비대칭 Tetradentate Schiff 염기 리간드의 전이금속 착물에 대한 합성 및 특성

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Synthesis and Characterization of Some Transition Metal Complexes of Unsymmetrical Tetradentate Schiff Base Ligand

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요 약. o-phenylenediamine, 3-acetyl-6-methyl-(2H) pyran, 2,4 (3H)-dione (dehydroacetic acid or DHA) 및 살리실 알데히드로부터 유도한 4-hydroxy-3-(1-{2-(2-hydroxy-benzylidene)-amino phenylimino}-ethyl)-6-methy-pyran-2-one (H_2L) 의 Cu(II), Ni(II), Co(II), Mn(II) 및 Fe(III) 고체 착물을 합성한 후, 원소분석, 전도도법, 수자율, 자외선-가시선, 적외선, ^{1}H-NMR 스펙트라, X-선 회절, 열분석을 통해 특성을 규명하고 항균 활성을 조사하였다. IR 스펙트럼 데이터로부터 이 리간드가 중심 금속이온에 대해 ONNO 주개원자 배열을 갖는 이염기성 네자리 리간드로 행동함을 제안하였다. 원소분석 데이터로부터 이들 착물의 화학량론이 1:1 (금속:리간드)임을 알았다. 물리-화학적 데이타로부터 Cu(II) 및 Ni(II) 착물이 사각평면 기하구조, 그리고 Co(II), Mn(II) 및 Fe(III) 착물이 팔면체 기하구조임을 제안하였다. X-선 회절 데이터로부터 Cu(II) 착물이 사방정계(orthorhombic) 결정계, Ni(II), Co(II) 및 Fe(III) 착물이 단사계(monoclinic) 결정계 그리고 Mn(II) 착물이 정방정계(tetragonal) 결정계임을 제안하였다. 착물의 열적 행동(TG/DTA)을 연구하였으며 Coats-Redfern 방법으로 반응속도 파라메터를 결정하였다. 리간드와 이들 금속 착물을 이용하여 *Staphylococcus aureus* 및 *Escherichia coli*에 대한 항균 활성과 *Aspergillus Niger* 및 *Trichoderma*에 대한 살균 활성을 조사하였다.

주제어: 디하이드로아세트산, 비대칭 네자리 리간드성 Schiff 염기, 전이금속 착물, 열분석, 분말 X-선 회절

ABSTRACT. The solid complexes of Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) with 4-hydroxy-3-(1-{2-(2-hydroxy-benzylidene)-amino phenylimino}-ethyl)-6-methy-pyran-2-one (H_2L) derived from o-phenylenediamine, 3-acetyl-6-methyl-(2H) pyran, 2,4 (3H)-dione (dehydroacetic acid or DHA) and salicylic aldehyde have been synthesized and characterized by elemental analysis, conductometry, magnetic susceptibility, UV-visible, IR, ^{1}H-NMR spectra, X-ray diffraction, thermal analysis, and screened for antimicrobial activity. The IR spectral data suggest that the ligand behaves as a dibasic tetradentate ligand with ONNO donor atoms sequence towards central metal ion. From the microanalytical data, the stoichiometry of the complexes has been found to be 1:1 (metal: ligand).

The physico-chemical data suggests square planar geometry for Cu(II) and Ni(II) complexes and octahedral geometry for Co(II), Mn(II) and Fe(III) complexes. The x-ray diffraction data suggests orthorhombic crystal system for Cu(II) complex, monoclinic crystal system for Ni(II), Co(II) and Fe(III) and tetragonal crystal system for Mn(II) complex. Thermal behaviour (TG/DTA) of the complexes was studied and kinetic parameters were determined by Coats-Redfern method. The ligand and their metal complexes were screened for antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* and fungicidal activity against *Aspergillus Niger* and *Trichoderma*.

Keywords: Dehydroacetic acid, Unsymmetrical tetradentate Schiff Base, Transition metal complexes, Thermal analysis, Powder X-ray diffraction

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INTRODUCTION

Tetradentate Schiff bases with N_2O_2 donor atoms are well known to coordinate with various metal ions and have attracted a great deal of interest in recent years due to their rich co-ordination chemistry.[1-5] Schiff bases of o-phenylenediamine reported to have variety of applications including biological,[6] clinical[7] and analytical[8] fields. Many symmetrical tetradentate bis-type Schiff bases of 1,2-diamines with o-hydroxy aldehyde/ketone have been prepared and studied intensively. However much less attention has been focused on unsymmetrical tetradentate Schiff bases derived from 1,2-diamines and different aldehydes/ketones. In particular those derived from aromatic 1,2 diamines have been under-investigated.[9] It is worthwhile to mention here that unsymmetrical Schiff bases of this type are difficult to obtain and are not easily isolated.[10]

A search of literature revels that no work has been done on the transition metal complexes of the unsymmetrical Schiff bases derived from aromatic 1,2-diamine, dehydroacetic acid and salicylic aldehyde. In this communication, we report the synthesis of unsymmetrical tetrdentate Schiff base formed by the condensation of o-phenylenediamine, dehydroacetic acid and salicylic aldehyde (*Fig.* 1). The solid complexes of Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) with this ligand have also been prepared and characterized by different physicochemical methods.

EXPERIMENTAL

Dehydroacetic acid obtained from Merck was used as supplied. O-phenylenediamine and salicylic aldehyde of A.R. grade were used for synthesis of ligand. A.R. grade metal chlorides were used for the complex preparation. The carbon, hydrogen and nitrogen contents were determined on Perkin Elmer (2400) CNS analyzer. IR spectra were recorded on FT-IR spectrometer, Perkin Elmer Company using KBr pellets. ^{1}H-NMR spectra of ligand were measured in $CDCl_3$ using TMS as internal standard. The TG/DTA and XRD were recorded on Perkin Elmer TA/SDT-2960 and Philips 3701 respectively. The uv-vis spectra of the complex were recorded on Shimadzu UV-1601 spectrometer. Magnetic susceptibility measurements of the metal chelates were determined on a Guoy balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant. Molar conductance of complexes was measured on Elico CM 180 conductivity meter using 10^{-3} M solution in DMF.

Synthesis of ligand

The ligand was prepared by a modification of the reported methods.[11-13] A typical procedure for synthesis of Schiff bases is as follows: a 50 mL solution of 10 mmol (0.168 g) of dehydroacetic acid, 10mmol (0.108 g) of o-phenylenediamine and 10
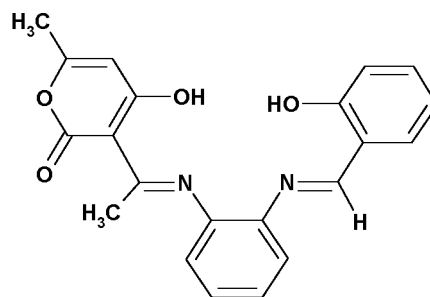

Fig. 1. Structure of ligand.

mmol (0.122 g) of salicylic aldehyde in super dry ethanol was refluxed for about 4 h. the precipitate thus formed was cooled to room temperature and collected by filtration. followed by recrystallization in ethanol (yield: 80%).

Synthesis of complexes

To a hot methanol solution (25 mL) of the ligand (0.01 mol), methnolic solution (25 mL) of metal chloride (0.01 mol) was added with constant stirring. The pH of reaction mixture was adjusted to 7.5 ~ 8.5 by adding 10% alcoholic ammonia solution and refluxed for about 3 h. the precipitated solid metal complex was filtered off in hot condition and washed with hot methanol. petroleum ether (40 ~ 60 °C) and dried over calcium chloride in vacuum desiccator (yield: 55%).

RESULT AND DISCUSSION

Physical characteristics. micro analytical. and molar conductance data of ligand and metal complexes are given in *Table* 1. The analytical data of complexes revels 1: 1 molar ratio (metal: ligand) and corresponds well with the general formula [ML] (where M = Cu(II) and Ni(II)) and [ML(H$_2$O)$_2$] (where M = Co(II), Mn(II) and Fe(III)). The magnetic susceptibilities of Cu(II) and Ni(II) complexes at room temperature are consistent with square-planar geometry and that of Co(II), Mn(II) and Fe(III)

complexes with high spin octahedral structure with two water molecules coordinated to metal ion. The presence of two coordinated water molecules was confirmed by TGA-DTA analysis. The metal chelate solution in DMF shows low conductance and this supports their non-electrolyte nature.

^{1}H-NMR spectra of ligand

The ^{1}H-NMR spectrum of the free ligand in CDCl$_3$ at room temperature shows the following signals. 2.18 δ (s. 3 H, C$_6$-CH$_3$), 2.55 δ (s. 3 H, N = C-CH$_3$), 5.5 δ (s. 1 H, phenolic OH), 5.8 δ (s. 1 H, C$_5$-H), 6.9 ~ 7.5 δ (m, 8H, Phenyl), 8.65 δ (s. 1 H, N = C-H) and 15.85 δ (s. 1 H, enolic OH of DHA moiety).

Infrared spectra

The IR spectrum of free ligand shows characteristic bands at 3060 ~ 3300, 1703, 1657, 1354, and 1219 cm^{-1} assignable to intramolecular hydrogen bonded (υ OH), lactone carbonyl (υ C = O), azomethine (υ C = N), aryl azomethine (υ C-N) and phenolic (υ C-O) stretching modes respectively.[14-15] The absence of a weak broad band in the 3060 ~ 3300 cm^{-1} region. noted in the spectra of the metal complexes indicates deprotonation of the intramolecular hydrogen bonded OH group on complexation and subsequent coordination of phenolic oxygen to the metal ion. This is further supported by upward shift in phenolic (υ C-O)[16] to the extent of 30 ~ 50 cm^{-1}. On complexation, the υ (C = N) band is shifted to

Table 1. Physical characterization, analytical and molar conductance data of compounds

Ligand/ Complexes	F. W.	M.P./ Decomp. Temp. °C	Color	Molar conduc. Mho cm^2 mol^{-1}	Found (Calculated)			
					C	H	N	M
(H$_2$L)	362.39	185	yellow	–	69.12 (69.60)	4.88 (5.01)	7.50 (7.73)	–
[CuL]	423.94	207	Green	17.10	58.92 (59.44)	4.01 (3.77)	6.50 (6.60)	14.02 (14.99)
[NiL]	419.16	212	Red	23.20	60.24 (60.13)	4.10 (3.82)	6.80 (6.68)	14.35 (14.01)
[CoL (H2O)$_2$]	455.32	215	Greenish	13.40	55.65 (55.35)	4.62 (4.39)	6.55 (6.15)	13.20 (12.94)
[MnL (H2O)$_2$]	451.33	270	Brown	18.46	55.80 (55.83)	4.50 (4.43)	6.40 (6.20)	12.78 (12.17)
[FeL (H2O)$_2$]	452.24	264	Brown	41.24	55.24 (55.83)	4.85 (4.43)	6.81 (6.20)	12.80 (12.17)

lower wave number with respect to free ligand, denoting that the nitrogen of the azomethine group is coordinated to the metal ion. This is supported by upward shift in υ C-N to the extent of $10 \sim 50$ cm^{-1}.[17] The IR spectra of metal chelates showed new bands in the $457 \sim 540$ and $407 \sim 478$ cm^{-1} regions which can be assigned to υ M-O and M-N vibrations respectively.[18] The IR spectra of Co(II), Mn(II) and Fe(III) show a strong band in the $3150 \sim 3600$ cm^{-1} region, suggesting the presence of coordinated water in these metal complexes. The presence of coordinated water is further confirmed by the appearance of non-ligand band in the $830 \sim 840$ cm^{-1} region, assignable to the rocking mode of water.[19] The presence of coordinated water is also established and supported by TG/DTA analysis of these complexes. Hence coordination takes place via phenolic oxygen and azomethine nitrogen of ligand molecule.

Magnetic susceptibility and electronic absorption spectra

The magnetic and electronic spectral data is given in *Table* 2. The spectra of ligand exhibit two main peaks at 31347 and 40816 cm^{-1} attributed carbonyl π-π^* and imino π-π^* transitions respectively. The electronic absorption spectrum of Cu(II) show three

bands at 17825, 26809 and 37313 cm^{-1}, assignable to the transitions $d_{xy} \rightarrow d_{x2-y2}$ and two intra-ligand transition bands. These electronic transitions and observed 1.71 B.M magnetic moment value suggests square-planar geometry around the Cu(II).[18,20] The electronic absorption spectrum of Ni(II) complex consists of two bands at about 17361 cm^{-1} and 26666 cm^{-1} assignable to $d_{xy} \rightarrow d_{x2-y2}$ and charge transfer transitions respectively. Observed electronic transitions, the diamagnetic nature and red colour of the complex suggests square-planar geometry for Ni(II) complex.[21,22] The electronic absorption spectrum of Co(II) complex show three bands at 10660, 18796 and 26385 cm^{-1} which may be attributed to the transitions $d_{xy} \rightarrow d_z{}^2$, $d_{yz} \rightarrow d_{x2-y2}$ and charge transfer respectively. Electronic transitions along with magnetic moment value 4.45 B.M. suggests high spin octahedral geometry for the Co(II) complex.[23,24] The octahedral geometry is further supported by ratio $\upsilon_2/\upsilon_1 = 1.763$ which is close to the value expected for octahedral geometry. The electronic absorption spectrum of Mn(II) complex show three bands at 14727, 21929 and 26455 cm^{-1} assignable to the transitions $d_{xy} \rightarrow d_{z2}$, MLCT and charge transfer respectively. Electronic transitions along with magnetic moment value 5.84 B.M. which is

Table 2. Magnetic and Electronic absorption spectral data of compounds

Ligand/Complexes	Magnetic moment μ_{eff} (B.M.)	Frequency in cm^{-1} (ε in L mol^{-1} cm^{-1})	Band Assignment	Geometry
(H$_2$L)	—	31347 (9060)	I N C T[a]	—
		40816 (9300)	I N C T	
[CuL]	1.71	17825 (15)	$d_{xy} \rightarrow d_{x2-y2}$	Square planar
		26809 (773)	MLCT[b]	
		37313 (1289)	I N C T	
[NiL]	Diamagnetic	17361 (92)	$d_{xy} \rightarrow d_{x2-y2}$	Square planar
		26666 (1085)	I N C T	
[CoL (H2O)$_2$]	4.55	10660 (7)	$d_{xy} \rightarrow d_{x2-y2}$	Octahedral
		18796 (208)	$d_{yz} \rightarrow d_{x2-y2}$	
		26385 (374)	I N C T	
[MnL (H2O)$_2$]	5.84	14727 (214)	$d_{xy} \rightarrow d_{x2-y2}$	Octahedral
		21929 (2008)	MLCT	
		26455 (1208)	I N C T	
[FeL (H2O)$_2$]	5.77	12787 (22)	$d_{xy} \rightarrow d_{z2}$	Octahedral
		18621 (82)	$d_{xy} \rightarrow d_{x2-y2}$	
		33898 (907)	I N C T	

[a]INCT: Intra-ligand charge transfer. [b]MLCT: Metal to ligand charge transfer.

almost close to spin only value (5.92 B.M.) suggests high spin octahedral geometry for the Mn(II) complex.[23,25] The electronic absorption spectrum of Fe(III) complex show three weak bands at 12787, 18621 and 33898 cm^{-1} which may be assigned to the transitions $d_{xy} \rightarrow d_{z^2} d_{xy} \rightarrow d_{x^2-y^2}$ and charge transfer respectively. Electronic transitions together with magnetic moment value 5.77 B.M. suggests high spin octahedral geometry for the Fe(III) complex.[23,26]

Thermal analysis

The simultaneous TG/DT analysis of metal complexes was studied from ambient temperature to 1000 °C in nitrogen atmosphere using α-Al$_2$O$_3$ as reference. In the TG curve of Cu(II) and Ni(II) complexes, no mass loss up to 270 °C indicates absence of coordinated water in these complexes.[17] In the TG curve of Cu(II) complex, the first step of decomposition from 285 to 400 °C, with a mass loss 24.70% (calcd. 23.11%), an exothermic peak $\Delta T max = 335$ °C in DTA may be attributed to the decomposition of non coordinated part of ligand. The second slow step from 410 ~ 905 °C with mass loss 58.80% (calcd. 61.46%), corresponds to decomposition of coordinated part of ligand. A broad endotherm in DTA is observed for this step. The mass of the final residue corresponds to stable CuO. 18.5% (calcd. 17.82%). the TG curve of Ni(II) complex, show two step decomposition. The first step from 288 °C to 435 °C, with a mass loss 24.00% (calcd. 23.38%), an exothermic peak $\Delta T max = 330$ °C in DTA may be attributed to the decomposition of non coordinated part of ligand. The slow decomposition in second step from 565 ~ 868 °C with mass loss 60.20% (calcd. 62.05%), corresponds to removal of coordinated part of ligand. A broad endotherm in DTA is observed for this step. The mass of the final residue 10% does not corresponds to any stoichiometry of end product.

The thermogram of Co(II) complex show mass loss 7.5% (calcd. 7.9%) in the range 180 ~ 230 °C, an endothermic peak in this region $\Delta T min = 207$ °C, corresponds to the removal of two coordinated water molecules.[27,28] The anhydrous complex first show slow decomposition from 240 ~ 550 °C, with

28% (calcd. 27.01%) mass loss, a broad exotherm $\Delta T max = 248$ °C in DTA may be attributed to removal of non coordinated part of ligand. The second step decomposition from 580 ~ 870 °C, with mass loss of 51.30% (calcd. 52.08%) corresponds to decomposition of coordinated part of ligand. A broad endotherm in DTA is observed for this step. The mass of the final residue corresponds to stable CoO. 10.25% (calcd. 12.94%). The TG curve of Mn(II) complex show first mass loss 7.20% (calcd. 7.97%) in the range 145 ~ 210 °C, an endothermic peak in this region $\Delta T min = 175$ °C, indicates removal of two coordinated water molecules. The anhydrous complex shows single step slow decomposition from 260 ~ 1000 °C, with 52% mass loss, a broad endotherm in DTA indicates that the complex is thermally quite stable. The thermal profile of Fe(III) complex shows mass loss 7.5% (calcd. 7.96%) in the range 160 ~ 250 °C, an endothermic peak in this region $\Delta T min = 207$ °C, indicates loss of two coordinated water molecules. The anhydrous complex first show slow decomposition from 250 ~ 625 °C, with 27% (calcd. 27.20%) mass loss, a broad exotherm $\Delta T max = 283$ °C in DTA may be attributed to removal of non coordinated part of ligand. The second step decomposition is sharp from 655 ~ 665 °C, with mass loss of 14.50%, a sharp endotherm in DTA at 655 °C is observed for this step. The third step decomposition is from 670 ~ 800 °C with 22% mass loss. The mass of the final residue 9.2% does not corresponds to any stoichiometry of end product.

Kinetic calculations

The kinetic and thermodynamic parameters *viz* order of reaction (n), energy of activation (E$_a$), frequency factor (log A), entropy of activation ($\Delta S^{\#}$) and free energy change ($\Delta G^{\#}$) together with correlation coefficient (r) for non-isothermal decomposition of metal complexes have been determined by Coats-Redfern integral method.[29] Kinetic study was not attempted for decomposition stage such as in Fe(III) chelate which occurs within a narrow temperature range resulting in a too steep TG curve for enough data to be collected. The data is given in

Table 3. The calculated free energy of activation is relatively low indicating the autocatalytic effect of metal ion on thermal decomposition of the complex.[30,31] $\Delta S^{\#}$ values were negative, which indicates a more ordered activated state that may be possible through the chemisorptions of oxygen and other decomposition products. The more ordered nature may be due to the polarization of bonds in activated state which might happen through charge transfer electronic transition.

Powder X-ray diffraction

The x-ray diffractogram of metal complexes was scanned in the range 5 ~ 100° at wavelength 1.543 Å. The diffractogram and associated data depict the 2 θ value for each peak, relative intensity and interplanar spacing (d-values). The diffractogram of Cu(II) complex had nine reflections with maxima at 2 θ = 8.473° corresponding to d value 10.427 Å. The diffractogram of Ni(II) complex shows twelve reflections with maxima at 2 θ = 22.504° corresponding to d value 3.954 Å. The diffractogram of Co(II) complex had thirteen reflections with maxima at 2 θ = 59.845° corresponding to d value 1.544 Å. Where as The diffractogram of Mn(II) complex had seven reflections with maxima at 2 θ = 36.129° corresponding to d value 2.484 Å. The x-ray diffraction pattern of these complexes with respect to major peaks having relative intensity grater than 10% have been indexed by using computer programme.[32] The above indexing method also yields miller indices (hkl), unit cell parameters and unit cell volume. The unit cell of Cu(II) complex yielded values of lattice constants a = 16.4410 Å, b = 13.8836 Å, c = 3.8408 Å and unit cell volume V = 876.8318 Å^3. In concurrence with these cell parameters, the condition such as a ≠ b ≠ c and α = β = γ = 90° required for sample to be orthorhombic were tested and found to be satisfactory. Hence it can be concluded that Cu(II) complex has orthorhombic crystal system. The unit cell of Ni(II) complex yielded values of lattice constants a = 14.8910 Å, b = 8.9216 Å, c = 8.4799 Å and unit cell volume V = 910.4587 Å^3. The unit cell of Co(II) complex yielded values of lattice constants a = 10.8962 Å, b = 5.4401 Å, c = 7.9007 Å and unit cell volume V = 441.7221 Å^3. In concurrence with these cell parameters, the condition such as a ≠ b ≠ c and α = γ = 90° ≠ β required for sample to be monoclinic were tested and found to be satisfactory. Hence it can be concluded that Ni(II) and Co(II) complex has monoclinic crystal system. The unit cell of Mn(II) complex yielded values of lattice constants a = 5.2046 Å, b = 5.2046 Å, c = 16.5209 Å and unit cell volume V = 447.5319 Å^3. In concurrence with these cell parameters, the condition such as a = b ≠ c and α = β = γ = 90° required for sample to be tetragonal were tested and found to be satisfactory. Hence it can be concluded that Mn(II) complex has tetragonal crystal system. The experimental density values of the complexes were determined by using specific gravity method [33] and found to be 3.222, 1.5024, 1.7200 and 3.3654 g·cm^{-3} for Cu(II), Ni(II), Co(II) and Mn(II) complexes respectively. By using experimental density values, mole-

Table 3. Kinetic parameters of metal complexes calculated by the Coats-Redfern (CR) method

Complexes	Step	n	E_a	logA	$\Delta S^{\#} \times 10^3$	$\Delta G^{\#}$	Corelation coefficient (r)
[CuL]	I	1.45	22.68	7.013	-234.15	38.73	0.9999
	II	0.89	14.34	0.151	-269.71	43.09	0.9936
[NiL]	I	1.01	26.13	8.334	-233.41	43.50	0.9929
	II	0.61	28.16	1.404	-252.02	57.80	0.9946
[CoL (H2O)₂]	I	1.20	12.56	1.080	-269.39	34.33	0.9991
	II	0.95	33.34	4.756	-241.93	62.93	0.9995
[MnL (H2O)₂]	—	1.42	24.28	1.766	-250.17	53.91	0.9832
[FeL (H2O)₂]	I	1.40	17.62	1.335	-249.54	38.33	0.9979
	II	0.35	32.91	2.362	-247.82	62.50	0.9971

E_a in kJ mol^{-1}, logA in min^{-1}, $\Delta S^{\#}$ in kJK^{-1}mol^{-1} and $\Delta G^{\#}$ in kJ mol^{-1}

Table 4. Antibacterial activity of compounds

Ligand/Complexes	inhibition zone (mm)			
	E. Coli		*Staphylococcus*	
	500 ppm	1000 ppm	500 ppm	1000 ppm
Ciproflaxin	29	32	31	35
(H$_2$L)	08	11	11	14
[CuL]	13	14	16	19
[NiL]	12	12	13	17
[CoL (H2O)$_2$]	12	13	14	17
[MnL (H2O)$_2$]	10	13	11	15
[FeL (H2O)$_2$]	10	13	11	15

Table 5. Yield of Mycelial dry weight in mg (% inhibition)

Ligand/Complexes	*Aspergillus Niger*		*Trichoderma*	
	250 ppm	500 ppm	250 ppm	500 ppm
Control	79	79	70	70
(H$_2$L)	61 (23)	24 (70)	40 (43)	19 (73)
[CuL]	40 (49)	10 (87)	20 (71)	02 (97)
[NiL]	43 (46)	13 (84)	22 (69)	03 (96)
[CoL (H2O)$_2$]	50 (37)	16 (80)	32 (54)	04 (94)
[MnL (H2O)$_2$]	53 (33)	18 (77)	34 (51)	08 (89)
[FeL (H2O)$_2$]	54 (32)	18 (77)	35 (50)	12 (83)

cular weight of complexes. Avogadro's number. volume of the unit cell. the number of molecules per unit cell were calculated by using equation $\rho =$ nM/NV and was found to be four. two. one and two for Cu(II), Ni(II). Co(II) and Mn(II) complexes respectively. With these values. theoretical density were computed and found to be 3.2109. 1.5287. 1.7114 and 3.3486 g·cm^{-3} for respective complexes. Comparison of experimental and theoretical density value shows good agreement within the limits of experimental error.[34]

Antimicrobial activity

The antimicrobial activity of ligand and metal complexes were tested *in vitro* against bacteria such as *Staphylococcus aureus* and *Escherichia coli* by paper disc plate method.[35] The compounds were tested at the concentration 0.5 mg·mL^{-1} and 1 mg·mL^{-1} in DMF and compared with known antibiotics *viz* ciproflaxin (*Table* 4). For fungicidal activity, compounds were screened *in vitro* against *Aspergillus Niger* and *Trichoderma* by mycelia dry weight method[16] with glucose nitrate media. The compounds were tested at the concentration 250 and 500 ppm in DMF and compared with control (*Table* 5). From *Tables* 4 and 5. it is clear that the inhibition by metal chelates is higher than that of a ligand and results are in good agreement with previous findings with respect to comparative activity of free ligand and its complexes.[16,35] Such enhanced activity of metal chelates is due to lipophilic nature of the metal ions in complexes.[36] The increase in activity with concentration is due to the effect of metal ions on the normal process. The action of compounds may involve the formation of hydrogen bond with the active center of cell constituents. resulting in interference with the normal cell process.[37]

CONCLUSION

In the light of above discussion we have proposed square-planar geometry for Cu(II) and Ni(II) complexes and octahedral geometry for Co(II). Mn(II) and Fe(III) complexes. On the basis of the physico-chemical and spectral data discussed above. one can assume that the ligand behave as dibasic. ONNO tetradentate. coordinating via phenolic oxygen and imino nitrogen as illustrated in *Fig.* 2. The complexes
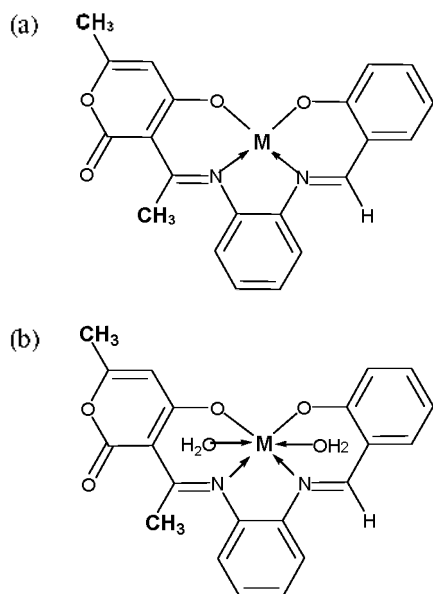
(a)

(b)

Fig. 2. The proposed structure of the complexes: (a) when M = Cu(II) and Ni(II); (b) when M = Co(II), Mn(II) and Fe(III).

are biologically active and show enhanced antimicrobial activities compared to free ligand. Thermal study reveals thermal stability of complexes. The XRD study suggests orthorhombic crystal system for Cu(II) complex and tetragonal crystal system for Mn(II) complex, where as monoclinic crystal system for Ni(II) and Co(II) complexes.

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