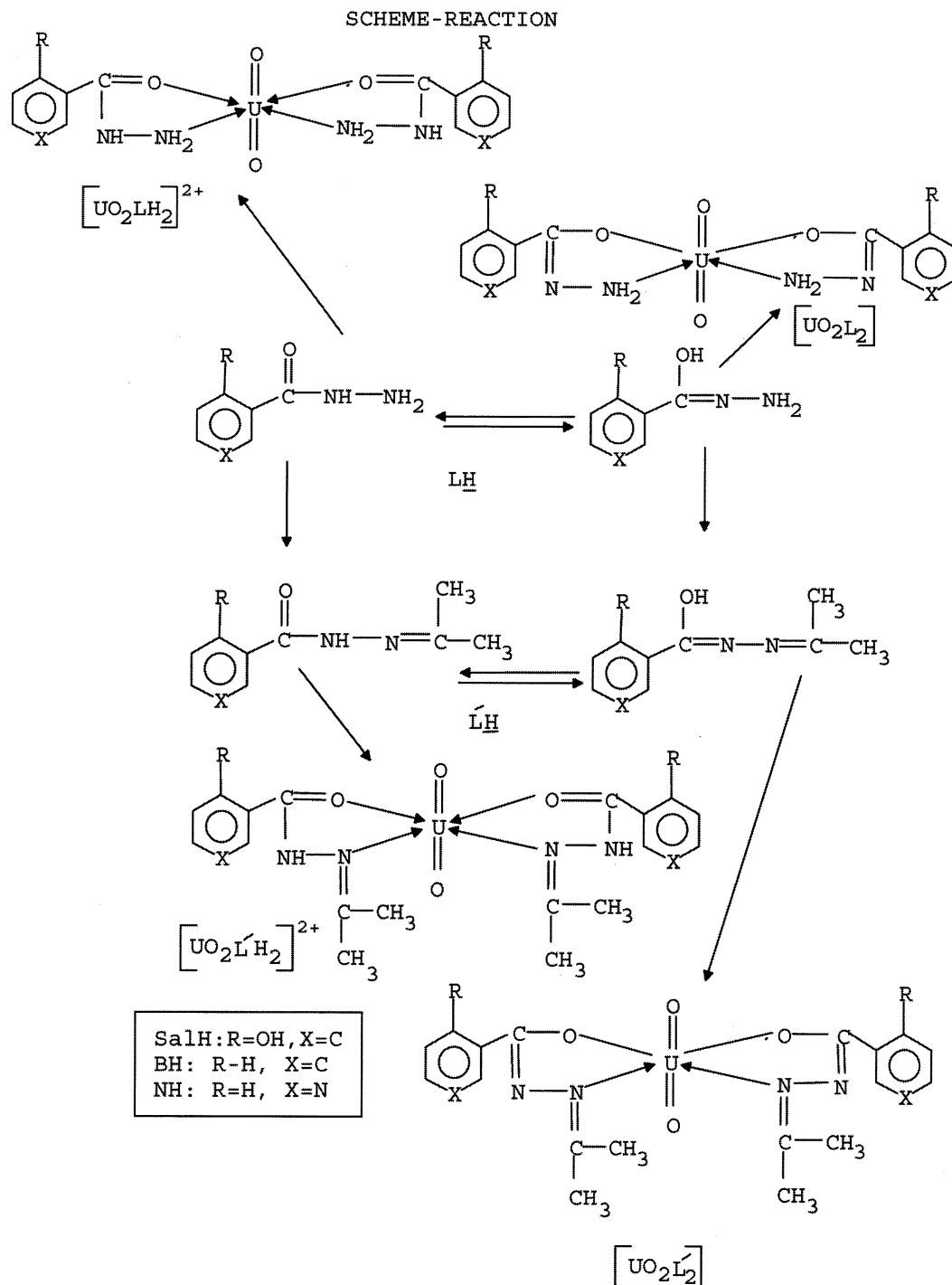
IR bands due to the  $\text{UO}_2$  group in the regions  $865\text{--}960\text{ cm}^{-1}$  and  $785\text{--}880\text{ cm}^{-1}$  have been assigned to  $\nu_{\text{as}}(\text{O=U=O})$  and  $\nu_{\text{s}}(\text{O=U=O})$ , respectively [6]. The bands appearing in presently prepared complexes in the region  $880\text{--}1000\text{ cm}^{-1}$  are attributed to the asymmetric stretching vibrations for  $\text{O=U=O}$  group [1,3,6,8,12-14,20,22,23]. The IR frequency of the  $\text{O=U=O}$  unit is found at  $908\text{ cm}^{-1}$  and is in accord with the expected value for a cationic uranyl complex [21]. The U=O double bonds show characteristic IR bands between  $900\text{--}905\text{ cm}^{-1}$ . This value is in accord with the neutral uranyl complexes in reference [21].

A band at  $\sim 1390\text{ cm}^{-1}$  which is not present in the spectra of the free ligands as well as in the corresponding product of  $[\text{UO}_2\text{L}_2]$  or  $[\text{UO}_2\text{L}'_2]$  suggests the presence of nitrate anions [10,12,24].

### 3.2 Electronic Spectra

The electronic spectral data for the present complexes are given in Table 2, which was recorded on DMF solution. Electronic spectra of the ligands and  $\text{UO}_2^{2+}$  complexes studied herein are almost identical with the slight splitting and shifting of the band positions. Upon complexation, the ligand band shifts to longer wavelength and infers that the uranium-ligand interaction is strong in these complexes. Electronic spectra of similar Schiff-base ligands have been reported. The absorption bands appear in the regions  $300\text{--}400$ ,  $260\text{--}284$  and  $223\text{--}258\text{ nm}$ . The weak band above  $260\text{--}285\text{ nm}$  is assigned to  $n\text{--}\pi^*$  transitions, while the absorption band at  $223\text{--}258\text{ nm}$  is assigned to  $\pi\text{--}\pi^*$  transitions, which involves molecular orbitals essentially localized





**Figure 2.** Suggested reaction mechanism and chemical structures of dioxouranium(VI) complexes.

on the C-N group and the benzene ring, thus the transition involves the azomethine group. The weak bands at  $\sim 400$  nm (DMF) are assigned to the  $^1E_g^+ \rightarrow ^3\pi_u$  transition. However, the typical band of  $\text{UO}_2^{2+}$  expected around 300-370 nm seems to be overlapped by fairly strong ligand-to-metal charge-transfer bands. These charge-transfer transitions probably occur from the n-orbitals of the Schiff base to the f-orbitals of uranium [1,9,20].

### 3.3 Conductivity Measurement

The molar conductance was performed on DMF solution and values are shown in Table 1. The low conductance of the complexes,  $[\text{UO}_2\text{L}_2]$  and  $[\text{UO}_2\text{L}'_2]$  indicates their non-electrolytic nature, when high conductance of the complexes,  $[\text{UO}_2(\text{LH})_2](\text{NO}_3)_2$  and  $[\text{UO}_2(\text{LH}')_2](\text{NO}_3)_2$  indicates their electrolytic nature which are tentative for the complexes. These data suggest that the nitrate ions are out of the coordination sphere in these complexes.

### 3.4 Magnetic Measurement

The magnetic susceptibility of the complexes were found to be negative indicating the complexes to be diamagnetic as expected  $f^0$ ,  $5f^06d^07s^0$ , U(VI) complexes possessing the 6+ oxidation state. The magnetic measurements of the dioxouranium (VI) complexes are independent of field strength and temperature and the ground states of dioxouranium(VI) compounds contain no unpaired electrons. This is consistent with diamagnetic behaviour expected for the U(VI) electronic spectra of complexes. The absence of any band above 500 nm in UV-visible region indicates the absence of d-d transition confirming the  $6d^0$ -system of  $\text{UO}_2^{2+}$  moiety.

### 3.5 Geometry

The  $\text{UO}_2^{2+}$  ion is coordinated to nitrogen and oxygen atoms of the ligand completing

the five coordinate chelate. The fact that the complexes with  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  involving 1:2  $\text{UO}_2^{2+}$  to ligand ratio giving solid complexes (Table 1), have been isolated. It clearly illustrates that the ligands under study does not introduce sufficiently severe steric hindrance as to preclude the formation of complexes, also steric features and arrangement in space can also favourably influence the stabilization of 1:2 complexes. The elemental analysis of the compound indicates the presence of two ligands per  $\text{UO}_2^{2+}$  unit. Uranyl nitrate reacts with LH, L'H in water to yield a yellow complex of the composition  $[\text{UO}_2\text{L}_2]$  or  $[\text{UO}_2\text{L}'_2]$  for neutral and in acetone for  $[\text{UO}_2(\text{LH})_2](\text{NO}_3)_2$  or  $[\text{UO}_2(\text{L}'\text{H})_2](\text{NO}_3)_2$  cationic complexes. Therefore both neutral and cationic complexes possess six coordinated geometry with the central metal ion for but it is absolutely difficult to elucidate without crystal experiment.

## 4. CONCLUSION

The proposed structure of uranyl complexes has been given in reaction scheme in Figure 2. The analytical and physical measurement data of the complexes indicate the ligands LH and L'H to act as bidentate coordinating through ON donor atoms and both types of ligand undergo deprotonation during complexation with  $\text{UO}_2^{2+}$  in presence of alkali to form neutral bis-ligated complex.

## REFERENCES

- [1] Signorni O., and Dockal E.R., Synthesis and characterization of aquo $[\text{N},\text{N}'\text{-ethylenebis(3-ethoxysalicylideneaminato)}]$ dioxouranium(IV), *Polyhedron*, 1996; **15**(2): 245-255.
- [2] Salbek S.A., and Teleb S.M., Infrared spectra of new dioxouranium(VI) solid complexes with tridentate Schiff bases  $[\text{UO}_2(\text{sal-OAP}(\text{L}))]$  ( $\text{L}=\text{H}_2\text{O}$ , Py, DMF AND  $\text{Et}_3\text{N}$ ), *J. Phys. Chem. Solids*, 1993; **54**(4): 489-493.

- [3] Nour E.M., Alnaimi I.S., and Alem N.A., Spectroscopic studies on the uranyl-Schiff bases solid complex  $[N,N'-p\text{-phenylene bis(salicylideneiminato)UO}_2]$ , *J. Phys. Chem. Solid*, 1992; **53**(1): 197-201.
- [4] Mandlik P.R., and Aswar A.S., Schiff base metal complexes of chromium(III), manganese(III), iron(III), oxovanadium(IV), zirconium(IV) and dioxouranium(VI), *Polish J. Chem.*, 2003; **77**:129-135.
- [5] Shoaib A.F., El-Bindary A.A., El-Sonbati A.Z., and Younes R.M., Stereochemistry of new nitrogen containing heterocyclic aldehyde VI. Novel structural and properties models of uranyl with quinoline azodyes, *Spectrochimica Acta Part A*, 2001; **57**: 1683-1691.
- [6] El-Sonbati A.Z., El-Bindary A.A., and Rashed I.G.A., Polymer complexes XXXVII novel models and structural of symmetrical poly-Schiff base on heterobinuclear complexes of dioxouranium(VI), *Spectrochimica Acta Part A*, 2002; **58**: 1411-1424.
- [7] Mubarak A.T., Novel supramolecular assembly of symmetrical mixed-metal-ligand complexes of dioxouranium(VI), *Spectrochimica Acta Part A*, 2006; **65**:1197-1207.
- [8] El-Sonbati A.Z., Belal A.A.M., El-Wakeel S.I., and Hussien M.A., Stereochemistry of new nitrogen containing heterocyclic compounds X. Supramolecular structures and stereochemical versatility of polymeric complexes, *Spectrochimica Acta Part A*, 2004; **60**: 965-972.
- [9] Mubarak A.T., Structural model of dioxouranium(VI) with hydrazono ligands, *Spectrochimica Acta Part A*: 2005; **61**: 1163-1170.
- [10] Maurya R.C., Mishra D.D., Pandey M., Shukla P., and Rathour R., Synthesis and spectral studies of octacoordinated dioxouranium(VI) complexes with some Schiff bases derived from 4-Acetyl-2,3-Dimethyl-1-(4-Methylphenyl)-3-Pyrazoline-5-One and aromatic amines, *Synth. React. Inorg. Met. Org. Chem.*, 1993; **23**(1): 161-174.
- [11] Agarwal R.K., and Prarash J., Synthesis and characterization of thorium(IV) and dioxouranium(VI) complexes of 4-[N(2-Hydroxy-1-Naphthalidene)amino] Antipyrine, *Polyhedron*, 1991; **10**(20/21): 2399-4403.
- [12] El-wahab Z.H.A., Mashaly M.M., and Fahemim A.A., Synthesis and characterization of cobalt(II), cerium(III), and dioxouranium(VI) complexes of 2,3-dimethyl-1-phenyl-4-salicylidene-3-pyrazolin-5-one mixed ligand complexes, pyrolytic products, and biological activities, *Chem. Pap.* 2005; **59**(1): 25-36.
- [13] Gatto C.C., Lang E.S., Jagst A., and Abram U., Dioxouranium(VI) complexes with 2,6-acetylpyridinebenzoylhydrazones and semicarbazones, *Inorg. Chim. Acta*, 2004; **357**: 4405-4412.
- [14] Gatto C.C., Lang E.S., Burrow R.A., and Abram U., Syntheses and structures of 2-acetylpyridine-(2-amino-benzoylhydrazone) and its dioxouranium(VI) complex, *J. Braz. Chem. Soc.*, 2006; **17**(8): 1612-1616.
- [15] Syamal A., and Singhal O.P., New dioxouranium(VI) complexes with tridentate dibasic Schiff bases containing ONO donor sets, *Transition Met. Chem.*, 1979; **4**:179-182.
- [16] Rajaram V., Paulraj K., and Ramalingam S.K., Dioxouranium(VI) complexes of some bidentate Schiff bases, *Transition Met. Chem.* 1983; **8**: 335-337.
- [17] Vogel A. I., *Quantitative inorganic analyses*, 1961; London.
- [18] Mubarak A.T., Supramolecular structures of oxovanadium(IV) polymeric complexes containing quinoline azodyes, *Designed Monomers and Polymers*, 2005; **8**(1): 1-10.

- [19] Mubarak A.T., and El-Assiery S.A., Supramolecular structures and properties models of macrocyclic polymer complexes, *Appl. Organometal. Chem.* 2004; **18**: 343-352.
- [20] Yang C.T., Ranford J.D., and Vittal J.J., Synthesis, characterization and biological activity of dioxouranium(VI) complexes of acyldipyridoxal hydrazones, *Synth. and React. in Inorg., Met.-Org. and Nano-Met. Chem.*, 2005; **35**:71-82.
- [21] Gatto C.C., Lang E.S., Kupfer A., Hagenbach A., Wille D., and Abram U., Dioxouranium complexes with acetylpyridine benzoylhydrazones and related ligands, *Z. Anorg. Allg. Chem.* 2004; **630**: 735-741.
- [22] Nag J.K., Das D., Pal S., and Sinha C., Synthesis and spectral characterization of homo- and hetero-dinuclear complexes with a new septadentate Schiff base ligand, *Proc. Indian Acad. Sci. (Chem. Sci.)*, 2001; **113**(1): 11-20.
- [23] El-Tabl H.M., El-Saied F.A., and Ayad M.I., Manganese(II), iron(III), cobalt(II), nickel(II), copper(II), zinc(II), and uranyl (VI) complexes of N-(4-formylantipyrine) benzothiazol-2-ylacetohydrazide, *Synth. and React. in Inorg. and Met.-Org. Chem.*, 2002; **32**(7): 1245-1262.
- [24] Gatto C.C., Lang E.S., Kupfer A., Hagenbach A., and Abram U., Mono-, Di- and trinuclear dioxo complexes of uranium containing hydrazonato and azomethine ligands, *Z. Anorg. Allg. Chem.*, 2004; **630**: 1286-1295.