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RESEARCH ARTICLE

NOVEL COPPER (II) COMPLEXES OF BIOLOGICALLY POTENT N-SUBSTITUTED PHENOTHIAZINES: SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

The novel biologically active two mononuclear tetra coordinated copper (II) complexes were synthesised and formulated as $[M(L)(L^1) H_2O].2H_2O$,where L=ligand and L^1=1,10-phenantholine. the newly synthesized complexes have been characterized by elemental analysis, molar conductance, UV-Visible, IR, mass spectra and magnetic property studies. The spectral studies have shown that the complexes are paramagnetic and tetrahedral structure. The metal complexes were tested for antibacterial and antifungal activities show some complexes exhibit moderate activity.

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INTRODUCTION

N-substituted phenothiazines are versatile compounds possessing anticholinergic, antihistaminic, antiamoebic and antiemetic activities. These compounds are found to be exhibiting fungicidal and antibacterial activities. They are extensively used in the field of psychiatry and chemotherapy [1]. They are good electron donors exhibiting low ionization potential. *N*-substituted phenothiazines fulfil the basic prerequisite for an active ligand possessing three active coordinate sites in the forms of a heterocyclic nitrogen and sulphur atoms in the side chain. Due to these multifaceted characteristic, they find widespread utilization in biology, medicine and chemical analysis. Recently, *N*-substituted phenothiazines have attracted a large interest in the photo ionization studies performed for solar energy conversion processes. It is used for pre-anesthetic medication, as a muscle relaxant and in the treatment of tetanus [2-4]. It has now been discovered that some derivatives of *N*-substituted phenothiazines show surprisingly high stabilizer activity and more solubility in a broad range of mineral and synthetic oils. Thus the subject matter of the instant invention is a lubricant composition comprising synthetic oils, mineral oils, mixtures thereof and an antioxidative compound. Such antioxidant combinations may show a synergistic action that is the stabilizing effect of such a mixture being greater than the sum of the performances of the individual antioxidant. Such synergistic performance can be obtained when combining the instant compounds along with certain aromatic amines or hindered phenols or with both types of antioxidants. Among the different transition metals, copper metal has gained a special position because of its appearances in biological systems, which are essentially needed to many biological processes. A number of proteins and enzymes have copper in their active sites, it is associated with a variety of biological functions like oxygen transport and activation, electron transfer etc [5-8]. The copper containing enzymes and proteins constitute an very important class of biologically active compounds [9]. The biological functions of copper proteins/enzymes include electron transfer, dioxygen transport, oxygenation, oxidation, reduction, and disproportionate[10,11]. The most common oxidation state of Cu is +2, and Cu(II) complexes have been extensively studied. These complexes have trigonal planar, tetrahedral, octahedral, distorted octahedral, pentagonal bipyramidal and square planar geometries [12]. Copper complexes of bis (thiosemicarbazones) are found to be hypoxia selective agents that can be used for imaging lack of oxygen in biological tissues. Recently Chen *et al* have shown that the copper complexes of plumbagin have higher anticancer properties and are less toxic to healthy cells than commonly used platinum-based drugs, such as cisplatin. Bernadette Creaven *et al.*[13] have been investigated the anticancer and antifungal activity of copper (II) complexes of quinolin-2(*1H*)-one derived Schiff bases. Antioxidant activity of Cu(II) complexes of Schiff bases derived from α- or β-alanine and

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salicylaldehyde were reported by Jan Vanco *et al.* [14]. Raman *et al.* [15] have studied the DNA interaction and antimicrobial activity of novel Cu (II) complexes with Schiff base derived from 2-aminophenol and o-aceteoacetotoluidide. Copper(II) complexes bind to CT-DNA through intercalative mode. The ligand biocidal activity was appreciably enhanced on complexation. DNA binding studies of Cu(II)-phenanthroline complexes have been studied by Senthil kumar *et al.*[16]. Various modes of DNA interactions of Cu(II) complexes in the presence of phenanthroline have been reported. Oxidative DNA damage of mixed Cu(II) complexes with sulfonamides and phenanthroline have also been reported by Benigno Macias *et al.* [17]. The scission of plasmid DNA by the Cu(II) complexes may be due to the steric effect. Copper is a bio-essential element and their complexes have been extensively utilized in metal-mediated DNA cleavage for the generation of activated oxygen species [18]. It has been reported that tetraaza macrocyclic copper coordination compounds have anti-HIV activities [19]. The above literature survey revealed that no attempt has been made for the synthesis of copper(II) complexes with synthesized-Substituted phenatiazine ligands. Therefore, in the present investigation the author has made an effort to synthesize Cu(II) complexes of the above cited ligands (L_1-L_6). The author has also studied the interaction of Cu(II) ion with 1,10-phenanthroline. The synthesized complexes were characterized by physical and spectroscopic techniques. The antimicrobial activity of the synthesized Cu(II) complexes were evaluated against antimicrobial by disc diffusion method.

MATERIALS AND METHODS

The ligands [L] were prepared as described in the literature [20] for phenothiazine. Metal salt, copper acetate and 1, 10-phenanthroline was obtained from Padmashri Scientific.. All organic solvents such as methanol, ethanol, diethyl ether, dimethyl form amide, dimethyl sulfoxide and DMSO-d6 were of analytical grade reagents and were used without further purification. Double distilled water was used in all preparations. Elemental analyses of complexes were estimated *in* an elementorvairo-EL instrument. Molar conductivity measurement in DMF was made on an ELICO-CM-180 conductivity bridge with a conductivity cell having cell constant 0.51cm^{-1}. UV-Visible spectra were recorded using a Shimadzu UV1601 spectrophotometer. IR spectra were recorded in KBr using a perkin Elmer 157 FT-IR spectrometer from 4000 to 400cm^{-1}. The magnetic susceptibilities of the complexes were measured in Johnson Matthey magnetic susceptibility balance which uses $HgCo(SCN)_4$ as calibrant, at room temperature. Melting points were determined on a Melt-Temp apparatus in laboratory devices .The mass spectra of ligands were recorded on TOF MS ES+ 9.25e4 spectrometer. .Nitrogen content was analysed by micro-combustion Dumas .The metal content was determined by atomic absorption spectrometry (perkin elmer Analyst 400 spectrophotometer). Metal content was estimated by standard procedures after decomposition in nitric acid [21]. The electronic spectra were recorded at 25^{0}C on a Jasco V560 in diffuse reflectance technique.

General Synthesis of metal Complexes: A Known concentration of the transition metal salt (1 m mol) (copper acetate in a minimum volume of methanol was added drop wise with stirring to a concentrated methanolic solution of ligand (1 m mol) followed by addition of 1:10-phenanthroline (1 m mol) in limited amount of methanol. The mixture was refluxed for 6 hr at 50^0-60^{0}C on water bath. On cooling, coloured solid product was obtained, the obtained metal complexes were collected by filtration and purified by washing with distilled cold ethanol and then with ether and dried over fused calcium chloride in vacuum. Each of the new complexes does not possesses a sharp melting points ranging from 250-300^{0}C.Some complexes have high melting point, which indicate their greater thermal stability.

Biological Activity: All the newly synthesized compounds are screened for biological activity such as antimicrobial by agar well diffusion method, antioxidant activity.

Antibacterial activity: The antibacterial activity were carried out against both positive and gram negative species B.Substilis, Ralstonia Solanacearum, Pseudomonas aeruginosa and Esherichia coli it is performed by disc diffusion technique method using nutrient agar medium.

Antifungal Activity: The antifungal activity was tested against Aspergillus flavus, Fusarium and phoma. The test organisms were sub-cultured in potato dextrose agar medium and incubated at 37 ^{o}C for 48 h .

RESULTS AND DISCUSSION

The molecular formula and structure of the complexes were determined on the basis of elemental analysis, mass, molar conductance, UV-visible, IR, and magnetic studies. The complexes are soluble in methanol, ethanol, acetonitrile , DMF, acetone & DMS

Physical properties of the complexes: The analytical data and physical properties of ligands and its metal complexes are given in table 1 .Complexes are coloured ,crystalline in nature and stable at room temperature as indicated by the melting point. The data shows that the ligand L forms a 1:1:1(M:L:L^1) complexes with Cu(II) ions. The prepared complexes were found to have formula

$[M(L)(L^1)H_2O].2H_2O$, $[M(L)(L^1)].2H_2O$.
Where M = Cu (II), L is ligand, L^1 is 1:10-phenathroline

Molar conductivity measurement: The molar conductance for the complexes measured at room temperature in DMF solution at 10^{-3}mol/dm^3 were measured to establish the charge of the metal complexes, it is in the range of 12-20 ohm^{-1} cm^2 mol^1, indicates that all the complexes exhibit non-electrolytic characteristic property, the nature is due to no counter ions in the proposed structures of the metal complexes [21].

Elemental analysis: The calculated elemental data are in agreement with the experimental results, except for halide ions.

UV-Visible spectra: The UV-Visible spectral data of the ligands and its complexes are presented in table-3. The broad band's observed in the region of 260-275 nm in the spectra of all complexes can be attributed to the intra-ligand transitions. The molar absorptivities of the complexes falling in the range of 0.24 x 10^4 to 1.10 x 10^4 L mol^{-1} cm^{-1}, are higher than that of the ligand in the free state which is 0.21 x 10^4 L mol-1 cm-1. The shift in the bands in UV- Vis spectra are attributed to the intramolecular transitions of $\pi\rightarrow\pi^*$ type.

Table 1. Physical characteristics and analytical data of the complexes

SL. NO	Complexes	Color	Melting point (^{o}C)	Molar conductance (mho cm^{2} mol^{-1}) (ionic ratio)	Yield (%)
1	$[Cu(L_1)(L^1)H_2O].2H_2O$	Light Green	$>260^{0}C$	12.4	68
2	$[Cu(L_2)(L^1)H_2O].2H_2O$	Light Green	$>260^{0}C$	12.8	69
3	$[Cu(L_3)(L^1)H_2O].2H_2O$	Light Green	$>260^{0}C$	14.0	75
4	$[Cu(L_4)(L^1)].2H_2O$	Light Green	$>260^{0}C$	16.0	76
5	$[Cu(L_5)(L^1)].2H_2O$	Light Green	$>260^{0}C$	15.6	65
6	$[Cu(L_6)(L^1)].2H_2O$	Light Green	$>260^{0}C$	18.2	82

Table 2. Elemental analysis of metal complexes

Molecular formula/	Mass	C Exp(Theor)%	H Exp(Theor)%	N Exp(Theor)%	M Exp(Theor)%
$C_{26}H_{27}ClN_3O_4SCu$	573	54.22(54.25)	4.52(4.54)	7.27(7.29)	11.00(11.02)
$C_{27}H_{26}ClN_3O_4SCu$	586	55.53(55.52)	4.46(4.48)	7.21(7.18)	10.03(10.08)
$C_{28}H_{28}ClN_3O_4SCu$	600	56.33(56.30)	4.70(4.71)	7.04(7.03)	9.85(9.86)
$C_{3o}H_{30}N_4O_4SCu$	605	59.90(59.85)	5.03(5.00)	9.29(9.30)	9.80(9.79)
$C_{31}H_{32}N_4O_4SCu$	619	60.42(60.46)	5.20(5.23)	9.10(9.09)	9.53(9.56)
$C_{32}H_{34}N_4O_4SCu$	633	61.04(61.02)	5.40(5.42)	8.86(8.88)	9.32(9.35)
$C_{26}H_{30}Cl_2N_2O_5S_2Cu$	673	49.95(49.97)	4.44(4.48)	4.16(4.15)	9.40(9.43)

Table 3. UV-visible spectral data of ligand and its metal complexes

Ligands and Complexes	ƛmax (nm)	Molar absorptivity (£)(10^{4},$M^{-1}cm^{-1}$)	transition
L_1	262	0.280	
$[Cu(L_1)(L^1)H_2O].2H_2O$	270	0.293	π-π^*
L_2	265	0.137	
$[Cu(L_2)(L^1)H_2O].2H_2O$	275	0.242	π-π^*
L_3	265	0.173	
$[Cu(L_3)(L^1)H_2O].2H_2O$	273	0.850	π-π^*
L_4	269	0.081	
$[Cu(L_4)(L^1)].2H_2O$	275	0.248	π-π^*
L_5	265	0.210	
$[Cu(L_5)(L^1)].2H_2O$	273	0.820	π-π^*
L_6	265	0.208	
$[Cu(L_6)(L^1)].2H_2O$	271	0.512	π-π^*

Table 4. IR absorption of ligand and its metal complexes

Complexes	Absorption (C=O)(cm^{-1})	Absorption (Ar-N)(cm^{-1})	Absorption (C-S-C)(cm^{-1})	Absorption (M-N)(cm^{-1})	Absorption (H_2O)(cm^{-1})
L_1	1674	1323	690	-	-
$[Cu(L_1)(L^1)H_2O].2H_2O$	1672	1308	688	445	3325
L_2	1675	1325	690	-	-
$[Cu(L_2)(L^1)H_2O].2H_2O$	1674	1309	689	435	3445
L_3	1670	1365	697	-	-
$[Cu(L_3)(L^1)H_2O].2H_2O$	1668	1342	698	435	3320
L_4	1671	1352	692	-	-
$[Cu(L_4)(L^1)].2H_2O$	1669	1338	691	440	3400
L_5	1683	1369	683	-	-
$[Cu(L_5)(L^1)].2H_2O$	1682	1340	682	445	3350
L_6	1686	1374	687	-	-
$[Cu(L_6)(L^1)].2H_2O$	1685	1345	687	435	3550

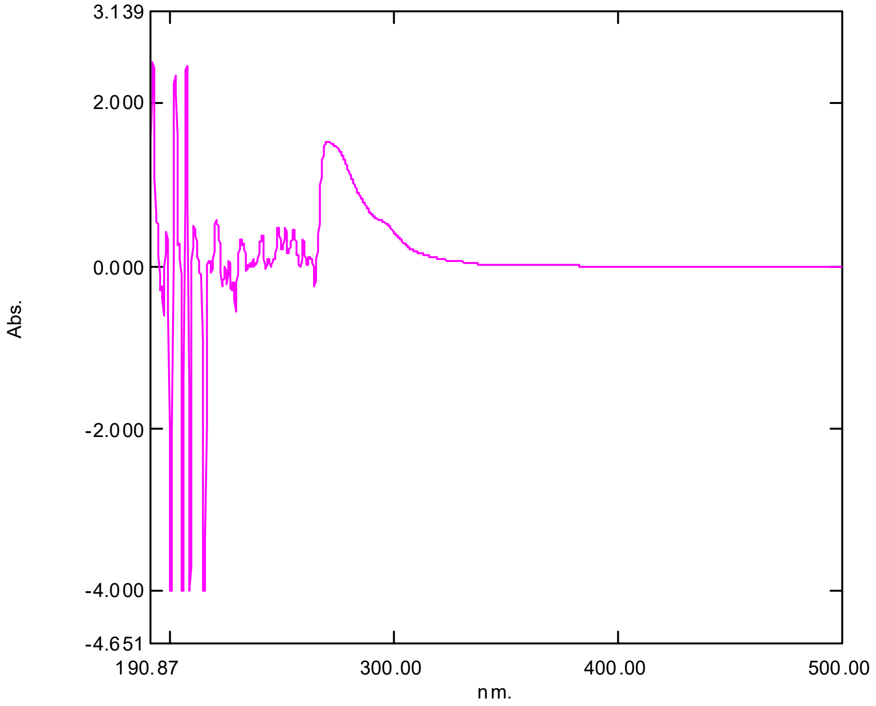
Complexes	μ_{eff} (BM)	Geometry proposed
$[Cu(L_1)(L^1)H_2O].2H_2O$	1.72	Tetrahedral
$[Cu(L_2)(L^1)H_2O].2H_2O$	1.72	Tetrahedral
$[Cu(L_3)(L^1)H_2O].2H_2O$	1.75	Tetrahedral
$[Cu(L_4)(L^1)].2H_2O$	1.73	Tetrahedral
$[Cu(L_5)(L^1)].2H_2O$	1.74	Tetrahedral
$[Cu(L_6)(L^1)].2H_2O$	1.74	Tetrahedral

Table-6: Antibacterial activity of ligands and their metal complex Zone of inhibition in mm

compounds	B.Substilis	Ralstonia Solanacearum	Pseudomonas aeruginosa	Esherichia coli
L_1	7.5	6.5	5	7
$[Cu(L_1)(L^1)H_2O].2H_2O$	8	12	12	14
L_2	8	6	8	7.2
$[Cu(L_2)(L^1)H_2O].2H_2O$	8	9	17.5	16.5
L_3	9	8	6	9.5
$[Cu(L_3)(L^1)H_2O].2H_2O$	12	14	18	18.8
L_4	7	3.5	13	8
$[Cu(L_4)(L^1)].2H_2O$	8	14	21	16.5
L_5	7.2	9	2	6.8
$[Cu(L_5)(L^1)].2H_2O$	10	16	18	14.5
L_6	7.4	4	4	7
$[Cu(L_6)(L^1)].2H_2O$	13	9	16.5	15
Standard	12	15	15	15

Table 7. Antifungal activity of ligands and their metal complexes Zone of inhibition in mm

compounds	Asperigillus flavour	Fusarium	Phoma
L_1	8	8	10
$[Cu(L_1)(L^1)H_2O].2H_2O$	10	12	16
L_2	7.5	8	12
$[Cu(L_2)(L^1)H_2O].2H_2O$	12.5	13.4	20.1
L_3	12	6	8.1
$[Cu(L_3)(L^1)H_2O].2H_2O$	14	14	19.9
L_4	14	12	8
$[Cu(L_4)(L^1)].2H_2O$	18.2	18.1	15
L_5	16	7	12
$[Cu(L_5)(L^1)].2H_2O$	17.9	16.6	17.8
L_6	14	7	8
$[Cu(L_6)(L^1)].2H_2O$	19	15	20
Standard	15	20	20



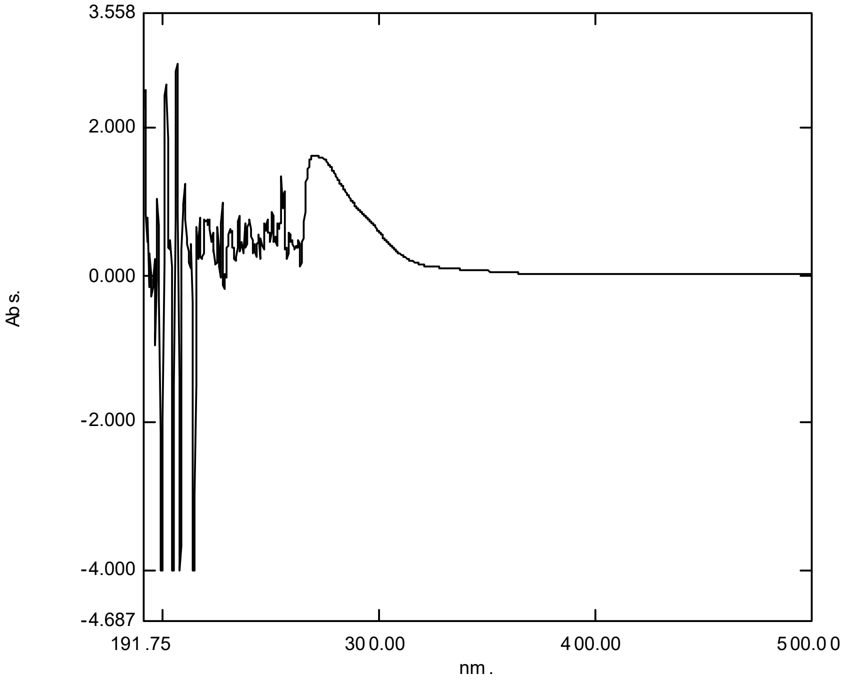


Figure 1: UV spectra of complexes 1 and 4

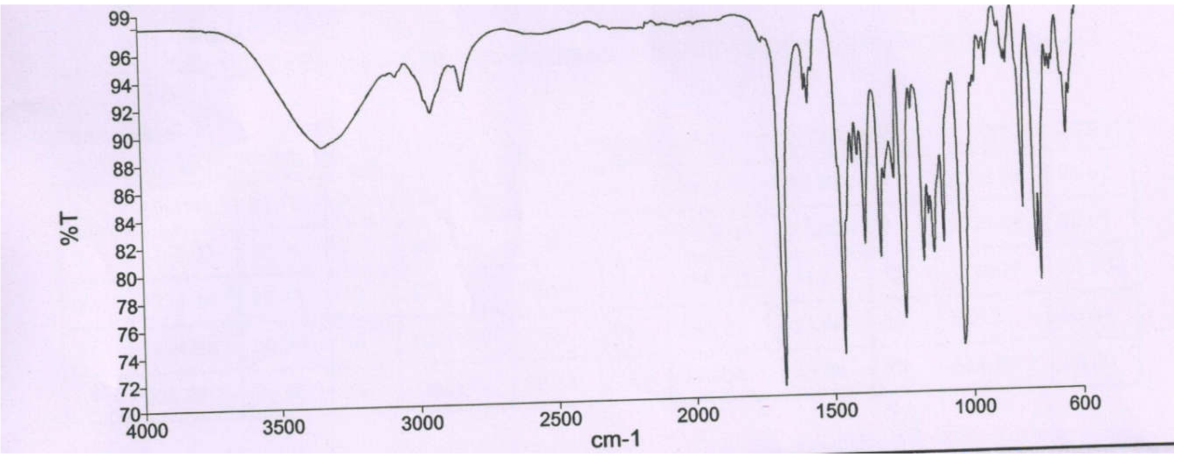


Figure 2: IR spectra of compound $[Cu(L_1)(L^1)H_2O].2H_2O$

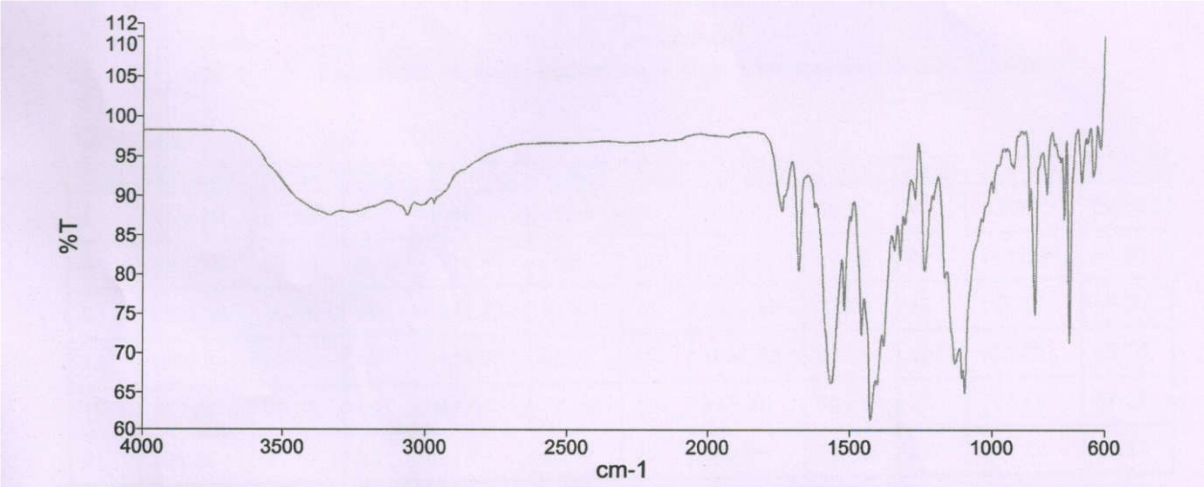


Figure 2: IR spectra of compound $[Cu(L_5)(L^1)].2H_2O$

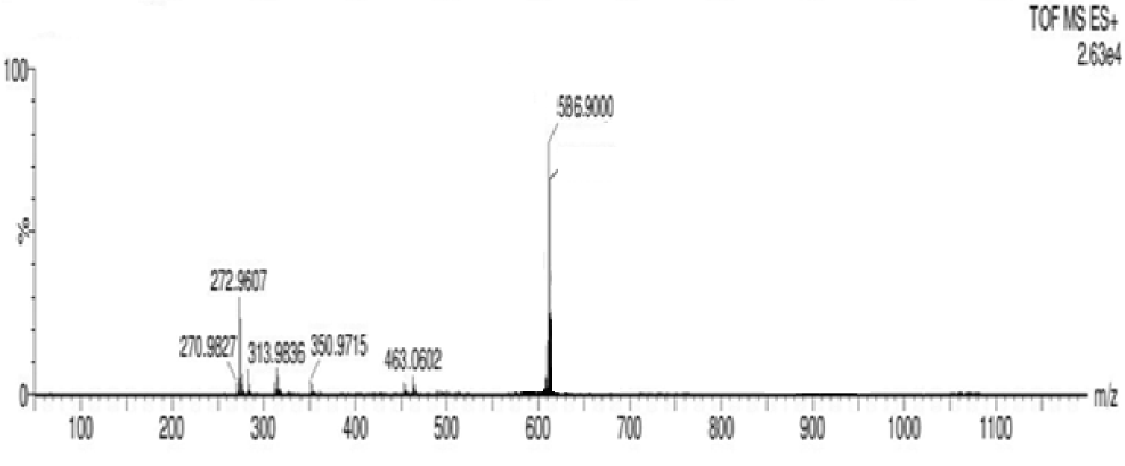
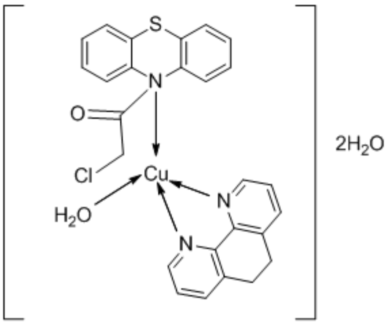


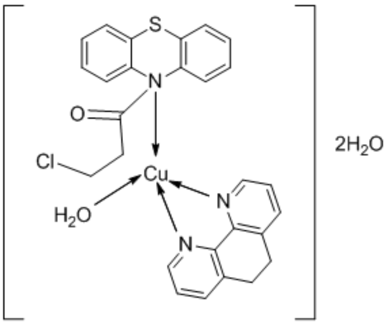
Figure 4. Mass spectrum of compound $[Cu(L_2)(L^1)H_2O].2H_2O$

This may be taken as an indirect evidence for the involvement of N atoms of ligand in the coordination process. The electronic spectra confirm the complexation between metal ions and the ligand [22].

Infrared spectra: The type of bonding in metal complexes is studied by comparing the IR spectra of ligands with the spectra of metal complexes. Relevant IR absorption frequencies of the ligand and its metal complexes are presented in Table 4. Figure 2. The ν(Ar-N) frequency in the complex is observed around 1300-1340 cm^{-1} which is lower than that observed in free ligand and this evidence supports to the coordination of phenothiazine nitrogen. Involvement of phenothiazine nitrogen in the complexation is also supported by the presence of a new band at 458-436 cm-1, assignable to ν(M-N) for these Cu(II) complexes [23]. The IR spectra of free ligands shows characteristic bands to lactum ν(C=O) in the region 1675-1657 cm-1 and ν(C-S-C) in the region 680-699cm^{-1}, These band were not shifted in the IR spectra of the Cu(II) complexes,



$[Cu(L_1)(L^1)H_2O].2H_2O$



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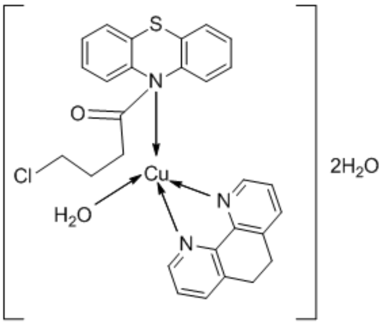
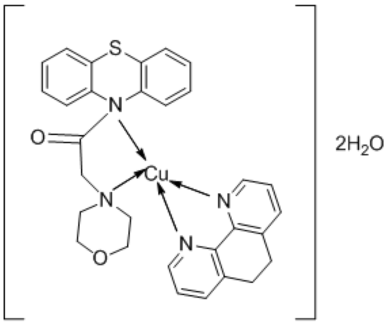
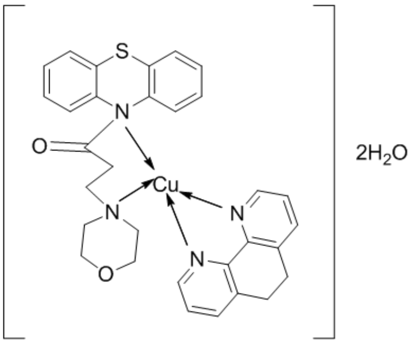


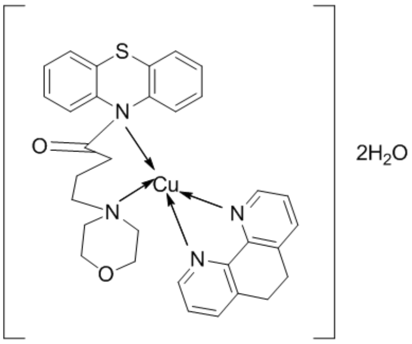
$[Cu(L_3)(L^1)H_2O].2H_2O$



$[Cu(L_4)(L^1)].2H_2O$



$[Cu(L_5)(L^1)].2H_2O$



$[Cu(L_6)(L^1)].2H_2O$

Figure 5. Structure of complex based on spectroscopic analysis

indicating the non participation of carbonyl oxygen and sulphur in coordination. In the uncomplexed ligands , the presence of a broad band in the 2000-2730 cm^{-1} range is assigned to the interaction of the quaternary ammonium ion, $(R_3NH)^+$ ion with a halide ion. In the IR spectra of the metal-ligand complexes, this band has shifted with diminished intensity suggesting that the exocyclic N atom of the amino group is indirectly involved in coordination with the metal center. A band observed in the 3000-2800 cm-1 region in the spectrum of ligands may be assigned to the heterocyclic nitrogen atom carrying an amine side chain. [24] This band of ligand shows a shift upon complexation suggesting its coordination to the metal (II) centre. In addition, complexes show a broad band in the 3250-3560 cm-1 region, supporting the hydrogen bonded OH interactions of the water molecules and sharp peak in the range of 1618-1624 cm^{-1} ,these peaks can be assigned to OH stretching and bending vibration which indicates the presences of coordinate water molecule in the complexes and also complex spectrum shows that bands in the 600-700 cm-1 and 715-740 cm-1 regions, attributable to the heterocyclic C-S-C vibrational modes of N-substituted phenothiazines. In the IR spectra of the corresponding metal complexes 4, 5 and 6, this band either disappeared or reduced to a small hump showing that the tertiary nitrogen atom of the side chain is another site of coordination. This shows that ligand act as a bidentate ligand with heterocyclic nitrogen atom and tertiary nitrogen atom as two coordination site[25].

Magnetic properties: The magnetic susceptibility measurements of the complexes were obtained at room temperature using Gouy balance. Pure $Hg[Co(SCN)_4]$ was and used as calibration standard [26]. The magnetic moment valves of the synthesized metal complexes are given in table-5. The effective magnetic moments (μeff) of copper(II) complexes obtained are in the range of 1.72-1.75 B.M. which is consistent with the presence of one unpaired electron [27]. It is possible to draw up the electronic transitions and predict the geometry with the aid of magnetic moments of most metal ions.

Mass Spectra: Mass spectrometry has been widely applied to the characterization of coordination compounds [28-29]. The mass spectra of all the Cu(II) complexes have been recorded. All the spectra exhibit parent peaks due to molecular ions. The proposed molecular formula of these complexes was confirmed by comparing their molecular formula weights with m/z values. Mass spectral studies provide evidence for the proposed constitution of the complexes. The two complexes are selected as representative show the molecular ion peaks $[M^+]=573.9890$, $[M^++2]=575.9924$ and $[M^+]=605.9249$, $[M^++2]=607.9355$ that correspond to the formula weight $[Cu(L)(L^1)H_2O]$.2H2O and $[Cu(L)(L^1)]$.2H2O respectively, for monomeric complexes. Besides, the spectra show some prominent peaks corresponding to various ion fragments. The peak intensity gives an idea of the stability of the fragments.

Biological activity

Antimicrobial activity: The newly synthesized Ligands and complexes were screened for their antimicrobial activities against the selected species of bacteria and fungi such as B.substilis Ralstonia Solanacrrum, Esherichia coli, Aspergillusflavus, Fusarium and phoma. The activities were compared with standard antibacterial and antifungal drugs such as Chloromphericol and Nystalin, respectively. The results were compared with standard drugs and depicted in table 6 and 7. The data pertaining to the antimicrobial potential of ligands and their Cu (II) complexes are presented in Table 5. The results indicate that the complexes show more activity than the free ligands against same microorganisms under similar experimental conditions. The remarkable activity was observed for complexes 3,4 and 5 may be arisen from the morpholine, which may play an important role in the antibacterialactivity.

This would suggest that the chelation could facilitate the ability of a complex to cross a cell membrane and can be explained by Tweedy's chelation theory [30]. All the test compounds show slightly lesser activity than the standard antibiotics. All Compounds were showing too good antifungal activity than antibacterial. All of the ligands showed lowest antimicrobial activity, but all the metal complexes under study were definitely showing better antimicrobial activity compared to the ligands and standard antibiotics Chloromphericol and Nystalin.

Proposed structure of metal complexes: The *N*-substituted phenothiazine complex crystal were poor in quality such that to permit X-ray crystallographic analysis of the structure .Therefore tentative complex structure for the compounds proposed in the study are based on various physic-chemical methods. The elemental analysis, mass magnetic susceptibility, spectroscopic, IR, UV and molar conductance data.

Conclusion

The synthesized complexes have been characterized by utilizing the various physic-chemical methods. The molar conductance of all the complexes in DMF shows that they are non-electrolytes. Non-electrolytic nature of the studied complexes showing the anions is coordinated to the central metal ion. The magnetic and electronic spectral studies support an tetrahedral geometry for all the metal complexes. Mass spectrum of the complexes shows two or three steps thermal degradation. Mass spectrum of the complex confirms the proposed structure. The proposed geometry of the complexes are given in figure-5. The antimicrobial activities of synthesized complex compounds were screened against two bacteria and three fungi using disc diffusion method. The result revealed that most of the synthesized complex compounds exhibited antimicrobial activities.

REFERNCES

1. Satoskar R.D. and S.D. Bhandarkar, Phamacology and Pharmacotherapeutics, 5th Ed., popular press, Bombay, 1976;181.
2. Perumal, R V M Adiraj and P Shanmugapandiyan , Indian Drugs.2001; 38:156-159.
3. Salamon , p. 4785095, (1988).
4. Salamon , p. 5157118, (1992).
5. Invert Dermatol J.1977;68: 313-317.
6. Solomon, E.I. K.W. Penfield, D.E. Wilcox, Struct. Bonding (Berlin).1983; 53:1-57.
7. MacPherson, I. S. M.E.P. Murphy, Cell. Mol. Life Sci, 2007; 64: 2887- 2899.
8. Kosman, D.J. J. Biol. Inorg. Chem, 2010;15:15–28.
9. Mukherjee, R.N. Indian J. Chem, 2003;42A : 2175.
10. Mukherjee, R.N. Comprehensive Coordination Chemistry-II: From Biology to Nanotechnology, 2003; 5.
11. Holm, R.H. P. Kennepohl, E.I. Solomon, Chem. Rev, 1996;96
12. Keshavan B and J Seetharamappa, Synth. React. Inorg, Met-org, chem.1988;18: 1449.
13. Vanco, J. Ol'ga Svajlevona, E. Racauska, J. Muselik and J. Valentova, Journal of Trace
14. Elements in Medicine and Biology,2004; 18:155.
15. Raman, N. Baskaran, T. A. Selvan and R. Jeyamurugan, Journal of Iranian Chemical residence, 2008;1: 129-139.
16. Kumar, R.S. S. Arunachalam, V.S. Periasamy, C.P. Preethy, A. Riyasdeen and M. A.
17. Akbarsha, European Journal of Chemistry, 2008; 43:2082.
18. Macias, B. I. Garcia, M.V. Villa, J. Borras, M. Gonzalez-Alvarez and A. Castineiras, Journal of Inorganic Biochemistry, 2003; 96: 367.
19. Liu, C. L. J. Y. Zhou, Q. X. Li, L. J. Wang, Z. R. Liao and H. B. Xu, J. Inorg. Biochem, 1999;75: 233.
20. Shionoyan M. and E. Kimura, *Chemistry*,1992;47: 878.
21. Liu, C. L. J. Y. Zhou, Q. X. Li, L. J. Wang, Z. R. Liao and H. B. Xu, Inorg. Chem. Acta,1998;3: 253.
22. Madhushree N N, Shiva Prasad K, Sudhir Nayak and Chandrashekara P G. N-substituted phenothiazine derivatives as potent antimicrobials: Synthesis and structural characterization. Der pharma Chemica, 2016;8(1):351-357.
23. Sreekanth A. and M.R.P. Kurup, *Polyhedron*, 2003; 23:3321.
24. Made Gowda N M, Lawrence Pacquette H, Kim Doo-Hyung, Jayaram, Beby. 1996. Coordination compounds of zinc(II) and *N*-alkylphenothiazines: synthesis and characterization. *Journal of Molecular Structure,* 382: 129-135.
25. Palaniandavar M. and C. Natarajan, *Australian J. Chem*, 1980; 33: 729.
26. Shearer, J., Dehestani A. and Abanda, F. 2008. *Inorg. Chem*, 47:2649.
27. Keshvan B. & Radhika, R T. 2000. Indian journal of chemistry, 39A:.425-429.
28. Lever, A.B.P. 1968. *Inorganic Electronic Spectroscopy, Elsevier,* New York.
29. Rehder, D. T. Pole nova and M. Buhl. Annual reports on NMR spectroscopy, *2007;* 62.
30. Lever, A.B.P. 1992. Inorganic Electronic Spectroscopy, 2nd ed., *Elsevier*, London.
31. Djebar-Sid, S., Benali-Baitich O. and J.P. Deloume, 2001. *J. Mol. Struct*, 121: 569.
32. Barry A 1991;Srivastava R S 1981

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