

Synthetic and physicochemical studies of uranium complexes with semicarbazone and hydrazone

B. V. Agarwala*, S. Hingorani

Department of Postgraduate Studies and Research in Chemistry, R.D. University, Jabalpur-482001 (India)

and G. A. Nagana Gowda

Sophisticated Instruments Facility, Indian Institute of Science, Bangalore-560012 (India)

(Received January 12, 1990; revised May 17, 1990)

Abstract

Uranyl complexes of two Schiff bases, semicarbazone and hydrazone containing OON donor atoms have been synthesized and characterized on the basis of NMR, IR and electronic spectral studies, conductance, magnetic susceptibility and thermogravimetric data. The ^1H NMR spectrum of the semicarbazone complex shows low field signals due to OH, NH and $-\text{CH}=\text{N}$ groups at 10.23, 9.31 and 8.17 ppm, respectively. The aromatic protons appear in the range 7.74–7.40 ppm. On complexation with U(VI) the signals due to OH and NH disappear evidently due to their participation in coordination. The coordination number of the *o*-vanillin semicarbazone (oVSC) complex is 6 whereas, that of the *o*-vanillin isonicotinic acid hydrazone (oVINAH) complex is 8, in addition to the two oxygen atoms already bonded to U(VI) in each species. The thermograms show the presence of 3 and 2 water molecules in these complexes, respectively and the IR spectral data also support the above conclusion. Suitable structures have been assigned.

Introduction

The Schiff base complexes of uranium have aroused interest on account of their high stability, usefulness in selective chemical separations and their formation in higher coordination numbers. Uranyl complexes with O and N donors have been extensively reviewed [1–4] and quite a few complexes of semicarbazone and hydrazone Schiff bases have been reported [5]. Eight coordinated U(VI) complexes of nine Schiff bases (L) derived from 4-aminoantipyrine and certain carbonyl compounds have also been investigated [6].

In view of the structural interest involved in the coordination chemistry of uranium with Schiff base ligands, the synthesis and characterization of two uranyl complexes with *o*-vanillin semicarbazone and *o*-vanillin isonicotinic acid hydrazone are reported in this paper.

Experimental

Chemicals

Uranyl acetate (B.D.H.), *o*-vanillin, isonicotinic acid hydrazide and semicarbazide hydrochloride

* Author to whom correspondence should be addressed.

(Sisco) were used. The solvents used were of reagent grade.

Preparation of the ligands

o-Vanillin semicarbazone was prepared by refluxing equimolar quantities of *o*-vanillin (0.05 mol; 7.60 g) and semicarbazide hydrochloride (0.05 mol; 5.55 g), previously neutralized and dissolved in hot water in an ethanolic medium for 4 h. The crystalline light yellow substance was filtered washed with ethanol, followed by acetone and ether and dried over CaCl_2 under vacuum. The melting point of the compound was found to be 185 °C and its purity was checked by TLC and NMR measurements. The yield was 9.31 g (90%) with respect to *o*-vanillin.

o-Vanillin isonicotinic acid hydrazone was also prepared in the same way using isonicotinic acid hydrazide (0.05 mol; 6.85 g). The yield was found to be 12.45 g (92%) with respect to *o*-vanillin and the melting point was about 200 °C. The elemental analysis data show that *o*-vanillin and semicarbazide/isonicotinic acid hydrazide have reacted in 1:1 stoichiometric ratio to yield the Schiff base ligands. Both of these are insoluble in alcohol, acetone, ether or chloroform, but they dissolve in hot dimethylformamide and dimethyl sulfoxide.

Preparation of the complexes

The complexes were synthesized by mixing together a hot aqueous solution of uranyl acetate (0.005 mol; 2.12 g) and the solution of the ligand (0.005 mol; oVSC = 1.05 g; oVINAH = 1.35 g) in 100 ml of dimethylformamide-ethanol (vol./vol.) solvent mixture. The reaction mixture was refluxed over a heating mantle for 6 h. The brown coloured precipitate was filtered and washed several times with alcohol, dimethyl sulfoxide and finally with ether. The resulting crystalline substance was dried using CaCl₂ under vacuum. The yields were 2 g (75%) and 2.5 g (60%) with respect to the ligands for the two uranium complexes of oVSC and oVINAH ligands, respectively. The metal to ligand stoichiometry is found to be 1:1 for oVSC and 1:2 for the oVINAH complexes as shown by analytical data (Table 1). The presence of water molecules is confirmed by IR spectral and TG data. The insolubility of the complexes is noted in water and non-aqueous solvents such as ethanol, methanol, acetone, chloroform and benzene but they are found to be soluble in dimethylformamide and dimethyl sulfoxide.

Physicochemical methods used for characterization of the complexes

The carbon, hydrogen and nitrogen analyses were carried out at RSIC, Lucknow. Proton NMR spectra of the ligands and the complexes were recorded on a WH-270 FTNMR spectrometer equipped with an ASPECT 2000 computer. The IR spectra were recorded using CsI pellets with a Perkin-Elmer 1430 IR spectrophotometer in the range 4000–200 cm⁻¹ and the electronic spectra were recorded with a Pye-Unicam SP 8-100 spectrophotometer. Magnetic susceptibilities were measured at 25 °C by Gouy's method using Hg[Co(SCN)₄] as a standard. The conductivity measurements were carried out on a direct reading

Toshniwal conductivity bridge employing a ~10⁻³ M solution of the complexes in dimethyl sulfoxide. Thermogravimetric analysis of the complexes was also carried out for both the complexes.

Results and discussion

NMR spectra

Proton NMR spectra of the ligands and the complexes were analysed by performing variable temperature and deuterium exchange experiments, in addition to the normal spectra at room temperature. Typical proton NMR spectra of the ligand oVINAH and the corresponding complex recorded at room temperature are shown in Fig. 1. Spectra of these complexes clearly show the disappearance of the OH and NH proton signals of the ligands in the complexed species indicating the site of coordination with the metal ion. The azomethine proton shifts downfield upon complexation, of the ligand oVSC from 8.1 to 8.8 ppm and of the ligand oVINAH from 8.7 to 9.3 ppm. This is due to the reduction of electron density of the azomethine linkage as a result of coordination of nitrogen with the metal ion resulting in the deshielding of the azomethine proton. This is in agreement with the IR spectra of the complexes, where $\nu(\text{C}=\text{N})$ in the complex is smaller than that in the respective ligand. Thus this observation clearly explains that the C=N nitrogen of the ligands is the third coordinating site with the metal ion (Table 2).

IR spectra

The bonding sites of the ligand involved in coordination with the metal ion have been further examined by careful comparison of the IR spectra of the ligand and the complexes (Table 3). The IR

TABLE 1. Colour, melting point, analytical data and molar conductivity of complexes

Complex ^a	Melting point (°C)	Colour	Composition: found (calculated) (%)				Molar conductance (Ω ⁻¹ cm ² mol ⁻¹)
			C	H	N	M	
[H ₂ L]	185	light yellow	52.07 (51.67)	5.49 (5.26)	20.10 (20.10)		3.5
[UO ₂ L·3H ₂ O]	> 360	brick red	20.64 (20.34)	2.76 (2.82)	7.73 (7.91)	45.05 (44.90)	8.10
[H ₂ L']	200	yellow	62.65 (61.99)	4.87 (4.79)	15.80 (15.49)		3.5
[UO ₂ L ₂ ·2H ₂ O]	> 360	violet	36.38 (39.71)	3.53 (3.54)	9.76 (9.92)	30.02 (27.5)	10.05

^aH₂L = *o*-vanillin semicarbazone, C₉H₁₁N₃O₃; H₂L' = *o*-vanillin isonicotinoylhydrazone, C₁₄H₁₁N₃O₃.

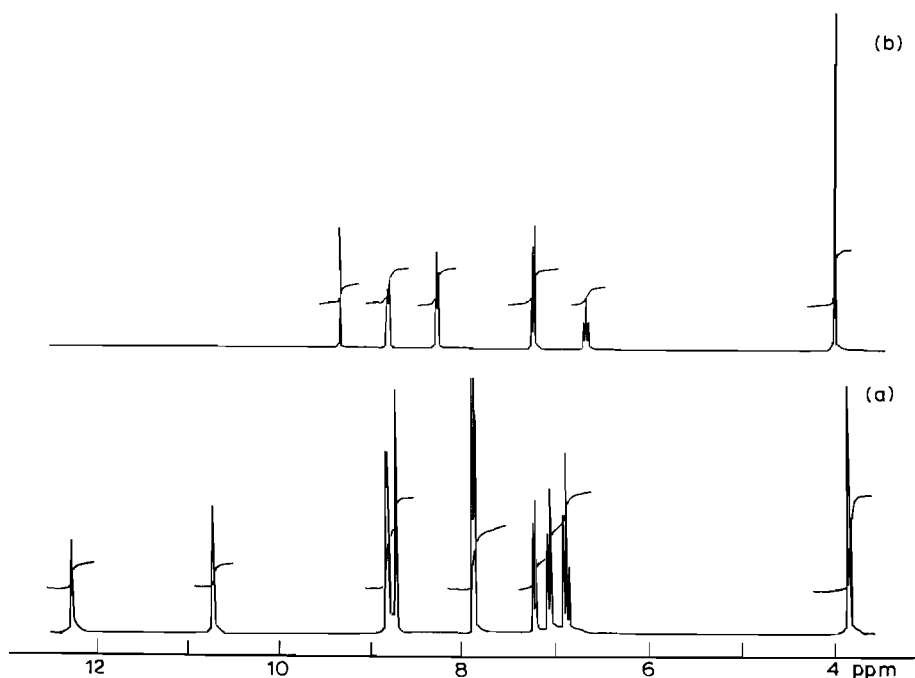


Fig. 1. ^1H NMR spectra: (a) oVINAH; (b) $\text{UO}_2\text{-oVINAH}$.

spectra of the ligands show bands at $3200\text{--}3250\text{ cm}^{-1}$ due to free hydroxyl groups which are absent in the complexes and a higher shift of the phenolic $\nu(\text{C}-\text{O})$ in the complexes, which is characteristic of phenolic oxygen coordination [7]. Bands due to $\nu(\text{C}=\text{N})$ in the ligands appearing at 1570 and 1608 cm^{-1} in oVSC and oVINAH, respectively, provide conclusive evidence for condensation of the amine with the aldehyde and formation of Schiff base with azomethine linkage. The coordination of nitrogen to the metal atom would be expected to reduce the electron density in the azomethine linkage and thus cause reduction in $\nu(\text{C}=\text{N})$. This is further substantiated by the presence of bands at 520 and 480 , 400 cm^{-1} assigned to $\nu(\text{U}=\text{O})$ and $\nu(\text{U}=\text{N})$ [8]. A significant shift to higher frequency of $\nu(\text{N}=\text{N})$ is due to the reduction of the lone pair-lone pair repulsive forces in the adjacent nitrogen atoms [9]. The disappearance of amine bands and appearance of new bands characteristic of $\nu(\text{NCO})^-$ in the $1350\text{--}1380\text{ cm}^{-1}$ region, is presumably due to the amide \rightleftharpoons imidol tautomerism of the ligand and subsequent coordination through the imidol oxygen [10]. The coordination of the ligand in the imidol form is also evidenced by the appearance of a sharp strong band characteristic of $\text{>C}=\text{N}-\text{N}=\text{C}<$ linkage at 1530 cm^{-1} in the spectra of both the complexes [11]. Both complexes show intense bands at $920\text{--}910\text{ cm}^{-1}$ and a medium intensity band at $800\text{--}700\text{ cm}^{-1}$ assignable to $\nu_{\text{as}}(\text{O}=\text{U}=\text{O})$ and $\nu_{\text{s}}(\text{O}=\text{U}=\text{O})$ modes, respectively [12]. This observation indicates that li-

nearity of the $\text{O}=\text{U}=\text{O}$ group is retained in the complexes. The doubly degenerate OUO bending mode ν_2 , was observed at 260 cm^{-1} in these complexes. No shift in the position of the stretching frequency of the pyridine nitrogen at 1570 cm^{-1} in the oVINAH complex and at $2840\text{--}2848\text{ cm}^{-1}$ due to the methoxy group in the oVSC and oVINAH complexes confirms their non-involvement in coordination.

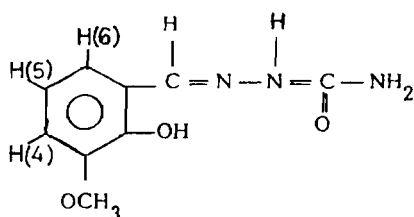
The presence of coordinated water is indicated by the presence of bands at 3430 and 3400 , 1620 and 1600 , and 940 and 970 cm^{-1} due to stretching, rocking and deformation modes of water in oVSC and oVINAH complexes, respectively [13].

Electronic spectra

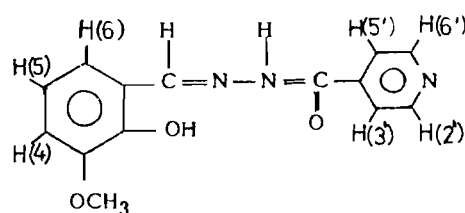
The electronic spectra of the uranyl complexes reveal that ligation has a relatively minor influence and the electronic spectra of such complexes are mainly dependent upon the triatomic UO_2 moiety [14]. Two absorption bands are observed in both the uranium complexes, one each in the visible and UV regions. A band observed at 350 and 300 nm in the case of the oVSC and oVINAH ligands, respectively indicates the $\pi\text{-}\pi^*$ transition of the $-\text{C}=\text{N}-$ moiety. This undergoes an upward shift to 400 and 340 nm in the spectra of the corresponding complexes showing the coordination of the azomethine nitrogen to the uranyl ion [15]. The second band observed at 520 and 460 nm in oVSC and oVINAH complexes, respectively is attributed to the transition from apical

TABLE 2. ¹H NMR spectral data at room temperature recorded on WH-270 FT-NMR spectrometer

Protons	Chemical shifts (ppm)		Protons	Chemical shifts (ppm)	
	L	UL		L'	UL'
H(6)	6.91	7.0	H(6)	7.05	7.24
H(5)	6.76	6.58	H(5)	6.88	6.64
H(4)	6.94	7.09	H(4)	7.22	7.24
-OCH ₃	3.80	3.94	-OCH ₃	3.83	3.97
-OH	10.23		-OH	12.27	
$\begin{array}{c} \text{H} \\ \\ -\text{C}=\end{array}$	8.17	8.80	$\begin{array}{c} \text{H} \\ \\ -\text{C}=\end{array}$	8.71	9.30
$\begin{array}{c} \text{H} \\ \\ -\text{N}- \\ \\ -\text{NH}_2 \end{array}$	9.30		-NH	10.71	
	6.41	6.29	H(2') and H(6')	8.81	8.77
			H(3') and H(5')	7.86	8.24



o-Vanillin semicarbazone



o-Vanillin isonicotinic acid hydrazone

TABLE 3. IR spectral data and their band assignments

Compound	$\nu(\text{OH})$ phenolic	$\nu(\text{NH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{N}=\text{N}=\text{C})$	$\nu(\text{N}-\text{N})$	$\nu(\text{U}-\text{O})$	$\nu(\text{M}-\text{N})$	$\nu\text{H}_2\text{O}, \delta\text{H}_2\text{O}$
[H ₂ L]	3430	3040	1660	1570		1055			
[UO ₂ L·3H ₂ O]				1580	1540	1068	520	400	3430, 1620, 940
[H ₂ L']	3200	3000	1695	1608		1000			
[UO ₂ L ₂ ·2H ₂ O]				1632	1520	1010	520	480	3400, 1600, 970

oxygen to orbitals of the uranyl moiety [16] and strong charge transfer bands arising from the ligand orbital to the 5f and/or 6d orbital of uranium. These ligand to metal charge transfer bands which are strongly affected by their chemical nature are responsible for the bright colours of these complexes [17].

Magnetic susceptibility and conductance measurements

The molar conductance measurements of 0.001 M solutions in dimethyl sulfoxide ($8\text{--}10 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)

show their non-electrolytic nature [18]. Magnetic measurements indicate that both the complexes are diamagnetic ($\mu_{\text{eff}}=0 \text{ BM}$) as generally expected for 5f⁰ U(VI) compounds, which is reminiscent of a spin-paired electronic configuration in an octahedral or square pyramidal complex geometry. Hence it can be concluded that reduction of the metal does not take place under the influence of the ligand [19].

Thermogravimetric analysis

The thermograms of the complexes reveal interesting features and corroborate some of the as-

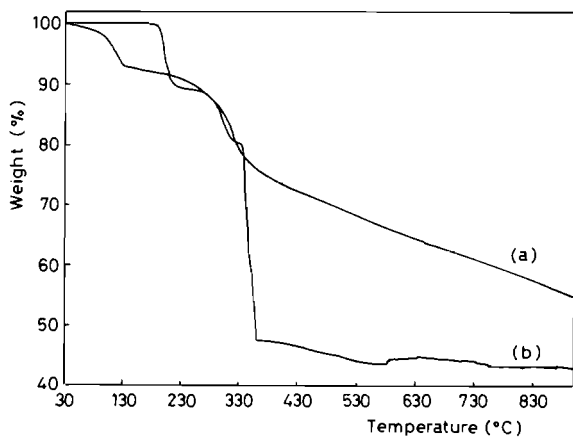


Fig. 2. TG curves: (a) $[\text{UO}_2(\text{L})3\text{H}_2\text{O}]$; (b) $[\text{UO}_2(\text{L}_2)2\text{H}_2\text{O}]$.

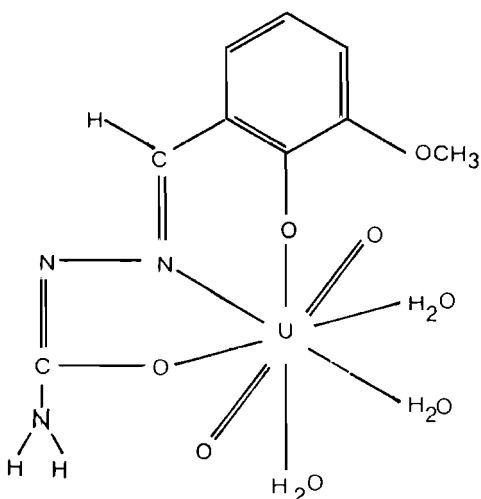


Fig. 3. Structure of $[\text{UO}_2(\text{L})3\text{H}_2\text{O}]$ ($\text{L}=\text{oVSC}$).

sumptions made on the basis of IR spectral studies. In the case of the oVSC complex, the loss of water starts below 190 °C and a weight loss of 6–6.5% is noticed between 60–140 °C. This is equivalent to elimination of two water molecules (calculated 6.9%). The third water molecule is lost from 140 to 250 °C gradually as seen by the inflexion in the thermogram suggesting its involvement in coordination. The complex gradually decomposes till the formation of its oxide at 750 °C. In the case of the $\text{UO}_2\text{-oVINAH}$ complex, it is fairly stable up to 200 °C after which two water molecules are lost and further decomposition proceeds till 369 °C. The plateaus in the thermograms correspond to the intermediates formed during the pyrolytic process (Fig. 2).

Conclusions

The various physicochemical studies on the uranyl complexes reveal that the ligands are binegatively

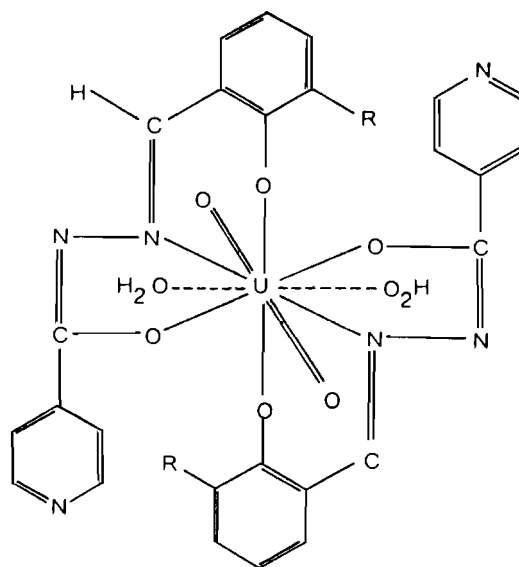


Fig. 4. Structure of $[\text{UO}_2(\text{L}_2)2\text{H}_2\text{O}]$ ($\text{L}'=\text{oVINAH}$) ($\text{R}=\text{oCH}_3$).

tridentate. The coordination number of the oVSC complex is 6 whereas that of the oVINAH complex is 8 in addition to the two oxygen atoms which have already bonded to U(VI) in each species. The structures proposed for both the complexes on the basis of the above studies are given in Figs. 3 and 4.

Acknowledgements

The authors thank the Council of Scientific and Industrial Research, New Delhi for financial assistance; Sophisticated Instruments facility, Indian Institute of Science, Bangalore for NMR spectral data; RSIC, Central Drug Research Institute, Lucknow for providing C,H,N analysis; and Professor C.L. Khetrpal, Indian Institute of Science, for useful discussions.

References

- 1 W. Radecka-Paryzek, E. Jankowska and E. Luks, *Polyhedron*, 7 (1988) 439.
- 2 R. C. Aggarwal and B. Prasad, *J. Inorg. Nucl. Chem.*, 33 (1971) 3984.
- 3 R. A. Lal, M. N. Singh and R. K. Thapa, *Indian J. Chem.* 26A, (1987) 883.
- 4 A. Syamal and B. K. Gupta, *Rev. Roum. Chim.*, 26 (1981) 857.
- 5 A. A. Sengupta and N. K. Dutta, *J. Inorg. Nucl. Chem.*, 37 (1975) 270.
- 6 G. S. Devi and P. Indrasenan, *Inorg. Chim. Acta*, 133 (1987) 157.

- 7 S. K. Gupta and L. K. Mishra, *J. Inorg. Nucl. Chem.*, *41* (1979) 890.
- 8 G. Percy, *Spectrochim. Acta, Part A*, *32* (1976) 1287.
- 9 S. P. Perleps, D. Nicholls and M. R. Harrison, *Inorg. Chim. Acta*, *102* (1985) 137.
- 10 K. M. Ibrahim, M. M. Bekheit and G. M. A. El-Reash, *Indian J. Chem.*, *28A* (1989) 261.
- 11 S. A. Abou Ali, G. V. Ali and M. M. Osman, *J. Chim. Chem. Soc. (Taipei)*, *31* (1984) 243.
- 12 N. S. Biradar, M. D. Patil and T. R. Gordar, *J. Inorg. Nucl. Chem.*, *37* (1975) 1437.
- 13 T. S. Lobana, H. S. Cheema and S. S. Sandhu, *Polyhedron*, *4* (1985) 717.
- 14 B. E. Douglas, *Inorg. Synth.*, *1* (1978) 18.
- 15 P. C. H. Mitchell and J. A. Valero, *Inorg. Chim. Acta*, *11* (1983) 179.
- 16 I. L. KimBong, C. Miyakoe and S. Imoto, *J. Inorg. Nucl. Chem.*, *37* (1975) 963.
- 17 U. Casellato, M. Vidali and P. A. Vigato, *Inorg. Chim. Acta*, *18* (1976) 77.
- 18 V. V. Savant and C. C. Patel, *J. Inorg. Nucl. Chem.*, *34* (1972) 1462.
- 19 K. M. M. S. Prakash, L. D. Prabhakar and M. C. Chowdary, *Polyhedron*, *6* (1987) 285.