

Dioxouranium(VI) Complexes of Some Monovalent Bidentate Schiff Base Ligands Derived from Aniline

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ABSTRACT

Several new dioxouranium(VI) complexes of Schiff bases [LH], derived from o-hydroxyaldehyde or ketone, 2-hydroxy-1-naphthaldehyde and aniline have been prepared and characterized on the basis of elemental analyses, IR and electronic absorption spectra and magnetic susceptibility measurements. The results suggest that the Schiff base is a monovalent anion with bidentate ON donor atoms of the phenolic oxygen and the azomethine nitrogen atoms. The formulae were found to be UO_2L_2 for the 1:2 non-electrolytic complexes and six-coordinate structure has been proposed for the complexes.

Key words: Aniline, dioxouranium(VI), o-hydroxyaldehyde or ketone, Schiff base

INTRODUCTION

Transition elements of Group IV, V and VI are known to form mononuclear oxocations of the type MO^{n+} and MO_2^{n+} . The most thoroughly investigated, best characterized and most stable oxometal cations are the dioxouranium(VI), dioxomolybdenum(VI) and oxovanadium(IV) ions. The strongly-bound oxygens of these oxometal cations remain intact during chemical reactions and produce one or more additional absorption bands beyond those normally available in transition metal complexes. The formation of multiple covalent bonds to oxygen by uranium has been explained theoretically. The tendency of oxygen to delocalise its $p\pi$ electrons away from its highly-compact valence shell by forming π bonds with π electron acceptor metals accounts for the formation of metal oxygen bond, at least qualitatively. Complexes of the uranyl ion, UO_2^{2+} , are of interest since they show seven-coordinate, pentagonal-bipyramidal geometry (Gatto et al., 2004). 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 (Signorni and Dockal, 1996).

The Schiff base ligands obtained by condensation of various amines with salicylaldehyde/substituted salicylaldehydes are a class of ligands widely studied. Most studies are especially those of the first transition series. The Schiff base complexes with many transition metal ions, focused on complexes of the d-block

elements, have attracted considerable interest because of their growing importance as model molecules for biological systems such as oxygen carriers (Soliman and Mohamed, 2004; Syamal, 1978; Salam and Chowdhury, 2000, 2003).

The dioxouranium(VI) complexes with tetradentate Schiff bases have been the subject of many investigations, while the oxouranium complexes with bi- or tridentate Schiff bases seem to be fewer in the literature (El-Tabl et al., 2002; Mandlik and Anwar, 2003). The tridentate dibasic Schiff base ligands behave as an ONO-donor ((El-Tabl et al., 2002) and react with the uranyl salts to form two types of complexes, depending on the molar ratio of the reactions.

However, little attention has been given to Schiff bases of ONS donor system. Co(II), Cu(II) and Zn(II) complexes of such Schiff base have been prepared and characterized (Soliman and Linert, 1999). Reaction modes of nickel(II) ion with the monodentate ligand diethylamine and the tridentate ligand 2-thiophenyl-1-hydroxysalicylaldimino were studied (Elerman et al., 1996). Square planar nickel(II) complexes of ONS donor Schiff base ligands and triphenylphosphine were reported (Tamizh et al., 2009). Several oxovanadium(IV) complexes of Schiff bases derived from salicylaldehyde and 3-aminothiophenol were described (Syamal, 1978). Dioxouranium(VI) complexes of some aroylhydrazines (benzoylhydrazine, salicyloylhydrazine, nicotinoylhydrazine) and their Schiff bases with acetone have been characterized where ligand acted as bidentate using NO-donor set (Chowdhury et al., 2008). The aim of this work is to study the behaviour, prepare and investigate the structure of the chelates dioxouranium(VI), UO_2^{2+} , complexes of the bidentate Schiff base ligands derived from o-hydroxyaldehyde or ketone, 2-hydroxy-1-naphthaldehyde and aniline, having as ON donor atoms.

EXPERIMENTAL

Uranyl nitrate hexahydrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, was obtained from BDH Chemicals Ltd. Salicylaldehyde (Sal)/substituted salicylaldehyde, 5-chloro-salicylaldehyde ($^5\text{Cl-Sal}$), 5-bromo-salicylaldehyde ($^5\text{Br-Sal}$), 2-hydroxyacetphenone (HAP), 2-hydroxypropiophenone (HPP), 2-hydroxy-1-naphthaldehyde (HNP), aniline (Ani) and other chemicals used were obtained from the M/S Aldrich Chemicals Co. Ltd.

Preparation of Ligand LH

Salicylaldehyde or substituted salicylaldehyde (Sal), 2-hydroxyacetphenone (HAP), 2-hydroxypropiophenone (HPP), 2-hydroxy-1-naphthaldehyde (HNP) (10 mmol each) were reacted with aniline (Ani) in a round bottom flask, containing 50 mL ethanol, fitted with a reflux condenser and a silica gel guard tube. Each mixture was refluxed for 30 min with continuous stirring, using magnetic stirrer. The mixture was then cooled in ice-bath and kept over night where upon crystalline precipitate of respective ligands separated out. The product was filtered off, washed with ethanol and dried in *vacuo* over calcium chloride. Colour, yield and melting points of prepared Schiff base ligands are given in Table 1.

Table 1. Colour, yield and melting points of the prepared Schiff base ligands.

Sl. No.	Ligands	Empirical formula	Physical state	Colour	% Yield	MP °C
1	Sal-AniH	HO(C ₆ H ₄)CH=N(C ₆ H ₅)	Solid	Pale green	80	48
2	BrSal- AniH	HO(C ₆ H ₃ Br)CH=N(C ₆ H ₅)	Solid	Orange	85	112
3	ClSal- AniH	HO(C ₆ H ₃ Cl)CH=N(C ₆ H ₅)	Solid	Orange	80	100
4	HAP- AniH	HO(C ₆ H ₄)C(CH ₃)=N(C ₆ H ₅)	Liquid	Lt. yellow	---	---
5	HPP- AniH	HO(C ₆ H ₄)C(C ₂ H ₅)=N(C ₆ H ₅)	Liquid	Lt. orange	---	---
6	HNP- AniH	HO(C ₁₀ H ₆)CH=N(C ₆ H ₅)	Solid	Deep orange	80	62

Preparation of complexes, UO₂L₂

4 mmol of respective ligand (LH) was taken in a round bottom flask containing 20 mL of mixed solvent of dichloromethane and ethanol by 10:1 (v/v). At reflux UO₂(NO₃)₂.6H₂O (2 mmol) was added to this with continuous stirring when colour changed immediately. The mixture was refluxed for one and half an hour on water bath when coloured precipitate came out. Mixture was then kept overnight. The precipitate was filtered in sintered funnel, washed with same solvent, and dried in *vacuo* over calcium chloride.

Physical Measurements

Melting point of the ligands and complexes were determined by an electro-thermal melting point apparatus. UV-absorption spectra were run on a Shimadzu UV-visible recording spectrophotometer (model-160). Infrared spectra were recorded on KBr pelletes 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. Metal analyses of the prepared complexes were done gravimetrically by oxine (Vogel, 1961). Some analytical and physical data of complexes are included in Table 2.

Table 2. Analytical and some physical data of the complexes.

Sl. No.	Complexes	Colour	Yield (%)	MP °C	Metal content (%)	μ _{eff} B.M.	Λ _m Ohm ⁻¹ cm ² mol ⁻¹
1	UO ₂ (Sal-Ani) ₂	Orange	80	250	34.49 (35.93)	Dia	1.4
2	UO ₂ (BrSal- Ani) ₂	Orange	70	247	27.92(29.02)	Dia	4.8
3	UO ₂ (ClSal- Ani) ₂	Deep yellow	75	250	31.83(32.55)	Dia	0
4	UO ₂ (HAP- Ani) ₂	Deep orange	75	208	33.02(34.47)	Dia	0
5	UO ₂ (HPP- Ani) ₂	Yellow	40	150	32.45(33.13)	Dia	0
6	UO ₂ (HNP- Ani) ₂	Orange	85	270	30.86(31.21)	Dia	1.0

M.P. = melting point, dia=diamagnetic

*Values in parentheses indicate calculated values.

RESULTS AND DISCUSSION

$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ reacts with the dinegatively-charged ligands in 1:2 ratio following the reaction scheme as shown in Figure 1 in slight warm conditions. As the ligand dissolved completely in general solvents, reaction proceed is shown by the colour change of the reaction mixture. Precipitates are formed upon cooling, which have been isolated and characterized by elemental analysis, IR and other conventional methods. All the complexes exhibit high melting points, indicating strong bonding between ligands upon complete deprotonation and neutral dioxouranium(VI) ion. All the 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 slightly soluble in methanol, ethanol, acetone and chloroform, and fairly soluble in dimethylformamide and dimethylsulfoxide. The analytical data support 1:2 metal-ligand stoichiometries. The Schiff bases behave as dibasic tridentate ligands coordinating via the phenolic oxygen, azomethine nitrogen and thiole sulphur atoms.

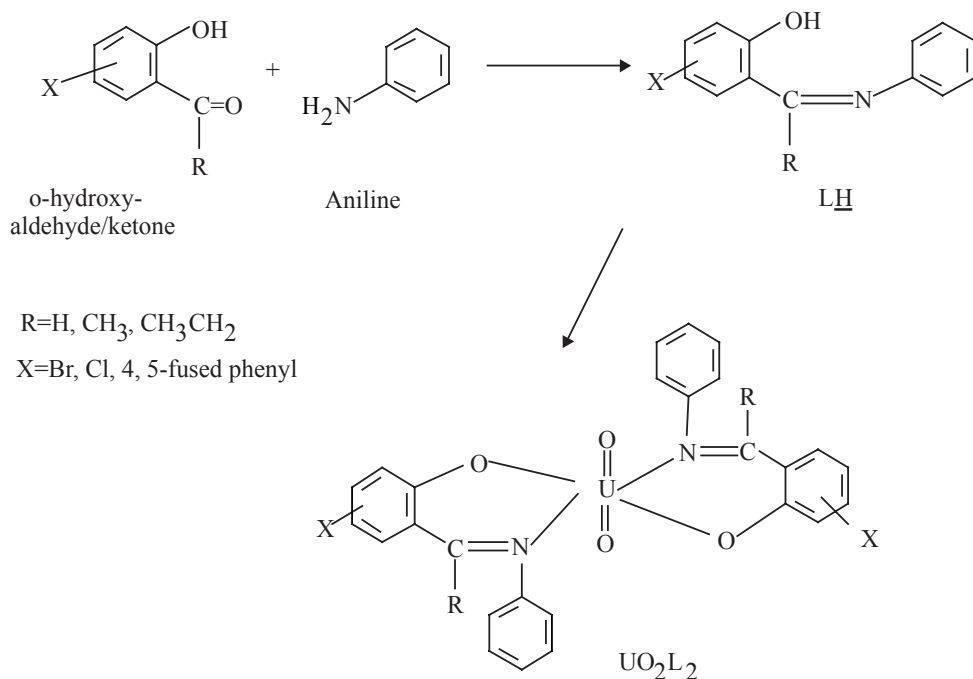


Figure 1. Reaction scheme and chemical structures of the ligands and the dioxouranium (VI) complexes.

IR Spectra

The infrared spectra of the present complexes are compared with those of corresponding ligand to determine the coordination sites of the ligands. The characteristic strong bands at 865-960 cm^{-1} and 785-880 cm^{-1} in the spectra of complexes have been assigned to $\nu_{\text{as}}(\text{O}=\text{U}=\text{O})$ and $\nu_{\text{s}}(\text{O}=\text{U}=\text{O})$, respectively (El-Sonbati et al., 2002; Yilmaz et al., 2008). The absorption bands appearing in the region 3205-3450 cm^{-1} are assigned to $\nu\text{O-H}$ (Chowdhury et al., 2008; Yilmaz et al., 2008). However, the O-H stretching frequency is dislocated to around 2583 cm^{-1} due to the hydrogen bridge $\text{OH}\cdots\text{N}=\text{C}$ (Figure 2) (Signorni, and Dockal, 1996; Chowdhury et al., 2008). These bands disappeared in the spectra of the complexes indicating coordination of phenolic oxygen atom (Soliman and Linert, 1999; Yilmaz et al., 2008). The negative shift of the $\nu(\text{C}=\text{N})$ in the spectra of the complexes indicates involvement of the azomethine nitrogen to coordination (Soliman and Linert, 1999). The absorption peaks appeared around 1550 cm^{-1} are attributable to $\nu(\text{C}=\text{C})$ (aromatic). The stretching frequencies of $\nu\text{C-O}$ (phenolic) and $\nu\text{C-N}$ (amino) appeared at 1261-1294 cm^{-1} and 1350-1381 cm^{-1} , respectively, in the spectra of the present complexes (Soliman and Linert, 1999). The U-O and U-N modes have been assigned most tentatively at 500-516 and 409-419 cm^{-1} , respectively (Salam et al., 1997; Chowdhury et al., 2008).

Table 3. Infrared spectral bands for the prepared complexes.

Sl. No.	Ligands	Assignments (cm^{-1})			
		$\nu\text{O-H}$	$\nu\text{C}=\text{N}$	$\nu\text{C-N}$	$\nu\text{C-O}$
1	Sal-AniH	3440 vs	1643 vs	1345 vs	1280 vs
2	BrSal-AniH	3450 vs	1632 vs	1340 vs	1270 vs
3	ClSal-AniH	3364 s	1645 vs	1381 vs	1266 vs
4	HAP-AniH	3205 vs	1638 vs	1377 vs	1270 vs
5	HPP-AniH	3250 vs	1600 vs	1379 vs	1258 vs
6	HNP-AniH	3240 vs	1618 vs	1347 s	1286 vs

Sl. No.	Complexes	Assignments (cm^{-1})					
		$\nu\text{C}=\text{N}$	$\nu\text{C-N}$	$\nu\text{C-O}$	$\nu\text{U}=\text{O}=\text{U}$	$\nu\text{U-O}$	$\nu\text{U-N}$
1	$\text{UO}_2(\text{Sal-Ani})_2$	1640 vs	1381 vs	1283 vs	924 vs	515 vs	410 s
2	$\text{UO}_2(\text{BrSal-Ani})_2$	1629 vs	1375 vs	1277 vs	923 vs	504 vs	409 vs
3	$\text{UO}_2(\text{ClSal-Ani})_2$	1643 vs	1376 vs	1286 vs	930 vs	516 vs	412 vs
4	$\text{UO}_2(\text{HAP-Ani})_2$	1596 vs	1377 vs	1279 vs	920 vs	500 vs	419 vs
5	$\text{UO}_2(\text{HPP-Ani})_2$	1601 vs	1371 vs	1261 vs	917 vs	509 vs	414 vs
6	$\text{UO}_2(\text{HNP-Ani})_2$	1628 vs	1350 s	1294 vs	924 vs	512 s	418 s

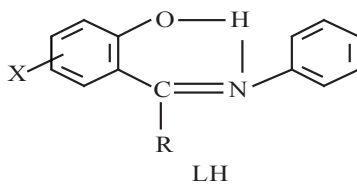


Figure 2. Hydrogen bonding in ligand molecule.

Electronic Spectra

The electronic spectrum of the ligand (LH) in ethanol shows absorption bands at 267-381 nm. The bands appearing at the UV region are attributable to $\pi - \pi^*$ transitions associated with the azomethine chromophores. The bands at higher energy arise from $\pi - \pi^*$ transitions within the phenyl rings. The absorption bands of the complex are shifted to longer wave length compared to those of the ligand. A moderately intensive band observed in the range of 330–395 nm is attributable to the $n - \pi^*$ transitions of the complex. However, the typical band of UO_2^{2+} expected around 400 nm seems to be overlapped by fairly strong ligand-to-metal charge-transfer bands. These charge-transfer transitions probably occur from the $n - \pi^*$ orbitals of the Schiff base to the f-orbitals of uranium (Elerman et al., 1996). Electronic spectral bands for prepared complexes are given in Table-4.

Table 4. Electronic spectral bands for the prepared ligands and their complexes.

Sl. No.	Ligands	Electronic spectra (nm)	Complexes	Electronic spectra (nm)
1	Sal-AniH	329, 306, 271	$\text{UO}_2(\text{Sal-Ani})_2$	400, 314, 305, 271
2	BrSal- AniH	321, 304, 271	$\text{UO}_2(\text{BrSal- Ani})_2$	348, 337, 319, 308, 272
3	ClSal- AniH	318, 304, 271	$\text{UO}_2(\text{ClSal- Ani})_2$	350, 339, 306, 272
4	HAP- AniH	315, 306, 268	$\text{UO}_2(\text{HAP- Ani})_2$	348, 315, 306, 270
5	HPP- AniH	313, 305, 267	$\text{UO}_2(\text{HPP- Ani})_2$	344, 316, 308, 270
6	HNP- AniH	381, 317, 304, 269	$\text{UO}_2(\text{HNP- Ani})_2$	438, 381, 319, 309, 270

Magnetic and Conductivity Measurement

The magnetic susceptibility of the complexes was found to be negative, indicating the complexes to be diamagnetic as expected for $f_0, 5f^06d^07s^0$, U(VI) complexes possessing its 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 molar conductance values (Table 2), measured in DMF (10^{-3} M) solution of the complex, gave a value of $0.4\text{--}4.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ which indicates their non-electrolytic behaviour as tentative for the complexes (El-Sonbati et al., 2002).

CONCLUSION

As a general conclusion, the prepared Schiff bases behave as a monobasic ligand in 1:2 complexes with bidentate ON donors derived from the phenolic oxygen and the azomethine nitrogen. Therefore, on the basis of elemental analyses and analytical data, an octahedral geometry has been proposed for the $[\text{UO}_2\text{L}_2]$ type complexes as in Figure 3. However, it is difficult to suggest the exact geometry of the present complexes without crystal structural evidence.

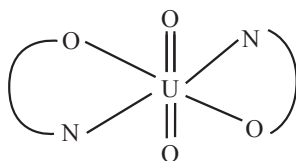


Figure 3. Proposed octahedral geometry for the prepared complexes.

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