International Archive of Applied Sciences and Technology
Int. Arch. App. Sci. Technol; Vol 8 [2] June 2017: 76-80

[ISO9001: 2008 Certified Organization]
www.soeagra.com/iaast.html

IAAST
ONLINE ISSN 2277- 1565
PRINT ISSN 0976 - 4828

CODEN: IAASCA **ORIGINAL ARTICLE**

DOI: .10.15515/iaast.0976-4828.8.2.7680

Physico-chemical Investigations on the Complexes of Mn (II) and Ni (II) with Newly Synthesized Mannich Bases

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ABSTRACT
Metal Mn(II) and Ni(II) complexes of Mannich bases 2-furfuryl-1-anilinomethyl-4-sulphacetamide (FAMSA) and 2-furfural-1-anilinomethyl-4-sulphanilamide (FAMSN) have been synthesized and characterized with the help of physico-chemical methods, elemental analysis, magnetic susceptibility measurements, IR and electronic spectral studies.
Keywords*: Schiff Base, Mannich Base, Metal Complexes, Spectral Studies*

Received 11.01.2017 Revised 10.03.2017 Accepted 14.04.2017

Citation of this article
Mahendra Pratap Singh. Physico-chemical Investigations on the Complexes of Mn (II) and Ni (II) with Newly Synthesized Mannich Bases. Int. Arch. App. Sci. Technol; Vol 8 [2] June 2017. 76-80

INTRODUCTION

The Mannich reaction [1] is widely used by both chemists and nature to form new carbon-carbon bonds via addition of enols or enolates to electrophilic iminium ions. This product are known as "Mannich bases". In the past few decades Mannich bases [2] of hetrocyclic molecules have played predominant and venerable role in the development of Co-ordination as well as medicinal chemistry and have attention of the synthetic chemists for their wide range of antimicrobial properties [3-4]. Several aminomethylated Mannich bases have several biological activities such as cytotoxic, anticancer, analgesic, antimicrobial and diuretic activities [5-10] and complexation characteristics with transition metals [11-13]. In the recent past, it was estimated that nearly 35% of mannich bases related articles were published in pharmaceutical journals [14, 15]. Several workers extended the studies of the transition metal complexes by using the Mannich reaction having antimicrobial, anticancerous and biological action [16-18]. Mannich bases had been reported as potential biological agents. These compounds play a vital role in pharmacological activities like antitubercular, antimalarial, anticancer, and antioxidant studies [19]. The present studies have been done by the reaction of furfuraldehyde and sulpha drugs (Sulphacetamide and sulphanilamide) and the reduction of the corresponding Schiff bases with sodium borohydride in methanol/alcohol.

EXPERIMENTAL

All the chemicals used were of analytical and G.R. grade. The Mannich bases FAMSA and FAMSN were synthesized by known method [20-22].

Synthesis of 2-furfural-1-anilinomethyl-4-sulphacetamide (FAMSA):

The titled Mannich base was prepared by refluxing sulphacetamide (10mmol, 2.14gm in 25ml alcohol) and 2-furfuraldehyde (10mmol, 0.96ml in 25ml alcohol) on water bath for 3-4 hours. The product was then cooled to 0^{o}C and sodiumborohydride (10mmol, 0.39gm) added over a period of 1 hour. Slowly the temperature was raised to room temperature. A deep yellow solution resulted and was stirred for 2-3 hours. The solvent was slowly evaporated. A solid colored powder was obtained. It was then washed with ethanol and ether successively and dried in air. Deep yellow crystals were obtained.

Synthesis of 2-furfural-1-anilinomethyl-4-sulphanilamide (FAMSN):

An equimolar amount of 2-furfuraldehyde (10mmol, 0.96ml in 25ml methanol) and sulphanilamide (10mmol,1.72gm in 25ml methanol) were mixed and stirred for 30 minutes. The mixture was refluxed for 3 hours. The resulting product was then cooled to 0^{o}C and $NaBH_4$ added over a period of 2 hours. Slowly

the temperature was raised to room temperature. A reddish yellow solution resulted and was stirred for 60 minutes. The solvent was evaporated and then recrystalised with ethanol and acetone and dried in air. Reddish yellow crystals were founded.

General Method For Preparing The Complexes:

A general method for the preparation of Mn(II) and Ni(II) transition metal complexes with Mannich base ligands were used. The metal chloride/metal sulphate (5mmol.) in 25ml ethanol/water was added slowly to a solution of the ligand FAMSA or FAMSN (10mmol in 25ml ethanol). The resulting mixture was stirred for 30 minutes and then refluxed for 2-3 hour on a water bath. The product was cooled and solvent was slowly evaporated then washed with ethanol, acetone and ether, dried in air. The different colored crystals of different complexes with different metal salts and ligands in 1:2 metal: ligand molar ratio have been isolated and their purety was checked by thin layer chromatography.

RESULTS AND DISCUSSION

The newly synthesized Mn(II) and Ni(II) complexes are colored solids, having sharp melting points. They are soluble in DMSO and DMF. These complexes were characterized with the help of following physico-chemical methods. Magnetic susceptibility measurements, electronic spectra,IR and elemental analysis. The analytical data indicates 1:2 metal : ligand stoichiometry for all the complexes. The analytical data of all the Mn(II) and Ni(II) complexes are given in Table-1.

Magnetic Susceptibility Measurements

The magnetic moments of all the four synthesized complexes were determined by using vibrating sample magnetometer (VSM) analysed data. Mn(II) complexes showed a value of magnetic moment in the range 5.45-5.74 B.M. Which is in the expected range of high spin octahedral Mn(II) complexes. The magnetic moment values of the newly synthesized Ni(II) Mannich base complexes observed in the range 2.98-3.08 B.M. at room temperature. These magnetic moment values are slightly higher from the spin only moment value 2.83 B.M. Based on this all the Ni(II) complexes can be assigned as distorted octahedral geometry[16] around the metal ion. The magnetic moment data of the Mn(II) and Ni(II) complexes in tabulated in table-1.

Electronic Spectral Studies

The electronic spectra provide the most detailed information about the electronic structure. The electronic spectral bands, observed in the present Mn(II) complexes in the range 19480-19900, 20400-21210, 25100-25600 and 26100-27000cm^{-1} assigned to $^6A_{1g}$-$^4T_{1g}$(4G), $^6A_{1g}$-$^4T_{2g}$, $^6A_{1g}$-^4E_g(4D) and $^6A_{1g}$-$^4T_{1g}$(4P) transitions respectively and shown octahedral geometry of Mn(II) complexes. The electronic spectra of the Ni(II) complexes exhibit five bands at 8200-8320, 10460-10850, 14100-14350, 16670-16900 and 25500-25800cm^{-1} which may be assigned to $^3B_{1g}$-$^3B_{2g}$(B), $^3B_{1g}$-^3E_g(E),$^3B_{1g}$-E_g(sh), $^3A_{2g}$(F)-$^3T_{1g}$ and $^3A_{2g}$(F)-$^3T_{2g}$(P) transitions respectively, considering octahedral geometry.

Infrared Spectral Studies

The main features of infrared spectra of the Mannich bases and their Mn(II) and Ni(II) complexes have been listed in Table-2.

The IR spectra of Mannich base (FAMSA) exhibit band at 3380$cm^{-1,}$ which is assigned V_{NH} modes. In the present complexes of Mn(II) and Ni(II), these bands are observed in the higher frequency region i.e. (3401-3391cm^{-1}) respectively, indicating the participation of nitrogen of $-CH_2$-NH- linkage in Coordination. It is also confirmed by presence of new band at 544-547 and 595cm^{-1} in the metal complexes of Mn(II) and Ni(II) due to V_{M-N} [23-24] respectively. A medium bands at 1268 cm^{-1} assigned to V_{C-O-C} of the furan ring in the ligand appeared at 1239-1420 and 1231-1245cm^{-1} in the Mn(II) and Ni(II) complexes respectively, which is suggestive of the Coordination of oxygen atom of the furan ring with metal. Appearance of a new bands at (370-385 cm^{-1}) [23-24] and (480-470cm^{-1}) in Mn(II) and Ni(II) complexes respectively due to $V_{(M-O),}$ also indicating the Coordination through oxygen with above described metal in chelation.

The IR spectrum of Mannich base (FAMSN) showed a medium band at 1040cm^{-1} due to V_{c-o-c} stretching vibration of furan ring. These bands in complexation remain unchanged indicating the nonparticipation of fural oxygen in Coordination. In(FAMSN), the V_{N-H} band due to anilinomethyl (-CH_2-NH-) group are observed at 3350 cm^{-1}, due to sulphonamide (-SO_2NH-) group is observed at 3269cm^{-1}[25]. On complexation band due to $-CH_2$-NH- group shifted to higher frequencies i.e.3408-3407 and 3408 cm^{-1} in Mn(II) and Ni(II) complexes respectively when band due to $-SO_2$NH- group is disappear in complexes indicating that both the nitrogen of Mannich base group (-CH_2-NH-) and sulphonamide group (-SO_2NH-) is in a participation in bonding. The nonligand band at(542-565cm^{-1}) [23-24] may be due to V_{M-N} also confirmed the Coordination through nitrogen with manganese.

The sulphato complex with (FAMSA) exhibit two band at 1089 and 626cm^{-1} in Mn(II) and 1090 and 628cm^{-1}[16] in Ni(II) indicating the participation of sulphate ion in complex formation. The nonligand band appear at (330cm^{-1}) [23-24][4] and 285cm^{1} due to V_{M-Cl} and also at 372cm^{-1} and 369cm^{-1} due to V_{M-S} [23, 26-27] in Mn(II) and Ni(II) respectively.

Absorption due to the bidentate sulphato group in the Mn(II) complex with (FAMSN) appear at 1099 and (617 cm^{-1}) [16] and in Ni(II) complex, these bands appear at 1099 and (680cm^{-1}) [28-29] indicating the participation of sulphate in chelate formation. The low frequency band observed at 310 and 361cm^{-1} in the Mn(II) complexes at 300cm^{-1} and 368 cm^{-1} in Ni(II) complexes is tentatively assigned to stretching vibrations of metal linked to bridge halogen and $V_{(M-S)}$ [23, 26-27] respectively. Mannich base ligands act as bidentate nature with ON and NN sides respectively.

Table-1
Analytical Estimations and Magnetic Moment Value of Mannich Bases and Their Mn(II) and Ni(II) Complexes

S.No.	Ligand/Metal Complexes	M.P. (0^0C)	Molecular Weight	Colour	Percentage of Elements							μ (B.M.)
					% C	% H	% O	% N	% S	%Cl	% M	
1	$C_{13}H_{14}N_2O_4S$	118	294.32	Deep Yellow	52.86	4.86	21.78	9.48	10.96	-	-	-
					53.04	4.79	21.74	9.51	10.89	-	-	
2	$Mn(C_{13}H_{14}N_2O_4S)_2Cl_2$	140	714.49	Yellowish Brown	43.68	3.90	17.95	7.86	8.97	9.90	7.70	5.45
					43.70	3.94	17.91	7.84	8,97	9.92	7.68	
3	$Mn(C_{13}H_{14}N_2O_4S)_2SO_4$	160	611.54	Dark Brown	42.18	3.83	25.92	7.60	12.98	-	7.45	5.70
					42.21	3.81	25.95	7.57	13.00	-	7.42	
4	$Ni(C_{13}H_{14}N_2O_4S)_2Cl_2$	165	718.25	Dark Brown	43.40	3.95	17.75	7.89	8.90	9.85	8.28	2.98
					43.47	3.92	17.82	7.70	8.92	9.87	8.17	
5	$Ni(C_{13}H_{14}N_2O_4S)_2SO_4$	175	615.30	Yellowish Brown	41.95	3.83	25.78	7.52	12.98	-	7.94	3.04
					42.00	3.79	25.82	7.56	12.94	-	7.81	
6	$C_{11}H_{12}N_2O_3S$	108	252.29	Reddish Brown	52.26	4.68	19.13	11.16	12.74	-	-	-
					52.36	4.79	19.02	11.10	12.70	-	-	
7	$Mn(C_{11}H_{12}N_2O_3S)_2Cl_2$	160	630.42	Light Brown	41.85	3.80	15.28	8.85	10.22	11.22	8.74	5.60
					41.90	3.83	15.22	8.88	10.17	11.20	8.70	
8	$Mn(C_{11}H_{12}N_2O_3S)_2SO_4$	125	655.58	Light Brown	40.24	3.74	24.32	8.60	14.70	-	8.37	5.74
					40.30	3.68	24.40	8.54	14.67	-	8.30	
9	$Ni(C_{11}H_{12}N_2O_3S)_2Cl_2$	190	634.18	Yellow	41.59	3.86	15.15	8.79	10.10	11.22	9.24	3.02
					41.68	3.81	15.13	8.81	10.11	11.10	9.00	
10	$Ni((C_{11}H_{12}N_2O_3S)_2SO_4$	140	659.33	Reddish Yellow	40.05	3.60	24.28	8.54	14.16	-	8.90	3.08
					40.07	2.66	24.26	8.49	14.50	-	8.70	

TABLE-2 : Electronic Data and Various Ligand Field Parameters (cm^{-1}) of Mn(II) Complexes

S.No.	Band Assignments and Parameters	Complexes	
		$Mn(C_{13}H_{14}N_2O_4S)_2Cl_2$	$Mn(C_{13}H_{14}N_2O_4S)_2SO_4$
		$Mn(C_{11}H_{12}N_2O_3S)_2Cl_2$	$Mn(C_{11}H_{12}N_2O_3S)_2SO_4$
1	$^6A_{1g}$-$^4T_{1g}$	19480/19750	19720/19900
2	$^6A_{1g}$-$^4T_{2g}$	20600/20400	20810/21210
3	$^6A_{1g}$-^4E_g	25100/25420	25400/25600
4	$^6A_{1g}$-$^4A_{1g}$	26420/26300	26100/27000
5	B	803/810	811/814
6	C	2514/2460	2540/2614
7	10Dq	8833/8910	8921/8954

8	F^2	1162/1161	1174/1187
9	F^4	71.82/70.28	72.57/74.68
10	B	0.93/0.94	0.94/0.94
11	β%	7.0/6.0	6.0/6.0
12	Λ	197/198.8	199/199.8
13	F	1104/1114	1115/1119
14	H	1.0/0.85	0.85/0.85
15	Π	13482.5/13220.0	13621.5/13995.0
16	Π /B	2.16/2.12	2.16/2.20

Table-3: Calculated Electronic Spectral Parameters (cm^{-1}) for Ni(II) Complexes

S.No.	Parameters	Complexes	
		$Ni(C_{13}H_{14}N_2O_4S)_2Cl_2$	$Ni(C_{13}H_{14}N_2O_4S)_2SO_4$
		$Ni(C_{11}H_{12}N_2O_3S)_2Cl_2$	$Ni(C_{11}H_{12}N_2O_3S)_2SO_4$
1	Dq^{XY}	1046/1068	1085/1078
2	Dq^Z	594/588	565/586
3	Dt	258.28/274.28	297.14/281.14
4	Ds	482/474	487/469
5	-DS	3374/3318	3409/3283
6	DQ	22546.27/27766.19	22683.70/22876.17
7	-DT	3497/3714	4026/3809
8	DQ^L	22540.52/22544	22076.67/22561.82
9	DQ^Z	30822.92/31556	32212.69/31891.55
10	DQ_A	14270.35/13977	13154.19/13862
11	DQ_E	26683.75/27160.40	27447.26/27382.80
12	-DT/DQ	0.15/0.16	0.17/0.16
13	Dσ	-1207/1225	-1287/-1230
14	Dπ	-70.05/-26.05	12.0/-1.01
15	Δ_1	156/52.03	-24.03/2.0
16	Δ_2	9709.3/9882.67	9986.97/9963.58
17	Δ_3	3218/3067	3228/3084
18	Dq^E	1121.21/1147.81	1171.64/1159.97
19	Dt/Ds	0.53/0.57	0.60/0.59

CONCLUSION

A newly synthesized Mannich bases FAMSA (**2-furfuryl-1-anilinomethyl-4-sulphacetamide**) and FAMSN (**2-furfuryl-1-anilinomethyl-4 sulphanilamide**) and its complexes have been investigated by physico-chemical and spectral studies and having octahedral geometry.

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