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Synthesis, Physico-Chemical and Antimicrobial Studies of N1',N6'-bis((2-hydroxyquinolin-3-yl)methylene)adipohydrazide and their metal (II) complexes

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ABSTRACT

The Cu(II), Co(II), Ni(II), Mn(II), Zn(II), Cd(II), and Hg(II), complexes of Schiff base N1',N6'-bis((2-hydroxyquinolin-3-yl)methylene)adipohydrazide has been synthesized and characterized by various spectral techniques. The complexes were prepared by reacting the ligand and metal chloride of Cu(II), Co(II), Ni(II), Mn(II), Zn(II), Cd(II), and Hg(II), in ethanol to get a series of mononuclear complexes. The complexes were characterized by CHN analysis, conductivity measurements, magnetic susceptibility, IR, NMR, ESR, UV-Vis and X-ray Powder diffraction studies. By these spectral studies it is found that Cu(II), Co(II), Ni(II), Mn(II), Zn(II), Cd(II), and Hg(II) complexes have exhibited octahedral geometry The ligand and its metal complexes have been screened for their antimicrobial activities. The prepared ligand shows low activity and its metal complexes shows moderate to good activity.

Key words: Quinoline, Schiff base, spectral studies, metal complexes and antimicrobial activity.

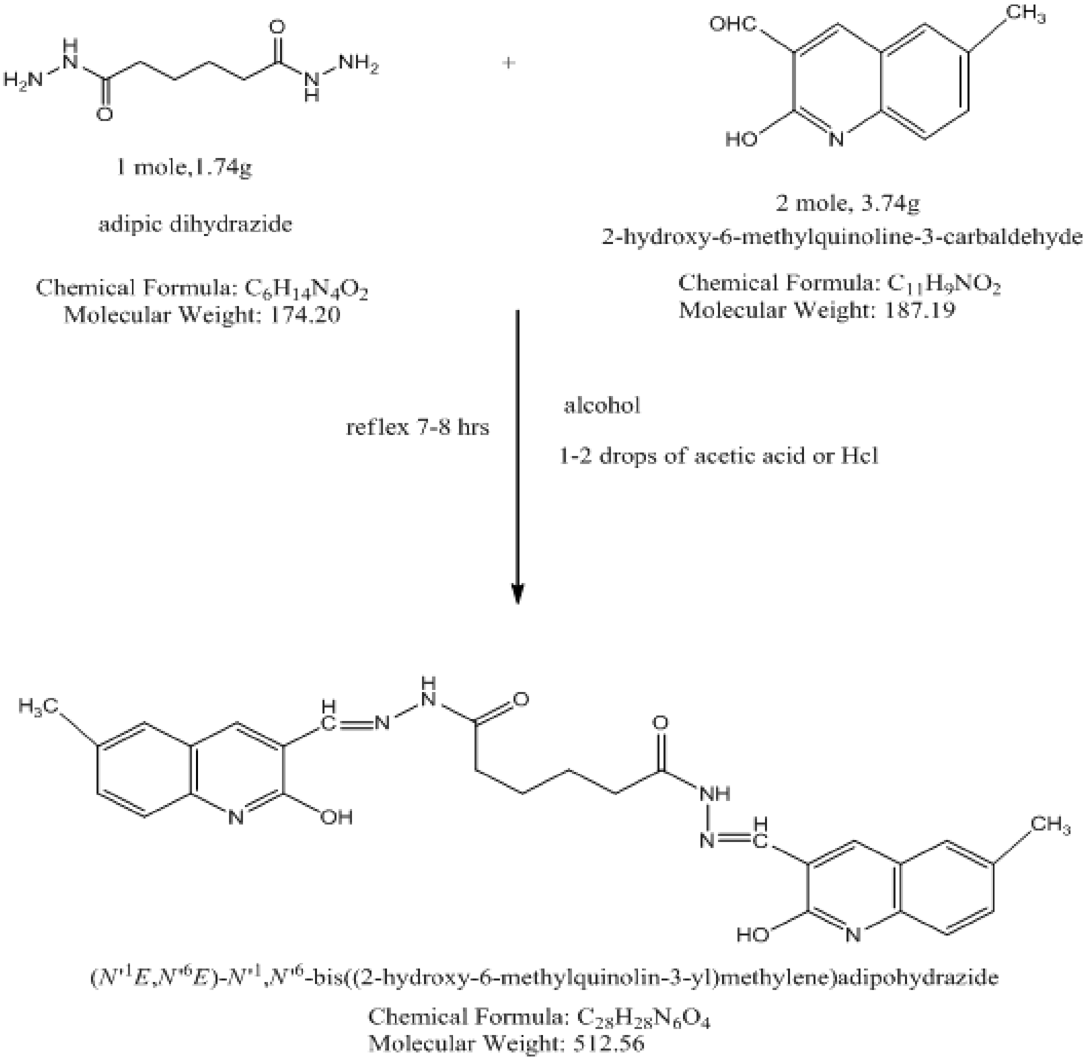
INTRODUCTION

Quinolines are a major class of alkaloids and play an important role in the fields of natural products and medicinal chemistry. Several methods for synthesizing Quinolines have been known since the late 1800s. Quinoline and their derivatives are also important constituents of organic and pharmacologically active synthetic compounds.[1-3] which possess a broad varieties of pharmacological activities such as antimalarial, antifungal, hypertensive, anticancer, anti-HIV, anti-inflammatory, analgesic, antiviral, antidepressant activity [1-4], cardiac stimulant and diuretic [5-9]. Quinoline derivatives as a source of valuable drug candidates and useful intermediates in organic chemistry [10], thus, the synthesis of this heterocyclic nucleus is of much used in pharmacopeia in treatment of malaria [11] and more recently tumors [12]. Our work is concerned with complexation in aqueous- organic solvents attract study researchers participation of the organic component. As a continuation of studies concerning the effect of an acid hydrazides [14-17], we examined in this study the complexing properties of adipicacid hydrazide ion aqueous-ethanol solutions [18]. The main goals of this study were describing the complexation of Cu(II), Co(II), Ni(II), Mn(II), Zn(II), Cd(II), and Hg(II), with ligand and revealing the effects of the central metal-ion.

EXPERIMENTAL SECTION

Materials and Methods

The chemicals were purified, acetophenone, hydrazine hydrate, sodium acetate, acetic acid, salicylaldehyde, diethyl melonate, ethyl acetoacetate, distilled alcohol and metal(II) salts were of AR grade.



Scheme1

Preparation of ligand
(N'^{1}E,N'^{6}E)-N'^{1},N'^{6}-bis((2-hydroxy-6-methylquinolin-3-yl)methylene)adipohydrazide

The Schiff base ligand were prepared by condensation of adipic dihydrazide (1 mole, 1.74g) and 2-hydroxyqninoline-3-carbaldehyde (2mole, 3.76g) in ethanol (30ml) was refluxed on water bath for 5-6 hours in presence of few drops of acetic acid. The reaction mixture was cooled to room temperature, the separated Schiff base were filtered and washed with hot alcohol and recrystalized from alcohol to get a pure sample. The purity of Schiff base was checked by TLC. Yield: 75%, MP; 285°C, Mol. Wt = 512.56

Preparation of Metal complexes

A solution of 0.01mole of metal chloride in ethanol was mixed with the ethanolic solution of 0.01 mole of ligand and refluxed for 3-4 hours on water both to get clear solution. 0.5gm of excess sodium acetate was added to the reaction mixture to adjust the pH 7-8 of the solution. The reaction mixture was further, refluxed for 2 hours more. The resulting mixture was decomposed by pouring into a 100ml of distilled water with constant stirring. The suspended solid complex was allowed to settle and collected by filtration, washed with sufficient quantity of distilled water and then with little hot ethanol to apparent dryness and dried in a vacuum over anhydrous calcium chloride in a desiccators. (Yield, 55-75%)

Physical Measurements

Infrared spectra of the ligand and its metal complexes in KBr pellets were recorded in the spectral range 4000 – 350 cm^{-1} with Perkin Elmer Spectrum One FT-IR spectrometer.^{1}H-NMR Spectra were recorded on AMX–400 NMR Spectrometer, using TMS as internal standard and DMSO as a solvent. The Electronic Spectra were recorded on an ELICO-SL-164 DOUBLE BEAM UV-Visible Spectrophotometer in the range of 200–1200nm in DMF. X-ray powder diffraction was recorded. Magnetic susceptibility measurements were recorded on Guoy balance method. The Conductance measurements were made on an ELICO-CM-82-conductivity bridge.

RESULTS AND DISCUSSION

Nature and Stoichiometry

All the complexes are colored in nature and were sparingly soluble in common organic solvents but soluble in DMF, DMSO and acetonitrile. The analytical data indicates that the complexes are agree well with 1:1 metal to ligand stiochiometry for Cu(II), Co(II), Ni(II) Zn(II), Cd(II) Hg(II) and Mn(II). The stoichiometry of all the complexes was confirmed by spectrophotometric method. The observed molar conductance values measures in DMF solution fall in the range 12 – 20 Ohm^{-1} cm^{2}mol^{-1}(Table 1). These observed values of the molar conductance are well within the expected range for non-electrolytic nature [16]. The physical characterization data of all the compounds has been summarized in Table 1.

Infrared Spectra

The significant IR bands for the ligand N1', N6'-bis((2-hydroxyquinolin-3-yl)methylene) adipohydrazide as well as for its metal complexes and their tentative assignments are complied and represented Table 2. The broad band observed at 3435 cm^{-1} in the IR spectra of the ligand assigned to $\nu_{(OH)}$, which were found to have disappeared in all their respective complexes, there by indicating the involvement of phenolic oxygen is bonding with metal ions through deprotonation. The band $\nu_{(NH)}$ observed at 3173 cm^{-1} in ligand and complexes $\nu_{(NH)}$ observed at 3173-3198 cm^{-1} respectively. A strong sharp band observed at 1660 cm^{-1} is assigned to adipic hydrazide ring $\nu_{(c=0)}$, which was shifted to 5-46 cm^{-1} in all complexes, indicates the involvement of adipic hydrazide ring carboxyl in complexation with metal ion, the band at 1598cm^{-1} is assigned to the azomethine $\nu_{(C=N)}$ group, lowering of $\nu_{(C=N)}$ 2-44cm^{-1} in the complexes as compared to its ligand, is due to reduction of double bond character carbon-nitrogen bond of the azomethine group[17]. The band observed at 1203 cm^{-1}, of the ligand is attributed to phenolic $\nu_{(C–O)}$ in view of previous observations [18]. This band is shifted to higher frequency and is found in the region 1203-1263 cm^{-1} (2-60 cm^{-1}) for the complexes. Thus, the low frequency skeletal vibrations due to $\nu_{(M-O)}$ and $\nu_{(M-N)}$ stretching provide direct evidence for complexation. In the present investigation the bands in the 552-566 cm^{-1} region for $\nu_{(M-O)}$ and 471 -494 cm^{-1} region for $\nu_{(M-N)}$ vibration respectively.

Table 1. Analytical, magnetic susceptibility, molar conductance of the ligand and its metal complexes

Ligand / Complex	**Mol. Wt.**	**M.P (°C)**	**Yield (%)**	**Found /Calculated (%)**					**μ_{eff} B.M.**	**Molar conductance Ohm^{-1} cm^{2} mol^{-1}**
				M	**C**	**H**	**N**	**Cl**		
$C_{28}H_{28}N_6O_4$	512.56	280	80	-	65.40 (65.61)	5.90 (5.51)	16.29 (16.40)	-	-	-
$[Cu(C_{28}H_{26}N_6O_4)]$	574.09	315	65	11.40 (11.07)	58.24 (58.58)	4.42 (4.56)	14.40 (14.64)	-	1.94	17
$[Co(C_{28}H_{26}N_6O_4)]$	569.48	314	70	10.44 10.35)	59.26 (59.05)	4.58 (4.60)	14.50 (14.76)	-	4.77	18
$[Ni(C_{28}H_{26}N_6O_4)]$	569.24	320	67	10.38 10.31)	58.12 (59.08)	4.56 (4.60)	14.65 (14.76)	-	2.94	19
$[Mn(C_{28}H_{26}N_6O_4)]$	565.48	331	65	9.80 (9.72)	59.32 (59.47)	4.50 (4.63)	14.85 (14.86)	-	5.71	16
$[Zn(C_{28}H_{26}N_6O_4)]$	575.95	354	68	11.40 (11.36)	58.45 (58.39)	4.25 (4.21)	13.45 (13.49)		Diamagnetic	16
$[Cd(C_{28}H_{26}N_6O_4)]$	622.95	361	70	18.18 (18.04)	54.02 (53.98)	4.15 (4.21)	13.52 (13.49)		Diamagnetic	13
$[Hg(C_{28}H_{26}N_6O_4)]$	711.13	371	79	27.98 (28.21)	47.30 (47.29)	3.58 (3.69)	11.75 (11.82)		Diamagnetic	17

Table 2. IR Spectral data of the ligand and its metal complexes (cm^{-1})

Ligand / complex	ν_{OH}	ν_{NH}	$\nu_{C=0}$	$\nu_{C=N}$	ν_{C-O}	ν_{M-O}	ν_{M-N}
$C_{28}H_{28}N_6O_4$	3435	3173	1660	1598	1203	-	-
$[Cu(C_{28}H_{26}N_6O_4)]$	-	3180	1614	1563	1234	552	471
$[Co(C_{28}H_{26}N_6O_4)]$	-	3194	1625	1560	1260	566	494
$[Ni(C_{28}H_{26}N_6O_4)]$	-	3184	1640	1574	1263	560	482
$[Mn(C_{28}H_{26}N_6O_4)]$	-	3194	1638	1580	1261	556	469
$[Zn(C_{28}H_{26}N_6O_4)]$	-	3198	1645	1558	1234	557	468
$[Cd(C_{28}H_{26}N_6O_4)]$	-	3192	1646	1554	1224	552	472
$[Hg(C_{28}H_{26}N_6O_4)]$	-	3194	1655	1560	1260	556	482

Magnetic movement and Electronic spectra of the complexes

Copper (II) complex

The complexes having temperature independent magnetic moment in the range of 1.74-2.2 B.M. agreeable to the spin only value. These complexes are mononuclear having no major spin-spin interactions; however no compromise can be set between the magnitude of the distortion and other variable factors. The Cu(II) complexes with this behavior indicate marked spin-exchange and strong coupling interaction between Cu(II) atoms. As the spin only value for a single unpaired electron is 1.72 B.M. The slight excess over this value for the Cu(II) complexes can be attributed to spin orbital coupling. The observed magnetic moment values for the present Cu(II) complexes is 1.94 B.M[19]. This value is expected for one electron system and is in the normal range of Cu(II) complex system. As the spin only values for a single unpaired electron is 1.72 B.M. The slight excess over this value found for the Cu(II) complex can be attributed to spin orbital coupling. In view of the above observations the magnetic moment values for the present Cu(II) complexes, suggest the distorted octahedral geometry around Cu(II) ions.

Electronic spectra of Cu(II) complexes exhibit a broad, low intensity shoulder band. The ^2E_g and $^2T_{2g}$ states of octahedral Cu(II) ion (d^9) split under the influence of the tetragonal distortion and the distortion can be such as to cause the three transition viz., $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2A_{1g}$, to remain unresolved in the spectra. It is concluded that all three transition lie within the single broad band in the region 25400 – 31000 cm^{-1}, have been assigned to charge transfer bands from ligand to metal. The observation favor distorted octahedral geometry around Cu(II) complexes. A broad asymmetric band in the region 13495-16605 cm^{-1}, the symmetry being on the lower energy side[20]. The broadness of the band may be due to dynamic John-Teller distortion. The band maxima observed for the present Cu(II) complexes is at 12195-16400cm^{-1}, 12305-16435 cm^{-1} and 12400 – 16360 cm^{-1} suggest that the complex displays coordination number six. In addition, we have observed a high intensity band around 15165cm^{-1} that can be attributed to the ligand-metal charge transfer transition.

Cobalt (II) complex

In octahedral Co(II) complexes the ground state is $^4T_{1g}$ and a large orbital contribution to the magnetic moment values for various Co(II) complexes are in the range 4.11-4.71 B.M. and 4.6-5.18 B.M. for tetrahedral and octahedral complexes respectively. In present investigation the observed magnetic moment values is in the range 4.77 B.M[21], which indicates octahedral geometry for these Co(II) complexes. This is due to partial quenching of orbital contribution to the magnetic moment. Electronic spectra of Co(II) complex exhibits three bands in the region 9528-10350 cm^{-1}, 14512-15385^{-1} and 20833- 26954 cm^{-1} due to the transition $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) = 9528-10350cm^{-1}, $^4T_1g(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) = 14512-15385cm^{-1} and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ ($\nu_{3)}$ = 20833-26954cm^{-1}. These transitions suggest octahedral geometry. The region at 25650-26870 cm^{-1} refers to the charge transfer band. These transitions suggest octahedral geometry for the Co(II) complexes. These assignments are in good agreement with the reported values [22].

Nickel (II) complex

Ni(II) complexes exhibits the magnetic moment value of 2.94 which are well within the range of expected value for octahedral geometry around the central metal ion[21]. Electronic spectra of Ni(II) complexes in octahedral coordination is $^3A_{2g}$, the Ni(II) complexes show three transition in an octahedral field, *viz.*,$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$; ($\nu_{1)}$ 7460- 8200cm^{-1}, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$; ($\nu_{2)}$ 16600-17100cm$^{-13}A_{2g}(F) \rightarrow {}^3T_{1g}(P)$; ($\nu_{3)}$ 24714 -26000cm^{-1}. The observed transition bands lie well within in the range of reported values. There values indicate considerable covalent character and support the octahedral geometry for the Ni(II) complex[23].

Manganese (II) complex

The observed magnetic moment values for Mn(II) complex of the ligand is in the range 5.71 B.M. The electronic spectra of Mn(II) complex shows three transition, which corresponds to the following transitions,$^6A_{1g} \rightarrow {}^4T_{1g}(4G)$; ν_1=15731-16500cm^{-1}, $^6A_{1g} \rightarrow {}^4E_g(4D)$; ν_2 = 17623-18600cm^{-1}, $^6A_{1g} \rightarrow {}^4T_{1g}(4D)$; ν_3= 21853-22700cm^{-1} These values indicate considerable covalent character and support the octahedral geometry[24]. Hence under the present study octahedral geometry is suggested for Mn(II) complex.

Table 3. Electronic spectral data of ligand field parameters of Cu(II), Co(II), Ni(II) and Mn(II) metal complexes

Complexes	ν_1(cm^{-1})	ν_2(cm^{-1})	ν_3(cm^{-1})	Dq (cm^{-1})	B^1	β	β%	ν_2/ν_1	ν_3/ν_2	LFSE k cal mol^{-1}
[Cu($C_{28}H_{26}N_6O_4$)]	12095 – 16400			1426	-	-	-	-	-	24.54
[Co($C_{28}H_{26}N_6O_4$)]	9628	14612	20733	932	826	0.94	15.05	1.51	1.41	14.28
[Ni($C_{28}H_{26}N_6O_4$)]	7470	16500	24814	910	834	0.80	19.87	1.20	1.50	32.87
[Mn($C_{28}H_{26}N_6O_4$)]	15632	17523	21753	937	865	0.78	22.39	1.12	1.24	14.59

^{1}H NMR Spectra

Spectrum of ^{1}HNMR is DMSO-d_6 solvent used. In ligand N1',N6'-bis((2-hydroxyquinolin-3-yl)methylene)adipohydrazide showed the sharp peak at δ 9.7 (S, 2H) due to OH at 2-position of phenyl ring of 2-hydroxy quinoline moiety has resonated, but in the case of Zn(II) complex which has been disappeared indicating the involvement of phenolic oxygen in the coordination *via*, deprotonation[25,26]. A single large peak showed at δ 3.4 (S, 3H, CH_3) due to protons of the azomethine group in ligand but in case of Zn(II) complex the peak observed at δ2.6 (S, 3H, CH_3)[27]. The Eight aromatic protons due to quinoline and phenyl rings have resonated in region δ 7.1- 7.9 (m, 8H, Ar-H) as a multiplet, in Zn (II) complex the eight aromatic protons have been observed in the region δ 7.1-8.6 (m, 8H, Ar-H) as a multiplet. The Zn(II) complex suggests coordination of the phenolic OH with metal ion.

ESR spectrum

The ESR spectrum of the powder Cu(II) complex was recorded at room temperature using DPPH as a standard showed a broadened feature without hyperfine splitting due to the dipolar interaction from the ESR spectrum of a set of magnetic parameter $g_{||}$ = 2.0523, $g_{\perp}$ = 2.0274. The observed ESR spectrum is characteristic of distorted octahedral geometry g value averaged to over all directions and G which is measure of extent of exchange interaction between metal ion have been calculated. In present case the value of G was found to be 4.0268 according to Hathway. If G value if greater then 4, the spin exchange interaction is negligible where as G value is less than 4 indicate considerable interaction between metal ions in solid complex clearly indicate that Cu(II) ion in the complex is mononuclear nature of the complex.

Table 4: ESR data of the Cu(II) complex

Complex	$g_{\|}$	$g_{\perp}$	g_{av}	g_{iso}	G
$[Cu(C_{28}H_{26}N_6O_4)]$	2.0523	2.0274	2.03985	2.2982	4.0268

X-ray powder diffraction studies

X-ray powder diffraction pattern for Cu(II) complex has characterized with a view to find the type of crystal system the XRD data given the table 5. The diffractogram of Cu(II) complex consists of ten reflections in the range of 10-30 (2θ value) with maxima at 2θ =10.59A^o The interplanar spacing(d) has been calculated from the position of intense peaks using Bragg's equation nλ=2dsin θ, □= 1.5406^{0}A. The observed and calculated values of 'd' are quite consistent (Table 5). The unit cell calculations have been carried out for the cubic system, the set of $h^2 + k^2 + l^2$ values of the complex were found to be 1, 2 and 4 which corresponds to the planes and absence of forbidden number its confirms the cubic symmetry from the above results the unit cell constants for cubic system were found to be a = b = c = 8.3548 ^{0}A for the Cu(II) complex of the ligand the complex showed broad peak indicates amorphous nature[28-29].

Table 5: X- Ray powder diffraction data of Cu(II) complex.

2θ	θ	sinθ	$sin^2θ$	$h^2+k^2+l^2$ (a)	$h^2+k^2+l^2$ (b)	h k l	d-spacing Cal.	d-spacing Abs	Relative intensity (%)	a (A°)
10.59	5.29	0.0922	0.0085	1	1	1 0 0	8.354	8.347	95.88	8.3548
15.64	7.82	0.1361	0.0185	2.176	2	1 1 0	5.659	5.661	44.60	8.0039
15.99	7.99	0.1390	0.0193	2.270	2	1 1 0	5.541	5.538	54.60	8.8412
16.15	8.07	0.1403	0.0197	2.317	2	1 1 0	5.490	5.483	57.20	8.7611
16.80	8.40	0.1460	0.0213	2.505	2	1 1 0	5.275	5.273	47.50	8.4639
20.18	10.90	0.1890	0.0357	4.200	4	2 0 0	4.075	4.396	51.80	8.1534
20.31	10.15	0.1762	0.0310	3.647	4	2 0 0	4.371	4.369	52.30	8.7497
21.59	10.79	0.1872	0.0350	4.117	4	2 0 0	4.114	4.112	55.60	8.2345
21.75	10.87	0.1885	0.0355	4.176	4	2 0 0	4.086	4.083	56.70	8.1754
22.23	11.11	0.1926	0.0371	4.364	4	2 0 0	3.999	3.995	61.70	8.0001
22.39	11.19	0.1941	0.0376	4.423	4	2 0 0	3.968	3.967	59.70	8.0191

Antibacterial activity

The antibacterial activity results revealed that the ligand and its complexes shown weak to good activity (Table 6). The ligand and its Cu(II), Zn(II) and Ni(II) complexes shows weakly active with the zone of inhibition 10-13 mm against the both organisms when compared to the standard drug streptomycin. The Mn(II), Co(II) and Cd(II) complexes shows moderate activity as compared to its ligand with zone of inhibition 15-17. The Hg(II) complex is a good activity with zone of inhibition 18-20 when compared to the standard drug streptomycin[31-32].

Antifungal Activity

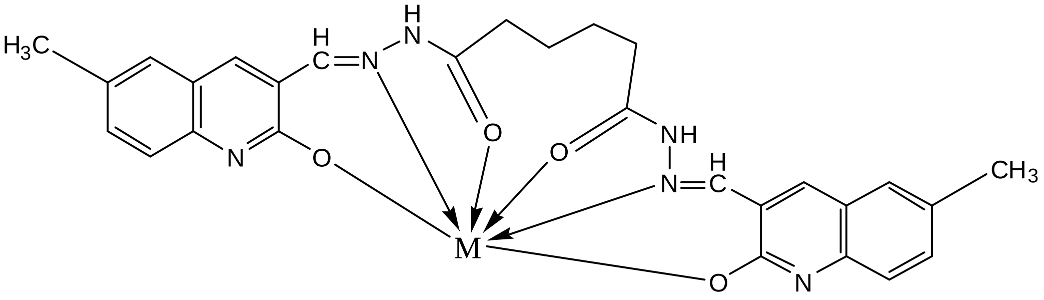
The antifungal activity, results revealed that the ligand and its Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), and Mn(II) complexes have exhibited weak to good activity (Table 6). The ligand and its Co(II) complexes shows weak activity with zone of inhibition, the Cu(II), Ni(II), Mn(II), Zn(II), Cd(II), Hg(II) shows moderate activity as compared to its ligand with the zone of inhibition 15-17mm, to good activity with the zone of inhibition of 18-20mm when compared to the standard drug chlotrimazole[33-34].

Table 6: Antimicrobial activity of the ligand and its metal complexes

Sl. No.	Compound	Antibacterial activity zone of inhibition (in mm)		Antifungal activity zone of inhibition (in mm)	
		E.Coli	***S.aureus***	***A.niger***	***A.flavus***
1.	$C_{28}H_{28}N_6O_4$	09	08	08	10
2.	$[Cu(C_{28}H_{26}N_6O_4)]$	10	11	15	12
3.	$[Co(C_{28}H_{26}N_6O_4)]$	14	13	14	13
4.	$[Ni(C_{28}H_{26}N_6O_4)]$	12	15	17	15
5.	$[Mn(C_{28}H_{26}N_6O_4)]$	15	13	20	19
6.	$[Zn(C_{28}H_{26}N_6O_4)]$	11	13	16	17
7.	$[Cd(C_{28}H_{26}N_6O_4)]$	16	15	18	16
8.	$[Hg(C_{28}H_{26}N_6O_4)]$	15	18	19	18
9.	Streptomycin	24	23	--	--
10.	Chlotrimazole	--	--	25	26
11.	DMF (Control)	0	0	0	0
12.	Bore size	08	08	08	08

CONCLUSION

The elemental analysis, Molar conductance, Magnetic Susceptibility, electronic spectra, IR, ^1H NMR, ESR spectra and X-ray data observations projects the following structures for these complexes where in Cu(II), Co(II), Ni(II), Mn(II), Zn(II), Cd(II), and Hg(II), are exhibit six coordinated octahedral geometry.



Where M = Cu(II), Co(II), Ni(II) , Zn(II), Cd(II), Hg(II)and Mn(II),

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REFERENCES

[1] GG Mohamed; Omar Md; Ahmed; Hindy Md; *Turk. J. Chem.*, **2006**, 60, 362.
[2] SK Hafijur Rahaman; G Rajarshi; Lu Tian-Huey; G Barindra Kumar; *Ind. J. Chem.*, **2005,** 11A, 2427.

[3] M Mustapha; BR Thorat; Sudhir Sawant; RG Atram; Ramesh Yamgar; *J. Chem. Pharm. Res.*, **2011**, 3(4), 5.
[4] Nirdosh Patil; BR Patil; *Oriental J. of Chemistry* **2002**, 18(3), 547.
[5] Dinesh kumar *et.al., J. Chem. Sci.*, **2009,** 121(1), 59.
[6] YM Issa; MM Omar; BA Sabrah; SK Mohamed; *J. Ind. Chem. Soc.* **1992,** 69, 186.
[7] K Maikawa; H Yoshikawa; *Adv Pestic Sci Plenary Session Symp. Pap. Int. Congr. Pestic. Chem.*, **1978,** 4, 104.
[8] S Nakajima; S Sugiyamer; M Suto; *Org. Prep. Proceed. Int.*, **1979,** 11, 77.
[9] L Jurd; AD King Jr.; K Mihara; *Experientia*, **1970**, 26**,** 1981.
[10] JA De. Geey; CF Vam Sumare; *Arch Int. Physiological Biochem.*, **1966,** 74, 512.
[11] R Fathi; Zhu Qus; *Appl Publ.*, **2004,** 43.
[12] P Sanket; Chaudhari; RP Nandini; *Ind. J. Het. Chem.* **2007,** 17, 149.
[13] E Okuyama; S Nishimura; S Ohmori; M Ozaki Sutake; M Yamazaki; *Chem. Pharm. Bull.*, **1993,** 41, 926.
[14] JB Hudson; Eds, "*In Antiviral Compounds from plants*", CRC Press, Boca Raton, Florida, **1990**.
[15] PP Hankare; SR Naravane; VM Bhuse; SD Debkar; AH Jagtap; *Ind. J. Chem.*, **2004,** 43A, 1464.
[16] NH El-Hammamy; MM El-Kholy; AI Kawana; GA Ibrahim; *J. Chem. Pharm. Res.*, **2010**, 2(4), 1112.
[17] KG Keser; Ulvi Avciata; Ahmet Gul; *Ind. J. Chem.*, **2007,** 46A, 1274.
[18] K Siddappa; RK Shikkargol; SD Angadi; *Proc. Indian Nat. Sci. Acad.*, **2009,** 75(2), 73.
[19] MA Hassan; *J. Islamic Acad. Sci*, **1991,** 4(4), 272.
[20] SJ Swamy; ER Reddy; D Nagaraju; S Jyothi; *Molecules*, **2006,** 11, 1000.
[21] GG Mohamed; *et.al., Turk J. Chem.*, **2006,** 60, 366.
[22] DP Singh; S Singh; VB Rana; *J. Ind. Chem. Soc.*, **2002,** 79, 889.
[23] G Chitra; *J. Ind. Council Chem.*, **2007,** 24(1), 16.
[24] S Chandra; LK Gupta; *Ind. J. Chem. Soc.*, **2005,** 82, 454.
[25] A.Eman , H.H Khaled, Saffaa Khalil and S.Nabil , Youssef, *AJBAS* **2008**, 2(2), 213.
[26] U.C Mashelkar and A.A Audi, *Ind. J. Chem.*, 4513, **2006,** 1464.
[27] Y.H. Zhang, Q.L. Wang, G.M. Yang, *Trans. Met. Chem.*, **2006,** 31, 856.
[28] K Siddappa; Tukaram Reddy; P Chandrakant Reddy; M Mallikarjun; K Mallikarjun; *Mat. Sci. Res. India.*, **2008**, 5(1), 131.
[29] MM Woolfson; *"An Introduction to X-ray Crystallography"* Cambridge, Cambridge University Press, **1980,** 125.
[30] K Siddappa; Tukaram Reddy; P Chandrakant Reddy; M Mallikarjun; Mahesh Tambe; K Mallikarjun; *Int. J. Pure & Appl. Chem.*, **2008,** 3(2), 87.
[31] K Siddappa; Tukaram Reddy; M Mallikarjun; CV Reddy; *E-J. Chem.* **2008,** 5(1), 155.
[32] MK Shivananda; Shet Prakash M; *J. Chem. Pharm. Res.*, **2011**, 3(5), 61.
[33] K Siddappa; K Mallikarjun; Tukaram Reddy, P Chandrakant Reddy; M Mallikarjun; Mahesh Tambe; *E-J. Chem.* **2009,** 6(3), 615.
[34] S Belaid; A Landreau; S Djebbar; O Benali-Baitich; G Bouet; JP Bouchara; *J. Inorg. Biochem.*, **2008,** 102, 63.