Pharmaceutical Significance Of Oxotungsten And Oxochromium Complexes Of Schiff's Bases Derived From Thiosemicarbazones

Abstract*— Metal complexes of bis (5-chlorosalicylaldehyde thiosemicarbazone, bis (trifluoroacetylacetone) thiosemicarbazone and their complexes with oxotungsten and oxocromium have been prepared. These complexes have been characterized by IR, electronic spectra, molar conductance and magnetic moment. These studies have indicated octahedral geometry around the metal ion. The complexes were also screened for antifungal and antibacterial activities.

Keywords—**Chromium complexes, tungsten complexes, Schiff base, thiosemicarbazide**

I. Introduction

In continuation of our earlier reports [1], on the medicinal significance of Schiff bases and their metal complexes,the present communication reports the synthesis of some new complexes of Schiff bases derived from condensation of 5-chlorosalicyldehyde, terephthaldehyde, 2,4- pentanedione and trifluoroacetylacetone with thiosemicarbazide.

II. Experiment

A. Preparation of Schiff bases

Schiff bases [2] were synthesized by the condensation of the respective aldehyde and ketone with thiosemicarbazide in the ratio of 2:1 in ethanolic solution. Metal complexes were prepared by refluxing their methanolic solution for 24h.The precipitate thus obtained was washed with DMSO and dried over fused calcium chloride.All the complexes used were of A.R. grade(B.D.H.Koch,Light and Fluka)

B. Preparation of metal complexes

Preparation of oxotungsten complexesTungsten and chromium complexes were synthesized by the addition of salt solution in methanol to the solution of ligand in DMSO/THF.The precipitate thus obtained was washed with DMSO/THF and dried over fused $CaCl_2$.

C. Preparation of oxochromium complexes

A methanolic solution of chromium chloride was added in small quantities with stirring to a hot solution of the ligands in methanol.The pH of the solution mixture was adjusted to 5.0 with NaOAcbuffer and stirring continued for 10-15 minutes.The solid complexes that separated was washed with aqueous methanol and dried over P_4O_{10} in vacuum.

The Infra red studies [3] [4] [5] were conducted in C.D.R.I.,Lucknow. and other studies in the Department of Chemistry,Bareilly College,Bareilly.

III. Results and discussion

All the complexes formed were found to be soluble in ethanol and insoluble in water. The molar conductance of all complexes of oxotungsten are found to be compatible with 1:1 electrolytic ratio and showed conductance in CH_3OH(70-90),DMF(85-95),DMSO(52-65) and for tungsten chloride complex the values are 180- 210, 130-158, 55-67,respectively,compatable with 1:2 electrolyte. The molar conductance of all the complexes of oxotungsten in CH_3OH, DMF and DMSO are 8.5-22.0,15.0-22.5 2.9-10.1 compatible with non-electrolytic nature.

The oxotungsten (IV) chloride and oxochromium (V) chloride complexes show magnetic moment values in the range of 1.20-2.82 B.M. which correspond to the diamagnetic nature of these complexes.

The electronic spectral bands [6] [7] of the present oxotungsten (IV) complexes show similar absorption peaks. The spectral bands at 16060-12900 cm^{-1} indicated octahedral environment for these complexes. A moderately intense band observed in the region of 14000-14560 cm^{-1} has been assigned to unresolved band resulting from dxy→dyz, dxz($2B_2 \rightarrow 2E_1$) and the third band at 20600-26000 cm^{-1} may either be assigned to the transaction dxz→ dz_2 ($2B_2 \rightarrow 2A_1$) which emerge from the low energy charge transfer.

IV. Infra-RedSpectra

The IR spectra of the ligands indicated two bands i.e., n(C=N) n(C=S) [8] [9] which on complexation, shifted to lower frequencies which clearly indicated the coordination through nitrogen of (C=N) group and Sulphur of (C=S) group [10]. The IR spectra of the complexes also exhibited more bands which may be due to (W=O),(Cr=O)stretching and (W - Cl), (Cr-Cl) bands, shown in Table- 2.

TABLE I Analytical and physical data of the ligands and the complexes

Compound	% of Metal (Found/ Calcd.	% of Hydrogen (Found/Calcd.	% of Carbon (Found /Calcd.)	% of Nitrogen (Found / Calcd.)	% of Sulphur (Found/ Calcd.)	% of Chlorine (Found/Calc)
bis (5-chlorosalicylaldehyde) thiosemicarbazone oxotungsten(IV)chloride	38.15 (38.20)	3.67 (4.80)	20.22 (20.12)	9.54 (9.0)	12. 98 (12.2)	7.50 (7.61)
bis(terephthaldicarboxaldehyde) thiosemicarbazone oxotungsten(IV)chloride	28.50 (29.50)	3.09 (3.21)	39.50 (40.49)	9.80 (10.39)	8.50 (7.92)	8.51 (8.60)
bis (2,4- pentanedione) thiosemicarbazone oxotungsten(IV)chloride	42.10 (41.17)	3.06 (4.70)	27.01 (26.56)	11.01 (11.63)	9.02 (8.86)	7.13 (7.14)
bis (trifluoroacetylacetone) thiosemicarbazone oxotungsten(IV)chloride	30.21 (30.09)	2.67 (2.02)	22.01 (23.70)	11.01 (11.63)	9.02 (8.86)	7.00 (7.50)
bis (5- chlorosalicyldehyde) oxochromium (V)chloride	26.67 (25.90)	1.66 (2.70)	31.22 (30.19)	8.00 (7.99)	9.98 (10.0)	7.90 (7.81)
bis (terephthaldicarboxaldehyde) thiosemicarbazone oxochromium(V)chloride	17.57 (18.29)	2.55 (2.78)	56.50 (56.65)	12.33 (11.81)	8.80 (9.40)	7.00 (7.3)
bis (2,4- pentanedione) thiosemicarbazone oxochromium(V)chloride	20.55 (19.23)	3.98 (3.31)	40.0 (41.01)	12.00 (13.14)	9.50 (10.0)	9.33 (9.6)
bis (trifluoroacetylacetone) thiosemicarbazone oxochromium(V)chloride	39.04 35.90	1.93 (2.21)	43.09 (40.82)	8.00 (8.40)	6.00 (6.0)	7.00 (7.10)

TABLE II Analytical and physical data of the ligand and the complexes

Compound Colour	Molar inductance in (Ω^{-1}cm^2 mol $^{-2}$)		Metal Chlorine (cm^{-1})	υ (C=S) cm^{-1}	Magnetic Moment B.M.	M.P (°C)	υ(C=N) cm^{-1}
	DMF	Me OH					
(CSALTSC)$_2$WOCl Dark brown	6.77	8.0	300	1800	1.50	201	1625
(TALDICTSC)$_2$WOCl Yellow	4.99	7.5	312	1500	1.20	212	1630
(PDIOTSC)$_2$ WOCl Brownish yellow	6.20	6.0	310	1500	1.02	215	1500
(TFAATSC)$_2$WOCl Dirty yellow	8.33	8.7	330	1615	1.57	210	1525
(CSALTSC)$_2$CrOCl Yellowish brown	7.82	6.0	323	1500	2.82	240	1515
(TALDICTSC) $_2$CrOCl Brown	6.91	7.9	315	1628	2.56	256	1600
(PDIOTSC) $_2$CrOCl Yellowish pink	6.74	8.6	325	1630	1.08	230	1650
(TFAATSC)) $_2$CrOCl Yellowish white	7.60	8.2	301	1576	2.20	240	1590

TABLE III Antibacterial screening at 2 µg disc (Zone formation in mm)

Compound	*S. aureus(mm)*	*B.subtilis(mm)*
(CSALTSC)$_2$WOCl Dark brown	9.0	8.0
(TALDICTSC)$_2$WOCl Yellow	6.0	8.0

(PDIOTSC)$_2$ WOCl Brownish yellow	7.0	8.9
(TFAATSC)$_2$WOCl Dirty yellow	8.9	8.7
(CSALTSC)$_2$CrOCl Yellowish brown	10.9	10.0
(TALDICTSC) $_2$CrOCl Brown	10.7	11.3
(PDIOTSC) $_2$CrOCl Yellowish pink	9.3	11.0
(TFAATSC)) $_2$CrOCl Yellowish white	9.6	10.0

V. Antimicrobial Screening

The antifungal activity [11] [12] [13] was evaluated by the radial growth method using agar-agar culture against various species using distilled water,glucose,starch and agar-agar adding a requisite amount of the compound after being dissolved in DMF so as to obtain certain final concentrations.Antibacterial [14] [15] and antifungal [16] activities of theSchiff bases and their metal complexes have been reported as anticarcinogenic [17] [18] antifungal, and antitubercular [19] [20]. All the complexes were screened for antibacterial and antifungal activities as shown in tables III and IV, respectively.

TABLE IV **Response of the test compound(1mg/ml) against fungi**

Compound	*Rhizopus species* (conc.in ppm)			*Aspergillus species* (conc. in ppm)		
	200	100	50	200	100	50
(CSALTS)$_2$ WOCl	60	56	45	65	78	46
(TALDICTSC$_{)2}$ WOCl	67	55	40	66	65	42
(PDIOTSC)$_2$ WOCl	65	50	45	75	58	45
(TFAATSC)$_2$WOCl	85	49	44	80	67	43
(CSALTSC)$_2$CrOCl	71	58	46	71	70	35
(TALDICTSTSC)$_2$ CrOCl	88	56	41	80	55	41
(PDIOTSC)$_2$ CrOCl	60	63	43	77	49	42
(TFAA TSC)$_2$CrOCl	70	53	37	76	49	38

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