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Synthesis and characterization of Mn (II), Co (II) and Ni (II) complexes of semicarbazone and thiosemicarbazone of 2-pyridylglyoxal

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ABSTRACT

The Mn (II), Co (II) and Ni (II) complexes of 2- pyridylglyoxal semicarbazone and thiosemicarbazone were synthesized and characterized by elemental analysis, melting points ,uv-visible analysis, I.R studies, magnetic susceptibility measurements and thin layer chromatography. Elemental analysis of the complexes shows 1:2 (Metal:ligand) stiochiometry for all the complexes having the general formula of $[M(L)_2]Cl_2$. On the basis of above studies an octahedral geometry is proposed for all above complexes.

Keywords: 2-pyridylglyoxal, semicarbazone, thiosemicarbazone

1. INTRODUCTION

Most of the chelating ligands containing nitrogen, oxygen and sulphur as donor atoms are of great interest due to different modes of coordination with metal ions and are very useful in biological and analytical chemistry [1- 2]. This is due to their capability of acting as multidentate N—O, N—N—O and O—N—N—O ligands with the formation of either mono/ bi or polynuclear complexes. Semicarbazones and thiosemicarbazones [3-4] act as a bidentate and tridentate ligands. The Schiff bases of semicarbazones and thiosemicarbazones derived from heterocyclic compounds have significant interest in antimicrobial, antiviral and antibacterial [5], antitumour [6], antifungal [7] and antimalarial [8] agents and their metal complexes show various biological properties [9-10].

Transition metal complexes of various amines with heterocyclic glyoxalic aldehydes have already been reported [11-12]. The literature survey has revealed that a very little work has been reported on transition metal complexes of the semicarbazones and thiosemicarbazones prepared from heterocylic glyoxalic aldehydes.

2. Experimental

All chemicals used were of AR grade. The solvents were purified before use.

2.1. Physico-chemical measurements

The C, H and N were analysed on Carlo – Erba -1106 elemental analyzer. The nitrogen content of the complexes was determined using Kjeldahl's method. Metal, sulphur [13] and chlorine were estimated by the standard methods. The magnetic susceptibility measurement were made at 300°K by Gouy`s Method using $Hg[Co(NCS)_4]$ as calibrant. The standard and diamagnetic corrections were applied using Pascal`s constants. I.R spectra of the ligands and complexes were recorded in KBr in the range 4000-200cm^{-1} on Beckmann IR 5A spectrophotometer.

2.2. Synthesis of 2-pyridylglyoxal

2-pyridylglyoxal was prepared by the method of Kipnis and Ornfelt [14]. 5.5 gm of selenium dioxide (50m mol) and 30.0 ml of dioxane were placed in 100 ml two necked flask, fitted with a thermometer and a reflux condenser. The mixture was refluxed at 55-60 °C. 6.55 g (50 mmol) of 2-acetylpyridine was added and refluxed with constant stirring for four to five hours. The reaction mixture was filtered, heated and solvent was removed by distillation at atmospheric pressure. The residual liquid was fractionated through 20 cm^{-1} column at 80-95 °C (11mm) to give 3.0 ml of oily- yellow coloured 2-pyridylglyoxal.

2.3. Synthesis of 2-pyridylglyoxal semicarbazone

The above semicarbazone was prepared by standard method [15]. To the solution of 5.57g (50 mmol) of semicarbazide hydrochloride and 5 g of sodium acetate in 20.0ml of water and 6.75 ml (50 mmol) of 2-pyridylglyoxal in ethanol were added. To the turbid mixture so obtained, 1.0 ml of alcohol was added and shaken for few minutes. Buff coloured solid separated, was filtered, washed with aqueous ethanol and dried in hot air oven. Purity of the product was checked by TLC.

2.4. Synthesis of 2- pyridylglyoxal thiosemicarbazone

This thiosemicarbazone was prepared by the method of Sah and Daniels [16]. An ethanolic solution of 6.75 g (50mmol) of 2-pyridylglyoxal was added to 4.55 g (50 mmol) of thiosemicarbazide, a dark red colour solution appeared which was refluxed for 5 hours. A solid substance separated on cooling, was filtered, washed with ethanol and dried in hot air oven.

2.5. Synthesis of Dichlorobis(2-pyridylglyoxal semicarbazone/ thiosemicarbazone) of Mn(II), Co(II) and Ni(II)

Hot ethanolic solution of ligand (5 mmol) was added to an ethanolic solution of metal salts (2.5 m mol). To this reaction mixture 1.0 g of sodium acetate was added and refluxed with stirring for 4 hours. Excess of the solvent was distilled off and on cooling, the crystals of the complexes separate out. These were filtered, washed with ethanol and dried over $CaCl_2$. Purity of the complex was checked by T.L.C

3. RESULTS AND DISCUSSION

3.1. Analytical data

Analytical data reveals 1:2 (metal: ligand) stoichiometry for the Mn (II) , Co (II) and Ni (II) complexes of 2-pyridylglyoxal semicarbazone / thiosemicarbazone. These compounds have high melting points and are soluble in DMF and DMSO. These compounds are insoluble in common organic solvents.

3.2. Magnetic moment studies

The magnetic moment for synthesized Mn (II), Co (II) and Ni (II) complexes were calculated at room temperature from the magnetic susceptibility measurements and found 5.80-5.84B.M, 4.01-4.03B.M and 2.90-2.91 B.M respectively, which is quite closer with spin only value of 5.92 B.M, 3.87 B.M and 2.83 B.M, favour the octahedral geometry of the metal complexes[17] (Table 1).

3.3. Infra-red spectroscopy:

The infrared spectrum of 2-pyridylglyoxal semicarbazone/ thiosemicarbazone exihibits bands at 1710-1700cm^{-1}, 1650 cm^{-1}, 1630-1620cm^{-1},610-590cm^{-1}, 3430-3420cm^{-1}, and 3185-3170cm^{-1} due to $\nu_{C=O}$ (glyoxalic), $\nu_{C=O}$ (amidic), $\nu_{C=N}$ (azomethine), $\nu_{C=N}$ (pyridine), ν_s NH_2 and $\nu_{as}NH_2$ and also one characteristic band due to thione group is found in the I.R region of 870 cm^{-1}. Out of these bands, some bands are changed after the complexation with metal ions.

The displacement $\nu_{C=O}$ (amidic) and $\nu_{C=S}$ (thione) frequencies at 1620-1610cm^{-1} and 855-830 cm^{-1} after the complex formation has been observed, which indicates the coordination of oxygen and sulphur of the ligands with the metal ions which is also supported by the observed bands of ν_{O-H} and ν_{S-H} in the spectra frequency of ligands. Some changes in the bands ν_s NH_2 and $\nu_{as}NH_2$ have been observed due to electron displacement. These bands were also observed in the complexes confirming that the free – NH_2 group of the ligands does not take part in complexation. It confirm the participation of the oxygen and sulphur atoms C=O and C=S of semicarbazones and thiosemicarbazones. ν_{C-N-C} stretching frequencies of pyridine ring are oberserved in the free ligands at 590-610cm^{-1} in free ligands of $C_8H_8O_2N_4$ and $C_8H_8ON_4S$ respectively ,which gets shifted to higher frequency region of 635-630cm^{-1}, 650-640cm^{-1} and 640-620cm^{-1} which confirm that nitrogen of pyridine ring also in coordination with metal ions. The pyridine nitrogen appears to be involved in coordination based on the in-plane and out- of -plane ring deformation bands shifting towards higher energies [18-19].

The shift in bands is also observed in the case of complexes due the coordination of νC=N of ligand to metal ion at 1615-1590 cm^{-1} towards lower wave numbers. The participation of the azomethine N atom in coordination is further supported by the displacement of N-N modes of the free ligands in the complexes. A similar change but of much greater magnitude is observed for N-N (1055-1040 cm^{-1}) of hydrazine in coordination to a metal ion.

There is no change in the frequencies of νC=O glyoxal moiety, which indicates non participation of oxygen of $\nu_{C=O}$ of glyoxalic group with metal ion on complexation. The bands appearing in the spectra of metal complexes in the region ν_{M-N} 495-460 cm^{-1}, ν_{M-O} 450-440 cm^{-1} and ν_{M-S} 365-355 cm^{-1} indicate the presence of M-N,M-O, and M-S bands which show the coordination of metal ion with nitrogen ,oxygen and sulphur atoms of the ligands [20-26]. (Table 2).

3.3. Electronic spectral studies

Table - 1: Elemental Analysis and Magnetic Moment of Ligands and Metal Complexes of 2-Pyridylglyoxalsemicarbazone/thiosemicarbazone

COMPOUNDS	Molecular Weight	M.P. (℃)	Colour	% FOUND / (CALC.)						μ_{eff} (B.M.)
				METAL	C	H	N	S	Cl	
				Obs./ Cal.	Obs./ Cal.	Obs./ Cal.	Obs./ Cal.	Obs./ Cal.	Obs./ Cal.	
$C_8H_8O_2N_4$	192	160	Brown	-	50.04/(50.00)	4.10/(4.16)	29.10/(29.16)	-	-	-
$C_8H_8ON_4S$	208	189	Light brown	-	46.12/(46.15)	3.90/(3.84)	26.98/(26.92)	15.40/(15.38)	-	-
$[Mn(C_8H_8O_2N_4)_2]\ Cl_2$	510	260	Buff crystalline	10.73/(10.78)	37.60/(37.64)	3.16/(3.13)	21.99/(21.96)	-	13.90/(13.92)	5.80
$[Mn(C_8H_8ON_4S)_2]\ Cl_2$	542	245	Yellow cryst.	10.12/(10.14)	35.43/(35.42)	2.97/(2.95)	20.64/(20.66)	11.82/(11.80)	13.05/(13.09)	5.84
$[Co(C_8H_8O_2N_4)_2]\ Cl_2$	514	210	Pink amorphous	10.43/(10.47)	37.30/(37.35)	3.10/(3.11)	21.8/(21.78)	-	13.85/(13.81)	4.01
$[Co(C_8H_8ON_4S)_2]\ Cl_2$	546	230	Light Pink	10.75/(10.80)	35.12/(35.16)	2.91/(2.93)	20.55/(20.51)	11.65/(11.72)	13.05/(13.00)	4.03
$[Ni(C_8H_8O_2N_4)_2]\ Cl_2$	546	190	Greenish Blue	11.53/(11.47)	37.38/(37.35)	3.02/(3.11)	21.80/(21.78)	-	13.85/(13.81)	2.90
$[Ni(C_8H_8ON_4S)_2]\ Cl_2$	490	215	Light Green	10.81/(10.80)	35.12/(35.16)	2.99/(2.93)	20.46/(20.51)	11.77/(11.72)	13.09/(13.00)	2.91

Table - 2: Infrared Spectral Data (in cm^{-1}) of Ligands and Metal Complexes of 2-pyridylglyoxal semicarbazone / thiosemicarbazone

Compound	$\nu_{C=O}$ (Glyoxalic)	$\nu_{C=N}$	$\nu_{C=O}$ (Amide)	$\nu_{C=S}$ (Thione)	ν_{C-N} (Pyridine)	$\nu_s NH_2$	$\nu_{as} NH_2$	ν_{M-N}	ν_{M-O}	ν_{M-S}
$C_8H_8O_2N_4$	1700	1630	1650	-	590	3420	3170	-	-	-
$C_8H_8ON_4S$	1710	1620	-	870	610	3430	3185	-	-	-
$[Mn(C_8H_8O_2N_4)_2]\ Cl_2$	1710	1605	1615	-	630	3460	3110	490 m	440 m	-
$[Mn(C_8H_8ON_4S)_2]\ Cl_2$	1715	1590	-	855	635	3485	3120	470 s	-	355 m
$[Co(C_8H_8O_2N_4)_2]\ Cl_2$	1715	1610	1610	-	640	3460	3115	485 m	450 m	-
$[Co(C_8H_8ON_4S)_2]\ Cl_2$	1710	1615	-	850	650	3475	3120	460 m	-	365 m
$[Ni(C_8H_8O_2N_4)_2]\ Cl_2$	1700	1610	1620	-	620	3465	3115	495 m	450 m	-
$[Ni(C_8H_8ON_4S)_2]\ Cl_2$	1705	1605	-	830	640	3480	3125	460 s	-	365 m

Table - 3: Electronic Spectral Data and Various Ligand Field Parameters of Mn(II) Complexes of 2-pyridylglyoxal semicarbazone/ thiosemicarbazone

Compounds	Band Position and their assignments												
	$^6A_{1g}\rightarrow{}^4E_g(4D)$	$^6A_{1g}\rightarrow{}^4E_{g,}{}^4A_{1g}(4G)$	$^6A_{1g}\rightarrow{}^4T_{1g}$ (4G)	B (cm^{-1})	C (cm^{-1})	10Dq (cm^{-1})	F_2 (cm^{-1})	F_4 (cm^{-1})	β	f	h	λ	CSFE (cm^{-1})
$[Mn(C_8H_8O_2N_4)_2]\ Cl_2$	27677	23450	19461	604	3481	6930	1101	99.48	0.70	0.81	4.2	142	0
$[Mn(C_8H_8ON_4S)_2]\ Cl_2$	27450	23500	19465	564	3572	6200	1074	102	0.65	0.72	5.00	139	0

Table - 4: Electronic Spectral Data and Various Ligand Field Parameters of Co(II) Complexes of 2-pyridylglyoxal semicarbazone / thiosemicarbazone

Spectral data and different Ligand field parameters from numerical fitting		$[Co(C_8H_8O_2N_4)_2]Cl_2$	$[Co(C_8H_8ON_4S)_2]Cl_2$
Experimental spin allowed bands (in cm^{-1})	ν_1	11620	11230
	ν_2	15590	14090
	ν_3	20215	20420
Racah parameters (in cm^{-1})	B	927	1108
	C	4282.74	5118.96
Slator-Condon-Shortley parameters (in cm^{-1})	F_2	1538.7	2451.1
	F_4	122.34	146.25
Crystal field stabilization energy (in cm^{-1})	E	6632	6501.6
Crystal field splitting energy (in cm^{-1})	10 Dq	8290	8127
Oscillator strength of transition	F	891.39	873.87
Nephelauxetic ratio	β_{35}	0.95	1.14
Ratio between ν_1, ν_2 and ν_3	ν_3 / ν_1	1.73	1.81
	ν_3 / ν_2	1.29	1.44
	$\nu_{2(obs)} / \nu_{1(cal)}$	2.23	2.01
Difference $\nu_{2(obs)}$ and $\nu_{1(cal)}$	$\nu_{2(obs)} - \nu_{1(cal)}$	8795	7108

The solution spectra of Mn (II) complexes exhibit a series of weak bands. The ground state of the d^5 system in a weak octahedral field has one electron in each d -orbital having their spin parallel the transition of the spectrum are assigned as from $^6A_{1g}$ ground term to the quartet excited terms [27].

The Orgel diagram for d^5 configuration for Mn(II) complexes show three bands at 27677-27450cm^{-1}, 23500-23450 and 19465-19461 cm^{-1} assigned for $^6A_{1g}\rightarrow{}^4E_g(4D)$ ν_1, $^6A_{1g}\rightarrow{}^4E_g,{}^4A_{1g}(4G)$ ν_2 and $^6A_{1g}\rightarrow{}^4T_{1g}(4G)$ ν_3 which are independent of the strength of the ligand field [28-33]. These transitions were used to calculate the values of B, C and 10Dq from the Tanabe- Sugano diagram for d^5 system [34].

The electronic transition observed for Mn(II) complex suggest the octahedral geometry. The value of 10 Dq has been calculated using the Dq /B = 1.1 relation.The Slater-Condon-Shortley parameters F_2 and F_4 have been calculated by using the values of Racah interelectronic repulsion parameters B ($B = F_2 - 5 F_4$) and C ($C = 35 F_4$). [35-36] The Nephelauxetic ratio β has been calculated by using free ion value of Racah parameter B (960 cm^{-1}) and the calculated B values for the complexes, as($\beta = B/ B_o$). (Table 3)

In the case of Co(II) complexes, three peaks were observed in their electronic spectra namely $^4T_{1g} \rightarrow {}^4T_{2g}(F)$ ν_1,$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $\nu_2$and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ ν_3 found at 11620-11230cm^{-1}, 15590-14090cm^{-1} and 20420-20215 cm^{-1} respectively. These spectra suggests octahedral geometry for Co (II) complexes. The spectral data and values of various ligand field parameters such as B, C, F_2, F_4, 10Dq, E, f, β_{35}, ν_3/ν_1 and ν_3 / ν_2 were calculated by the standard methods [37-43].The results obtained are in favour of octahedral geometry of the complexes. The ratio of $\nu_{2(obs.)}/ \nu_{1(calc.)}$ agrees with the required range (2.23 -2.01) for the octahedral Co(II) complexes [44]. The 10 Dq values calculated from method (c) are in good agreement with the $\nu_{2\,(obs.)} - \nu_{1(calc.)}$ values. The lower values of β-$_{35}$ indicate the covalent character of the metal-ligand bond, and the high intensity of the absorption bands. The values of ratios between ν_1, ν_2 and ν_3 indicate the octahedral geometry for the complexes (Table 4)

The electronic spectra for the Ni(II) complexes exhibits absorption bands at 10512-10500 cm^{-1}, 17260-17250cm^{-1} and 26400-25980 cm^{-1} assigned to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ν_1 ,$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ν_2 and $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)\nu_3$ transitions respectively, which support an octahedral geometry around Ni (II) ion. B value has been taken as an average of β_{35} values calculated by the literature methods [44]. The spectral data and values of various ligand field parameters such as 10Dq, B [45],C, β_{35}, ν_2 / ν_1, Dq / B, λ, E, f and h. The 10Dq and β_{35} values of the complexes indicate the presence of strong covalent bonds in the complexes [46]. This is also supported by the β_{35} values in the complexes. The ratio of ν_2/ν_1 for the complexes is 1.64 as expected for octahedral Ni(II) complexes [47]. Lowering in these values from the theoretical value of ν_2/ ν_1 (1.8) suggests some distortion in the octahedral geometry. [48] In all the complexs of Ni(II), the best fit was obtained using

Table - 5: Electronic spectral data and various ligand field parameters of Ni(II) complexes of 2-pyridylglyoxal semicarbazone/ thiosemicarbazone.

Spectral data and different Ligand field parameters from numerical fitting		$Ni(C_8H_8O_2N_4)_2]\ Cl_2$	$Ni(C_8H_8ON_4S)_2]\ Cl_2$
Experimetal Spin allowed bands (in cm^{-1})	ν_1	10512	10500
	ν_2	17250	17260
	ν_3	25980	26400
Racah parameters (in cm^{-1})	B	780	810
	C	3603.6	3742.2
Slater-Condon-Shortley parameters (in cm^{-1})	F_2	1294.8	1344.6
	F_4	102.96	106.92
Crystal field stabilization energy (in cm^{-1})	E	12614.4	12600
Crystal field splitting energy (in cm^{-1})	10Dq	1051.12	10500
Oscillator strength of transition	f	1181.12	1179.77
Nephelauxetic function of Ligand	h	2.16	1.91
Nephelauxetic ratio	β_{35}	0.74	0.77
Ratio between ν_2 & ν_1	ν_2 / ν_1	1.64	1.64
Spin- orbit coupling constant	λ	154	171

the method (c) because there is least difference in the calculated and observed transition energies in this method. The ν_2 band in all cases shows some sign of splitting, which may be attributed to spin-forbidden transitions occurring due to spin-orbit coupling to ‘E(D) lying close to the $^3T_{1g}\ (F)$ state [49-50]. Values of λ were found to be considerably lower than the value for the free ion (λ_0) (Table 5).

4. CONCLUSION

Mn(II), Co (II) and Ni (II) complexes of 2-pyridylglyoxal semicarbazone and thiosemicarbazone were synthesized and characterized by analytical and spectral studies. On the basis of these studies an octahedral geometry is proposed for all the above complexes.

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