

Study of Uranyl Complexes of Some Schiff Bases

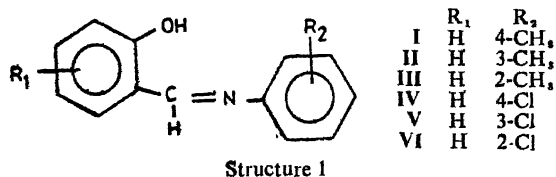
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Dioxouranium(VI) complexes of some Schiff bases, obtained by condensing chloroanilines and toluidines with salicylaldehyde are synthesised and characterised by elemental analysis, spectral and conductance data. All the complexes are orange red in colour, microcrystalline in nature and form compounds of the type $[UO_2(LH)_2](NO_3)_2$, where LH is a Schiff base molecule. The bonding with the metal in the complexes takes place from hydroxyl oxygen and imine nitrogen of the ligand. It is observed that dioxouranium(VI) forms 1 : 2 adducts with these Schiff bases. Conductivity measurements, analytical data and spectral study show that these complexes have coordination number eight with hexagonal bipyramid structure.

A large number of metal complexes with Schiff base ligands formed from salicylaldehyde or substituted salicylaldehydes with various aromatic amines are known¹⁻⁴. Solution stability constants of the complexes of a number of Schiff bases with various divalent metal ions have been studied by Dodwad, Datar and Patil⁵. In the present communication, we report the synthesis and spectral properties of a few uranium(IV) complexes with Schiff bases shown below :



Experimental

Uranyl nitrate hexahydrate used for preparing the complexes was of B.D.H, A.R. grade. Salicylaldehyde, toluidines and chloroanilines were of L.R. grade which were purified by conventional methods.

Preparation of Schiff bases :

These were prepared by refluxing calculated quantities of salicylaldehyde and corresponding

substituted anilines in ethanolic medium for 0.5-1.0 hr. The bases produced solidified rapidly on cooling. The solid was separated and recrystallised from methylated spirit. All the Schiff bases crystallised⁶ as light yellow to orange yellow coloured crystals.

Preparation of complexes :

The complexes were prepared by refluxing one part of uranyl nitrate and two parts of Schiff base in ethanolic medium for 1 to 2 hr. The orange red coloured complexes separated on cooling. They were filtered, washed with alcohol and dried in vacuum over fused CaCl₂.

Elemental analysis :

The purity of the complexes was ascertained by elemental analysis. Uranium in the complexes was estimated gravimetrically⁶ as U₃O₈. Nitrogen was estimated microanalytically by Duma's method. The results of elemental analysis are given in Table 1.

Physical measurements :

The conductance measurements of all the complexes in DMF were made with a Phillips PR 9500 conductivity bridge having a cell constant of 0.6831. Molar conductance of the complexes

TABLE 1—COLOUR, ELEMENTAL ANALYSIS AND CONDUCTANCE DATA FOR URANYL COMPLEXES OF SCHIFF BASES

Ligand No.	Complex No.	Empirical formula	Colour of the complex	Analysis % ; Found/(Calcd.)		Conductivity ohm ⁻¹ cm ² mole ⁻¹
				U	N	
I	VII	$[UO_2(C_{11}H_{11}ON)_2](NO_3)_2$	Orange	29.70 (29.10)	7.50 (6.86)	124.531
II	VIII	$[UO_2(C_{11}H_{11}ON)_2](NO_3)_2$	Orange	29.25 (29.10)	7.43 (6.86)	123.331
III	IX	$[UO_2(C_{11}H_{11}ON)_2](NO_3)_2$	Orange red	29.46 (29.10)	7.31 (6.86)	124.531
IV	X	$[UO_2(C_{11}H_{10}ONCl)_2](NO_3)_2$	Orange red	27.40 (27.77)	6.74 (6.53)	129.631
V	XI	$[UO_2(C_{11}H_{10}ONCl)_2](NO_3)_2$	Orange	27.75 (27.77)	6.90 (6.53)	127.031
VI	XII	$[UO_2(C_{11}H_{10}ONCl)_2](NO_3)_2$	Orange	27.66 (27.77)	7.13 (6.53)	129.131

TABLE 2—SELECTED IR FREQUENCIES (CM⁻¹) OF SCHIFF BASES AND THEIR URANYL COMPLEXES

Compd. No.	Aromatic C-H stretching vibration	C-N stretching vibration	Aromatic C-C stretching vibrations	C-O stretching vibrations	OH bending vibration	$\nu_1(\text{O}-\text{U}-\text{O})$	$\nu_2(\text{O}-\text{NO}_2)$
I	3100 (w)	1620 (s)	1600 (m) 1580 (s) 1500 (sh)	1370 (sh) 1190 (sh)	1280 (s)	—	—
II	3125 (w)	1640 (s)	1620 (sh) 1590 (sh) 1520 (sh)	1400 (sh) 1195 (s)	1290 (s)	—	—
III	3100 (w)	1630 (s)	1610 (sh) 1580 (s) 1500 (sh)	1390 (sh) 1190 (sh)	1290 (sh)	—	—
IV	3100 (w)	1615 (s)	1590 (sh) 1570 (sh) 1490 (s)	1380 (sh) 1185 (sh)	1280 (s)	—	—
V	3120 (w)	1630 (sh)	1610 (sh) 1590 (sh) 1510 (m)	1385 (s) 1200 (s)	1290 (s)	—	—
VI	3100 (w)	1630 (s)	1600 (m) 1580 (s)	1390 (sh) 1195 (s)	1280 (s)	—	—
VII	3100 (w)	1650 (s)	1610 (sh) 1520 (m)	1380 (s) 1195 (m)	1280 (s)	920 (s)	1240 (sh)
VIII	3125 (w)	1660 (s)	1630 (sh) 1610 (w) 1510 (s,b)	1400 (sh) 1195 (sh)	1300 (s,b)	930 (s) 920 (sh)	1260 (sh)
IX	3130 (w)	1650 (s)	1620 (s) 1500 (s,b)	1400 (s) 1190 (m)	1290 (s)	$\nu_1 = 820$ (sh) 930 (s) 900 (sh)	1260 (sh)
X	3120 (w)	1640 (s)	1615 (sh) 1490 (s)	1380 (sh) 1190 (sh)	1290 (s,b)	$\nu_1 = 830$ (s) 930 (s) 890 (sh)	1240 (sh)
XI	3100 (w)	1650 (s)	1620 (s) 1600 (s)	1385 (s) 1190 (sh)	1280 (s,b)	930 (s) 910 (s)	1240 (s)
XII	3150 (w)	1660 (s)	1640 (sh) 1620 (m)	1400 (s) 1195 (s)	1300 (s)	950 (s)	1260 (s)

b = broad, m = medium, sh = sharp, s = strong, w = weak.

were calculated and are reported in Table 1. Infrared spectra of the ligands and their complexes, in *nujol*, were recorded on Perkin Elmer-700 spectrophotometer in the region 4000-650 cm⁻¹ and selected frequencies with their tentative assignments are presented in Table 2.

Results and Discussion

The complexes obtained are orange red in colour, microcrystalline in nature and are insoluble in common organic solvents. They are, however, soluble in DMF. This insolubility did not permit the determination of their molecular weights. The results of elemental analysis suggest that the complexes have 1 : 2 stoichiometry.

Conductance : It is observed that the molar conductance in DMF at 10⁻³M are in the range of 120-130 ohm⁻¹cm²mole⁻¹ indicating that the complexes behave as 1 : 2 electrolytes. This is in accordance with the observations of Geary⁷. It is clear from the conductivity data that the complexes behave as strong electrolytes and that the DMF molecules replace the weakly coordinated unidentate nitrate groups from the coordination sphere⁸.

Infrared spectra : The infrared spectra of the Schiff bases and their complexes exhibit a weak band characteristic of aromatic C-H stretching vibration in the range of 3150-3100 cm⁻¹. The

spectra of the ligands as well as their complexes show a strong, sharp or medium band in the region 1640-1490 cm⁻¹ which is assigned to the C=C stretching vibration. In the complexes as well as the ligands a strong and sharp band in the regions 1400-1370 cm⁻¹ and 1200-1185 cm⁻¹ is attributed to the C-O stretching vibration. Two characteristic frequencies, 950-890 cm⁻¹ and 830-820 cm⁻¹ can be predicted⁹ for UO₂ ion in all the complexes. A strong, sharp or broad band in the 1300-1280 cm⁻¹ region is assigned to the OH bending vibration⁴. Absence of measurable absorption in the infrared region characteristic of OH absorption (3650-3590 cm⁻¹) has been attributed to the existence of intramolecular hydrogen bonding¹⁰. Some representative ir spectra are shown in Figs. 1 and 2.

Some of the Schiff bases studied in the present investigation exhibit the property of thermochromism¹¹ and photochromism¹¹⁻¹³. This property has also been attributed to the existence of intramolecular hydrogen bonding^{10,14} between the phenolic proton and the imine nitrogen.

The formation of a coordinate bond between the oxygen of the OH group and the metal increases the electron density on the latter. Consequently, the $\nu_{\text{C}=\text{N}}$ will shift towards higher wave number side due to increase in C-N bond order¹⁵. A strong band found in the 1640-1615 cm⁻¹ region, assignable to the C=N stretch¹⁶ of the Schiff bases, is

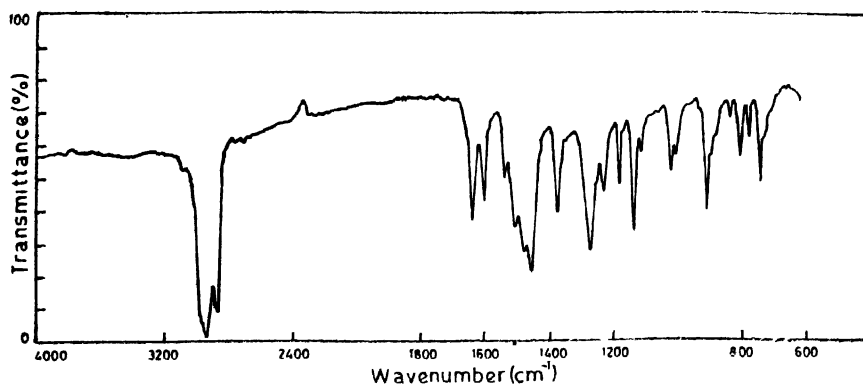


Fig. 1. IR spectra of complex VII.

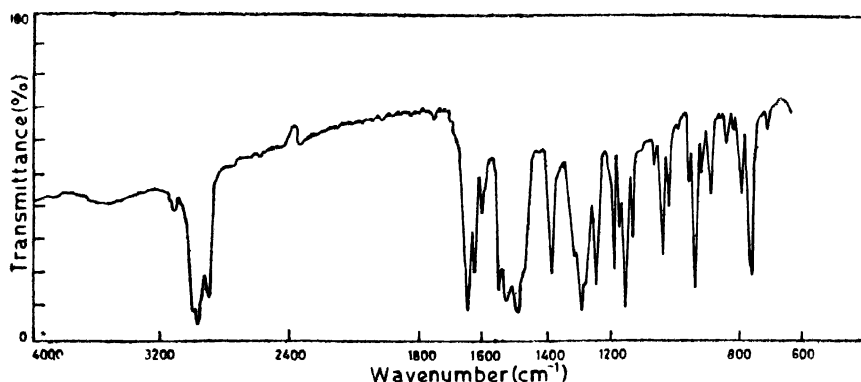


Fig. 2. IR spectra of complex XII.

observed in the complexes in the 1660-1640 cm^{-1} region. The observable shift obtained in the $\text{C}=\text{N}$ stretch after complexing confirms the formation of coordinate bond from oxygen of the OH group and imine nitrogen to the metal ion.

A strong and sharp band for all the complexes appears in the region 1260-1240 cm^{-1} and has been assigned¹⁷ to the NO_2 group. This is, however, not observed in case of the Schiff base ligands. This fact confirms the interpretation of conductivity

data and it also confirms the presence of NO_2 ions in the suggested structure of the complexes.

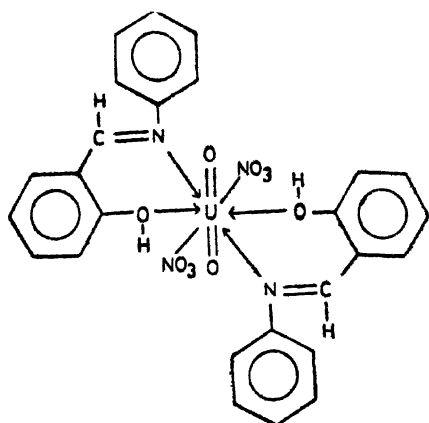
On the basis of the analytical data, conductivity measurements and infrared spectral data, it may be suggested that the complexes have coordination number eight with hexagonal bipyramid structure and is represented by structure 2.

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Structure 2

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