



Preparation and Characterisation of Manganese and Vanadium Complexes of Schiff Bases

KEYWORDS

Complexes, Octahedral stereochemistry, Antibacterial activity.

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ABSTRACT Metal chelates of Mn(III) and V(III) with schiff bases have been synthesized by the condensation of 1,3-diaminopropanol-2 with 3-aminopyridine-2-carbaldehyde/2,6-dihydroxyacetophenone and characterized by using physicochemical and spectroscopic methods. The ligands DAPAPC and DAPDHAP were found to behave in tetradentate (N, O) manner. The complexes formed by these ligands have been found to have octahedral stereochemistry. The ligands and their respective complexes were also screened for their antibacterial activity.

INTRODUCTION

Transition metal coordination compounds containing the schiff base ligands have been interest for many years. These complexes play an important role in the development of coordination chemistry related to enzymatic reactions, magnetism and molecular architectures [1-3]. Imines are an important class of ligands in coordination chemistry and have various applications in analytical chemistry and in catalysis [4-5]. Keeping the above facts in mind, transition metal complexes of schiff bases derived from 1,3-diaminopropanol-2 and pyridine-2-carboxaldehyde/2,5-dihydroxyacetophenone with Mn(III) and V(III) metal ions are reported.

EXPERIMENTAL

All chemicals used were of AR grade (Aldrich, Lancaster, Sisco and E. Merck). The ligands 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 spectrometer 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 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as a calibrant. The analytical data, colour, magnetic moment and important IR spectral bands are recorded in table 1 and table 2 respectively.

PREPARATION OF THE LIGANDS

The schiff bases were prepared by the condensation of carbonyl and amino-compounds. The amino compound was dissolved in ethanol and refluxed for about half an hour. Now, the requisite amount of carbonyl compound was added to the flask and this mixture was refluxed for about 6hr. and kept for 24hr. The crystals of ligand were obtained and purified by recrystallisation in the same solvent. The purity of ligand was checked by elemental analysis and melting point.

PREPARATION OF METAL-COMPLEXES

Metal complexes were prepared by refluxation precipitation method. To the hot methanolic solution of ligand, methanolic solution of metal salts was added dropwise from dropping funnel and the resulting mixture was refluxed for 6hr. on a water bath and cooled. The pH of the solution was adjusted. The metal complexes obtained were filtered, washed with water and then with hot methanol and dried in an electrical oven.

RESULTS AND DISCUSSION

All the complexes are coloured, stable in air and decompose at higher temperature. The elemental analyses of metal complexes suggest 1:1 metal to ligand stoichiometry. The solid

complexes were found to be soluble in DMSO and DMF and the molar conductance was measured at 10^{-3} M dilution (at 25°C). The values of molar conductance in these solvents suggest 1:3 electrolytic nature for Mn(III) and V(III) complexes. Magnetic measurements and the electronic spectra of Mn(III) and V(III) complexes were also obtained in order to have information on their probable geometries.

Magnetic moments for Mn(III) complexes lie in the range of 4.73-4.95 B.M. revealing the high spin nature of the complexes, corresponding to four unpaired electrons. This value is indicative of square pyramidal configuration for the Mn(III) complexes [6]. The electronic spectra of Mn(III) complexes show an intense charge-transfer band at 27000 cm^{-1} and two d-d transitions at 19000 cm^{-1} and 13000 cm^{-1} . Since, Mn(III) ion is easily reducible, charge transfer will be from ligand to the metal corresponding to $\pi \rightarrow t_2$ (transition) [7]. The other two bands may be assigned to ${}^5B_1 \rightarrow {}^5B_2$ (13000 cm^{-1}) and ${}^5B_1 \rightarrow {}^5E$ (19000 cm^{-1}), respectively. These are characteristic of square pyramidal geometry around Mn(III) ion [8].

The V(III) complexes show magnetic moment in the range of 2.70-2.82 B.M. which is very nearly equal to the value expected for d^2 system like V(III) ion. The value also suggested paramagnetic nature and octahedral geometry for the complexes [9-10]. The electronic spectra of the V(III) complexes show weak and broad bands in the range 15820-17200 cm^{-1} with a shoulder in the range 19980-22730 cm^{-1} . The bands at higher wave numbers were considerably more intense and better resolved. Of the two bands mentioned above, the low energy band may be assigned to the ${}^3T_{1g} \rightarrow {}^3T_{2g}$ transition in pseudo octahedral symmetry and higher energy band to ${}^3T_{1g} \rightarrow {}^3T_{1g}(P)$ [11]. These are characteristic of octahedral geometry around V(III) ion [12].

The characteristic infrared bands (4000-200) cm^{-1} for the free ligands [DAPAPC] and [DAPDHAP] when compared with those of its Mn(III) and V(III) complexes provide meaningful information regarding the bonding sites of the ligands (given in Table 2). In the IR spectra the bands at 1590 cm^{-1} and 1585 cm^{-1} in (DAPAPC) and (DAPDHAP) respectively due to $\nu(\text{C}=\text{N})$ have shifted to a higher wave-number indicating coordination through the azomethine nitrogen to the central metal ion. The pyridine ring vibrations are observed at higher frequencies (1020-1023) cm^{-1} and 670 cm^{-1} in (DAPAPC) indicating an additional bonding through pyridine nitrogen [13] in the complex. The bands at 1510 cm^{-1} in (DAPDHAP) due to $\nu(\text{C}-\text{O})$ phenolic oxygen have shifted to 1540 cm^{-1} in the metal complexes, suggesting deprotonation and complexation of phenolic oxygen during complex formation. The non ligand bands in the range of 510-525 cm^{-1} and 385-410 cm^{-1}

can be assigned to $\nu(\text{M-N})$ and $\nu(\text{M-O})$, respectively, the appearance of which further supports bonding of the ligand to the metal through nitrogen and oxygen. The IR spectrum of the complexes thereby excluding the involvement of any other group in coordination and suggesting tetradentate nature of the ligands (DAPAPC) and (DAPDHAP). The presence of coordinated water molecules is indicated by the appearance of new bands at $(3400-3200) \text{ cm}^{-1}$ and $(840-825) \text{ cm}^{-1}$ due to stretching mode of -OH and rocking mode of coordinated water molecules [14]. The TGA also supported the inference of IR spectra. The thermogram shows the loss of two water molecules for V(III) complexes while loss of only one water molecule for Mn(III) complexes.

On the basis of available evidences, square pyramidal geometry may be suggested for all Mn(III) complexes, fig.no.1 and octahedral geometry may be suggested for all V(III) complexes, fig.no.2.

All synthesized compounds were evaluated for their antibacterial activities by inhibition zone technique [15] against different gram positive and gram negative bacteria e.g. Escherichia coli, Staphylococcus aureus, Salmonella typhi, Bacillus subtilis etc. All the ligands were found to be less potent than their corresponding metal complexes.

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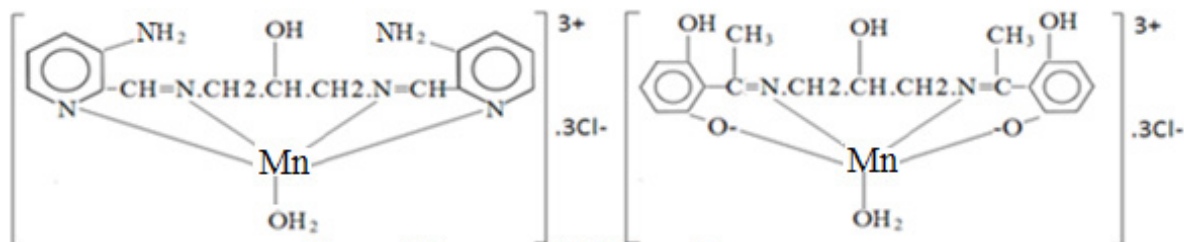


Fig. no. 1 Structure of Mn(III) complexes

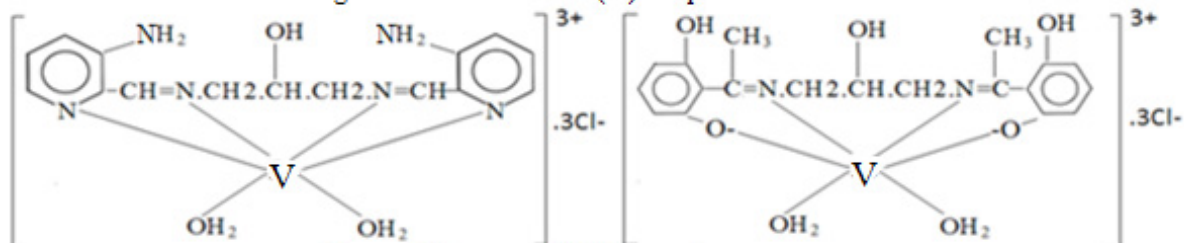


Fig. no. 2 Structure of V(III) complexes

Table 1: ANALYTICAL DATA AND PHYSICAL DATA OF THE METAL COMPLEXES.

S.No.	Compound (colour)	M.P. (°C)	Elemental Analysis (%): Found (Calculated)						Mag. Moment (B.M.)
			C	H	N	O	M	Cl	
1.	[Mn(DAPAPC).(H ₂ O)]. Cl ₃ (Yellow)	151	37.70 (37.65)	4.18 (4.10)	17.59 (17.49)	6.70 (6.68)	11.50 (11.44)	22.30 (22.21)	4.77
2.	[Mn(DAPDHAP).(H ₂ O)]. Cl ₃ (yellowish Brown)	163	42.58 (42.56)	4.10 (4.06)	5.22 (5.19)	17.92 (17.89)	10.25 (10.19)	19.89 (19.79)	4.95
3.	[V(DAPAPC).(H ₂ O) ₂].Cl ₃ (Brown)	126	36.62 (36.59)	4.47 (4.40)	17.09 (17.00)	9.76 (9.65)	10.36 (10.31)	21.67 (21.58)	2.72
4.	[V(DAPDHAP).(H ₂ O) ₂].Cl ₃ (Light Brown)	139	41.49 (41.42)	4.36 (4.25)	5.09 (4.90)	20.38 (20.29)	9.27 (9.19)	19.38 (19.31)	2.79

Table 2: KEY IR SPECTRAL BANDS OF LIGANDS [DAPAPC], [DAPDHAP] AND THEIR METAL COMPLEXES.

S. No.	Compound	Key IR spectral bands (cm ⁻¹)		M:L ratio	Electrolytic nature
		v(C=N)	v(C-O)		
1.	(DAPAPC)	1590	----	----	----
2.	(DAPDHAP)	1585	1510	----	----
3.	[Mn(DAPAPC).(H ₂ O)].Cl ₃	1611	----	1:1	1:3
4.	[Mn(DAPDHAP).(H ₂ O)].Cl ₃	1630	1545	1:1	1:3
5.	[VDAPAPC).(H ₂ O) ₂].Cl ₃	1605	----	1:1	1:3
6.	[V(DAPDHAP).(H ₂ O) ₂].Cl ₃	1625	1540	1:1	1:3

REFERENCES

- | 1. Goyal, S. and Lal, K. (1989), J. Indian Chem. Soc., 66, 477. | 2. Dash, B., Mahapatra, P.K., Panda, D. and Patnaik, J.M. (1984), J. Indian Chem. Soc., 61, 1061. | 3. Parashar, R.K., Sharma, R.C., Kumar, A. and Mohan, G. (1988), Inorg. Chim. Acta., 151, 201. | 4. Nath, M. and Yadav, R. (1997), Bull. Chem.Soc., (Japan), 70, 1331. | 5. Wilkinson, G., Gillard, R.D. and McCleverty, J.A. (1987), Comprehensive Coordination Chemistry, Pergamon Book Ltd., New York, edn.2, Vol. 6. | 6. Ismail A. Patel, Thaker, B.T. & Thaker, P.B. (1998), Indian J. Chem., 37A: 429-433. | 7. Sharma B.C. & Patel C.C. (1973), Indian J. Chem., 11: 941. | 8. Rastogi, R.K., Garg, P. and Ahmad, S. (2008), Asian J. Chem., Vol. 21, No. 8, 6144-6148. | 9. Alok K. Pareek, Joseph, P.E. and Daya S. Seth (2010), Oriental J. Chem., 26 (3), 1195-1197. | 10. Kamalendu Dey, Bhaumik, Bijali Bikash and Sarkar, Saikat (2004), Indian J. Chem., 43A: 773-777. | 11. Machin, D.J. and Murray K.S. (1967), J. Chem. Soc., A: 1498. | 12. Rastogi, R.K., Garg, P. and Ahmad, S. (2013), Oriental J. Chem., Vol. 29, No. (1), 327-331. | 13. Marsh, W.E., Egglestone, D., Hatfield, W.E. and Hodgson, D.J. (1983), Inorg. Chim. Acta, 70 (2), 137. | 14. Nakamoto, K. (1969), Infrared Spectra of Inorganic and Coordination Compounds, John Wiley, New York, p.159, 173, 214. | 15. Bansal, A. and Singh, R. V. (2009), Bol Soc Chil Quim, 45, 479.