

Synthesis and characterization of dioxouranium (VI) complexes of schiff bases derived from isatin, isovanillin and *o*-vanillin

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Received 1 March 1995; revised 29 May 1995;
accepted 18 July 1995

Three schiff bases viz. isatin semicarbazone, isovanillin thiosemicarbazone, *o*-vanillin *para*-anisidine and their dioxouranium(VI) complexes have been synthesised and characterized by elemental analysis, IR and NMR spectral studies.

The schiff base complexes of uranium have aroused interest on account of their high stability, usefulness in chemical separations and their novel structural features in higher coordination numbers. Uranyl complexes with O and N donors have been extensively reviewed and quite a few complexes of semicarbazone and hydrazone schiff bases have been reported¹⁻⁴. Eight coordinated dioxouranium(VI) complexes of some schiff bases derived from 4-aminoantipyrine and certain carbonyl compounds have also been investigated⁵. In continuation of our earlier work on schiff base complexes, the present note deals with dioxouranium(VI) complexes of isatin semicarbazone (ISC), isovanillin thiosemicarbazone (IVTSC) and *o*-vanillin *para*-anisidine (*o*-VPA). The ligands are identified by ¹H NMR and the uranyl complexes have been investigated by other physicochemical methods.

Experimental

Isatin, isovanillin, *ortho*-vanillin, semicarbazide hydrochloride, thiosemicarbazide, *para*-anisidine (all Sisco) and the uranium salts (E Merck) were used. Ethanol and other solvents used were of reagent grade.

The IR spectra were recorded on an Acculab 10 spectrophotometer using CsI discs in the 4000-200 cm⁻¹ region. The NMR spectra were measured on an AMX-400 FT NMR spectrometer using DMSO-*d*₆

as solvent and TMS as internal standard. The TG data were obtained using a Perkin-Elmer Thermal Analyser at temperature upto 860°C in dinitrogen atmosphere at a heating rate of 10-15°C/min. Diffuse reflectance spectra were recorded on a Perkin-Elmer 2300 spectrophotometer using MgO pellets in the 200-1000 nm range. The magnetic susceptibility was measured by Gouy's method using Hg[Co(SCN)₄] as a calibrant. Elemental analyses were obtained by microanalytical procedures.

Preparation of ligands

An ethanolic solution of *o*-vanillin (0.05 mol, 7.6 g) was gradually added to an ethanolic solution of thiosemicarbazide (0.05 mol, 4.55g) with vigorous shaking. The mixture was then refluxed over a water bath for 4-5 h. The resulting solution was concentrated for half an hour and allowed to stand overnight. On cooling, crystalline mass of isovanillin thiosemicarbazone was obtained which was filtered, washed with ethanol and dried at room temperature. The purity was checked by m.p., IR spectrum and elemental analysis data.

o-Vanillin *para*-anisidine was prepared by mixing an ethanolic solution of *o*-vanillin (0.05 mol, 7.60g) and ethanolic solution of *para*-anisidine (0.05 mol, 6.15 g) in 1:1 ratio. The mixture was refluxed over heating mantle at 90°C for 5 h. This brown colour solution was left overnight at 0°C. The crystalline product was filtered, washed with acetone and dried over calcium chloride *in vacuo*. Isatin semicarbazone was prepared as described earlier⁶.

Syntheses of uranium complexes

The complexes were synthesised by mixing an ethanolic solution of uranyl nitrate (0.005 mol, 2.51 g) and the ligand solution (0.005 mol, ISC = 1.02 g, or IVTSC = 1.12 g) dissolved in 60 cm³ DMF. The reaction mixture was heated under reflux on a heating mantle for 4 h and a few drops of ammonia was added after cooling the reaction mixture. The refluxing was continued on a heating mantle for another 3 h. The coloured precipitate was separated out which was filtered, washed with ethanol and finally with ether. The resulting crystalline substance was dried over CaCl₂ *in vacuo*. The 1:2 complex was synthesised by adding an ethanolic solution of *o*-VPA (2.57 g) to an ethanolic solution of uranyl acetate (2.12 g). The mixture was heated under reflux for 4 h and the

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Table 1—Characterization data of uranium complexes

Compound Colour	M.pt. (°C)	Found (Calcd.), %			
		C	H	N	U
ISC canary yellow	265	52.40 (52.94)	3.48 (3.92)	27.80 (27.45)	—
[UO ₂ (L)NO ₃ ·2H ₂ O] dark yellow	315	18.67 (18.92)	2.08 (1.92)	12.10 (12.25)	42.08 (41.68)
IVTSC cream	225	49.00 (48.00)	5.20 (4.88)	19.00 (18.66)	—
[UO ₂ (L')NO ₃ ·H ₂ O] yellow	325	18.62 (18.82)	2.00 (2.09)	9.68 (9.75)	41.83 (41.45)
<i>o</i> -VPA brown	230	69.72 (70.06)	6.04 (5.83)	6.02 (5.44)	—
[UO ₂ (L'')] yellow	335	46.00 (46.06)	3.42 (3.57)	3.52 (3.57)	31.02 (30.42)

HL = ISC, HL' = IVTSC, HL'' = *o*-VPA

separated crystalline compound was isolated as described above.

Results and discussion

The elemental analyses and physical properties of schiff bases and their uranium complexes are listed in Table 1. The results show that the ligand coordinates to the metal ion in 1:1 molar ratio except in the case of *o*-VPA complex where the stoichiometric ratio is 2:1. The ligands dissolve only in strong polar solvents such as DMF, DMSO and THF, and do not coordinate as has been observed in the case of DMF. The complexes are partially soluble in DMF and DMSO. The yield is 55–60%.

In the infrared spectra, the chelating ligand ISC exhibits absorption bands at 1706 and 1638 cm⁻¹ due to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ whereas *o*-VPA shows bands at 3430 and 1600 cm⁻¹ due to $\nu(\text{O}-\text{H})$ and $\nu(\text{C}=\text{N})$ respectively. In their NMR spectra, two distinct N-H proton singlets appear at 10.70 and 10.17 ppm for ISC dissolved in DMSO-*d*₆. The benzene ring protons appeared as two doublets at 8.06 (1H), 6.85 (4H) and two triplets at 7.34, 7.03 ppm due to 5H/6H. The coupling constants J_{16} , J_{45} and J_{56} were 8.78, 8.82 and 8.6 Hz respectively. These results indicate that the semicarbazide group is present in ISC in its keto form. Obviously, signals due to azomethine proton is not observed in ISC due to absence of $-\text{CH}=\text{N}$ group but remarkably noticed in *o*-VPA at 8.93 ppm. For *o*-VPA, the O-H proton (*o*-vanillin ring) singlet

appeared at lowest field 13.47 and multiplets due to ring protons appeared between 7.43 and 6.88 ppm. Two signals due to two methoxy groups (each present in *o*-vanillin and *p*-anisidine ring) resonate \sim 3.80 ppm. The coupling constants J_{45} , J_{56} and J_{78} were 7.76, 7.47 and 8.85 Hz respectively. The results of IR and NMR spectra of the two ligands compliment each other. In case of IVTSC, IR absorption bands are observed at 1432, 1587 cm⁻¹ due to $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{N})$ followed by a characteristic band due to $>\text{C}=\text{N}-\text{N}=\text{C}<$ (ref. 7) linkage at 1533 and $\nu(\text{C}=\text{N})$ at 1570 cm⁻¹.

The IR spectra of uranium complexes show significant changes compared to the ligand. The band due to $\nu(\text{C}=\text{N})$ shows a bathochromic shift (17–68 cm⁻¹) on complexation^{8–10} which is further substantiated by the presence of new bands at 454 and 520 cm⁻¹ unambiguously assigned to $\nu(\text{M}-\text{N})$ ¹¹. Both the complexes formed by ISC and IVTSC exhibit a hypsochromic shift of $\nu(\text{N}-\text{N})$ and is due to the reduction of lone pair repulsive forces in the adjacent nitrogen atoms¹². In case of the uranium complex of ISC, the disappearance of amine bands and appearance of new bands characteristic of $\nu(\text{NCO}^-)$, in the region 1349 cm⁻¹ is presumably due to amide \rightleftharpoons imidol tautomerism of the ligand and its subsequent coordination through the imidol oxygen¹³. The bands exhibited at 820 and 380 in the uranium complex of IVTSC are due to $\nu(\text{C}-\text{S})$ and $\nu(\text{U}-\text{S})$ whereas a medium intensity band is observed in the uranium complex of ISC at 414 cm⁻¹ due to $\nu(\text{U}-\text{O})$. The IR spectra of both the dioxouranium(VI) complexes have an additional strong bands at 880, 960 cm⁻¹ which is attributed to $\nu_a(\text{OUO})$ mode¹⁴. The spectra of these complexes display strong bands at 1440, 1430; 1305, 1285 and 1020, 1005 attributed to ν_4 , ν_1 , ν_2 modes of the coordinated nitrate group, respectively¹⁵. Since the separation between ν_4 and ν_1 is \sim 140 cm⁻¹ in both the complexes, it is suggested that the nitrate groups are coordinated unidentately to the metal ion. The presence of water (coordinated) is indicated by the bands at 3534, 3230; 1603, 1620 and 1005, 950 cm⁻¹ due to stretching, rocking and deformation modes of water respectively^{16,17}. In the uranium complex formed with *o*-VPA, the disappearance of OH mode of free ligand indicates coordination to metal ion via deprotonation¹⁸. This is further confirmed by the appearance of a new band at 432 cm⁻¹. This complex exhibits intense band at 916 and a medium intensity band at 732 cm⁻¹ assignable to $\nu_{as}(\text{O}=\text{U}=\text{O})$ and $\nu_s(\text{O}=\text{U}=\text{O})$ modes respectively¹⁹.

The thermogram of dioxouranium(VI)–ISC complex shows weight loss of 6.2% (Calcd. 6.3%)

between 170 and 240°C corresponding to the presence of two water molecules in the coordination sphere. The complex decomposes rapidly at 280°C due to the breaking up of the organic moiety of the complex. Decomposition continues with a gradual breaking up beyond 690°C indicating that no stable residue of a definite composition is formed.

The dioxouranium(VI)-IVTSC complex shows weight loss of 3.6% (Calcd. 3.1%) between 180° and 360° C corresponding to elimination of one water molecule in coordination sphere. The complex decomposes at 310° C and TGA curve shows continuous weight loss upto 580°C. At temperature > 760°C, a stable residue is seen which may be due to the formation of impure U₃O₈. The complex dioxouranium(VI)-*o*-VPA starts decomposing at 90° C which continues upto 580°C. A stable residue is formed beyond 780° C due to the formation of U₃O₈ (obs. 32.5, calcd. 32.4%). This complex does not contain any water molecule.

All the uranium complexes are diamagnetic. The complexes formed in 1:1 stoichiometry display broad band in the UV region (26880, 25770 cm⁻¹) and a weak band in the visible region (16180, 15625 cm⁻¹). This may be due to M→LCT as noticed from their diffuse reflectance spectra. The critical study of all the physicochemical data along with their degradation pattern in the pyrolytic curve of uranium complexes give enough evidence for our tentative structural assignments. The presence of coordinated water molecule is substantiated by the IR and TGA data. The IR data also support monodentate coordination of nitrate group in such complexes formed in higher coordination numbers.

Acknowledgement

The authors thank Prof. C L Khetrpal, Bangalore for his help in recording NMR spectra and useful discussion. Financial assistance received from DAE, Govt. of India is gratefully acknowledged.

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