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RESEARCH ARTICLE

SYNTHESIS, SPECTRAL AND BIOLOGICAL STUDIES OF Mn(II), Co(II) AND Cu(II) COMPLEXES OF [2-CHLORO-5-(2,4-DIHYDROXYPHENYL AZO)PHENYL] PHENYLMETHANONE.

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Abstract

[2-chloro-5-(2,4-dihydroxyphenyl azo)phenyl] phenylmethanone is an azodye derived from (2-amino-5-chlorophenyl)PhenylMethanone. Three new complexes of this azodye with the metal ions Mn(II), Co(II), and Cu(II) have been prepared and characterized by various analytical methods like microanalytical method, metal estimation, anion estimation, conductance and magnetic moment measurements. These complexes were also characterized by spectral techniques like FTIR, Electronic, and ESR. The azodye and the selected complexes were subjected to antimicrobial study, antioxidant study and anticancer study. The spectral and analytical data confirms that the azodye acting as tridentate ligand with the metal ions Mn(II), Co(II), and Cu(II) and. The ligand and the metal ions in the complexes are found to be 1:1 ratio.

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Introduction:-

Azodyes and their metal complexes are very important compounds receiving attention in scientific research and industry. These compounds are highly coloured and used as dyes and pigments for long time (Pooja, T., 2004). Azodyes have wide spread application as redox, acidbase indicators, metalochrome and histological stains have attracted many investigators. Azo compounds are also used as inkjet printers and electro-optical devices. Synthetic dyes containing –N=N- groups are known as non-biodegradable in aerobic condition (Park, H., *et al.*, 2003).

(2-amino-5-chlorophenyl)PhenylMethanone {2-amino-5-chloro benzophenone}, 2-Aminobenzophenone derivatives are important compounds because of their application in heterocyclic synthesis and medicines (Mini, S., *et al.*, 2015). This compound is used as the starting material for the synthesis of benzodiazepam. All the drugs synthesized from 2-aminobenzophenone possess CNS activity (Rajesh K. Singh, *et al.*, 2011). So the derivatives were considered to be of our interest because of having the CNS activity of benzodiazepines to obtain drugs with high therapeutic index than diazepam.

The present work deals with the synthesis and characterization of some new complexes of Cu(II), Co(II), and Mn(II) ions with the azodye, [2-Chloro-5-(2,4-dihydroxyphenylazo)phenyl]phenylmethanone, derived from 2-amino-5-chlorobenzophenone and resorcinol.

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Experimental:-

Materials and methods:-

The reagents 2-amino-5-chlorobenophenone, resorcinol, were purchased from their manufactures (BDH-AR, Merck-GR) and used as such for the synthesis of ligand. All of the metal salts used for the preparation of the complexes were AR grade samples.

Estimation of the metal and chloride present in the complexes were done by standard methods (Vogel, A.I., 1989). Elemental analyses were determined by CHNS analysis at SAIF, Cochin. The molar conductivity measurements were made using Systronics direct reading conductivity meter. Infrared spectra were recorded on a Perkin–Elmer Spectrum 65 infrared spectrophotometer using KBr pellets. ESR spectra of Cu(II) complexes in solid state, solution and frozen states were recorded on a Varian-E-112 spectrophotometer at X- band using TCNE as marker at the SAIF, IIT, Mumbai. The magnetic moments were measured at room temperature on a Sherwood Scientific Magnetic Susceptibility balance. Electronic absorption spectral measurements of the ligand and the complexes in methanol were recorded on a Perkin–Elmer Lamda 25 UV-Visible spectrophotometer.

Preparation of [2-chloro-5-(2,4-dihydroxy phenylazo) phenyl] phenylmethanone [RABP]:-

The ligand RABP is prepared by diazotizing 2-amino-5-chlorobenzophenone and coupling with resorcinol (Mini S., *et al.,* 2013). The resulting product was recrystallised from DMF.

Preparation of complexes:-

The complexes of [2-chloro-5-(2,4-dihydroxyphenylazo)phenyl]-phenyl methanone [RABP] with Mn(II), Co(II), and Cu(II), were prepared by the following general method. A methanolic solution of the corresponding metal salt [$CuCl_2.2H_2O$, $Mn(Ac)_2.4H_2O$, $Co(NO_3)_2.6H_2O$] was added to a solution of RABP in acetone. The metal salt to ligand molar ratio was kept 1:1. The resulting mixture was stirred and refluxed for 3-4 hours. The solution thus obtained was concentrated to get the solid complex. It was filtered, washed with ethanol-acetone mixture, dried and kept in a desiccator over anhydrous $CaCl_2$.

Results and Discussion:-

All complexes are stable non-hygroscopic solids and are soluble in DMSO, DMF and $CHCl_{3.}$ The analytical data of the complexes of RABP are presented in Table 1. The analytical data obtained are in good agreement with the calculated values which suggest that the metal and the ligand are coordinated in the ratio 1:1. Based on the analytical data, [Cu(RABP)Cl], [$Co(RABP)(NO_3)(H_2O)_2$], and [$Mn(RABP)(Ac)(H_2O)_2$] are the empirical formulae suggested for the complexes. The molar conductance at room temperature was determined using 10^{-3}M solutions of the complexes in the solvents methanol and DMF. These values support the non-electrolytic nature of all the complexes (Geary, W. J., 1971). The conductance values along with the magnetic moments are also shown in Table 1.

Infrared spectra:-

The infrared spectra of the ligand and the metal complexes were recorded in the range 4000-400 cm^{-1}. The important spectral bands and the tentative assignments are given in Table 2. The infrared spectra of the complexes exhibit characteristic absorptions of all functional groups of ligand but at a shifted position in the case of coordinated groups. The strong absorption band shown by the ligand RABP at 1460 cm^{-1} corresponds to $\nu_{N=N}$ suffers a shift to higher wave number may taken as an evidence for the participation of -N=N group in coordination (Gaber, M., *et al*., 2008). This is supported by the appearance of new band in the region of 423-467 cm^{-1} assignable to ν_{M-N} (Beecroft, B., *et al*., 1974). The considerable shift shown by strong $\nu_{C=O}$ band at 1619 cm^{-1} of RABP to lower value in complexes is a clear evidence for the participation of >C=O in coordination (Radhakrishnan, P.K., *et al*., 1984). The appearance of new bands in the region 503-523 cm^{-1} assignable to ν_{M-O} confirms the involvement >C=O in coordinate bond formation (Speca, A.N., *et al*., 1974).

The two hydroxyl groups in the resorcinol part of the ligand exhibit a broad band at 3418 cm^{-1}. From the anion analysis, it is found that one chloride ion is present per copper complex molecule. This indicates that RABP is acting as tridentate univalent anion. This is achieved via deprotonation of one of the OH group of the resorcinol part of the ligand. The broad peak shown by Cu(II) complex at 3320 cm^{-1} may due to the uncoordinated phenolic OH group.

As in the case of Cu(II), the IR band shown by Ni(II) complex at 3352 cm^{-1} may due to the presence of one uncoordinated hydroxyl group in the resorcinol part of the ligand.

In Co(II) and Mn(II) complexes the broad band appeared respectively at 3411 and 3344 cm^{-1}, may due to the uncoordinated phenolic OH and ν_{OH} of coordinated water. It is supported by the univalent behavior of RABP and the bands corresponding to ν_{HOH} (def) at 1627 and 1631 cm^{-1} and ν_{HOH} (rock) at 948, 949 cm^{-1} respectively (Nakamoto, K., 1970). In the newly synthesized Co(II) complex, the presence of two medium intensity bands at 1380 cm^{-1} and 1225 cm^{-1} due to ν_1 and ν_2 vibration and 1485 cm^{-1} is due to ν_4 vibration respectively. The frequency separation ν_4- ν_1 is in the range 100-150 cm^{-1} is reasonable to infer that nitrate group is coordinated as monodentate anion in the Co(II) complex of RABP. In the present complex of Mn(II) the acetate group act as monodentate ligand. This is evidenced by the difference of 215 cm^{-1} between ν_{COO} (asym) 1621 cm^{-1} and ν_{COO} (sym) 1406 cm^{-1} vibrations.

Electronic spectra:-
The electronic spectral data of different metal complexes with RABP are presented in Table 3. Copper (II) being a d^9 system is highly susceptible to Jahn-Teller distortion and perfectly octahedral configuration can never be expected (Sadasivan, V., 2004). Generally a distorted octahedral, square planar or tetrahedral configuration is formed. The electronic spectra of Cu (II) complex of RABP shows a broad band around 430 nm corresponds to $n \rightarrow \pi^*$ transition of ligand RABP. Two weak bands present at 668 nm and 525 nm assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, suggests square planar geometry for the Cu(II) complex (Rajendra K. Jain and Anand P. Mishra, 2012). The newly synthesized Mn(II) complex exhibit a very intense band around 438 nm and a very faint shoulder around 550 nm. The intense peak may be attributed to the ligand absorption and weak shoulder may due to the overlapping of spin forbidden d-d transition with the ligand absorption. The newly synthesized Co(II) complex shows three absorption bands at 691 nm 580 nm and 428 nm. These are attributed to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and $\| n \rightarrow \pi^*$ transition originated from the ligand. These bands support an octahedral geometry for the complex (Ballhausen, C.J., 1979).

ESR spectrum:-
In the ESR spectrum of the newly synthesized Cu(II) complex, there is an absorption around 3200 G, characteristic of Cu^{2+} species. The absence of half- field peak around 1600G corresponding to $\Delta Ms = \pm 2$ rules out the Cu-Cu interaction in this complex (Sharma A.L., *et al.*, 2001). The ESR spectra of the Cu(II) complex in polycrystalline state and in DMF solution and at LNT are shown in fig:1 and 2. The spectrum taken at the frozen state shows hyperfine splitting in the parallel component with low intensities in the low field region and one intense peak at the high field region. The G value is calculated using the relation $G=\frac{g_{\parallel}-2.0027}{g_{\perp}-2.0027}$

If the G value is larger than four, the exchange interaction is negligible because the tetragonal axes are aligned parallel or are slightly misaligned; and the unpaired electrons are present in the $d_{x^2-y^2}$ orbital. If the G value is less than four, the exchange interaction is considerable and the local tetragonal axes are misaligned (Benial, A.M.F., *et al.*, 2000).

The copper (II) complex of RABP shows the $g_{\parallel}$ value 2.38 and $g_{\perp}$ value 2.04. These values indicate that the unpaired electron is localized in the $d_{x^2-y^2}$ orbital of copper ion. g_{avg} calculated is 2.15 and G value calculated using this $g_{\parallel}$ and $g_{\perp}$ value is 10.09 indicates negligible exchange interaction of Cu-Cu in the complex. The covalency parameter α^2 calculated using the above mentioned equation is 0.83, which is <1.0, indicates that the complex has some covalent character in the ligand environment (Raman, N., *et al.*, 2004). The ESR spectral data of Cu(II) complex of RABP is given in Table 4.

Antimicrobial Activity:-

The antibacterial and antifungal activity results of ligands and their metal complexes were presented in Table 5 and 6. A comparative study of the ligands and their metal complexes indicate that most of the metal chelates exhibit higher antimicrobial activity than those of the free ligands. The activities of these complexes depend on the structure and orientation of various moieties of chelates. The number of binding sites and the effect of chelation may be responsible for the increased antimicrobial activity of the complexes. Besides this, many other factors such as solubility, dipole moment and conductivity of complexes also may be the reason for remarkable antimicrobial activities of the complexes (Coombs, R.V., *et al.*, 2005; Chohan, Z.H., *et al.*, 2001, 2010). The antimicrobial activities of RABP and its complexes are shown in fig: 3 and 4.

Antitumour activity:-

The antitumour activity of Co(II) complex was determined by MTTassay. The result obtained from MTT assay method is recorded in Table 7. It is clear that as the concentration of the drug increases relative cell viability decreases. The cell viability of the complex is shown in fig:5

Antioxidant study:-

The antioxidant values of the ligand and Mn(II) complex studied by DPPH assay are shown in Table 8. These values indicate that the antioxidant activity of the ligand have been enhanced on complexation with Mn^{2+} ion and the complex $[Mn(RABP)(Ac)(H_2O)_2]$ has comparable activity to the standard.

Table 1:- Analytical data of RABP complexes.

Complex	Metal%	Anion%	C%	N%	H%	μeff	Conductivity	
							Methanol	DMF
[Cu(RABP)Cl]	14.1 (14.5)	7.9 (7.8)	59.6 (59.3)	6.2 (6.4)	2.6 (2.9)	1.8	15.4	32.6
$[Co(RABP)(NO_3)(H_2O)_2]$	11.6 (11.2)	-	44.8 (45.0)	5.5 (5.9)	3.1 (3.4)	5.1	21.8	18.2
$[Mn(RABP)(Ac)(H_2O)_2]$	10.9 (11.0)	-	45.4 (45.2)	5.5 (5.4)	2.3 (2.5)	6.7	21.7	11.8

Ac = acetate

Table 2:- IR Spectral bands of RABP and its complexes

RABP	[Cu(RABP)Cl]	$[Co(RABP)(NO_3)(H_2O)_2]$	$[Mn(RABP)(Ac)(H_2O)_2]$	Assignments
3418	3320	---- 3411	---- 3344	ν_{OH} phenolic ν_{OH} phenolic & water
2873	2875	2873	2872	ν_{C-H} (aromatic stretching)
1619	1594	1596	1594	$\nu_{C=O}$
-	-	-	1625	ν_{COO}(asy)
1460	1484	1478	1475	$\nu_{N=N}$
-	-	-	1406	ν_{COO}(sym)
-	-	1380	-	ν_1 NO_3 coordinated
-	-	1225	-	ν_2 NO_3 coordinated
832	830	824	832	ν_{C-H} aromatic bond
-	450	445	462	ν_{M-N} bond
-	510	509	517	ν_{M-O} bond

Table 3:- Electronic spectral bands of RABP and its complexes.

Compound	λ_{max} nm	Assignments
RABP	426	$n \rightarrow \pi^*$
	262	$\pi \rightarrow \pi^*$
[Cu(RABP)Cl]	430	$n \rightarrow \pi^*$
	525	$^2B_{1g} \rightarrow {}^2E_g$
	668	$^2B_{1g} \rightarrow {}^2B_{2g}$
$[Co(RABP)NO_3(H_2O)_2]$	428	$n \rightarrow \pi^*$
	580	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
	691	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
$[Mn(RABP)Ac(H_2O)_2]$	438	$n \rightarrow \pi^*$
	550	d→d

Table 4:- ESR Spectral data of [Cu(RABP)Cl]

Complex	$g_{\parallel}$	$g_{\perp}$	g_{avg}	$A_{\parallel}$	G	α^2
[Cu(RABP)Cl]	2.38	2.04	2.15	0.0170	10.09	0.832

Table 5:- Antibacterial activity of RABP and its complexes.

Compound	*Escherichia coli*	*Staphylococcus aureus*
Chloroform	NZ	NZ
RABP	0.8 cm	NZ
[Cu(RABP)Cl]	1.1 cm	0.8 cm
[Co(RABP)(NO_3)(H_2O)$_2$]	0.7 cm	NZ
[Mn(RABP)(Ac)(H_2O)$_2$]	NZ	0.9 cm

Table 6:- Antifungal activity of RABP and its complexes.

Compound	*Aspergillus Niger*	*Candida Albicans*
Chloroform	NZ	NZ
RABP	NZ	NZ
[Cu(RABP)Cl]	NZ	0.7 cm
[Co(RABP)(NO_3)(H_2O)$_2$]	NZ	NZ
[Mn(RABP)(Ac)(H_2O)$_2$]	NZ	NZ

NZ- No zone

Table 7:- The percent viability of cells as determined by MTT assay method for [Co(RABP)NO_3(H_2O)$_2$]

Sample concentration (µg/ml)	OD at 540 nm	% viability
Control	0.4522	100
[Co(RABP)(NO_3)(H_2O)$_2$]		
10	0.3049	67.42
50	0.2306	50.99
100	0.1301	28.77

Table 8:- Percentage inhibition of antioxidant activity of RABP and their Mn(II) complex Optical density of control at 517 nm is 0.389

Sample concentration (µg/ml)	OD at 517nm	% inhibition
RABP		
12.5	0.274	29.56
25	0.185	52.44
50	0.180	53.72
100	0.176	54.75
200	0.162	58.35
[Mn(RABP)(Ac)(H_2O)$_2$]		
12.5	0.220	43.44
25	0.181	53.47
50	0.108	72.23
100	0.097	75.06
200	0.090	76.86

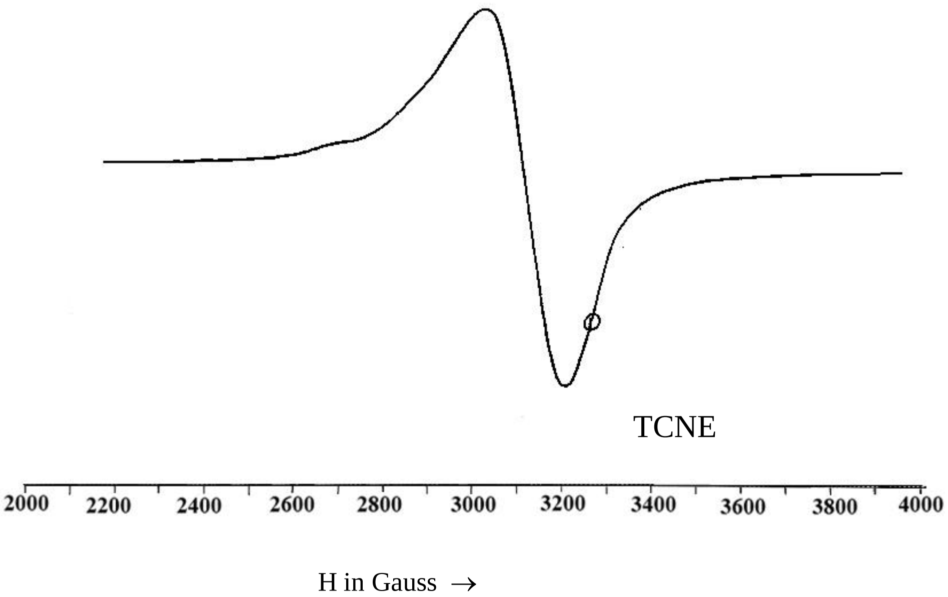


Fig 1:- Polycrystalline ESR Spectrum of [Cu(RABP)Cl].

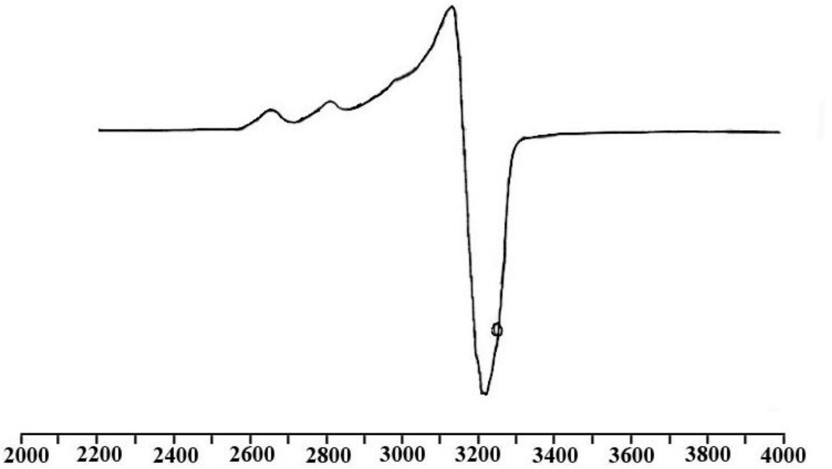


Fig 2:- ESR Spectrum of [Cu(RABP)Cl] in DMF at 77K.

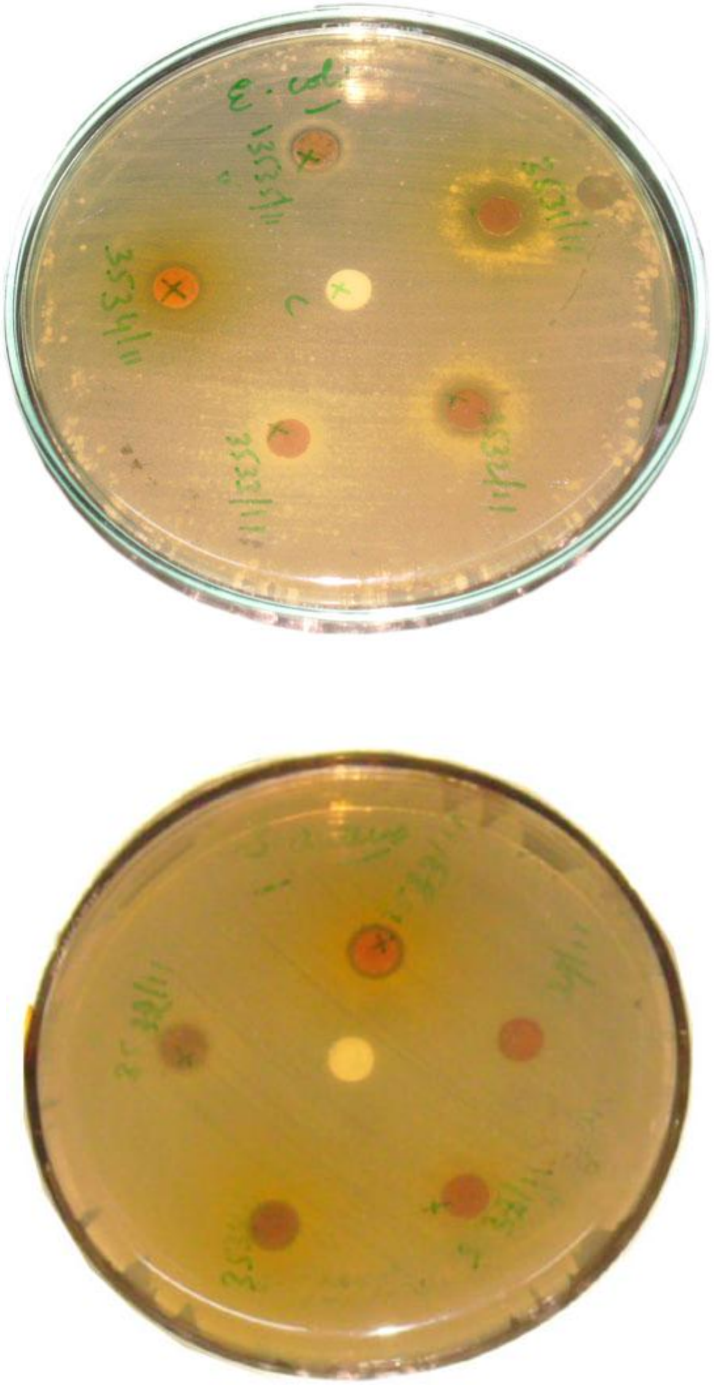


Fig 3:- Antibacterial activity of RABP and its complexes against *Escherichia coli* and *Staphylococcus aureus.*

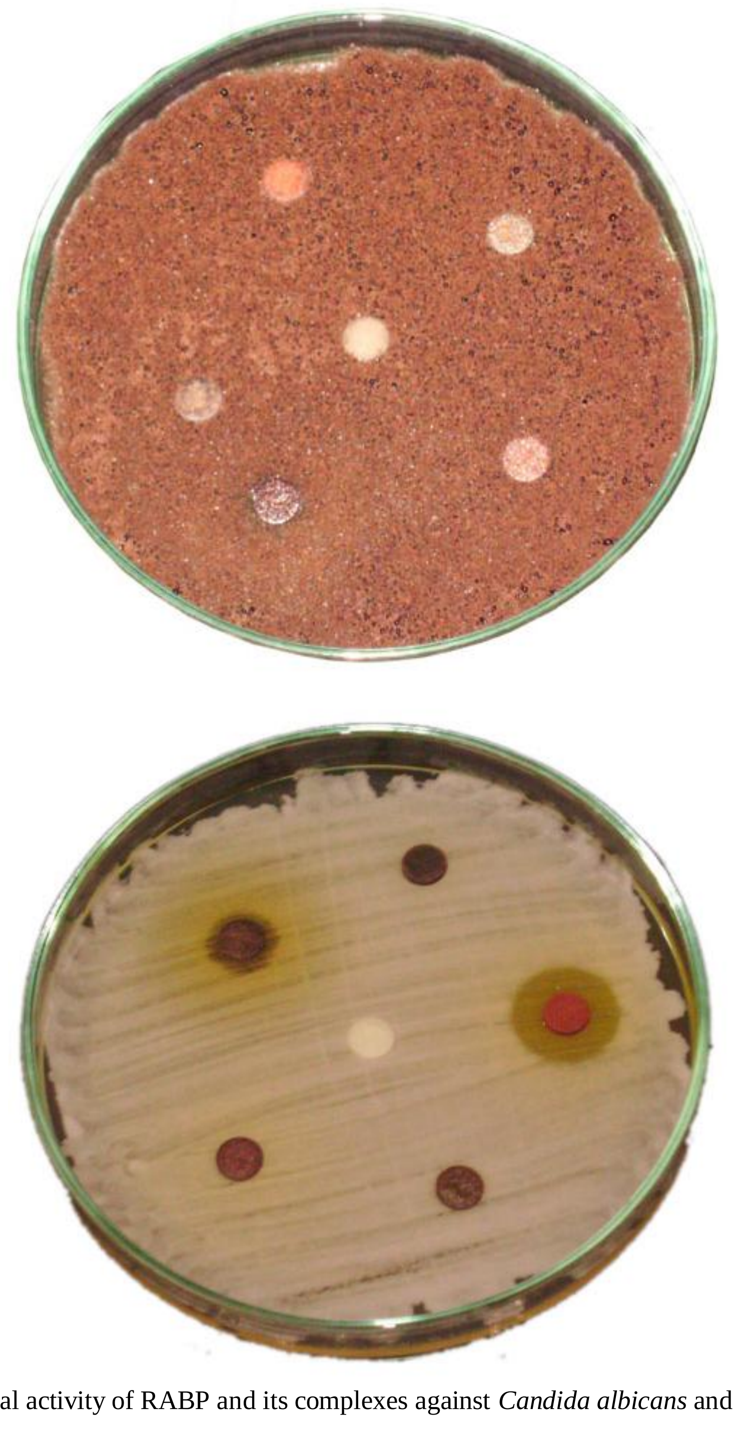
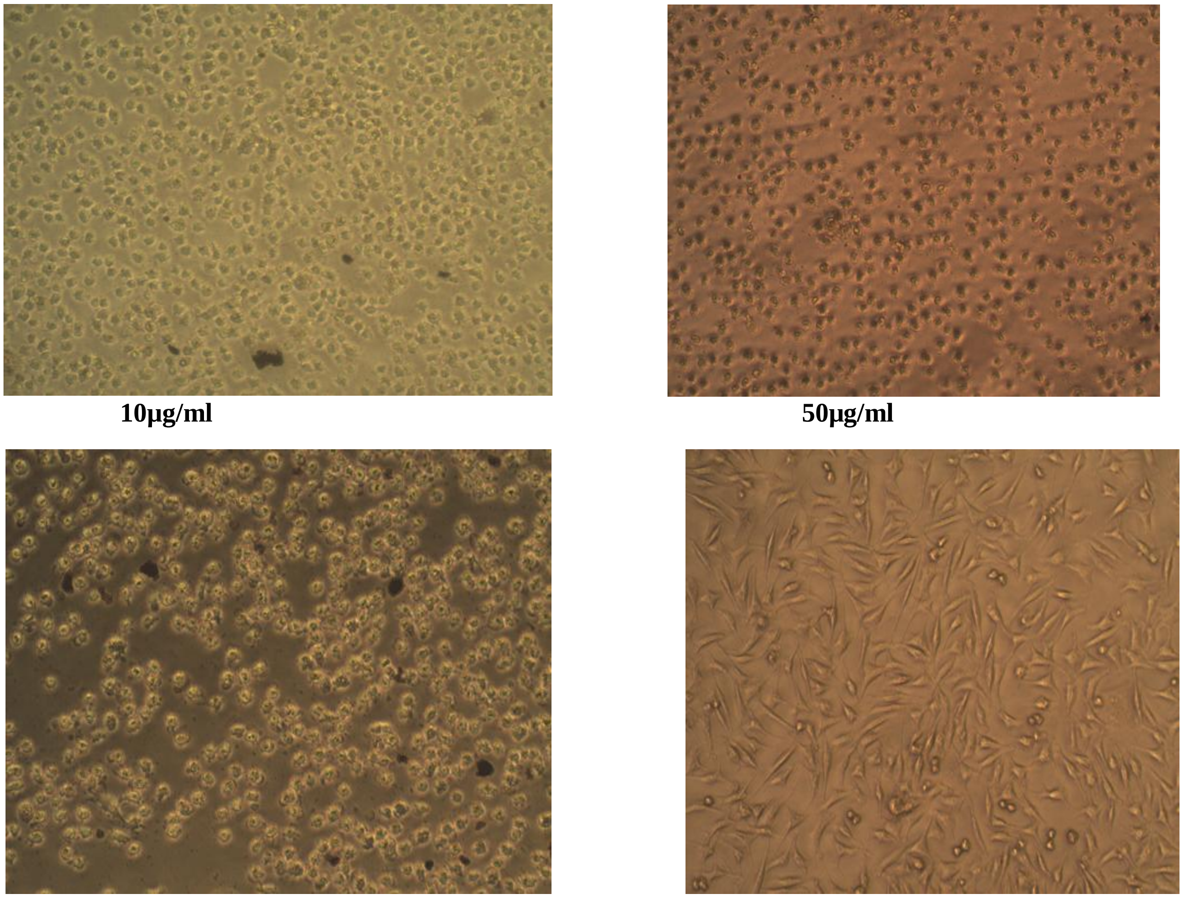


Fig 4:- Antifungal activity of RABP and its complexes against *Candida albicans* and *Aspergillus niger*



10µg/ml **50µg/ml**

10µg/ml **50µg/ml**

Fig 5:- Image of MTT assay done with [Co(RABP)$NO_3(H_2O)_2$] at different concentrations.

Conclusion:-

Three complexes of [2-Chloro-5-(2,4-dihydroxyphenylazo)phenyl]phenyl methanone, (RABP) with Mn(II), Co(II), and Cu(II), were synthesized and characterized by physico-chemical studies. On the basis of spectral and physicochemical analyses, square planar and octahedral geometries have been proposed for the complexes. IR spectral data reveals that RABP is acting as univalent in all the complexes. It acts as tridentate manner through nitrogen and oxygen. The ligand is coordinated in 1:1 with the metal ions. All the complexes show non-electrolytic behavior. With the help of all analyses the complexes are formulated as [Cu(RABP)Cl], [Co(RABP)$(NO_3)(H_2O)_2$], and [Mn(RABP)(Ac)$(H_2O)_2$].

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