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Antimicrobial activities of titanium and vanadium complexes of 6-nitro-3-(Indolin-2-One) hydrazine carbothioamide and 6-nitro-3-(Indolin-2-one) hydrazine carboxamide

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ABSTRACT

The reaction of titanium (III) chloride and vanadium (III) chloride with monofunctional bidentate thiosemicarbazone (TSCZH) and semicarbazones (SCZH) derived from the condensation of 6-nitro-1H-indol-1-2,3-dione with thiosemicarbazide and semicarbazide hydrochloride, respectively have been carried out in 1:2 molar ratios. The resulting derivaties are coloured solids and are monomeric in nature. Octahedral geometry has been proposed on the basis of elemental analyses, magnetic susceptibility, molar conductance, electronic and I.R. spectra. The ligands and their complexes have been screened for antimicrobial activity.

Key words: Antimicrobial activities, II, V, complexes.

INTRODUCTION

The coordination derived from Schiff bases are being investigated for their therapeutic activities[1-3], Schiff bases act as intermediates in many biological process such as pyridoxal enzyme, aldol condensation, decarboxylation, transamination etc. Several Schiff base complexes have been synthesized some of metalloproteins[4-6] shiff base complexes also find application as super oxide dismutase mimics[7] and their catalytic role in the epoxidation of olefines[8].

Transition metals form some specific and important drugs with diphenyle pyridine and isothiopendyl. These drugs are found to be antiserothenine, antihistaminic, anticonvulsant, and antifungal in nature and hence used in medicinal chemistry[9]. It has been established that certain platinum and palladium[10-11] complexes are of biological importance due to their carcinostatic activity and interest in biological chemistry. Charlson *et. al.,*[12], have reported that cesium cis dichloroserinetopalladate(II) induces filament growth in *E. coli*. The complexes of palladium (II) with aminoacids such as glycine, serine and gludamine have also been reported[13,14] to be active against certain tumors. It is also wel known[15] that carcinostatic action of drugs is due to their interaction with nuclear D.N.A. Keeping these facts in consideration, we report here the synthesis, spectroscopic elucidation and antimicrobial properties of titanium (III) and vanadium (III) complexes with N and S/O based ligands.

MATERIAL AND METHODS

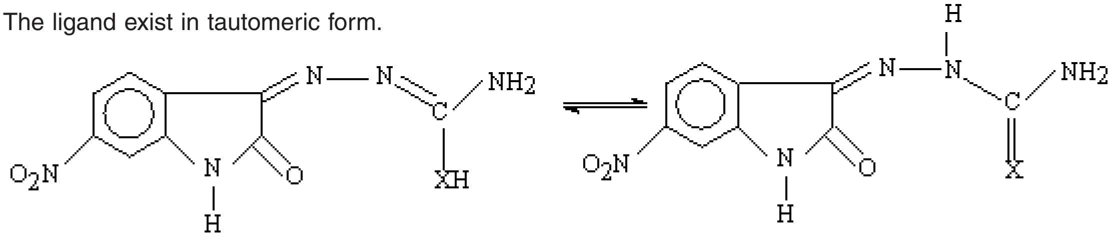
All the chemicals used were of A.R. grade. Titanium (II) chloride was prepared by standard method in the lab whereas vanadium (III) chloride (BDH, England) was used as such 6-nitroisatin was prepared in the lab by Sandmeyer isonitroacetanilide synthesis method[16]. The ligand TSCZH and SCZH were prepared by the condensation of 6-nitroisatin with hydrazinecarbothioamide and hydrazine carboxamide in the presence of sodium acetate in

1:1 molar ratio in absolute alcohol. The reaction mixture was refluxed for 4-6 hours over water bath. The product so obtained was recrystallised from ethanol and dried in vacuo. Their analytical data given in table 1.

Preparation of complexes

The metal chloride and the ligand were dissolved in ethanol and the solutions were allowed to react when the precipitate of the complexes was obtained. It was filtered, washed and dried in vacuo over fused $CaCl_2$.

The ligand exist in tautomeric form.



X = O or S

Analytical methods and physical measurments

Purity of the ligands and their metal complexes was checked by TLC on silica gel using anhydrous dimethylsuphoxide and benzene as solvent. Each of the compounds moves as a single spot, thus proving the presence of only one component.

The ligands used and the complexes were subjected to elemental analyses for C, H, N/S. The metal was estimated gravimetrically I.R., electronic spectra were recorded. The magnetic susceptibility was determined by Gouy's balance. Molar conuctance was measured at 10^{-3}M dilution at room temperature.

RESULTS AND DISCUSSION

The analytical data indicates that the metals have reacted with the monobasic bidentate thiosemicarbazone (TSCZH) and semicarbazone in the molar ratio of 1:2

The molar conductance measurements carried out at 10^{-3}M dilution (25°C) in DMSO and DMF reveal the 1:3 electrolytic nature of the complexes. The calculation of magnetic moments from magnetic susceptibility measured by Gouy,s balance indicated paramagnetic nature and octahedral geometry of the complexes[16].

The electronic spectra of titaniuum (III) complexes exhibit only one band in the range of 15000-15500cm^{-1} which may be assigned to $^{2}T_{2g}\rightarrow{}^{2}Eg$ transition. This is characteristic of octahedral geometry[17].

The electronic spectra of vanadium (III) complexes show wead broad bands in the range of 15800-16200 cm^{-1} with a shoulder in the range of 19000-19900 cm^{-1}. The bands at higher wave number were more intense and better resolved and have been assigned to $^{3}T_{2g}\rightarrow{}^{3}T_{2g}(P)$. Transition lower energy bands have been assigned to $^{3}T_{1g}\rightarrow{}^{3}T_{2g}(P)$. transition octahedral enviroment[18].

The I.R. spectra of the ligands and the complexes were recorded in KBr phase and compared. The I.R. spectra of the free ligands exhibit a band at Ca 3285 cm^{-1} assignable to NH Vibrations of the functional group. This band disappeared in the corresponding $[M(TSCZ)_2]Cl_3$ and $[M(SCZ)_2Cl_3$ complexes indicating deprotonation of the functional group on complexation[19].

The bands at 1615cm^{-1} and 1610cm^{-1} TSCZ and SCZ respectively may be due υC=N. These bands have shifted to higher wave numbers, suggesting coordination through azomethine nitrogen atom. The bands at 1680-1690cm^{-1} and 995-1050cm^{-1} may be assigned to υC=O and υC=S

Table 1: Physical properties and analytica data of TSCZH and their complexes

Comp.	Colour	m.p. (°C)	Found M	N	S	Cl	O	C	H	Magnetic moment (in B.M.)	Molar conductance (ohm^{-1} cm^2 mole^{-1}) DMSO	DMF
TSCZH (265.41)	Grey	221	-	26.16	12.24	-	-	-	-	-	-	-
SCZH (249.18)	Brown	232	-	27.86	-	-	-	-	-	-	-	-
$[Ti(TSCZ)_2]Cl_3$ (684.32)	Light brown	310	6.99	20.46	9.37	15.54	14.01	131.70	1.89	1.70	110	200
$[Ti(TSCZ)_2]Cl_3$ (652.17)	Brown	330	7.33	21.47	-	16.30	19.61	33.27	1.99	1.71	110	230
$[V(TSCZ)_2]Cl_3$ (687.4)	Light	290	7.41	20.37	9.32	15.47	13.95	31.56	1.89	2.84	115	220
$[V(SCZ)_2]Cl_3$ (655.25)	Grey	310	7.77	21.37	-	16.23	19.52	33.11	1.98	2.86	120	215

respectively. These bands show downward shifting on complexation indicating coordination of oxygen and sulphur to the central metal atoms and formation of M-O and M-S types of bonding[19]. The bands due to υC=O around 1670cm^{-1} appeared unchanged in the I.R. spectra of complexes. This indicates non participcation of this group in coordination. Similar is the case with the bands in the region 3430-3360cm^{-1} attributed ot asymmetric modes of NH_2 group. This also suggest the non participation of amino group in coordination[20].

Few new peaks have been observed in the I.R. spetra of the complexes. Out of these peaks at Ca 360-370 cm^{-1}, 440-445 cm^{-1}, 310-315 cm^{-1} and 418-425 cm^{-1} may be assigned to $\upsilon(Ti \leftarrow N)$, $\upsilon(V \leftarrow N)$, υ(M-S) and υ(M-O) respectively[19]. The bands in the range of 3200-3250cm^{-1} may be due to υO-H mode of coordinated water[21] and those Ca 850-875 cm^{-1} may be assigned to wagging and rocking modes of OH group of coordinated water[22]. The presence of coordinated water molecules is also nidicated by TGA. The thermogram show the loss of two water molecules around 170°C.

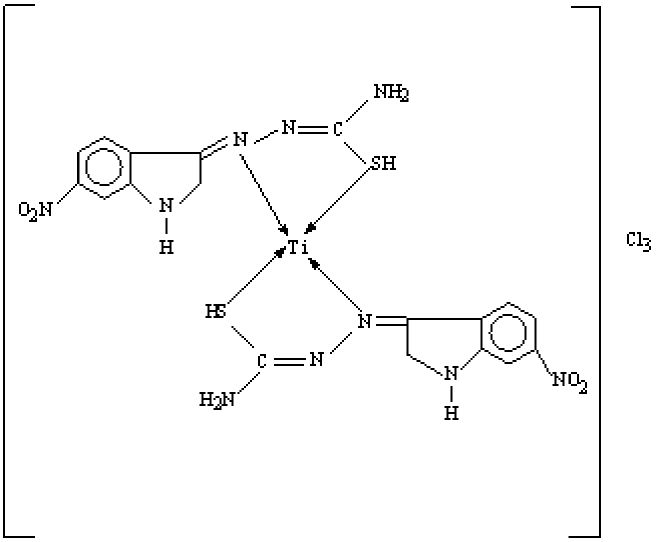
On the basis of above mentioned facts, octahedral geometry has been proposed for all the complexes, four positions are occupied by two bidentate ligand molecules and two by water molecules.

Antimicrobial activities

The ligands and the complexes were screened for antifungal and antibacterial activities. The antifungal activity was evaluated against Macrophomina phaseolina and Fusarium oxysporum using a procedure recommended for testing new chemicals[23].

The linear growth of the fungus was recorded by measuring their diameter of the fungus colony after 96hrs. and the percentage inhibition was calculated by the formula $10^2 (d_c - d_t)/d_c$ where d_c and d_t are the diameters of fungus colony in the control and test plates respectively.

Antibacterial activity was tested against *Bacillus substilis* and Salomenlla species using the paper disc plate method[24].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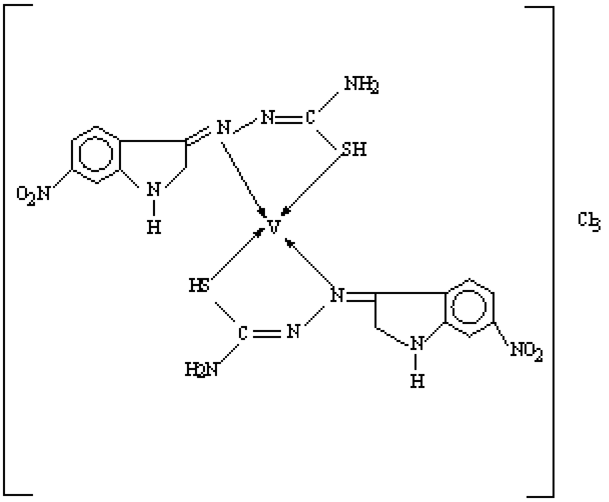
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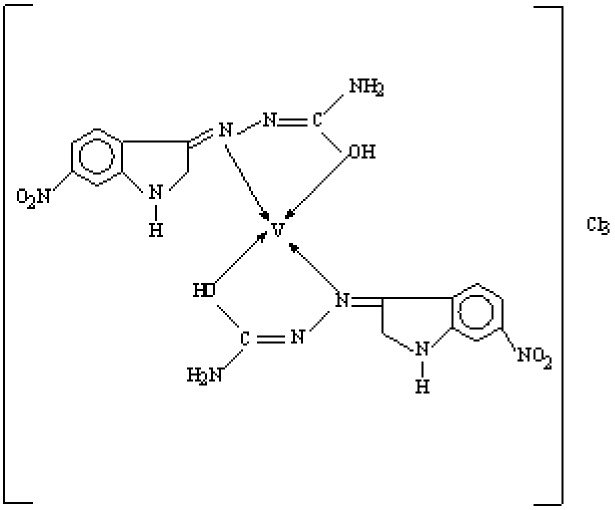
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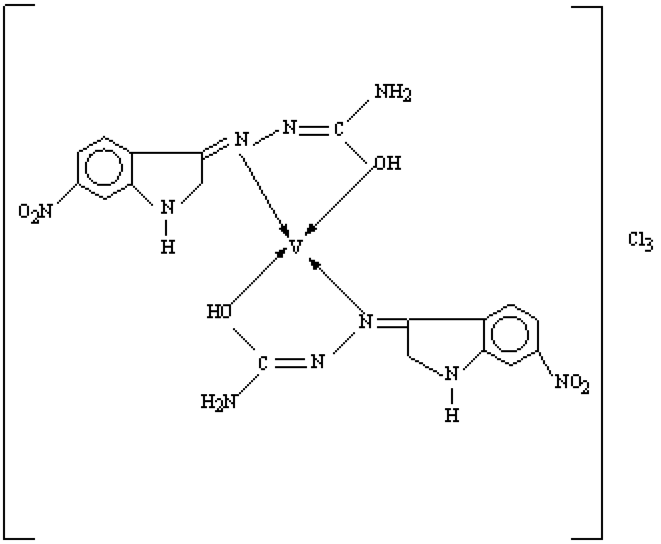

Scheme 1: Proposed sturcture of the complexes

Table 2: Fungicidal screening and antibacterial screening data of the ligands and their metal complexes

Comp.	**Inhibition after 96h(%) (conc. in ppm)**				**Diameter of inhibition zone (mm) (conc. in ppm)**			
	Fusarium oxysporum		***Macrophomina phaseolina***		***Bacillus substiles***		***Salmonella* species**	
	100	**200**	**100**	**200**	**500**	**1000**	**500**	**1000**
TSCZH	55	65	57	62	8	9	6	11
SCZH	53	56	52	58	7	9	6	10
$[Ti(SCZH)_2]Cl_3$	59	66	62	64	11	14	13	15
$[Ti(SCZ)_2]Cl_3$	57	60	58	59	9	13	11	14
$[V(SCZ)_2]Cl_3$	67	72	67	71	10	12	9	12
$[V(SCZ)_2]Cl_3$	63	69	61	65	7	9	7	11

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