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Microwave Assisted Synthesis, Spectral and Antibacterial Investigations on Complexes of Cu (II) With Pyrimidine Derivatives

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Abstract: The Present research work describes the synthesis, spectral and antibacterial studies on the few complexes of Copper (II) with pyrimidine derivatives. The characterizations of the compounds have been carried out on the basis of elemental analysis, infrared, electronic spectra and magnetic susceptibility studies. Antibacterial activities of these ligands and complexes have also been reported on S.aureus and E.coli microorganisms. The diffuse reflectance spectrums of the complexes show bands in the region around 11000 cm^{-1} to 25000cm^{-1} assignable to $^2E_g \rightarrow {}^2T_{2g}$, $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions. These are also typical of octahedral environment around the Copper. The magnetic moment (1.87 BM) of the complex indicates high octahedral environment. The microwave method of synthesis of complexes have been found easier, convenient and ecofriendly.

Keywords: Microwave, amide, Copper (II).

1. INTRODUCTION

Amides play vital roles in nature. All proteins are polyamides and make up a large part of the animals body1. They are found in all living cells and are principle materials of skin, muscles, nerves, blood, enzymes, antibodies and many harmones. Metal or metalloid amide are compounds which contain one or more $–CONH_2$ ligand groups or a simple derivative [such as –CONHR, $-CONR_2$, where R = methyl, phenyl, $SiMe_3$ etc.) attached to metal. Amides of sodium and potassium are the first examples of metal amides. Metal or metalloid amides may be mono, di- or poly nuclear and nitrogen is in a three coordinated environment. Metal amides include many important natural products such as haemin (a porphyrin), chlorophyll (a dihydroporphyrin), vitamin B_{12} etc. Importance of amide group containing compounds has also been recognized in various fields of chemistry and biology 2-6.

Copper doorknobs are used by hospitals to reduce the transfer of disease and Legionnaire's disease is suppressed by copper tubing in air-conditioning systems. Copper sulfate is used as a fungicide and as algae control in domestic lakes and ponds. It is used in gardening powders and sprays to kill mildew. Copper-62 radioisotope is used as a positron emission tomography radiotracer for heart blood flow measurements 7.

On copper rich soil only a limited number of plants have a chance survival and there is not much plant diversity near copper-disposing factories. Due to effects upon plants copper is a serious threat to the production of farmlands. The decompositions of organic matter may seriously slow down because of this.

When the soil of farmland is polluted with copper, animals will absorb concentration that are damaging to their health. Mainly shelves suffer in great dear from copper poisoning, because the effect of copper are manifesting at fairly low concentration 8.

Further included in the concept that portrayed "tyrosine metabolism and melanin biosynthesis" were multiple protein-protein complexes involving the protein Dopochrome tautomerase, Tyrosinase and Tyrosinase-related protein, all of which are copper binding proteins and play a critical role in the bioprocess. Similarly copper binding proteins, potentate amino acid metabolism, by having a functional role in two biological process namely amine oxidase and oxidoreductase activity 9-11.

2. EXPERIMETAL

2.1 Apparatus

(i) EC Double Beam UV-VIS Spectrophotometer (UV 5704SS), with quartz cell of 10 mm light path was used for Electronic spectral measurement at GCRC (Green Chemistry Research Center) Govt. Dungar College (NAAC A-Grade) Bikaner, (Raj.).

(ii) IR spectra were recorded on Bruker Optic Model Alpha (FT-IR) (Zn-Se Optics, ATR) (4000-500 cm-1) using KBr disc at SIL, P.G. Dept. of chemistry, Govt. Dungar College (NAAC-A- Grade) Bikaner, Rajasthan.

(iii) Microwave synthesis was carried out in domestic microwave oven and GMBR (Green Microwave Biochemical Reactor) at GCRC, P.G. Dept. of Chemistry, Govt. Dungar College (NAAC-A- Grade) Bikaner, Rajasthan.

(iv) All biological activities have been carried out with horizontal laminar, BIFR, Bikaner.

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2.2 Materials and method

For the synthesis of Copper (II) complexes with amide group containing ligands, a solution of Copper Chloride (0.001 mole in 30 ml ethanol) has been taken in a 250 ml round bottom flask, in this solution respective amide ligand[((i)N-(pyrimidin-2-yl) benzamide, N2PB (ii)N-(pyrimidin-2-yl) acetamide ,N2PA (iii)N-(4, 6dimethylpyrimidin-2-yl) benzamide,N46DM2PB (iv)N-(4, 6dimethylpyrimidine-2-yl) acetamide ,N46DM2PA] (0.003 mole) was added slowly with constant stirring. The reaction mixture was placed on a magnetic stirrer with constant stirring for 6-7 hours at room temperature.

In the alternative green synthesis, the reaction mixture was irradiated in a microwave reactor at 600 W for 2-10 minutes. The solid precipitate obtained in both the methods was separated and crystallized. Crystals were purified and recrystalized with alcohol and dried under vacuum.

3. RESULTS AND DISCUSSION

All the complexes synthesized and investigated were found to be coloured crystalline/powder substances, stable under normal laboratory conditions over a long period of time, non-hygroscopic, insoluble in most organic solvents and water except DMF and methyl alcohol. The conductivities measured for some complexes in DMF indicated the complexes to be non-electrolyte or covalent (12). The physical features and results of elemental analysis are presented in Table 1. The analytical data is in good agreement with the proposed molecular formula of the complexes.

(i). Vibrational Spectra

Selected infrared spectral bands are presented in Tables 3. A careful comparison of the characteristic IR bands of the amide group containing ligands and their copper complexes has led to fairly important structural conclusions and mode of coordination.

The IR bands due to amide ν (N-H) mode observed at 3175-3382 cm^{-1} for the free amide ligands are shifted towards higher frequencies indicating the non-participation of the nitrogen atoms in coordination. Carbonyl oxygen of amide-I group are participates in metal ligand bonding, which confirmed by 14-66 cm^{-1} negative shift of amide-I (ν C=O) frequency in complexes to the comparision of ligands (13).

The amide II and III bands arising from ν (C-N) as well as from δ(N-H) modes, (although the two modes are coupled to one another) shift towards higher frequencies further confirm the coordination via carbonyl oxygen of amide group. These facts may be explained by the decrease of the double bond character of C=O and the subsequent increase of the C-N double bond character (14). In complexes, pyrimidinyl nitrogen participates in bonding, which has been confirmed by the 16-50 cm^{-1} negative shifting of pyridine ring peak in complexes to the comparison of ligands.

These observations have ambiguous and support the final structural conclusions of the complexes and the mode of bonding in them.

(ii). Magnetic Susceptibility Measurements

Magnetic susceptibility of bivalent copper compounds has been measured at room temperature. The spin only value of 1.73 BM calculated from spin only formula for Cu (II) ion with electronic configuration of d^9 is generally not observed for all copper complexes. It seems well established that under conditions of adequate magnetic dilution the cupric ion exhibits a moment somewhat above the spin only value, for the one unpaired electron configuration of d^9. Ray and Sen (15) reported for a number of typical cupric complexes, the moments at room temperature and, in some instances at unspecified lower temperatures. They correlated the magnetic moments of 1.7-1.9 BM on one hand with red-yellow colour of the complex and on the other hand magnetic moment of 1.9-2.2 BM with a green-blue colour of the complex. The octahedral arrangements of ligands lead to 1.7-1.9 BM value. The larger moments reported by Ray and Sen have often been associated with very high values of Qi, the Weiss constant in the Curie-Weiss law up to 373ºk. The copper (II) ion gives rise to ^2D spectroscopic state as the ground state which splits by an octahedral crystalline field into lower lying doublet ^2E_g and an upper orbital triplet $^2T_{2g}$. The green-blue colours frequently observed for cupric complexes can be attributed to transitions between $^2Eg \rightarrow {}^2T_{2g}$ energy states and have low value of extinction coefficient. Although E_g levels cannot give rise to orbital contribution, yet there is a considerable interaction between the doublet and triplet states by means of the fairly large spin orbit coupling constant of cupric ion (λ=-830cm^{-1}). This effect gives rise to the quite appreciable orbital contribution observed in the moment of a complex and the moment is given by the spin only value of 1.73 BM multiplied by the factor $(1+2\lambda /\Delta)$ where λ is the separation between E_g and T_{2g} states which is in the range of 10,000-20,000 cm^{-1}. According to Polder (16), the orbital contribution observed is independent of the magnitude of tetragonal splitting or its sign, provided that only the mean susceptibility is considered. The extension of tetragonal distortion of the octahedral case to the complete removal of two trans ligands leading to square planar complex is expected to change the magnetic properties comparatively little from those of octahedral complexes. In such cases, the concept of triplet and doublet ligand field states loses much of its significance. J Thus Δ in the expression;

$$\mu = \mu_{spin\text{-}only}\ (1+2\lambda/\Delta)$$

can be considered to be the energy separation between $dx^2\text{-}y^2$ and d_{xz}/d_{yz} orbitals (17).

The magnetic moments calculated from the magnetic susceptibility measurements at room temperatures for all the complexes are presented in Tables 2. The solid state magnetic moments at room temperature for all the copper complexes of the amide ligands have been found to be in the range 1.78 to 2.01 BM. These values are indicative of the fact that all the copper complexes are paramagnetic in nature. However, the values of magnetic moment in combination to electronic spectra can only lead to geometrical adoptions of the central metal ion in the complexes.

(iii). Electronic Spectra

Copper has electronic configuration [Ar] $(3d^{10})$ $(4s^{1})$ and in its bivalent state it shows a configuration of [Ar] $3d^9$. A d^9 state is the whole equivalent of d^1, so the spectra of copper (II) complexes are analogous to those of titanium (III), d^1 complexes but with the energy levels inverted. Cu (II) complexes are susceptible to considerable distortion which renders their absorption spectra to be quite complex. Copper (II) forms a large number of complexes with various donor ligands and with interesting stoichiometries but perfect octahedral and tetrahedral complexes of Cu (II) are very few. Cu (II) gives rise to only one free ion ground term ^2D, which is tenfold spin and orbitally degenerate. ^2D term splitting in an octahedral or tetrahedral crystal field and may be understood using appropriate orgel diagram (18, 19). The levels in the octahedral symmetry further split in an elongated tetragonal crystal field (D_{4h} symmetry). These may be understood by considering tries splitting pattern of d-orbitals of the copper (II) ions in crystal fields of different symmetry. The d-d transition of Cu (II) ion is predominantly electric dipolar in nature (20) and obeys two selection rules viz. spin multiplicity and Laporte. Forbidden transitions, due to electric dipole selection rules, between d-orbitals in centrosymmetric molecules become allowed due to vibronic coupling and ligand field transitions gain some intensity three weak transitions to the $d_{x^2-y^2}$ orbitals of tetragonal Cu (II) would thus be expected. These usually appear depending on field strength of the coordinating ligand in the red spectral region (λ=600-700 (nm). The energies of these absorption maxima depend somewhat on tetragonal distortion (21). In general, as the strength of the ligand increases, the energies of these transitions will increase. The electronic absorption spectra of the copper (II) complexes of the amide group containing ligands were recorded in UV and visible regions and the electronic absorption spectral bands are given in Tables 2 with their tentative assignments. The UV spectra of the uncomplexed amide group containing ligands show a characteristic band in the region 208-220 nm which is assigned to $n \rightarrow \pi^*$ transition of the chromophoric C=O group of amide bond. This band shows a bathochromic shift in the copper complexes of the entire amide group containing ligands. This shift is attributed to the involvement of carbonyl group in metal complexation as indicated by IR studies. A strong; band observed around 25000 cm^{-1} in all complexes may be assigned to M ← L charge transfer transition from 'O' atom of amide group containing ligand to Cu (II), but a band in the similar region is also present in the uncomplexed ligands, so either the charge transfer band is missing in the complexes or is overlapped by intraligand transition band. The result of electronic spectra has been suggested distorted octahedral geometry of the complexes. The magnetic moment values also supported this assumption.

CONCLUSIONS

Changes in characteristic ir bands of amide group containing ligands on complexation reveal the mode of coordination through carbonyl oxygen of amide group and pyrimidinyl nitrogen around metal centre in all the complexes of all the ligands. The IR spectra predict the possibility of coordination through deprotonated or non-deprotonated nitrogen and involvement of exogenous ligand is seen in the complexes. In the light of above facts on the basis of experimental observations, the tentative structures have been assigned to the complexes and which are shown in Fig. 1 to 4. Recapitulating the experimental data, it is concluded that these amide group containing ligands act as bidentate ligands with stoichiometry of two amide ligand molecule and two exogeous ligand per metal ion in the complexes, which adopt distorted octahedral geometry. Antibacterial activity of amide ligand and their Cu (II) metal complexes are shown in Fig 5, 6.

Table- 1 Physico-chemical Data of Cu (II) Metal Complexes (C.M. = Conventional method, M.M.= Microwave method)

S. N.	Complexes	Colour	Reaction period		Yield %		Elemental analysis Calculated (Found)%		
			C.M. hrs.	M.M. min.	C.M.	M.M.	C	H	N
1	$[Cu\text{-}(N2PB)_3]Cl_2$	Light Green	6	2.00	35	50	54.47 (54.40)	3.71 (3.65)	17.33 (17.25)
2	$[Cu\text{-}(N2PA)_3]Cl_2$	Pale Yellow	6.5	2.30	40	50	39.92 (39.85)	3.88 (3.84)	23.29 (23.20)
3	$[Cu\text{-} (N46DM2PB)_3]Cl_2$	Dark yellow	6.5	2.00	45	45	57.77 (57.70)	4.81 (4.75)	15.55 (15.45)
4	$[Cu\text{-} (N46DM2PA)_3]Cl_2$	Orange	6.5	2.30	45	45	46.08 (46.00)	5.28 (5.15)	20.16 (20.10)

Table-2 Magnetic moments and electronic Spectral data of ligand and Cu (II) metal complex

S.N.	Ligand and Complex	R_f value	μ_{eff} (BM)	Electronic Spectral Bands λ_{max} (cm^{-1})	Tentative assignments	Expected Geometry
1	$[Cu\text{-}(N2PB)_3]Cl_2$	$(0.750)^c$	1.84	12642, 12836, 1302013227, 13422, 15619, 13661, 15698, 24952	$^2T_{2g} \leftarrow {}^2E_g$ $^2B_{1g} \rightarrow {}^2A_{1g}$	Distorted Octahedral
2	$[Cu\text{-}(N2PA)_3]Cl_2$	$(0.571)^a$	1.90	11682, 14858, 15384, 24509	$^2T_{2g} \leftarrow {}^2E_g$ $^2B_{1g} \rightarrow {}^2A_{1g}$	Distorted Octahedral
3	$[Cu\text{-}(N46DM2PB)_3]Cl_2$	$(0.700)^b$	1.88	12285, 12836, 13888, 14598, 23696, 24691,	$^2T_{2g} \leftarrow {}^2E_g$ $^2B_{1g} \rightarrow {}^2A_{1g}$	Distorted Octahedral
4	$[Cu\text{-}(N46DM2PA)_3]Cl_2$	$(0.777)^d$	1.96	12437, 16155, 17730, 18315, 20080, 24691	$^2T_{2g} \leftarrow {}^2E_g$ $^2B_{1g} \rightarrow {}^2A_{1g}$	Distorted Octahedral

a= ethyl acetate:carbon tetrachloride(6:4), b= acetone: carbon tetrachloride (5:5) ,
c= acetone: carbon tetrachloride (6:4), d= acetone: carbon tetrachloride (7:3)

Table- 3 IR Vibrational frequencies of Cu (II) transition metal complexes

S N	Complexes	ν_{N-H} (amide)	$(\nu_{C=O})^a$	$(\nu_{C-N+\delta N-H})^b$	$(\nu_{N-H+\delta C-N})^c$	Pyrimidinyl	ν_{M-N}	ν_{M-O}	ν_{M-cl}
1	N2PB	3382	1674	1410	1288	1621			
	$[Cu\text{-}(N2PB)_3]Cl_2$	3379	1620	1507	1345	1578	485	496	----
2	N2PA	3339	1735	1408	1288	1618			
	$[Cu\text{-}(N2PA)_3]Cl_2$	3378	1649	1496	1313	1591	483	519	----
3	N46DM2PB	3319	1673	1474	1319	1643			
	$[Cu\text{-}(N46DM2PB)_3]Cl_2$	3320	1643	1475	1334	1611	477	514	----
4	N46DM2PA	3318	1739	1447	1369	1642			
	$[Cu\text{-}(N46DM2PA)_3]Cl_2$	3321	1673	1474	1411	1610	476	513	----

a: - amide - I band, b: - amide - II band, c: - amide – III band

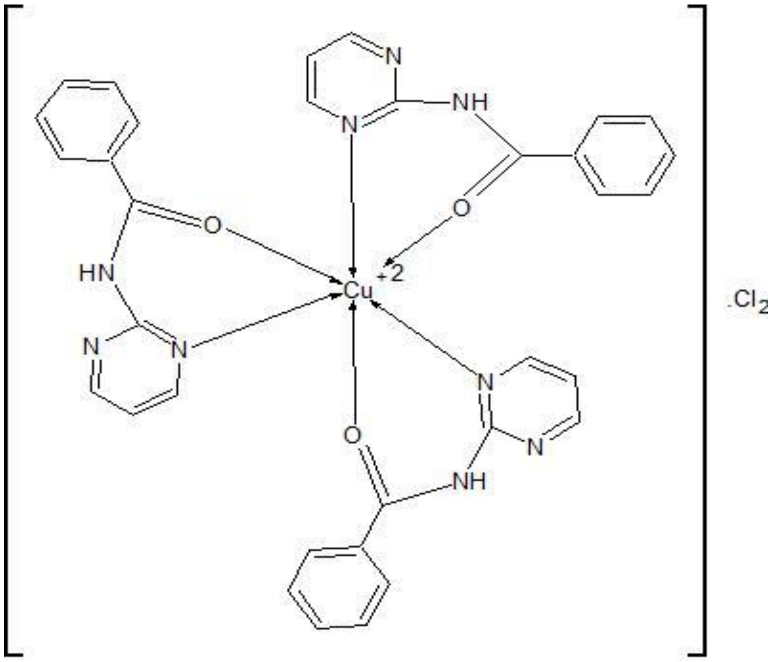

Fig. 1. Tentative Structure of Complex $[Cu\text{-}(N2PB)_3]Cl_2$

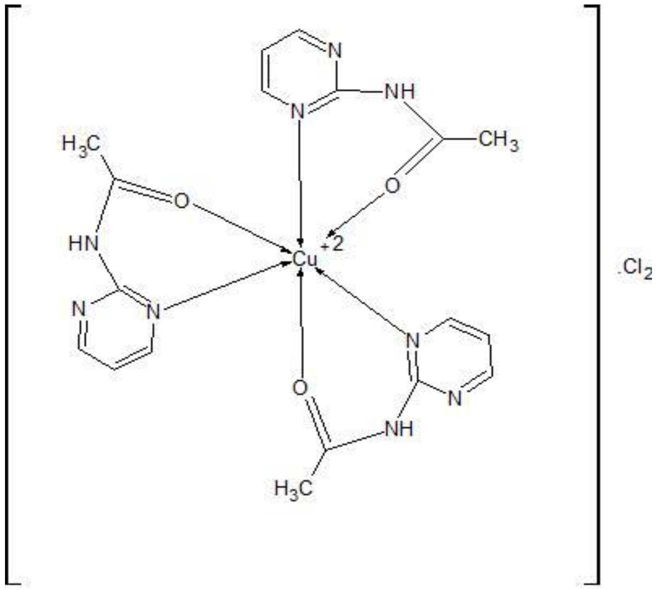

Fig. 2. Tentative Structure of Complex [Cu-(N2PA)$_3$]Cl$_2$

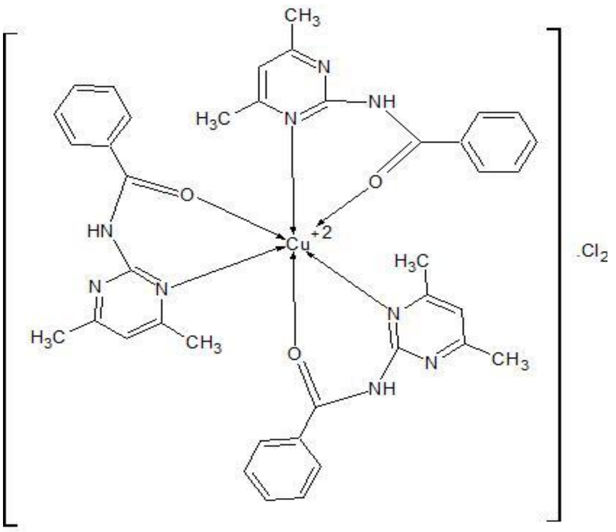

Fig. 3. Tentative Structure of Complex [Cu-(N46DM2PB)$_3$]Cl$_2$

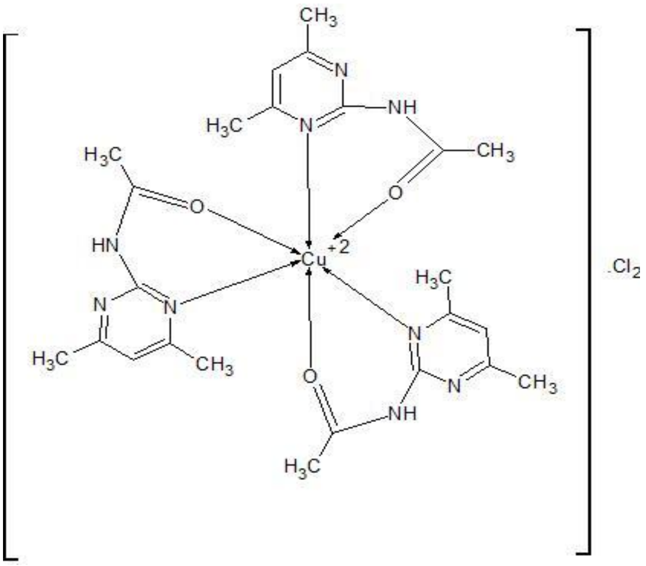

Fig. 4. Tentative Structure of Complex [Cu-(N46DM2PA)$_3$]Cl$_2$

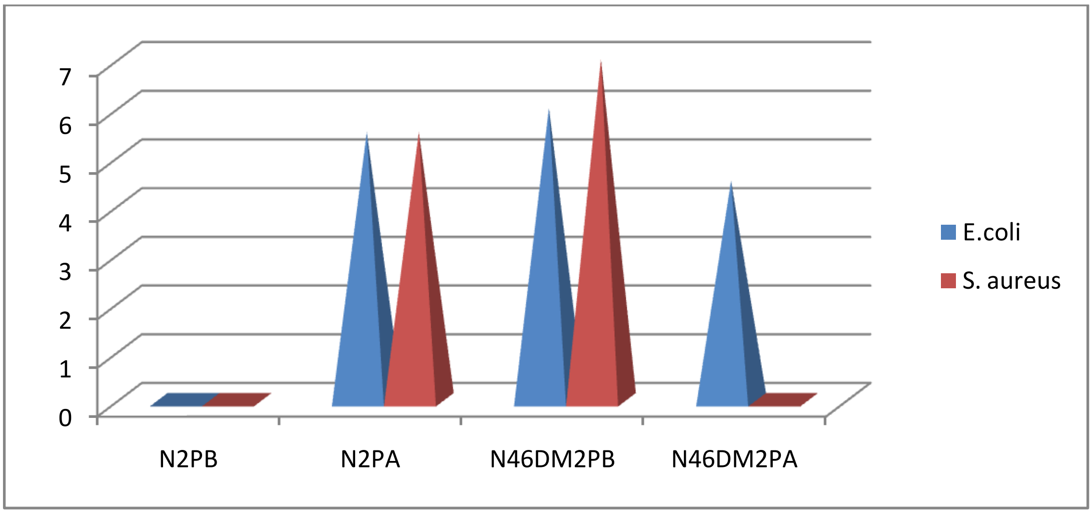

Fig.5. Biological activity of amide Ligands

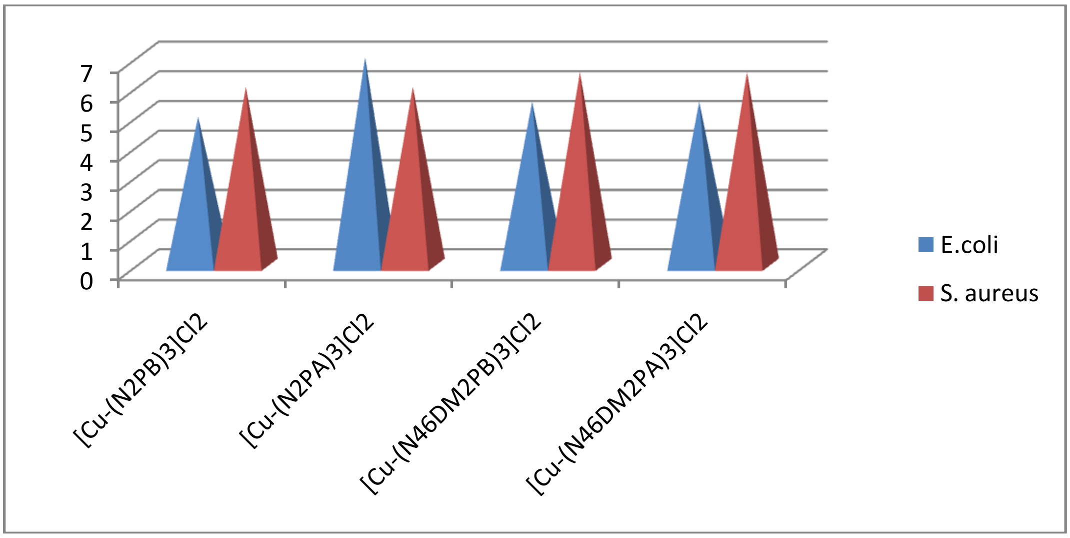

Fig.6 Biological activity of metal complexes containing amide Ligands

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