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Synthesis and spectral characterisation of Mn(II) complexes with amide group containing 1,8-Naphthyridines

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ABSTRACT

Complexes of Mn(II) with 1,8-naphthyride containing amide group ligands 2-amino-1-8,naphthyride-3-carboxamide (ANC), 2-amino-N-phenyl-1,8-naphthyride-3-carboxamide (APNC), 2-amino-N-(p-methyl phenyl)-1,8-naphthyridine-3-carboxamide(AMPNC), 2-amino-N-)p-bromo phenyl)1,8-naphthyridine-3-carboxamide(ABPNC), 2-amino-N-(p-chloro phenyl)-1,8-naphthyridine-3-carboxamide (ACPNC), 2-amino-N-(p-methoxy phenyl)-1,8-naphthyridine-3-carboxamide (AMYPNC), 2-methyl-N-O-carboxyphenyl-1,8-naphthyridine-3-carboxamide (MCNC) and 2-phenyl-N-O-carboxphenyl-1,8-naphthyridine-2-carboxamide (PCNC) have been prepared characterized by elemental analysis, conductance, thermal magnetic, IR and electronic spectral studies of these complexes.

Key words: Manganese, 1,8-naphtyridine.

INTRODUCTION

An amide group offers two potential bending atoms, the oxygen and nitrogen, for complexation of metal ions. A number of complexes have been reported with amide group ligands which exhibit diverse coordinating behaviours with different metal ions[1-4]. However, studies on the metal complexes of the derivatives of amide groups are limited, Pannu *et. al.,*[5] have proposed the structure for this complexes with oxygen, of the amide group coordinating. On the other hand, Wiersema and Windle, on the basis of the Mn(II) salicylamide complexes, have reported that the salicylamide coordinates through nitrogen of the amide group. The majority of amide ligands form monomeric complexes with Mn(II). In view of these differences, investigation of the coordinating behaviours of the amide group containing ligands is worth while.

EXPERIMENTAL

Material

All the chemicals used were of A.R. grade, ANC, APNC, AMPNC, ABPNC, ACPNC, AMYPNC[7]. MCNC[8] and PCNC[8] were prepared by the literature method. The purity of these compounds was checked by TLC and melting determination.

Measurements

The magnetic susceptibility measurements were made at room temperature were obtained using CAHN 2000 Faraday balance (using $Hg[Co(CNS)_2]\chi_g$-16.44×10^{-6}g cc^{-1} as standard). Molar conductivities of the complexes in DMF were measured using a Digisun Digital Conductivity Meter, Model DI 909 with 0.1 M KCl solution was employed for conductivity measurements. The thermal data of the complexes were obtained using Mettler-Toledo, DSC and TGA 822e series at Central Instrumentation Center, Kakatiya University, Warangal. The IR spectra of ligands and metal complexes were recorded in KBr pellets or Nujol nulls on Perkin Elmer-BX system-The scanning time was 6 minutes in the range of 4000-400 cm^{-1}. The electronic spectra of complexes in solution of DMF were recorded on Shimadzu UV-Vis Spectrometer, Model 2401 PC.

Analysis

The percentage of Carbon, Hydrogen and Nitrogen present in organic compounds (ligands) and metal complexes were carried out a Central Drug Research Institute, Lucknow using Elementar Vario EL III Carlo Erba 1108. Manganus estimated by Complexometric Titrations.

Preparation of complexes

All the complexes were prepared by mixing methanolic solution acetate (0.001 m mol) was dissolved in methanol. To this solution (30ml) of ligand solution (0.002 m mol) was added with constant stirring over a period of 15 min then the reaction mixture was refluxed on a water both 2-3 hours or until solid separated purified by repeated washing with diethyl ether, methanol and dried in vacuum over a fused $CaCl_3$ in a desiccator.

RESULTS AND DISCUSSION

Microanalysis and conductance

The theoretica percentage of elements are calculated for different formulae expected for the reaction in Stochiometric ratios like 1:2. The experimentally obtained values are very close to the data calculated for the metal: ligand: acetate molecule ratio as 1:2:2 in the case of complexes[1-6] and metal: ligand: water molecule ratio as 1:2:2 in the case of 7 and8. Thus the formulae can be proposed tentatively as $[Mn(ANC)_2(OAc)_2]$, $[Mn(APNC)_2(OAc)_2]$, $[Mn(AMPNC)_2(OAc)_2]$, $[Mn(ABPNC)_2(OAc)_2]$, $[Mn(ACPNC)_2(OAc)_2]$, $[Mn(AMYPNC)_2(OAc)_2]$, $[Mn(MCNC)_2(H_2O)_2]$. The analytical data of these complexes are presented in Table 1. The molar conductance values of all complexes are recorded at 10^{-3} m concentration in DMF solution. The values are in the range of 5.9 to 9.2Ohm^{-1} cm^2 mol^{-1}. The conductance in this range suggests that the complexes are non-electrolytes[8]. The conductance measurements were made at regular intervals of time, over a period of 48 hours to know about any reactions between the complex species and the coordinating solvent.

Table 1: Analytica data and Physicochemical data of Mn (II) complexes

S. No.	Complex	Mol. wt.	Found (Calcd%) C	H	N	M	Molar Conductance λ_M ohm^{-1} cm^2 mol^{-1}	M_{eff} B.M.
1.	$[Mn(ANC)_2(OAc)_2]$	549.37	48.21 (48.09)	4.02 (4.04)	20.02 (20.38)	9.78 (9.99)	8.90	5.89
2.	$[Mn(APNC)_2(OAc)_2]$	701.57	57.892 (58.20)	4.21 (4.31)	15.2 (15.96)	7.09 (7.82)	9.20	5.90
3.	$[Mn(AMPNC)_2(OAc)_2]$	729.63	58.92 (59.25)	4.27 (4.70)	15.64 (15.35)	7.23 (7.52)	6.70	5.88
4.	$[Mn(ABPNC)_2(OAc)_2]$	859.36	46.92 (47.51)	3.33 (3.29)	13.15 (13.03)	6.02 (6.39)	7.90	5.94
5.	$[Mn(ACPNC)_2(OAc)_2]$	770.55	52.40 (52.99)	3.07 (3.67)	14.11 (14.53)	7.29 (7.12)	5.90	5.93
6.	$[Mn(AMYPNC)_2(OAc)_2]$	761.63	56.34 (56.76)	4.62 (4.50)	14.42 (14.69)	7.29 (7.21)	7.00	5.89
7.	$[Mn(MCNC)_2(H_2O)_2]$	703.55	58.24 (58.30)	3.92 (4.01)	11.27 (11.93)	7.49 (7.80)	6.30	5.91
8.	$[Mn(PCNC)_2(H_2O)_2]$	827.69	63.28 (63.84)	3.74 (3.90)	10.26 (10.14)	6.25 (6.63)	6.90	5.92

Thermal

The thermograms are obtained by heating the samples in nitrogen atmosphere at the rate of 20°C per minute. The date of all the complexes were critically examined to ascertain the decomposition process and the presence of different species, like ligand, acetate and water molecules.

Thermorgram of $[Mn(ANC)_2(OAc)_2]$ complex is thermally stable up to 240°C and then undergoes decomposition in one step this decomposition occurs between 240° and 690°C with a weight loss of 84.17 (cal. 84.17%) corresponding to the loss of two acetate ions and two ligands molecules. The weight of the residue left suggests the formation of MnO_2 and agrees with weight of the residue 15.08% and calculated 15.83%. Thermogram of $[Mn(PCNC)_2 (H_2O)_2]$ complex is thermally stable up to 195°C and then undergoes decomposition in two steps. The information about the extract nature of the complex and the existence of water molecule inside the coordination sphere can be obtained from thermal studies. The loss of water on heating is evidenced by and endothermic peak in DTA analysis[9].

I.R. Spectra

The selected ligands exhibit ?(CO) vibrations at 1671 (ANC), 1673 (APNC), 1670 (AMPNC), 1672 (ABPNC), 1674(ACPNC), 1670(AMYPNC), 1685(MCNC) and 1680 cm^{-1}(PCNC). The v(NH_2) frequency in ligands 1-6 appears at 3447 (ANC), 3448 (APNC), 3449 (AMPNC), 3445 (ABPNC), 3448(ACPNC) and 3485 cm^{-1}(AMYPNC). The amide v(NH) frequency shows up in ligands 2-8 around 3240, 3250, 3215, 3270, 3368, 3300 and 3250 cm^{-1} respectively. The v(OH) of carboxylic group absorbs in the range of 2500-2700cm^{-1} in MCNC and PCNC.

The complexes exhibit v(C=H) vibrations at down field shifted in the corresponding complexes 1652, 1654, 1651, 1652, 1651, 1659, 1669 and 1671 cm^{-1}, The v(NH_2) frequency in the complexes in 1-6 down field shifted appears at 3421, 3415, 3388, 3427, 3419 and 3429cm^{-1}. The v(NH) frequency in the complexes in 2-8 high field shifted shows up 3258, 3265, 3224, 3279, 32348, 3270 and 3212 cm^{-1}. The characteristic infrared absorption of Mn(II) complexes are presented in Table 2 indicate that the coordinating atoms are amide group oxygen and nitrogen in the case of 1-6 ligands. The ligands 7and8 bond through carboxylate oxygen (on deprotonation) and amide nitrogen.

Magnetic properties

The magnetic moments of the Mn(II) complexes were calculated from the magnetic susceptibilites measured using vibrating sample magnetometer. Thes susceptibility has been corrected for the diamagnetic corrections of all atoms and constitutive corrections of all bonds[10]. The values are presented in Table 1.

A majority of Mn(II), a d^5 ion complexes from high spin complexes (S=5/2). As is excepted from $^6S_{5/2}$ or $^6A_{1g}$ state[11], most of these have magnetic moments close to the spin only values of 5-92 B.M. The magnetic moments of all the Mn(II)

Table 2: Infrared spectral data (cm^{-1}) of Mn (II) complexes

S.No.	Complexes	v(NH_2)	v(NH)	v(C=O)	v(C-N)
1.	$[Mn(ANC)_2(OAc)_2]$	3421	-	1652	1427
2.	$[Mn(APNC)_2(OAc)_2]$	3415	3258	1654	1431
3.	$[Mn(AMPNC)_2(OAc)_2]$	3388	3265	1651	1421
4.	$[Mn(ABPNC)_2(OAc)_2]$	3427	3224	1652	1419
5.	$[Mn(ACPNC)_2(OAc)_2]$	3419	3279	1651	1420
6.	$[Mn(AMYPNC)_2(OAc)_2]$	3429	3248	1659	1413
7.	$[Mn(MCNC)_2(H_2O)_2]$	-	3270	1669	1423
8.	$[Mn(PCNC)_2(H_2O)_2]$	-	3212	1671	1463

complexes prepared in the presented study have magnetic moments in the range of 5-91 B.M. and the hence all the complexes are high spin. The results obtained from other physicochemical investigations revealed that the Mn(II) ion is hexacoordinated in all complexes. Therefore, octahedral geometry could be proposed for these complexes, this if further confirmed by the electronic spectra data.

Electronic spectra

The electronic spectra of Manganese (II) complexes showed a weak absorption bans (spin forbidden). These absorptions bands are observed at about 18,000 cm^{-1}, 25,000 cm^{-1} and 29,000cm^{-1} assignable to $^4T_{1g}(G) \leftarrow {}^6A_{1g}$, $^4E_g(G)$, $^4A_{1g}(G) \leftarrow {}^6A_{1g}$ and $^4T_{2g}(D) \leftarrow {}^6A_{1g}$. The absorption bands below 18,500 cm^{-1} and of low intensity observed in all the Mn(II) complexes are characteristics of octahedral complexes[22]. A narrow range observed in the first band of three Mn(II) complexes suggests that all the ligands create almost equal field strength around the Mn(II) ions.

The structure of the Mn(II) complexes 2-amino-N-(p-methyl phenyl) 1,8-naphthyridine-3-carboxamide (AMPCNC) ***a*** and 2-phenyl-N-O-carboxyphenyl 1,8-naphthyridine-3-carboxamide (PCNC) ***b*** complexes are presented in Fig.1.

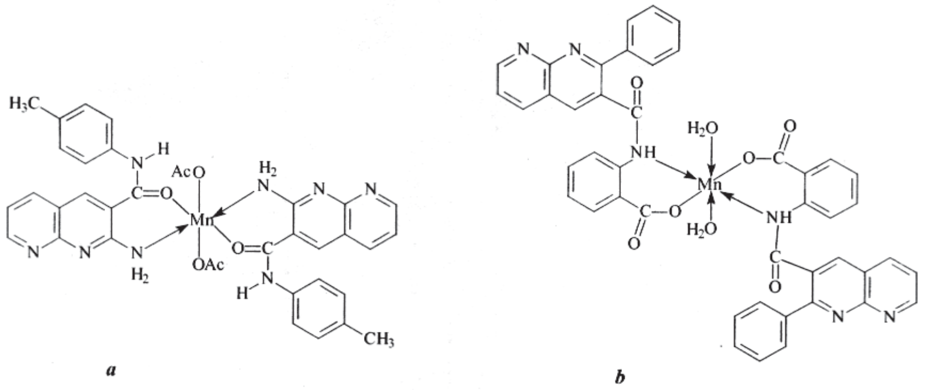

Fig. 1: Mn(II) complexes of (a) AMPCNC and (b) PCNC

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