

Divalent metal complexes of 2-pyrrolylgyoxal semicarbazone and thiosemicarbazone: Synthesis, characterization and biocidal activity

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ABSTRACT

The synthesis and characterization of Mn (II), Co (II), Ni (II) and Cu (II) complexes of 2-pyrrolylgyoxal semicarbazone (L) and 2-pyrrolylgyoxal thiosemicarbazone (L¹) are reported. The complexes have been characterized by elemental analysis, melting points, molar conductance, magnetic studies, uv-visible and I.R spectral studies. They have the stoichiometry of the type [ML₂Cl₂] for all the metal ions. The antibacterial and antifungal activity of the metal complexes has been investigated. Both ligands and their complexes show good antibacterial and antifungal activity. The activity data showed that the metal complexes have more antifungal and antibacterial activity than the present ligands.

Keywords: 2-Pyrrolylgyoxal, semicarbazone, thiosemicarbazone, Divalent metal complexes, Biocidal activity.

1. INTRODUCTION

Semicarbazones and thiosemicarbazones are actually Schiff bases which are formed by condensation of aldehydes or ketones with semicarbazide and thiosemicarbazide [1] and behave as chelating ligands and usually react with metallic cations giving complexes. These are very versatile ligands² and can coordinate with metal as neutral molecule or after deprotonation, as an anionic ligand and adopt a variety of different coordination modes [3-5]. These are now well established as an important class of sulphur donor ligands particularly for transition metal ions [6]. Semicarbazone and thiosemicarbazone and their metal complexes are of great significance for their pharmacological properties such as antibacterial, antifungal, antitumoral, antiviral and anticancer [7-13]. Interest in the metal complexes with semicarbazone and thiosemicarbazone ligands has been stimulated because biological activities are often enhanced on complexation [14-16].

Transition metal complexes of various amines with heterocyclic glyoxalic aldehydes have already been reported [17]. The literature survey has revealed that a very little work has been reported [18] on transition metal complexes of the semicarbazones and thiosemicarbazones prepared from heterocyclic 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 [19]. Metal, sulphur and chlorine were estimated by the standard methods. The magnetic susceptibility measurement was 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. The bacterial culture for *B. Subtilis*, *E. Coli*, *S. Aureus*, *S. Varidence* and pathogenic stains of *H. gramineum* and *C. capisici* were obtained from Department of Microbiology, BSA College, Mathura.

Antibacterial and antifungal activity of ligands and their metal complexes were evaluated by agar disc diffusion method [20] in the department of microbiology, BSA College, Mathura.

2.2. Synthesis of 2-pyrrolylgyoxal

2-pyrrolylgyoxal was prepared by the method of Kipnis and Ornfelt. [21] 5.5 gm of selenium dioxide (50mmol) 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, 5.45 g (50 mmol) of 2-acetylpyrrole 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 yellowish brown coloured 2-pyrrolylgyoxal.

2.3. Synthesis of 2-pyrrolylgyoxal semicarbazone

The above semicarbazone was prepared by standard method²². To the solution of 5.57g (50 mmol) of semicarbazide hydrochloride and 5 g of sodium acetate in 20.0ml of water and 6.15 ml (50 mmol) of 2-pyrrolylgyoxal in ethanol were added. To the turbid mixture so obtained added 1.0 ml of alcohol and shaken for few minutes. Buff coloured solid obtained, 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-pyrrolylgyoxal thiosemicarbazone

This thiosemicarbazone was prepared by the method of Sah and Daniels [23]. An ethanolic solution of 6.15g (50mmol) of 2-pyrrolylgyoxal was added to 4.55 g (50 mmol) of thiosemicarbazide, a dark red coloured solution appeared which was refluxed for 5 hours. A solid substance obtained on cooling, was filtered, washed with ethanol and dried in hot air oven.

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

Hot ethanolic solution of ligand (5 mmol) was added to an ethanolic solution of metal salts (2.5 mmol). 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 CaCl₂. Purity of the complexes was checked by T.L.C

3. RESULTS AND DISCUSSION

3.1. Analytical data

The analytical data of the reported complexes reveals 1:2 (metal: ligand) stoichiometry for the Mn (II), Co (II), Ni (II) and Cu (II) of 2-pyrrolylgyoxal semicarbazone / thiosemicarbazone. These compounds have high

melting points and are soluble in DMSO and Dioxane. These compounds are insoluble in common organic solvents such as ethanol, acetone, benzene, ethyl acetate etc.

3.2. Magnetic moment studies

The magnetic moment for reported complexes of Mn (II), Co (II), Ni (II) and Cu (II) were calculated at room temperature from the magnetic susceptibility measurements and found 5.85-5.99B.M, 4.04-4.05B.M, 2.89-2.93 B.M and 1.84-1.91 B.M respectively, which is quite closer with spin only value of 5.92 B.M, 3.87 B.M, 2.83 B.M and 1.73B.M favours the octahedral geometry for Mn (II), Co (II) and Ni (II) [24-27] and distorted octahedral geometry for Cu(II) complexes [28-29]. (Table 1)

3.3. Infra-red spectroscopy

The infrared spectrum of 2-pyrrolylgyoxal semicarbazone/ thiosemicarbazone exhibits bands at 1720-1715cm⁻¹, 1710cm⁻¹, 840cm⁻¹, 1670-1640cm⁻¹, 740-720cm⁻¹, 3440-3410cm⁻¹ and 3190-3175cm⁻¹ due to $\nu_{C=O}$ (glyoxalic), $\nu_{C=O}$ (amidic), $\nu_{C=S}$ (thione), $\nu_{C=N}$ (azomethine), ν_{N-H} (pyrrole), $\nu_{symm} NH_2$ and $\nu_{asymm} NH_2$. Out of these bands, some bands are changed after the complexation with metal ions.

There was displacement in the I.R spectrum of metal complexes and new bands of $\nu_{C=O}$ (amidic) and $\nu_{C=S}$ (thione) frequencies at 1690-1670cm⁻¹ and 825-815 cm⁻¹ have been observed, which indicates the coordination of oxygen and sulphur of the ligands with the metal ions, and 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 $\nu_s NH_2$ and $\nu_{as} NH_2$ have been observed due to electron displacement. These bands were also observed in the complexes confirming that the free -NH₂ group of the ligands does not take part in complexation. It confirms the participation of the oxygen and sulphur atoms C=O and C=S of semicarbazones and thiosemicarbazones. There was no shift in the frequency of ν_{N-H} stretching vibration of pyrrole ring, which indicates that nitrogen of pyrrole does not take part in complexation [30].

The shift in bands is also observed in the case of complexes due to the coordination of $\nu_{C=N}$ (azomethine) of ligand to metal ion at 1650-1590 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(1080-1030 cm⁻¹) of hydrazine in coordination to a metal ion.

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

COMPOUNDS	Molecular Weight	M.P (°C)	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 ₇ H ₈ O ₂ N ₄	180	200	Yellowish brown	-	46.60/46.66	4.42/4.44	31.10/31.11	-	-	-
C ₇ H ₈ ON ₄ S	196	210	Oily yellowish	-	42.83/42.85	4.12/4.08	28.60/28.57	16.30/16.32	-	-
[Mn(C ₇ H ₈ O ₂ N ₄) ₂ Cl ₂]	542	245	Light yellow	11.25/11.31	34.58/34.56	3.22/3.29	23.01/23.04	-	14.62/14.60	5.85
[Mn(C ₇ H ₈ ON ₄ S) ₂ Cl ₂]	516	270	Pale yellow	10.60/10.65	32.57/32.55	3.15/3.10	21.73/21.70	12.45/12.40	13.71/13.75	5.99
[Co(C ₇ H ₈ O ₂ N ₄) ₂ Cl ₂]	490	250	Dark pink	12.01/12.04	34.29/34.28	3.29/3.26	22.82/22.85	-	14.50/14.48	4.04
[Co(C ₇ H ₈ ON ₄ S) ₂ Cl ₂]	522	280	Violet	11.29/11.30	32.12/32.18	3.10/3.06	21.49/21.45	12.29/12.26	13.52/13.60	4.05
[Ni(C ₇ H ₈ O ₂ N ₄) ₂ Cl ₂]	522	240	Greenish	12.03/12.04	34.30/34.28	3.28/3.26	22.83/22.85	-	14.44/14.48	2.89
[Ni(C ₇ H ₈ ON ₄ S) ₂ Cl ₂]	519	270	Dark Green	11.33/11.30	32.22/32.18	3.00/3.06	21.42/21.45	12.19/12.26	13.58/13.60	2.93
[Cu(C ₇ H ₈ O ₂ N ₄) ₂ Cl ₂]	495	255	Blue	12.93/12.92	39.95/40.00	3.25/3.23	22.60/22.62	-	14.30/14.34	1.91
[Cu(C ₇ H ₈ ON ₄ S) ₂ Cl ₂]	527	295	Greenish blue	12.16/12.14	31.89/31.88	3.01/3.03	21.30/21.25	12.04/12.14	13.50/13.47	1.84

Table - 2: Infrared Spectral Data (in cm⁻¹) of Ligands and Metal Complexes of 2-pyrrolylgyoxal semicarbazone / thiosemicarbazone

Compound	$\nu_{\text{C=O}}$ (Glyoxalic)	$\nu_{\text{C=N}}$	$\nu_{\text{C=O}}$ (Amide)	$\nu_{\text{C=S}}$ (Thione)	$\nu_{\text{sym NH}_2}$	$\nu_{\text{asy NH}_2}$	$\nu_{\text{N-N}}$	$\nu_{\text{N-H}}$ (pyrrole)	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-S}}$	$\nu_{\text{M-Cl}}$
C ₇ H ₈ O ₂ N ₄	1720	1650	1710	-	3410	3190	-	720	-	-	-	-
C ₇ H ₈ ON ₄ S	1715	1640	-	840	3440	3175	-	740	-	-	-	-
[Mn (C ₇ H ₈ O ₂ N ₄) ₂ Cl ₂]	1730	1615	1675	-	3405	3180	1050	750	460 m	360s	-	310 w
[Mn (C ₇ H ₈ ON ₄ S) ₂ Cl ₂]	1720	1670	-	820	3430	3170	1040	780	420s	-	320m	350b
[Co(C ₇ H ₈ O ₂ N ₄) ₂ Cl ₂]	1720	1670	1670	-	3400	3165	1030	760	480 m	370s	-	320 w
[Co(C ₇ H ₈ ON ₄ S) ₂ Cl ₂]	1730	1590	-	825	3430	3160	1070	770	430s	-	335m	340b
[Ni(C ₇ H ₈ O ₂ N ₄) ₂ Cl ₂]	1715	1625	1680	-	3400	3175	1080	760	440 m	370s	-	320 w
[Ni(C ₇ H ₈ ON ₄ S) ₂ Cl ₂]	1710	1610	-	825	3420	3160	1060	770	445s	-	340m	350b
[Cu(C ₇ H ₈ O ₂ N ₄) ₂ Cl ₂]	1710	1620	1690	-	3445	3175	1055	790	480 m	420s	-	320 w
[Cu(C ₇ H ₈ ON ₄ S) ₂ Cl ₂]	1710	1610	-	815	3430	3170	1070	810	460s	-	370m	340b

Table - 3: Electronic Spectral Data and Various Ligand Field Parameters of Mn(II) Complexes of 2-pyrrolylgyoxal 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 ₇ H ₈ O ₂ N ₄) ₂ Cl ₂]	27980	23985	19560	571	3655	6280	1273	104	0.66	0.73	4.8	140	0
[Mn (C ₇ H ₈ ON ₄ S) ₂ Cl ₂]	28571	23810	20000	680	3402	7480	1166	97.2	0.79	0.88	3.00	166	0

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

Spectral data and different Ligand field parameters from numerical fitting		[Co(C ₇ H ₈ O ₂ N ₄) ₂ Cl ₂]	[Co(C ₇ H ₈ ON ₄ S) ₂ Cl ₂]
Experimental spin allowed bands (in cm^{-1})	ν_1	11235	10753
	ν_2	14085	14493
	ν_3	20408	18868
Racah parameters (in cm^{-1})	B	996	877
	C	4601.52	4051.74
Slator-Condon-Shortley parameters (in cm^{-1})	F ₂	1653.036	1455.82
	F ₄	131.34	115.76
Crystal field stabilization energy (in cm^{-1})	E	6053.6	6208
Crystal field splitting energy (in cm^{-1})	10 Dq	7567	7760
Oscillator strength of transition	F	813.65	834.40
Nephelauxetic ratio	β_{35}	1.02	0.90
Ratio between ν_1, ν_2 and ν_3	ν_3 / ν_1	1.81	1.75
	ν_3 / ν_2	1.44	1.30
Difference $\nu_{2(obs)}$ and $\nu_{1(cal)}$	$\nu_{2(obs)} / \nu_{1(cal)}$	2.16	2.15
	$\nu_{2(obs)} - \nu_{1(cal)}$	7572	7760

There is no change in the frequencies of $\nu_{C=O}$ 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} , ν_{M-S} 365-355 cm^{-1} and ν_{M-Cl} 350-310 cm^{-1} indicate the presence of M-N, M-O, M-S and M-Cl bands which show the coordination of metal ion with nitrogen, oxygen, sulphur and chlorine atoms of the reported ligands [31-34]. (Table 2)

3.4. Electronic spectral studies

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 transitions of the spectrum are assigned as from ${}^6A_{1g}$ ground term to the quartet excited terms. The Tanabe-Sugano diagram corresponding to such a system shows that the only high spin state Russell-Saunders term is 6s which is in octahedral geometry, change its notation ${}^6A_{1g}$ to ${}^6A_{1g}$ since there is no excited state with the spin multiplicity. All electronic transition in high spin d^5 complex are closely forbidden / Laporte forbidden and spin forbidden [35].

The Orgel diagram for d^5 configuration for Mn(II) complexes shows three bands at 27980-27571 cm^{-1} , 23985-23810 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 field³⁶. These transitions were used to calculate the values of B, C and 10Dq from the Tanabe-Sugano diagram for d^5 system [37].

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 ($C = 35 F_4$) [38-40]. 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 ($\beta = B/B_0$). The intensity of absorption bands in terms of a parameter 'f' (Oscillator strength of the transition) and nephelauxetic function of the Ligand in complex 'h' have been calculated as follows [41] [$f = 10 Dq/g$ and $(1 - \beta) = h$. K, Where 'g' is Lange's splitting factor value and the nephelauxetic function value of the metal 'k' have been used as 8000 cm^{-1} and 0.07 respectively]. (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 , ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ ν_2 and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ ν_3 found at 11235-10753 cm^{-1} , 14493-14085 cm^{-1} and 20408-18868 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 [42-46]. The results obtained are in favour of octahedral geometry of the complexes. The ratio of $\nu_2(\text{obs.})/\nu_1(\text{calc.})$ agrees with the required range (2.16 -2.15) for the octahedral Co(II) complexes [47-51]. The 10 Dq values calculated from method (c) are in good agreement with the $\nu_2(\text{obs.}) - \nu_1(\text{calc.})$ 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 10638-10417 cm^{-1} , 17857-16667 cm^{-1} and 27027-26000 cm^{-1} assigned to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ν_1 , ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ν_2 and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ν_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 [47]. The spectral data and values of various ligand field parameters such as 10Dq, B [48], C, β_{35} , ν_2/ν_1 , Dq/B, λ , E, f and h are observed. The 10Dq and β_{35} values of the complexes indicate the presence of strong covalent bonds in the complexes [49]. This is also supported by the β_{35} values in the complexes. The ratio of ν_2/ν_1 for the complexes is 1.67-1.59 as expected for octahedral Ni (II) complexes [50]. Lowering in these values from the theoretical value of ν_2/ν_1 (1.8) suggests some distortion in the octahedral geometry. [51-52] In all the complexes of Ni (II), the best fit was obtained using 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 ${}^1E(D)$ lying close to the ${}^3T_{1g}(F)$ state [53]. Values of λ were found to be considerably lower than the value for the free ion (λ_0). (Table 5)

The coordinated Cu (II) Complexes of 2-pyrrolyl glyoxal semicarbaone/thiosemicarbaone exhibited a single broad band in the region of 12350-16300 cm^{-1} . The broadness of the band indicated the three transition as shoulders in the range which are similar in energy and give rise to only broad absorption band. The broadness of the

Table - 5: Electronic Spectral Data and Various Ligand Field Parameters of Ni(II) Complexes of 2-pyrrolylgyoxal semicarbazone/ thiosemicarbazone

Spectral data and different Ligand field parameters from numerical fitting		[Ni(C ₇ H ₈ O ₂ N ₄) ₂ Cl ₂]	[Ni(C ₇ H ₈ ON ₄ S) ₂ Cl ₂]
Experimental Spin allowed bands (in cm ⁻¹)	v ₁	10638	10417
	v ₂	17857	16667
	v ₃	27027	26000
Racah parameters (in cm ⁻¹)	B	865	761
	C	3996.3	3515.82
Slater-Condon-Shortley parameters (in cm ⁻¹)	F ₂	1375	1263.26
	F ₄	114.18	100.45
Crystal field stabilization energy (in cm ⁻¹)	E	12765.6	12500.4
Crystal field splitting energy (in cm ⁻¹)	10Dq	10638	10417
Oscillator strength of transition	F	1195.28	1170.44
Nephelauxetic function of Ligand	H	1.41	2.25
Nephelauxetic ratio	β ₃₅	0.83	0.73
Ratio between v ₂ & v ₁	v ₂ / v ₁	1.67	1.59
Spin- orbit coupling constant	λ	204	149

Table - 6: Electronic Spectral Data and Various Ligand Field Parameters of Cu (II) Complexes of 2- pyrrolylgyoxal Semicarbazone/ Thiosemicarbazone

Compound	Band Positions	Assignments	10 Dq (in cm ⁻¹)	CFSE
[Cu(C ₇ H ₈ O ₂ N ₄) ₂ Cl ₂]	12350	$2B_{1g} \rightarrow 2A_{1g}$	8475	5085
	13370	$2B_{1g} \rightarrow 2B_{2g}$		
	15800	$2B_{1g} \rightarrow 2E_g$		
[Cu(C ₇ H ₈ ON ₄ S) ₂ Cl ₂]	12850	$2B_{1g} \rightarrow 2A_{1g}$	9275	5565
	14500	$2B_{1g} \rightarrow 2B_{2g}$		
	16300	$2B_{1g} \rightarrow 2E_g$		

band may have been due to dynamic John-Teller distortion. The bands as shoulders in the range 12350-12850cm⁻¹, $2B_{1g} \rightarrow 2A_{1g}$ (v₁), 13370-14500cm⁻¹, $2B_{1g} \rightarrow 2A_{2g}$ (v₂), and 15800-16300 cm⁻¹, $2B_{1g} \rightarrow 2E_g$ (v₃) were observed. All of these data suggested a distorted octahedral geometry around the Cu(II) ion [54-56].

3.5. Antibacterial activity

The purified products were screened for antimicrobial activity by using four different concentrations of 1000 ppm, 750 ppm, 500 ppm and 250 ppm using DMF as a solvent for a time period of 24 hours. From the experiment data, it was observed that all the semicarbazone and

thiosemicarbazone and their corresponding Mn(II),Co(II),Ni(II) and Cu(II) complexes were found to be inactive at a concentration of 1000 ppm. It was also observed that most of the complexes show good activity against different strains of *B. Subtilis*, *E. Coli*, *S. Aureus* and *S. Varidence* at concentrations 750 ppm, 500 ppm and 250 ppm. Experimentally observed data are represented in Table 7. The highest dilution of the test chelates which inhibited the visual growth of the test organism was taken as the minimum inhibitory concentration [57].

3.6. Antifungal activity

Czapeck's agar medium (sucrose, KH₂PO₄, NaNO₃, KCl, FeSO₄, MgSO₄, agar-agar and water) was used as medium for checking the fungicidal activity of 2-pyrrolyl glyoxal semicarbazone and 2-pyrrolyl glyoxal thiosemicarbazone with their corresponding Mn (II), Co (II), Ni (II) and Cu(II) complexes. It has been found that all the complexes and ligands were found to be highly active against *H. Gramineum* and *C. Capisici*. Cu (II) complexes possess higher antifungal activity among all the

complexes of semicarbazone and thiosemicarbazone at concentration 750 ppm whereas Mn (II), Co (II) and Ni (II) complexes of semicarbazone and thiosemicarbazone possess greater fungicidal activity against *H. Gramineum* and *C. Capisici* at 500 ppm. In all the cases the most complexes are found to possess greater antifungal activity than their ligands, which is in accordance with the previously established fact that on chelation of metal to ligand increases the fungitoxicity of the molecule [58-59].

Table - 7: Inhibitory zone*(in mm) observed against indicated bacteria and fungi

Substance	Concentration in ppm	Bacteria				Fungi	
		Mean diameter after 24 hours **				Mean diameter after 120 hours	
		B. Subtilis	E. Coli	S. Aureus	S. Varidence	H. Gramineum	C. Capisici
C ₇ H ₈ O ₂ N ₄	1000	-	-	-	-	-	+
	750	-	+	+	+	++	+++
	500	+	-	-	+	+	++
	250	++	++	-	-	+	++
[Mn(C ₇ H ₈ O ₂ N ₄) ₂ Cl ₂]	1000	-	-	-	-	+	+
	750	+	+	+	+	++	++
	500	-	++	-	+	+++	+++
	250	-	++	-	-	+	++
[Co(C ₇ H ₈ O ₂ N ₄) ₂ Cl ₂]	1000	-	-	-	-	+	++
	750	-	-	-	++	++	++
	500	-	-	-	-	+++	+++
	250	+	+	-	-	+	++
[Ni(C ₇ H ₈ O ₂ N ₄) ₂ Cl ₂]	1000	-	-	-	-	++	+
	750	+	-	-	+	++	++
	500	+	++	-	+	+++	+++
	250	++	-	-	-	++	++
[Cu(C ₇ H ₈ O ₂ N ₄) ₂ Cl ₂]	1000	-	-	-	-	++	++
	750	++	+	++	++	++++	++++
	500	++	+	++	+	++	++
	250	-	++	++	-	+	+
C ₇ H ₈ ON ₄ S	1000	-	-	-	-	-	++
	750	++	++	++	-	++	++
	500	++	-	-	+	+++	+++
	250	-	-	-	-	++	+
[Mn(C ₇ H ₈ ON ₄ S) ₂ Cl ₂]	1000	-	-	-	-	+	++
	750	++	++	++	+	++	++
	500	+	-	-	-	+++	+++
	250	-	+	-	-	++	+

[Co(C ₇ H ₈ ON ₄ S) ₂ Cl ₂]	1000	-	-	-	-	++	++
	750	+	+++	-	++	++	++
	500	++	-	-	-	+++	+++
	250	-	+	-	-	++	+
[Ni(C ₇ H ₈ ON ₄ S) ₂ Cl ₂]	1000	-	-	-	-	+	++
	750	++	-	-	++	++	++
	500	-	-	-	-	+++	+++
	250	+	+	++	-	++	++
[Cu(C ₇ H ₈ ON ₄ S) ₂ Cl ₂]	1000	-	-	-	-	++	+++
	750	++	++	++	-	++++	++++
	500	+	+	+	+	+++	+++
	250	-	-	-	-	++	+

*DMF was used a control and showed nil activity against above bacteria ; **Zone size : (+)=6 -10mm, (++)=10-14mm, (+++)=14-18mm, (++++)=18-22mm, (+++++) >22mm; (-)=no inhibition

4. CONCLUSION

Mn(II), Co(II), Ni(II) and Cu(II) complexes of 2- pyrrolyglyoxal semicarbazone and thiosemicarbazone were synthesized and characterized by analytical and spectral studies. An octahedral/distorted octahedral geometry is proposed for all the above complexes. Biocidal activity of all these complexes have also been determined which shows that complexes are more potential than ligands.

5. REFERENCES

- Rai BK. **Journal of Indian Council of Chemists**, 2005; 22; 2: 1-5.
- Bermejo E, Castineiras A, Garcia I and West DX. **Polyhedron**, 2003; 22(8): 1147-1154.
- West DX, Padhye SB, Sonawane PB and Chikate RC. **Structure and Bonding**, 1991; 76: 1.
- West DX, Padhye SB, Sonawane PB and Chikate RC. **Asian Journal of Chemistry Reviews**, 1990; 4(1):125.
- Nandi AK, Chaudhary S, Mazumdar SK and Ghosh S. **Journal of the Chemical Society, Perkin Transaction**, 1984; 2(11): 729-1733.
- Casas JS, Garcia MS and Tarende. **J.Sordo, Coordination Chemistry Review**, 2000; 209(1): 197-261.
- Patil SA, Naik VH, Kulkarni AD and Badami PS. **Spectrochimica Acta A**, 2010; 75: 347-354.
- Sharma K, Singh R, Fahmi N and Singh RV. **Spectrochimica Acta A**, 2010; 75: 422-427.
- Al-Amiery AA, K.Al-Majedy Y, Abdulreazak H, and Abood H. **Bioinorganic Chemistry and Applications**, 2011; 1-6.
- Wiecek J, Kovala-Demertzi D, Ciunik Z, Zervou M and Demertzi MA. **Bioinorganic Chemistry and Applications**, 2010; 1-9.
- Ferraz KO, Wardell SMSV, Wardell JL, Louro SRW and Beraldo H. **Spectrochimica Acta A**, 2009; 73: 140-145.
- Graminha AE, Batista AA, Mendes IC, Teixeira LR and Beraldo H. **Spectrochimica Acta A**, 2008; 73(69): 1277-1282.
- Raja N and Ramesh R. **Spectrochimica Acta A**, 2010; 75: 713-718.
- Rajesh D. Hunashal and Satyanarayana D. **Int.J Pharm Bio.Sci**, 2012; 3(4): 183-192.
- Tarafder MTH, Ali MA, Wee DJ, Azahari K, Silong S. **Transition Metal Chemistry**, 2000; 25(4): 456-460.
- Zahid H. Chohan and Muhammad M. Naseer. **Applied Organo Metal Chemistry**, 2007; 21: 728-738.
- Uma agrawal and Saxena GC. **Eghpt J. Chem**, 1985; 28(1): 81.
- Pramod Kumar Agrawal, Renu Singhal, Satnam Singh Arora and Ajay Agrawal. Accepted for Publication, **IJCPS**, 2015.
- Wiles DM and Suprunchuk T. **Can.J.Chem.**, 1969; 47: 1087.
- Gomathi V and Selvameena R. **International Journal of Scientific Research**, 2013; 2: 24-25.
- Kipnis F and Ornfelt J. **Am. Chem. Soc.**, 1946; 68: 2734.
- Vogel AI. **A Text BOOK of Practical Organic Chemistry**. (Longmans Green, London), 1956; 344.

23. Sah PTT and Daniels TC. **Rec.Trav.Chim.,Pays.Bas.Belg.**, 1950; 69: 1545.
24. Fenton DE. **Advances in Inorganic and Bioorganic Mechanisms**, Ed.AGskyes, Academic,London, 1983;12B:187.
25. Figgis BN and Lewis J. **In Progress in Inorganic Chemistry**, F.A.Cotton, Ed.; Interscience, NewYork,1964.
26. Khan TA, Naseem S, Azim Y, Parveen S and Shakir M. **Trans.Met.Chem.**2007; 32,706-710.
27. Saied KEM. **Ind.J.Chem.**1994; 35A: 830.
28. Earanshow A. **Introduction to Magnetochemistry**, Academic Press Inc., Limited, London, 1968.
29. Figgis BN and Lewis J. **Modern Coordination Chemistry**(N.Y.,Wiley Interscience),1960.
30. Chandra S, Prewm Ballabh and Chaudhary SK. **International Journal of Applied Biology and Pharmaceuticals Technology**, 2013; 4: 3.
31. Larabi L, Benali O, Mekelleche SM and Harek Y. **Applied Surface Science**, 2006; 253, 1371.
32. Helena Otmacic and Ema Stupnisek-Lisac. **Electrochimica Acta**, 2003; 48: 985.
33. Ferraro JR. **Low Frequency Vibrations of Inorganic and Coordination Compounds**. Plenum Press, N.Y, 1971.
34. Nakamoto K. **Coordination Compounds in Infrared and Raman Spectra of Inorganic and Coordination Compounds**. 4th Ed; John-Wiley and Sons, Inc., New York, 1986.
35. Cotton FA and Wilkinson G. **Advanced Inorganic Chemistry**, InterScience Pub. Illrd Ed., 1972; 579.
36. Naryana I. **Chem Acta**, 1981; 130: 2808.
37. Hubey JE. **Principles of Structure and Reactivity**. Harper and Row, New York, 1977; 363.
38. Jorgenson CK. **Oxidation number and Oxidation states**. Springer, Newyork, 1969; 106.
39. Gingras BA and Sirianni AF. **Can. Chem.**, 42, 17, 1964.
40. Akbar Ali M, Kabir MH, Nazimuddin M, Tarafdar SMMH and Khair MA. **Indian J.Chem.**,1988; 27A: 1064-67.
41. Jorgensen CK. **Absorption Spectra and Chemical Bonding in Complexes**. (Oxford,London, N.Y., Paris)1962.
42. Konig E. **Structure and Bonding**. 1971; 9: 175.
43. Jorgenson CK. **Absorption Spectra and Chemical Bonding in Complexes**, (Pergamon Press,London)1962.
44. Lever ABP. **Advances in Chemistry Series**, 1966; 62: 435.
45. Orgel LE. **J.Chem.Phys.**, 1955; 23: 1004.
46. Douglas BE and McDaniel DH. **Concept and Models of Inorganic Chemisty**. (Oxford and I.B.H.Publishing CO.,Calcutta) 1970; 233.
47. Chandra S and Gupta K. **Indian Journal of Chemistry**, 2001; 40A: 775-779.
48. Lever ABP. **Inorg. Electronic Spectroscopy**, Elsevier, Amsterdam,1984.
49. Thaker BT. **J.Ind.Chem.Soc.**, LVII, 1980; 682-684.
50. Bertrand JA, Howard WJ and Kalyanaraman AR. **Chem.Commun**, 1971; 437.
51. Lever ABP. **Advances in Chemistry Series**, 1966; 62: 435..
52. Raman N, Ravichardran S and Thangaraja C. **Journal of Chemical Science**, 2004; 116: 40 & 215.
53. Liehr AD and Ballhausen CJ. **Ann.Phys.**, 1959; 6: 134.
54. Mishra AP and Gautam SK. **J.Indian Chem.Soc.**, 2004; 81: 324.
55. Dunn TM. **The visible and UltraViolet Spectra of Complex Compounds in Modern Coordinated Chemistry**, N.Y. Interscience, 1960.
56. Meek DW, Drago RS and Piper TS, **Inorg. Chem.**, 1962;1: 285
57. Ispir E, Toroglu S and Kayraldiz A.**Transition Met.Chem.** 2008; 33: 953.
58. Gudasi KB, Patil MS, Vadavi RS, ShenoyRV, Patil SA. **Transition Metal Chemistry**, 2006; 31: 580.
59. Raman N, Muthuraj V, Ravichandran S and Kulandaisamy A. **Proc. Indian Acad. Sciences**, 2003; 115: 161-167.