

Preparation, Characterization and Antimicrobial Properties of Some Vanadium(III) and Manganese(III) Complexes of Schiff Bases

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Few complexes of V(III) and Mn(III) have been prepared by reacting their metal(III) chlorides with pyridine-2-carboxaldehydehydrazinecarboxamide [PCHC], pyridine-2-carboxaldehydethiosemicarbazone [PCTSC], 2,5-dihydroxyacetophenonehydrazinecarboxamide [DHAPHC], 2,5-dihydroxyacetophenonethiosemicarbazone [DHAPTSC], (Schiff-bases) in ethanol medium. The chelates are coloured solids and electrolytes of the type $[ML]^{+n}.X^{-n}$ and $[ML_2]^{+n}.X^{-n}$. The IR spectra of the ligands and complexes suggest involvement of hydroxy group, carbonyl group, thionyl group and azomethine group in bonding through oxygen, sulfur and nitrogen atoms, respectively. The electronic spectra and magnetic data suggest the octahedral and square-pyramidal stereochemistry for the complexes of vanadium(III) and manganese(III), respectively. The ligands and complexes have been tested for their antimicrobial activity.

Key Words: V(III), Mn(III), Complexes, Schiff bases, Antimicrobial activity.

INTRODUCTION

The metal complexes of semicarbazones and thiosemicarbazones have aroused considerable interest in view of their industrial and biological importance. Many of these compounds possess a wide spectrum of medicinal properties. The multifarious roles of transition metals in biochemistry¹, suggest that considerable potential exists for the development of new chemistry with these metals in ligand system, specifically designed to serve these roles. Thiosemicarbazides and thiosemicarbazones react as chelating agents with transition metal ions by bonding through the sulfur and hydrogenic nitrogen atom^{2,3}.

Therefore, an attempt has been made to synthesize and characterize some of the biologically active Schiff base complexes of vanadium(III) and manganese(III).

EXPERIMENTAL

All the chemicals used were of AR grade (Aldrich, Lancaster, Sisco and E. Merck). The ligand as well as metal complexes were analyzed by standard methods. Conductivity measurements were carried out on Philips Conductivity Bridge model PR9500 using 10^{-3} M DMF solution. The IR spectra were recorded on Perkin-Elmer spectro-

meter using KBr pellets. Electronic spectra were recorded on Beckmann DU-2-spectrophotometer in the range of 750-350 cm⁻¹. Magnetic susceptibility was measured on a Gouy-balance using CuSO₄·5H₂O as a calibrant.

Preparation of the ligands: The new ligands, [PCHC], [PCTSC], [DHAPHC] and [DHAPTSC] were prepared by the condensation of ethanolic solutions of pyridine-2-carboxaldehyde and 2,5-dihydroxyacetophenone with ethanolic solutions of semicarbazide and thiosemicarbazide hydrochloride (in presence of sodium acetate), respectively. On cooling, crystals separated out, which were recrystallized in the same solvent and finally dried in vacuum. The purity of ligand was checked by elemental analyses and m.p.

Preparation of metal complexes: A mixture of ethanolic solutions of the ligands in ethanol and corresponding chlorides of V(III) and Mn(III) were refluxed for 3-4 h. The complexes were cooled, filtered and washed with ethanol several times to remove any excess of the metal chloride and/or ligand. Finally, it was washed with anhydrous diethylether and dried in an electrical oven.

RESULTS AND DISCUSSION

The analytical data of compounds are given in the Table-1. The characteristic infrared bands (4000-200 cm⁻¹) for the free ligands [PCHC], [PCTSC], [DHAPHC] and [DHAPTSC] when compared with those of its V(III) and Mn(III) complexes provide meaningful information regarding the bonding sites of the ligands.

TABLE-1
ANALYTICAL, PHYSICAL DATA AND IR BANDS (cm⁻¹) OF THE COMPLEXES

Compound (colour)	m.p. (°C)	Elemental analysis (%): Found (Calcd.)					
		C	H	N	S	Cl	M
[V(PCHC) ₂ (H ₂ O) ₂]Cl ₃ (Brown)	230	32.10 (32.23)	3.60 (3.83)	21.39 (21.48)	–	20.29 (20.37)	9.70 (9.78)
[V(PCTSC) ₂ (H ₂ O) ₂]Cl ₃ (Green)	267	30.29 (30.36)	3.40 (3.61)	20.11 (20.24)	11.47 (11.56)	19.05 (19.19)	9.11 (9.21)
[V(DHAPHC) ₂]Cl (Light brown)	286	41.80 (42.99)	3.90 (3.98)	16.60 (16.71)	–	6.96 (7.04)	10.00 (10.15)
[V(DHAPTSC) ₂]Cl (Yellow)	290	40.32 (40.41)	3.60 (3.74)	15.56 (15.71)	11.90 (11.97)	6.47 (6.62)	9.46 (9.54)
[Mn(PCHC) ₂ H ₂ O]Cl ₃ (Blackish brown)	315	33.03 (33.12)	3.47 (3.54)	22.00 (22.08)	–	20.78 (20.93)	10.67 (10.84)
[Mn(PCTSC) ₂ H ₂ O]Cl ₃ (Blackish green)	321	31.02 (31.15)	3.21 (3.33)	20.56 (20.77)	5.76 (5.93)	19.51 (19.69)	10.03 (10.20)
[Mn(DHAPHC)(H ₂ O) ₂]Cl ₂ (Deep brown)	333	29.09 (29.20)	3.67 (3.78)	11.21 (11.35)	–	19.00 (19.14)	14.70 (14.87)
[Mn(DHAPTSC)(H ₂ O) ₂]Cl ₂ (Brownish yellow)	336	27.89 (27.99)	3.54 (3.62)	10.75 (10.88)	8.21 (8.29)	18.27 (18.35)	14.15 (14.25)

Compound	Key IR spectral bands (cm ⁻¹)			M:L ratio	Electrolytic nature	μ_{eff} (BM)
	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{S})$			
[V(PCHC) ₂ (H ₂ O) ₂]Cl ₃	1560	1710	–	1:2	1:3	2.88
[V(PCTSC) ₂ (H ₂ O) ₂]Cl ₃	1590	–	780	1:2	1:3	2.89
[V(DHAPHC) ₂]Cl	1575	1715	–	1:2	1:1	2.91
[V(DHAPTSC) ₂]Cl	1615	–	795	1:2	1:1	2.93
[Mn(PCHC) ₂ H ₂ O]Cl ₃	1553	1706	–	1:2	1:3	4.90
[Mn(PCTSC) ₂ H ₂ O]Cl ₃	1598	–	782	1:2	1:3	4.86
[Mn(DHAPHC)(H ₂ O) ₂]Cl ₂	1569	1711	–	1:1	1:2	4.70
[Mn(DHAPTSC)(H ₂ O) ₂]Cl ₂	1610	–	790	1:1	1:2	4.85

It is well known that the semicarbazone and thiosemicarbazone ligands can coordinate as bidentate ligands⁴, in most cases, *via* the azomethine nitrogen and oxygen/sulfur atoms⁵. The band in the range of 1640-1620 cm⁻¹ due to $\nu(\text{C}=\text{N})$ in the IR spectra of all the ligands show a downward shift in their corresponding metal complexes suggesting coordination of the azomethine nitrogen to the central metal ion. This is further supported by the appearance of non-ligand bands in the range of 530-510 cm⁻¹ in the IR spectra of all the complexes, assignable to $\nu(\text{M}-\text{N})$. The IR spectra of the ligands [PCHC] and [DHAPHC] show a band in the range of 1740-1720 cm⁻¹ which may be assigned to $\nu(\text{C}=\text{O})$ ⁶. These bands have shifted downwards in the IR spectra of their corresponding complexes suggesting coordination through carbonyl oxygen to the central metal ion which is further confirmed by the appearance of non-ligand bands in the range of 400-385 cm⁻¹ assignable to $\nu(\text{M}-\text{O})$.

Another important bands in the range of 840-820 cm⁻¹ showing a shift is due to $\nu(\text{C}=\text{S})$ indicating coordination through thione sulfur of thiosemicarbazone moiety in the metal complexes of [PCTSC] and [DHAPTSC]. This is further confirmed by the appearance of new bands in the range of 440-410 cm⁻¹ assignable to (M-S). The bands appearing in the range of 1468-1460 cm⁻¹ and 744-740 cm⁻¹ in the spectra of [PCHC] and [PCTSC] have been assigned to stretching and out of plane bending vibrations of pyridine-ring. These bands remain unchanged in the spectra of their respective complexes suggesting that pyridine nitrogen is not involved in coordination to the metal ion⁷.

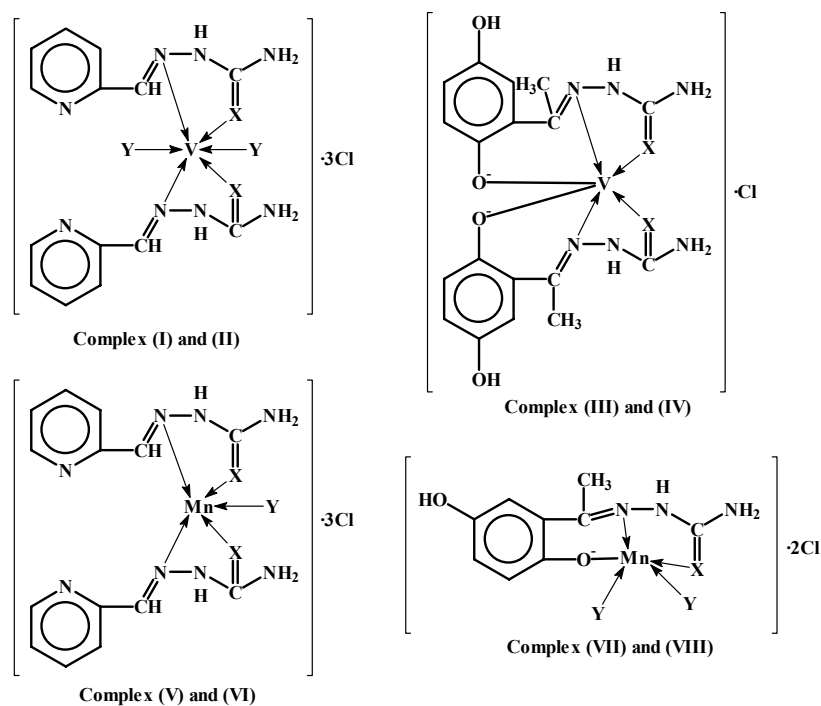
The IR spectra of [PCHC], [PCTSC], [DHAPHC] and [DHAPTSC] shows a band in the range of 3220-3200 cm⁻¹ which may be assigned to $\nu(\text{NH})$ vibrations. These bands remains practically unchanged in the spectrum of their respective complexes suggesting non-involvement of this group in the coordination.

Broad and weak bands have been observed in the range of 2800-2790 cm⁻¹ in [DHAPHC] and [DHAPTSC] ligands. The disappearance of these bands in the IR spectra of their respective complexes indicated the deprotonation and subsequent coordination of phenolic oxygen atom. This was further supported by a negative shift of the $\nu(\text{C}-\text{O})$ phenolic from higher frequency region to lower frequency region in the IR spectra of their corresponding metal complexes⁸.

All other bands appeared unchanged indicating bidentate nature of ligands ([PCHC] and [PCTSC]) and tridentate nature of ligands ([DHAPHC] and [DHAPTSC]), respectively.

The IR spectrum of all manganese(III) complexes and some vanadium(III) complexes with ligands ([PCHC] and [PCTSC]) exhibit nonligand broad absorption bands in the region of 3300-3310 cm⁻¹ which may be attributed to $\nu(\text{OH})$ group of coordinated water-molecules⁹. This is further confirmed by the appearance of new peaks in the range of 840-825 cm⁻¹ which is assigned to wagging mode of coordinated water molecules¹⁰.

The electronic spectrum of V(III) complexes was recorded in pyridine solution which showed bands at 16,000 cm⁻¹ with a shoulder at 21,000 cm⁻¹. The low-energy band has been assigned to ${}^3T_{1g} \rightarrow {}^3T_{2g}$ whereas the high-energy band to ${}^3T_{1g} \rightarrow {}^3T_{1g}(\text{P})$ transitions, respectively. These are characteristic of octahedral geometry¹¹ around V(III) ion, which is further confirmed by the μ_{eff} value in the range of 2.88-2.93 BM. for all V(III) complexes. The electronic spectrum of Mn(III) complexes exhibited an intense charge-transfer band at 27,000 cm⁻¹ and two $d-d$ transitions at 19,000 and 13,000 cm⁻¹. Since, Mn(III) ion is easily reducible, the charge transfer will be from ligands to the metal corresponding to $\pi \rightarrow t_2$ transition. The other two bands may be assigned to ${}^5B_1 \rightarrow {}^5B_2$ and ${}^5B_1 \rightarrow {}^5E$, respectively. All these are characteristic of square pyramidal geometry¹², around Mn(III) ion, and which is further confirmed by the μ_{eff} value in the range of 4.70-4.90 B.M. for all Mn(III) complexes.



Conductivity of the complexes was measured in DMF solvent and all the complexes were found to be electrolytic in nature of the type $[ML]^{n+} \cdot X^{n-}$ and $[ML_2]^{n+} \cdot X^{n-}$, where M = V(III) or Mn(III), while n = 1 for complexes(III) and (IV), n = 2 for (VII) and (VIII) and n = 3 for complexes (I), (II), (V) and (VI), respectively. The aforesaid physico-chemical evidences suggested octahedral geometry for V(III) complexes while square-pyramidal geometry for Mn(III) complexes.

All the ligands and their complexes were screened for their antibacterial activity against *Escherichia coli*, *Staphylococcus aureus*, at 10 mg/mL concentration and antifungal activity against *Aspergillus niger* at the same concentration. All the ligands were found to be less potent than their corresponding metal complexes.

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