



Synthesis, Spectral, Powder X-Ray Diffraction and Antimicrobial Studies of Some Transition Metal(II) Complexes of Schiff Base Derived from 3-[(2-hydroxy-6-methylquinolin-3-ylmethylene)-amino]-2-methyl-3H-quinazoline-4-one

K. SIDDAPPA*, PATIL CHANDRAKANT REDDY, MALLIKARJUN KOTE, TUKARAM REDDY, MAHESH TAMBE and MALLIKARJUN METRE

Department of Studies and Research in Chemistry, Gulbarga University, Gulbarga-585 106, India

*Corresponding author: E-mail: siddappa_65@rediffmail.com

(Received: 8 December 2010;

Accepted: 27 June 2011)

AJC-10088

Complexes of the type ML_2 and $M'L$ [where, $M = Cu(II), Co(II), Ni(II)$ and $Mn(II)$; $M' = Zn(II), Cd(II)$ and $Hg(II)$] with the Schiff base $L = 3-[(2-hydroxy-6-methylquinolin-3-ylmethylene)-amino]-2-methyl-3H-quinazoline-4-one$, (HMQMAMQ) have been synthesized. Their characterizations have been done by elemental analysis, conductance data, magnetic susceptibility measurements, 1H NMR, electronic, IR, ESR and X-ray studies. Ligand field parameters of some of the complexes have also been calculated. On the basis of spectral studies, complexes of $Co(II), Ni(II)$ and $Mn(II)$ have been assigned octahedral geometry, whereas the complexes of $Zn(II), Cd(II)$ and $Hg(II)$ have been assigned tetrahedral geometry. The complex of $Cu(II)$ has been assigned distorted octahedral geometry. The ligand and its complexes have also been screened for their antimicrobial activity against selected fungi and bacteria.

Key Words: Quinazoline, X-ray data, quinoline, antimicrobial activity.

INTRODUCTION

Quinazolines are a big family of heterocyclic compounds, which have shown broad variety of biological activity profiles^{1,2}. Quinazolines and condensed quinazolines exhibit diverse pharmacological activities^{3,4}. Among the various quinazolines reported, the substituted quinazolines exhibit interesting pharmacological activities like analgesic⁵, antiinflammatory⁶, antibacterial⁷ and anticonvulsant activities⁸. Amino quinazoline derivatives were found to be inhibitors of the tyrosine kinase or dehydrofolate reductase enzymes⁹, so they work as potent anticancer agents¹⁰. They are also used to work out medicines against hypertension, malaria and to fight infections involving AIDS^{11,12}. Some substituted quinazolines have been found to be potential and highly selective inhibitors of human immunoglobulin E¹³ and epidermal growth factor receptor tyrosine kinase¹⁴, which regulates the cell growth and proliferation, so they work as potent antiallergic or anticancer agents^{15,16}. Among the other pharmacological activities, quinazoline derivatives show remarkable antimicrobial properties against microorganisms associated with death in patients due to immunocompromized diseases¹⁷. Quinazoline Schiff bases possess potent analgesic and antiinflammatory activities¹⁸.

A survey of literature reveals that, the reaction of methyl quinazoline hydrazide and methyl quinoline aldehyde Schiff base have not been reported so far. Hence, it was thought

worthwhile to synthesize new substituted quinazoline ligand (HMQMAMQ) and its metal(II) complexes.

The present paper discusses the synthesis, spectral studies and antimicrobial activities of the complexes of $Cu(II), Co(II), Ni(II), Mn(II), Zn(II), Cd(II)$ and $Hg(II)$ with the following ligand [(2-hydroxy-6-methylquinolin-3-ylmethylene)-amino]-2-methyl-3H-quinazoline-4-one (HMQMAMQ) (Fig. 1).

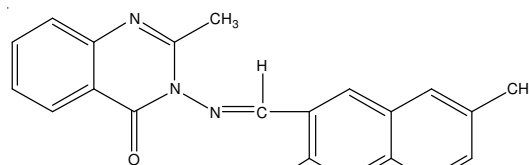


Fig. 1. Structure of ligand

EXPERIMENTAL

All the reagents used were of analytical grade and used without further purification. The metal chlorides/salts were of E. Merck and used as received.

Synthesis of ligand

Preparation of 3-amino-2-methylquinazoline-4-one: A mixture of methyl-N-acetyl anthranilate (0.1 mol) and hydrazine hydrate (0.1 mol) in ethanolic solution was refluxed for 6 h. The excess of solvent was then distilled off and the resulting

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF THE LIGAND AND ITS METAL(II) COMPLEXES

Ligand/Complex	m.w.	m.p. (°C)	Yield (%)	Elemental analysis (%): Found (calcd.)					μ_{eff} (BM)	Molar conductance (λ_{M} Ohm ⁻¹ cm ² mol ⁻¹)
				C	H	N	M	Cl		
C ₂₀ H ₁₆ N ₄ O ₂	344.37	250	75	69.56 (69.70)	4.59 (4.68)	16.17 (16.27)	-	-	-	-
[Cu(C ₂₀ H ₁₅ N ₄ O ₂) ₂]	750.26	278	65	63.43 (64.03)	3.65 (4.03)	14.52 (14.94)	8.32 (8.47)	-	1.95	15.50
[Co(C ₂₀ H ₁₅ N ₄ O ₂) ₂]	745.65	280	66	64.03 (64.43)	3.89 (4.06)	14.80 (15.03)	7.76 (7.90)	-	4.86	18.20
[Ni((C ₂₀ H ₁₅ N ₄ O ₂) ₂)]	745.41	282	65	64.22 (64.45)	3.85 (4.06)	14.85 (15.03)	7.73 (7.87)	-	2.98	19.30
[Mn(C ₂₀ H ₁₅ N ₄ O ₂) ₂]	741.66	279	65	64.59 (64.78)	3.91 (4.08)	15.01 (15.110)	7.21 (7.41)	-	5.70	19.85
[Zn(C ₂₀ H ₁₅ N ₄ O ₂)Cl]	444.20	280	67	53.88 (54.08)	3.21 (3.40)	12.46 (12.61)	14.59 (14.72)	7.81 (7.98)	Diamag	13.20
[Cd(C ₂₀ H ₁₅ N ₄ O ₂)Cl]	491.22	287	65	48.78 (48.90)	2.89 (3.08)	11.21 (11.41)	22.70 (22.88)	7.10 (7.22)	Diamag	16.25
[Hg(C ₂₀ H ₁₅ N ₄ O ₂)Cl]	579.40	290	60	41.29 (41.46)	2.46 (2.61)	9.47 (9.670)	34.42 (34.62)	5.98 (6.12)	Diamag	15.50

solid was dried and recrystallized from absolute ethanol¹⁹ (m.p. 186 °C, yield 75 %).

Preparation of 2-chloro-3-formyl-6-methylquinoline:

Dimethyl formamide (9.13 g, 0.12 mol) was cooled to 0 °C in a flask equipped with drying tube and phosphorous oxychloride (53.7 g, 32.2 mL) was added drop wise with stirring. To this solution, methyl acetanilide (7.5 g, 0.05 mol) was added and after 5 min the solution was refluxed for 16 h on water bath. The reaction mixture was poured into ice cold water and stirred for 0.5 h at 0-10 °C. The yellow precipitate formed was filtered, washed with water and recrystallized from ethyl acetate as yellow needles (m.p. 176 °C, yield 70 %).

Preparation of 3-formyl-2-hydroxy-6-methylquinoline:

A mixture of 2-chloro-3-formyl-6-methylquinoline (2.2 g, 0.01 mol) and aqueous hydrochloric acid (35 mL, 4 mol) was heated under reflux on water bath for *ca.* 1 h and then allowed to cool to room temperature. 3-Formyl-2-hydroxy-6-methylquinoline separated as solid, was collected by filtration and recrystallized from aqueous acetic acid into yellow silky needles (m.p. 185 °C, yield 65 %).

Preparation of 3-[(2-hydroxy-6-methylquinolin-3-ylmethylene)-amino]-2-methyl-3H-quinazolin-4-one: The Schiff base ligand (HMQMAMQ) was prepared by the reaction of 3-amino-2-methylquinazolin-4-one (0.01 mol) with 3-formyl-2-hydroxy-6-methylquinoline (0.01 mol) in ethanol by refluxing on water bath for 7-8 h in the presence of a few drops of acetic acid. The reaction mixture was cooled to room temperature, the separated ligand was filtered, washed and recrystallized from alcohol. The purity of the ligand (HMQMAMQ) was checked by TLC (m.p. 250 °C, yield 75 %).

Preparation of complexes: To the hot solution of the Schiff base ligand (HMQMAMQ) (0.001 mol) in ethanol (35 mL), a hot ethanolic solution of respective metal chlorides (0.001 mol) in ethanol (15 mL) was added and the reaction mixture was then treated with sodium acetate (0.5 g) and the refluxing was continued further for 2 h. The resulting reaction mixture was then decomposed by pouring into distilled water (80-100 mL), the coloured complex separated out was collected by filtration, washed with distilled water, then with hot

ethanol and dried in vacuum over anhydrous calcium chloride. The complexes were analyzed for their metal and chloride contents by standard methods²⁰. Elemental analysis data is shown in Table-1.

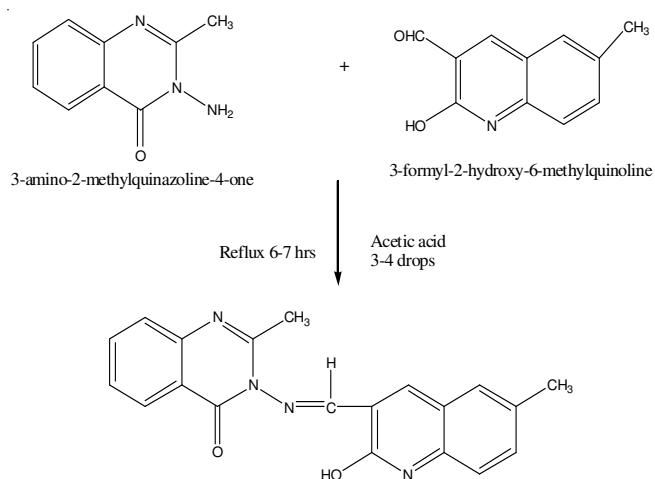


Fig. 2. Scheme for preparation of ligand

Physical measurements: Infrared spectra of the ligand and its metal(II) complexes in KBr pellets were recorded in the spectral range 4000-350 cm⁻¹ with Perkin elmer spectrum one FT-IR spectrometer. UV-Visible spectra were recorded on an Elico SL-164 double beam UV-VIS spectrophotometer in the range of 200-1200 nm. Magnetic susceptibilities were measured on a Guoy balance at room temperature using Hg[Co(SCN)₄] as calibrant. The molar conductance of the complexes was measured on ELICO CM-82 conductivity bridge in DMF solution at a concentration of 10⁻³ M. ¹H NMR spectra were recorded on AMX-400 NMR spectrometer, using TMS as internal standard and DMSO as a solvent. X-ray diffraction spectrum was obtained on the Philips P.W. 3710 diffractometer at CIL, University of Hyderabad, Hyderabad. The elemental analysis (CHN) were obtained from Thermo finnigam, Italy, FLASH EA 1112 series and ESR spectra recorded on VARIAN, USA, E-112 Spectrometer at IIT Mumbai.

RESULTS AND DISCUSSION

The prepared complexes were sparingly soluble in common organic solvents but soluble in DMF, DMSO and acetonitrile. The analytical data indicates that the stoichiometry of the complexes are 1:2 (metal to ligand ratio) for Cu(II), Co(II), Ni(II) and Mn(II) and 1:1 (metal to ligand ratio) for Zn(II), Cd(II) and Hg(II) complexes. The observed molar conductance values measured in DMF solution fall in the range 15-20 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$, indicating that the complexes are non-electrolytic in nature²¹.

Magnetic susceptibility: The magnetic susceptibility measurements of the complexes were performed at room temperature (Table-1). The mononuclear Cu(II) complex having no major spin interaction shows magnetic moment in the range of 1.75-2.20 BM. The present Cu(II) complex has a magnetic moment value 1.95 BM. The magnetic moment value observed for Cu(II) complex under present study is due to distorted octahedral geometry^{22,23}. The Co(II) complex shows magnetic moment of 4.86 BM. The spin free octahedral complex of Co(II) are reported to exhibit magnetic moment in the range of 4.70- 5.53 BM²⁴. The magnetic moment value obtained for the Co(II) complex under study indicates that it has an octahedral configuration. For Ni(II) complex, the observed magnetic moment value is 2.98 BM, which is well within the expected range for Ni(II) complex with octahedral geometry 2.83-4.0 BM²⁵. The magnetic moment value of Mn(II) complex is 5.70 BM, indicating it to be high spin type paramagnetic, which lies within the octahedral range, which is close to spin only value of 5.90 BM as the ground term is $^3A_{2g}$ and thus supports the octahedral stereochemistry²⁶. The Zn(II), Cd(II) and Hg(II) complexes showed a diamagnetic behaviour.

Electronic spectra: The electronic spectral data of Cu(II), Co(II), Ni(II) and Mn(II) complexes of the ligand (HMQMAMQ) were recorded in DMF solution at 10^{-3} M concentration and are given in Table-2. They have been studied with a view to obtaining more information on the stereochemistry of the complexes and to procure more support for the conclusion deduced with the help of magnetic data. The Cu(II) complex exhibits a broad asymmetric band in the region 12150-16325

cm^{-1} with a maxima at 14145 cm^{-1} in an distorted octahedral geometry²⁷. The broadness of the band may be due to dynamic Jahn-Teller distortion and is assigned to $^2T_{2g} \rightarrow ^2E_g$ transitions.

The electronic spectra of the Co(II) complex gave two absorption bands at 9970 cm^{-1} and 20040 cm^{-1} , due to $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)(v_1)$ and $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)(v_3)$ transitions²⁸. The bands due to the $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)(v_2)$ transitions could not be observed because of its low intensity. The position of v_2 band has been calculated (15411 cm^{-1}) by using the equation $v_2 = v_1 + 10 Dq$. These transitions suggest octahedral geometry for Co(II) complex. The ligand field parameters such as Dq, B', β and $\beta \%$ have been calculated by using band-fitting equation given by Billing and Underhill²⁹. The crystal field splitting energy (Dq) value of 819 cm^{-1} , is well within the range reported for most of the octahedral Co(II) complexes. The Co(II) complex under present investigation possess Racah parameter B' 925 cm^{-1} . The Racah parameter B' is less than free ion value 971 cm^{-1} , suggesting a considerable orbital overlap and delocalization of electrons on the metal ion. The nephelauxetic ratio (β) for the present Co(II) complex is 0.94 cm^{-1} . This is less than one, suggesting partial covalency in the metal ligand bond. The values Dq, $\beta \%$, LFSE and v_2/v_1 suggest the octahedral geometry for Co(II) complex³⁰. The electronic spectrum of Ni(II) complex shows three bands at 10750 , 15150 and 25300 cm^{-1} (Table-2), assignable to $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)(v_1)$, $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)(v_2)$ and $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)(v_3)$ transitions respectively³¹. The values v_2/v_1 and $\beta \%$ further support the octahedral geometry around the Ni(II) ion³². The observed bands for Mn(II) complex are at 10210 , 15130 and 23400 cm^{-1} due to the transitions $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)(v_1)$, $^3A_{2g}(F) \rightarrow ^3A_{1g}(F)(v_2)$ and $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)(v_3)$ respectively. The position of bands indicates that the complex has six coordinated octahedral geometry³³ (Table-2).

Infrared spectra: The IR spectral data of the ligand (HMQMAMQ) and its metal(II) complexes are represented in Table-3. The sharp band observed at 1700 cm^{-1} in ligand is assigned to quinazoline ring $\nu(\text{C}=\text{O})$, which was shifted to $20\text{-}30 \text{ cm}^{-1}$ in all complexes, indicating the involvement of carboxyl group of quinazoline ring ($\text{C}=\text{O}$) in complexation with metal ion³⁴. The band exhibited at 1615 cm^{-1} is assigned

TABLE-2
ELECTRONIC SPECTRAL DATA AND LIGAND FIELD PARAMETERS OF Cu(II), Co(II), Ni(II) AND Mn(II) COMPLEXES (cm^{-1})

Complexes	v_1	v_2	v_3	Dq	B'	β	$\beta \%$	v_2/v_1	v_3/v_2	LFSE (kcalmol^{-1})
[Cu(C ₂₀ H ₁₅ N ₄ O ₂) ₂]	-	12150	16325	1421	-	-	-	-	-	24.15
[Co(C ₂₀ H ₁₅ N ₄ O ₂) ₂]	9970	15411	20040	819	925	0.94	15.00	1.54	1.30	14.16
[Ni(C ₂₀ H ₁₅ N ₄ O ₂) ₂]	10750	15150	25300	932	833	0.80	19.78	1.41	1.67	31.85
[Mn(C ₂₀ H ₁₅ N ₄ O ₂) ₂]	10210	15130	23400	935	858	0.77	22.26	1.48	1.55	16.50

TABLE-3
IR SPECTRAL DATA OF THE LIGAND AND ITS METAL(II) COMPLEXES(cm^{-1})

Ligand/ complexes	$\nu(\text{OH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{O})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{Cl})$
C ₂₀ H ₁₆ N ₄ O ₂	3400	1700	1615	1260	-	-	-
[Cu(C ₂₀ H ₁₅ N ₄ O ₂) ₂]	-	1675	1560	1305	530	450	-
[Co(C ₂₀ H ₁₅ N ₄ O ₂) ₂]	-	1680	1565	1300	525	455	-
[Ni((C ₂₀ H ₁₅ N ₄ O ₂) ₂)]	-	1670	1558	1310	529	452	-
[Mn(C ₂₀ H ₁₅ N ₄ O ₂) ₂]	-	1672	1557	1307	531	449	-
[Zn(C ₂₀ H ₁₅ N ₄ O ₂)Cl]	-	1676	1562	1304	535	448	353
[Cd(C ₂₀ H ₁₅ N ₄ O ₂)Cl]	-	1677	1557	1310	534	452	352
[Hg(C ₂₀ H ₁₅ N ₄ O ₂)Cl]	-	1674	1560	1307	537	450	352

to the azomethine $\nu(\text{C}=\text{N})$ group in the ligand, but in complexes it has lowered to $50\text{--}58\text{ cm}^{-1}$ due to the reduction of double bond character in carbon-nitrogen of the azomethine group³⁵. The broad band observed at 3400 cm^{-1} in the ligand (HMQMAMQ) is assigned to $\nu(\text{OH})$, which disappeared in all the complexes, thereby indicating the involvement of phenolic oxygen in bonding with metal ions through deprotonation³⁶.

The frequency observed at 1260 cm^{-1} of the ligand is attributed to phenolic $\nu(\text{C}-\text{O})$, but this band is shifted to higher frequency in the region $40\text{--}50\text{ cm}^{-1}$ for the complexes³⁷. This confirms the involvement of phenolic OH in the complex formation. The low frequency skeletal vibrations due to (M-O) and (M-N) stretching provide direct evidence for complexation. In the present investigation the frequencies observed in the region of $537\text{--}525\text{ cm}^{-1}$ are due to $\nu(\text{M}-\text{O})$ and the frequencies observed in the region of $455\text{--}448\text{ cm}^{-1}$ are due to $\nu(\text{M}-\text{N})$ vibrations^{38,39}. The frequencies observed in the region $353\text{--}352\text{ cm}^{-1}$ were due to $\nu(\text{M}-\text{Cl})$ bonding⁴⁰. These are characteristic of chlorine atom in Zn(II), Cd(II) and Hg(II) complexes and is further confirmed by quantitative chloride estimation.

¹H NMR spectra: The ligand (HMQMAMQ) showed sharp peak at δ 12.6 (s, 1H) due to OH at 2-position of phenyl ring of quinoline moiety has resonated, but in the case of Cd(II) complex, which disappeared indicate the involvement of phenolic oxygen in the coordination via deprotonation⁴¹. The peak appeared at δ 8.6 (s, 1H, $-\text{CH}=\text{N}$) is due to the azomethine group in the ligand, but in the case of Cd(II) complex the peak was observed at δ 8.3 (s, 1H, $-\text{CH}=\text{N}$). The Schiff base ligand showed two separate singlet peaks at δ 2.75 and δ 2.78 (s, $2 \times 3\text{H}$) due to protons of the two $-\text{CH}_3$ groups which are attached to the quinazoline and quinoline moiety, but in Cd(II) complex it appears at δ 2.73 and δ 2.75. The eight aromatic protons due to quinazoline and phenyl rings resonated in the region δ 7.00–8.50 (m, 8H, Ar-H) as a multiplet, in Cd(II) complex the eight aromatic protons have been observed in the region δ 6.70–8.20 (m, 8H, Ar-H) as a multiplet. On comparing the ¹H NMR spectra of the ligand (HMQMAMQ) and the Cd(II) complex, it was observed that the signals of protons of different functionalities of the ligand have been shifted to the downfield region indicating the coordination of the ligand to the metal Cd(II) ion.

ESR spectrum: The ESR spectrum of the powder Cu(II) complex was recorded at room temperature, on X-band at a frequency of 9.1 GHz under the magnetic-field strength of 3200 G. One unpaired electron in Cu(II) complex with ²B_{1g} as ground state lies in $d_{x^2-y^2}$ orbital and follows the trend $g_{\parallel} > g_{\perp} > g_{\text{av}}$. The analysis of spectra gives the data $g_{\parallel} = 2.270$, $g_{\perp} = 2.062$, $g_{\text{av}} = 2.034$, $g_{\text{iso}} = 2.192$ and $G = 4.850$ and are given in Table-4. The observed g_{\parallel} value for the Cu(II) complex was less than 2.3, which is in agreement with the covalent character of the metal ligand bond. The $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$, which measures the negligible exchange interaction between the metal centers

in polycrystalline solid, has been calculated. According to Hathaway and Billing⁴² if $G > 4$, the exchange interaction is negligible, but if $G < 4$ it indicates considerable exchange interaction in the solid complex. The Cu(II) complex has the G value > 4 , indicating that the exchange interaction is negligible in solid complex. The observed value of $G = 4.850$ for the complex under the present study gives evidences of mononuclear nature of the complex.

Complex	g_{\parallel}	g_{\perp}	g_{av}	g_{iso}	G
[Cu(C ₂₀ H ₁₅ N ₄ O ₂) ₂]	2.270	2.062	2.034	2.192	4.850

X-ray diffraction studies: The Zn(II) complex has been characterized by powder XRD studies with a view to finding the type of crystal system. The XRD data of Zn(II) complex are given in the Table-5. There are 3 reflections (2θ) between 5.44685° and 57.42692° with maxima at $2\theta = 30.3350^\circ$ corresponding to the value of $d = 2.9440\text{ \AA}$. The interplanar spacing (d) has been calculated from the positions of intense peaks using Bragg's relation $n\lambda = 2d \sin\theta$ (where $\lambda =$ wavelength of X-ray used, $\text{CuK}\alpha = 1.5406\text{ \AA}$). The observed and calculated values of d are quite consistent. The unit cell calculation has been carried out for the cubic system⁴³.

The cell parameters have been calculated by using the equation for cubic system, $\text{Sin}^2\theta = \lambda^2/4a^2 (h^2+k^2+l^2)$, where $\lambda^2/4a^2$ is a common factor. The Zn(II) complex has a value of $\lambda^2/4a^2 = 0.0022$. The $h^2+k^2+l^2$ values are given in the Table-5. The absence of forbidden number indicates that the Zn(II) complex may belong to cubic symmetry. The complex showed broad peak indicating its amorphous nature.

Antimicrobial activity: The prepared ligand (HMQMAMQ) and its Cu(II), Co(II), Ni(II), Mn(II), Zn(II), Cd(II) and Hg(II) complexes have been tested for antimicrobial activity by cup-plate method⁴⁴. The antimicrobial activity results of the screened compounds are given in the Table-6. Antibacterial activity against *E. coli* and *S. aureus* and antifungal activity against *A. niger* and *A. flavous* at 1000 mg/mL concentration⁴⁵ were carried out. The standard drugs streptomycin and clotrimazole were also tested for their antibacterial and antifungal activity at the same concentration under the conditions similar to that of the test compounds⁴⁶.

The antibacterial activity results revealed that the ligand (HMQMAMQ) and its complexes show weak to good activity. The ligand and its Ni(II), Zn(II) and Hg(II) complexes are weakly active with the zone of inhibition 11–14 mm against both the organisms when compared with the standard drug streptomycin. The Co(II) and Cd(II) complexes show moderate activity as compared with its ligand with the zone of inhibition 15–17 mm. The Cu(II) and Mn(II) complexes exhibited good activity with the zone of inhibition 18–20 mm when compared with the standard drug streptomycin.

TABLE-5
POWDER X-RAY DIFFRACTION DATA OF Zn(II) COMPLEX

Peak No.	2θ	θ	$\text{Sin}\theta$	$\text{Sin}^2\theta$	$h^2+k^2+l^2$	h k l	d		Intensity	a (Å)
							Calc.	Obs.		
1	5.446	2.723	0.047	0.002	1	1 0 0	16.211	16.211	14.59	16.211
2	30.335	15.167	0.261	0.068	30	5 2 1	2.944	2.944	39.17	16.211
3	57.426	28.713	0.480	0.230	102	10 1 1	1.603	1.603	100.00	16.211

TABLE-6
ANTIMICROBIAL ACTIVITY OF THE LIGAND AND ITS METAL(II) COMPLEXES

Compound	Antibacterial Activity zone of inhibition (in mm)		Antifungal Activity zone of inhibition (in mm)	
	<i>E. coli</i>	<i>S. aureus</i>	<i>A. niger</i>	<i>A. falyvous</i>
C ₂₀ H ₁₆ N ₄ O ₂	12	11	11	10
[Cu(C ₂₀ H ₁₅ N ₄ O ₂) ₂]	20	18	15	16
[Co(C ₂₀ H ₁₅ N ₄ O ₂) ₂]	17	15	13	14
[Ni((C ₂₀ H ₁₅ N ₄ O ₂) ₂)]	13	14	12	13
[Mn(C ₂₀ H ₁₅ N ₄ O ₂) ₂]	18	19	19	18
[Zn(C ₂₀ H ₁₅ N ₄ O ₂)Cl]	12	13	18	20
[Cd(C ₂₀ H ₁₅ N ₄ O ₂)Cl]	15	16	14	12
[Hg(C ₂₀ H ₁₅ N ₄ O ₂)Cl]	12	13	16	17
Streptomycin	24	25	-	-
Clotrimazole	-	-	24	26
DMF (Control)	0	0	0	0
Bore size	08	08	08	08

The antifungal activity results revealed that the ligand (HMQMAMQ) and its Cu(II), Co(II), Ni(II), Mn(II), Zn(II), Cd(II) and Hg(II) complexes exhibit weak to good activity. The ligand and its Co(II), Ni(II) and Cd(II) complexes show weak activity 10-14 mm, when compared with the standard drug clotrimazole. The Cu(II) and Hg(II) complexes showed moderate activity as compared with its ligand with the zone of inhibition 15-17 mm. The Mn(II) and Zn(II) complexes exhibited good activity with the zone of inhibition 18-20 mm when compared with the standard drug clotrimazole.

Conclusion

The elemental analysis, conductivity data, magnetic susceptibility, electronic, IR, ¹H NMR, ESR and X-ray diffraction spectral observations reveal the mononuclear nature of all the complexes. The non-electrolytic behaviour of the complexes confirms the presence of chlorides within the coordination sphere. The Cu(II), Co(II), Ni(II) and Mn(II) complexes exhibit octahedral geometry, whereas Zn(II), Cd(II) and Hg(II) complexes exhibit tetrahedral geometry (Figs. 3 and 4). The prepared complexes show better antibacterial and antifungal activity than the ligand 3-[(2-hydroxy-6-methyl-quinolin-3-ylmethylene)-amino]-2-methyl-3H-quinazoline-4-one.

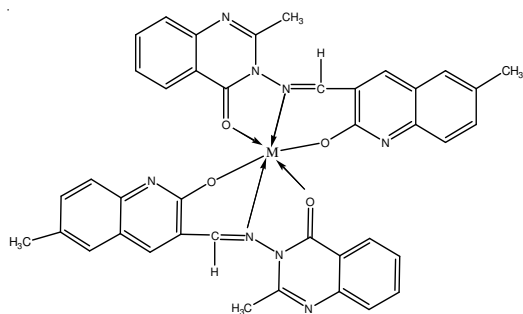


Fig. 3. Proposed structure of complexes of Cu(II), Co(II), Ni(II) and Mn(II)

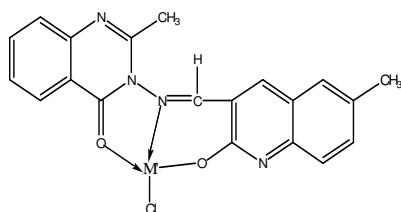


Fig. 4. Proposed structure of complexes of Zn(II), Cd(II) and Hg(II)

ACKNOWLEDGEMENTS

The authors are thankful to the Chairman, Department of Chemistry, Gulbarga University, Gulbarga for providing the facilities needed for the experiments. They also thank the Chairman of the Department of Microbiology and the Department of Botany, Gulbarga University for providing the facilities to carryout antimicrobial activity studies. They also thank CIL, University of Hyderabad, Hyderabad; IISc Bangalore and IIT Bombay for providing X-ray diffraction spectrum, ¹H NMR, ESR and Elemental analysis.

REFERENCES

- E. Brollosy, R. Nasser, A. Megeed, F. Mohmed and A.R. Genday, *Alexandria J. Pharm. Sci.*, **17**, 17 (1982).
- D.J. Brown, *The Chemistry of Heterocyclic Compounds*, J. Wiley & Sons, New York (1996).
- P.M. Traxler, *Expert Opinion on Therapeutic Patents*, Vol. 7, pp. 571-588 (1997).
- V. Alagarsamy, V. Muthukumar, N. Pavalarani, P. Vasanthanathan and R. Revathi, *Biol. Pharm. Bull.*, **26**, 557 (2003).
- M. Koizumi and Y. Marakuni, *Japan Kokai*, **77**, 51 (1971).
- R. Nigam, S. Swarup and V.K. Saxena, *Indian Drugs*, **27**, 238 (1990).
- V. Alagarsamy, U.S. Pathak, D. Sriram, S.N. Pandeya and E. De Clercq, *Indian J. Pharm. Sci.*, **62**, 433 (2000).
- H. Manabu, I. Rivichi and H. Hideaki, *Chem. Pharm. Bull.*, **38**, 618 (1990).
- T.M. Traxler, P. Furet, H. Melt, E. Buchdunger, T. Meyer and N. Lydon, *J. Med. Chem.*, **39**, 2289 (1996).
- J.B. Hynes, A. Tomazic, A. Kumar, V. Kumar and J.H. Friesheim, *Heterocycl. Chem.*, **28**, 1981 (1991).
- N.V. Harris, C. Smith and K. Bowden, *J. Med. Chem.*, **27**, 7 (1992).
- R.O. Dempcy and E.B. Scibo, *Biochemistry*, **30**, 848 (1991).
- M. Berger, B. Albrecht, A. Brecher, W. Neruda and M. Woisetschlager, *J. Med. Chem.*, **44**, 3031 (2001).
- A. Bridges, *J. Chem. Rev.*, **101**, 2541 (2001).
- T. Herget, M. Frietag, M. Morbitzer, R. Kupfer, T. Stamminger and M. Marschall, *Antimicrob. Agents Chemother.*, **48**, 4154 (2004).
- A.J. Barker, D.H. Davies, D.S. Brown and J.R. Woodburn, *Breast Cancer Res. Treat.*, **38**, 67 (1996).
- V. Alagarsamy, V. Rajasoloman, R. Meena and K.V. Ramseshu, *Biol. Pharm. Bull.*, **28**, 1091 (2005).
- S.N. Pandeya, D. Sriram and V. Alagarasamy, *Acta Pharm. Turc.*, **41**, 391 (1999).
- A. Kumar, S. Singh, A. Saxena and K. Shankar, *Indian J. Chem.*, **27B**, 443 (1998).
- A.I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, ELBS and Longman Group Ltd. London, edn. 3 (1962).
- W.J. Geary, *Coord. Chem. Rev.*, **1**, 81 (1972).
- K. Siddappa, P.T. Reddy, P.C. Reddy, M. Mallikarjun, T. Mahesh and K. Mallikarjun, *Int. J. Pure Appl. Chem.*, **3**, 87 (2008).
- D. Bulent, K. Fatma and C. Mustafa, *J. Chem. Sci.*, **121**, 163 (2009).

24. R.S. Baligar and V.K. Revankar, *J. Serb. Chem. Soc.*, **17**, 1301 (2006).
25. J.S. Sreedharsyam, R.R. Erra, N.R. Devanuri and S. Jyothi, *Molecules*, **11**, 1000 (2006).
26. D. Kumar, A. Syamal, Jaipal and L.K. Sharma, *J. Chem. Soc.*, **121**, 57 (2009).
27. R.N. Prasad and A. Jain, *J. Indian Chem. Soc.*, **81**, 319 (2007).
28. D.P. Singh, R. Kumar, R. Mehani and S.K. Verma, *J. Serb. Chem. Soc.*, **71**, 939 (2006).
29. A.E. Underhill and D. Billing, *Nature*, **210**, 834 (1996).
30. K.S. Siddiqi, A. Umar, S.A. Nami and S. Khan, *J. Serb. Chem. Soc.*, **71**, 1137 (2006).
31. A.P. Mishra and K. Krishna, *J. Indian Chem. Soc.*, **86**, 1150 (2009).
32. G. Chitra, *J. Indian Counc. Chem.*, **24**, 16 (2007).
33. C. Sulekha, G. Rachna, G. Nidhi and S.S. Bawa, *Synth. React. Met-Org. Nano-met. Chem.*, **35**, 683 (2005).
34. T. Bhawana, S. Shweta, S. Chirag and G.L. Talesara, *J. Indian Chem. Soc.*, **86**, 1204 (2009).
35. E.A. Elzahany, K.H. Hegab, S.K.H. Khalil and N.S. Youssef, *Aust. J. Basic Appl. Sci.*, **2**, 210 (2008).
36. B.B. Mahapatra and P. Nilachala, *J. Indian Chem. Soc.*, **88**, 518 (2009).
37. Y.M. Balasaheb, Y.S. Agasimundin and B. Shivakumar, *Indian J. Chem.*, **49B**, 264 (2010).
38. M.L. Harikumar Nair and L. Shamla, *Indian J. Chem. Soc.*, **86**, 133 (2009).
39. D. Prakash, C. Kumar, A.K. Gupta, S. Prakash and K.R.R.P. Singh, *J. Indian Chem. Soc.*, **85**, 252 (2008).
40. C. Spinu, M. Pleniceanu and C. Tigale, *Turk. J. Chem.*, **32**, 487 (2008).
41. Y.H. Zhang, Q.L. Wang and G.M. Yang, *Transition Met. Chem.*, **31**, 856 (2006).
42. B.J. Hathaway and D.E. Billing, *Coord. Chem. Rev.*, **6**, 143 (1970).
43. M.M. Woolfson, *An Introduction to X-ray Crystallography*, Cambridge University Press Cambridge, 125 (1980).
44. A.L. Barry, *Procedure and Theoretical Consideration for Testing Antimicrobial Agents in Agar media*, Williams Wilkins Baltimore, edn. 5 (1991).
45. A. Simmons, *Practical Medical Microbiology*, Churchill Livingstone Edinberg, 11, edn. 4, 163 (1996).
46. J.A. Kovacs, C.A. Allegra, J.C. Swan, J.C. Drake, J.C. Parillo, B.A. Chabner and H. Masur, *Antimicrob. Agents Chemother.*, **43**, 430 (1998).