

PREPARATION OF SCHIFF BASE COMPLEXES OF URANIUM (VI), TIN (II) TIN (IV) AND THORIUM (IV) AND DETERMINATION OF THEIR STRUCTURE BY SPECTROPHOTOMETRIC METHODS

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ABSTRACT

UO₂(II), Th (IV) Tin (II) and (IV) complexes with Schiff bases derived from o-nitrobenzaldehyde and p-dimethylaminobenzaldehyde with allylamine have been prepared. The complexes have been characterized by IR spectra and elemental analysis. Magnetic susceptibility of complexes measured. It is concluded that ligand coordinated to metal with allylicnitrogen and coordination number changed according to central atom.

INTRODUCTION

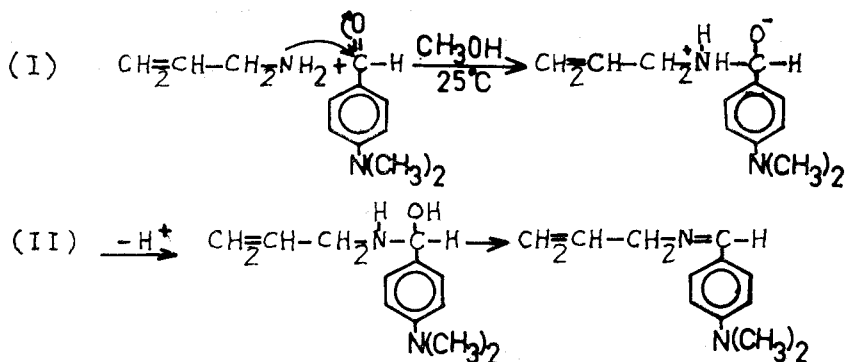
Though, a large number of papers have appeared on metal complexes with Schiff bases derived from aromatic aldehydes and substituted amines, very few ones have been published on Actinide complexes of Schiff bases. The limited information on actinide complexes of Schiff bases prompted us to undertake a systematic search in this field.

In this paper, uranium, thorium and tin complexes of Schiff bases prepared and their structure examined. Schiff bases will be obtained by the condensation of carbonyl compounds, especially aldehyde and ketones, with primary amines. If carbonyl compounds or amins contain effective functional groups, Schiff bases will form effective chelate groups. Chelates can serve as multiple electron-pair donor through several different atoms to a single acceptor atom or ion.

In the present paper Schiff bases derived from p-dimethyl-amino-benzaldehyde and o-nitrobenzaldehyde by the reaction of allylamine in methanol at 25°C. These Schiff bases have been characterized by N.M.R, IR and Mass spectrum. Solid complexes have been characterized by IR and elemental analysis. Magnetic susceptibility measurements have shown that all the complexes are diamagnetic. All the Schiff bases in complexes are coordinated to the metal as monodentate ligand where the allylic nitrogen is bonding site.

EXPERIMENTAL

Materials: All the substance in this investigation were reagent grade (Aldrich). Schiff bases were prepared by the condensation of aldehydes with the same mol number of allylamine in methanol as reported earlier (Tiollois, 1962). Schiff bases are obtained as liquid in methanol. This was confirmed by the colour change of the solution. Schiff base have taken from methanol in rotary evaporator at 30°C. Reaction mechanizm of Schiff bases (Zlatkis, 1973):



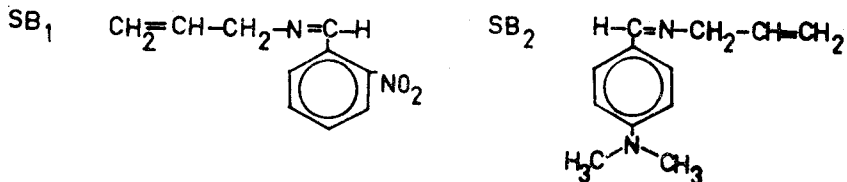
Synthesis of metal complexes: All the complexes were prepared by adding calculated amount of Schiff base to the metal salt in methanol at room temperature.

Metals: Th (NO₃)₄ · 4H₂O, UO₂ (NO₃)₂ · 6H₂O, SnCl₄ · 5H₂O, SnCl₂ · 2H₂O Reaction mixture refluxed 15 minutes and NaOH solution was added untill the complex precipitate. Coloured solid complex was filtered and dried in vacuum dessicator.

Solid complexes were analysed for their carbon, nitrogen and hydrogen contents and results are recorded in table 1.

Table I

Complex	Formula	% C		% N		% H	
		found	calc	found	calc	found	calc
(SB ₁) UO ₂ (II)	(UO ₂ C ₄₀ H ₄₀ N ₁₀ O ₁₄)	40.1	41.59	11.92	12.13	3.25	3.46
(SB ₁) Th (IV)	(ThC ₄₀ H ₄₀ N ₁₀ O ₁₄) OH ₄	44.20	45.28	10.11	11.56	3.70	4.15
(SB ₁) Sn (IV)	(SnC ₃₀ H ₂₀ N ₄ O ₄ Cl ₄)	37.1	37.46	8.1	8.74	2.96	3.12
(SB ₂) UO ₂ (II)	(UO ₂ C ₆₉ H ₄₈ N ₂ O ₆)	49.15	50.26	11.9	12.21	5.15	5.28
(SB ₂) Th (IV)	(Th C ₁₄ H ₈ N ₂) OH ₄	53.25	54.75	10.15	10.64	6.02	6.46
(SB ₂) Sn (IV)	(SnC ₃₂ H ₂₄ N ₄ Cl ₄)	44.0	45.23	8.5	8.79	4.8	5.02
(SB ₂) Sn (II)	(SnC ₃₂ H ₂₄ N ₄ Cl ₃)	45.0	46.1	8.5	8.97	4.92	5.12



Magnetic susceptibility measurements were made by Gouy balance and results are recorded in table 2

Table 2

Complex	Gram susceptibility of complex
(SB ₁) UO ₂ (II)	$X_g - 7,65 \cdot 10^{-7} (\text{erg gauss}^{-2})\text{g}^{-1}$
(SB ₁) Th (IV)	$X_g - 6,92 \cdot 10^{-7} (\text{erg gauss}^{-2})\text{g}^{-1}$
(SB ₁) Sn (IV)	$X_g - 7,24 \cdot 10^{-7} (\text{erg gauss}^{-2})\text{g}^{-1}$
(SB ₂) VO ₂ (II)	$X_g - 1,04 \cdot 10^{-6} (\text{erg gauss}^{-2})\text{g}^{-1}$
(SB ₂) Th (IV)	$X_g - 5,14 \cdot 10^{-7} (\text{erg gauss}^{-2})\text{g}^{-1}$
(SB ₂) Sn (IV)	$X_g - 6,94 \cdot 10^{-7} (\text{erg gauss}^{-2})\text{g}^{-1}$
(SB ₂) Sn (II)	$X_g - 5,92 \cdot 10^{-7} (\text{erg gauss}^{-2})\text{g}^{-1}$

IR spectrum of the complexes have taken with Perkin-Elmer double beam spectrophotometer in nujol. N.M.R spectrum of Schiff bases have taken with Varian T 60 A spectrometer in CDCl_3 . Electronic spectra of Schiff bases were measured with Hitachi model spectrophotometer using 1 cm matched quartz cell. Mass spectrum of the Schiff bases have taken with Fenningen Nat 1020 mass spectrometer and molecular weights were recorded as expected.

RESULT AND DISCUSSION

Characterization of Schiff bases were made by using N.M.R, IR and Mass spectrum. From N.M.R spectrum, it can be easily seen that there are six kinds of protons that have different chemical shifts. Aromatic protons observed at 7 and 8 ppm as double doublet, -N(CH₃)₂ protons have peak at 3,1 ppm as singlet, terminal hydrogens at 5,05 ppm as triplet, aldehyde hydrogen at 8,5 ppm, a multiplet at 6,5 ppm and doublet at 4,20 ppm which belong to -N-CH₂-protons (Parikh, 1974 Functional group peaks are observed on IR spectrum. -NH(CH₃)₂ peaks are observed at 1260-1380 cm^{-1} , C=N

peak is at 1640 cm^{-1} and aromatic, aliphatic CH stretching peaks at 3080 and 2800 cm^{-1} . Absorption spectrum of Schiff bases also have taken and three peaks are observed at 377 nm , 333 nm and 250 nm which are resulted from $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ conjugation transitions.

Eight complexes were prepared from two Schiff bases and to explain the structure of these complexes, their IR spectra have been taken. In all complexes donor atoms are imine nitrogen. It is observed that $\text{C}=\text{N}$ peak which is observed at 1640 cm^{-1} disappeared in complex (Mahmoud, 1980) This is resulted from bonding of nitrogen to metal atom. Thus, disappearance of the stretch of $\text{C}=\text{N}$ on complexation is due to the decrease in electron density within this band as a result of high positive charge of coordinated metal ion.

From this study, we concluded that:

- i) All the ligands (Schiff bases) are monodentate and imine nitrogen is bonding site.
- ii) All the complexes are diamagnetic.
- iii) They have very high melting points.
- iv) They are insoluble in CCl_4 , CHCl_3 , pyridine, acetone, CS_2 , DMSO, H_2O , benzene and dioxane.

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