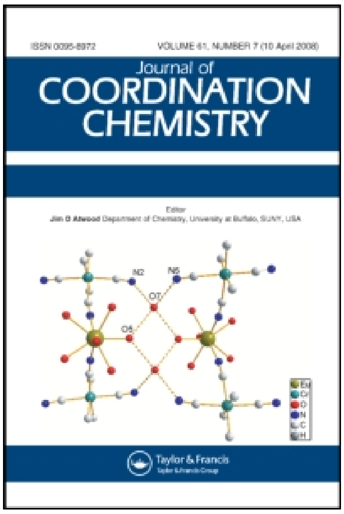

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Mononuclear and binuclear Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes of Schiff-base ligands derived from 7-formyl-8-hydroxyquinoline and diaminonaphthalenes

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Mono- and binuclear Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes of Schiff-base ligands derived from 7-formyl-8-hydroxyquinoline with diaminonaphthalenes were prepared and characterized by elemental and thermal analysis, conductance measurements and IR spectroscopy. The structures of the solid complexes under study are established by using electronic and ESR spectroscopy and magnetic susceptibility measurements. The results show that Co(II), Zn(II) and Cd(II) complexes are tetrahedral, Ni(II) complexes are octahedral and Cu(II) complexes are either tetragonally distorted octahedral or square planar. All complexes and ligands were found to be highly active against fungi.

Keywords: Transition metals; Schiff bases; Antifungal tetrahedral; Octahedral

1. Introduction

Schiff-base derivatives of various transition metals have been investigated for their coordinating capability, pharmaceutical and biological activities [1–5]. These complexes are used as catalysts for water photolysis [6] or for oxygen reduction at a modified carbon cathode [7]. Some compounds have been used for catalytic hydrogenation of unsaturated hydrocarbons [8]. Schiff bases have also been used for analytical purposes [9] in the determination of metal ions, and some Schiff-base derivatives have been used in the solvent extraction of metals [10]. The applications of such complexes depend to a large extent on their molecular structure. The present work provides a new series of mono- and binuclear complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with Schiff-base ligands derived from 7-formyl-8-hydroxyquinoline and 1,5- or 1,8-diaminonapthalene. These complexes were characterized by elemental analysis, conductance, TGA, IR, magnetic susceptibility studies, and electronic and ESR

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spectroscopy to determine the mode of bonding and geometry biological activities of the ligands and complexes were also studied.

2. Experimental

All compounds used in the present investigation were pure BDH chemicals.

2.1 *Preparation of 7-formyl-8-hydroxyquinoline (FHQ)*

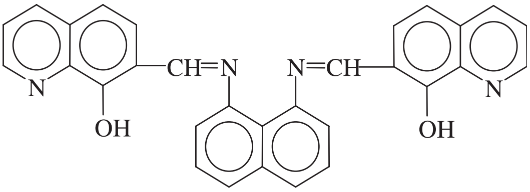
7-Formyl-8-hydroxyquinoline was prepared as reported earlier [11]. 1.45 g (0.1 mol) of 8-hydroxyquinoline was added to 8.5 ml (0.01 mol) of chloroform and 90 ml of 15% NaOH. The reaction mixture was heated under reflux for 4 h, on a water bath, during which time the solution became brown in color. After cooling, the pH of the solution was adjusted to 5.5–5.8 using 0.01 M HCl. A pale brown product separated and was left to coagulate, then filtered off and recrystallized from 80% ethanol, mp 225°C and yield 75%. The purity of the FHQ was checked by results of elemental analysis (table 1) and IR spectroscopy (table 3).

Table 1. Elemental analysis of FHQ and the free ligands L_{Ia} and L_{IIb} and their metal(II) complexes, and molar conductance values for the solid complexes.

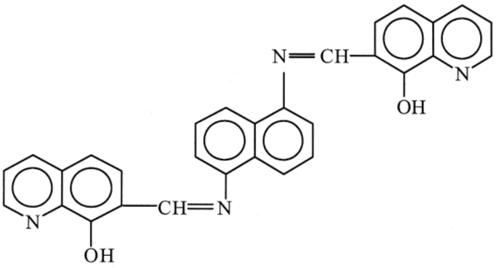
No.	Compound	M : L	Color	Mp (C°)	Analysis (Calculated %) Found % C	 H	 N	 M	Λ(ohm^{-1} cm^2 mol^{-1})
	FHQ	–	Pale brown	225	(69.36) 69.11	(4.46) 4.71	(8.09) 8.40	–	–
	L_{Ia}	–	Brown	260	(76.92) 76.53	(4.27) 4.61	(11.97) 12.33	–	–
1	$[CoL_{Ia}]_2H_2O$	1 : 1	Orange	298	(64.81) 64.40	(3.11) 3.22	(10.2) 10.02	(10.40) 10.61	16
2	$[NiL_{Ia}(H_2O)_4]H_2O$	1 : 1	Green	>350	(58.42) 58.70	(3.20) 2.94	(8.73) 9.14	(9.42) 9.62	22
3	$[CuL_{Ia}]EtOH \cdot H_2O$	1 : 1	Brown	>350	(60.90) 60.86	(3.11) 3.04	(9.30) 9.47	(11.00) 10.74	20
4	$[ZnL_{Ia}]H_2O$	1 : 1	Yellow	297	(65.75) 65.45	(3.65) 3.80	(10.23) 9.91	(11.90) 12.02	18
5	$[CdL_{Ia}]2H_2O$	1 : 1	Dark yellow	305	(58.78) 59.10	(3.60) 3.71	(9.14) 8.85	(9.14) 9.05	15
	L_{IIb}	–	Brown	277	(76.92) 77.20	(4.27) 4.51	(11.97) 11.44	–	–
6	$[Co_2L_{IIb}(H_2O)_4]Cl_2 \cdot H_2O$	2 : 1	Reddish brown	320	(48.71) 48.45	(2.73) 2.42	(7.41) 7.54	(16.10) 15.90	142
7	$[Ni_2L_{IIb}(H_2O)_8]Cl_2 \cdot H_2O$	2 : 1	Green	>350	(43.85) 44.17	(2.43) 2.21	(7.21) 6.87	(14.82) 14.50	152
8	$[Cu_2L_{IIb}(H_2O)_4]Cl_2 \cdot H_2O$	2 : 1	Brown	>350	(46.80) 46.75	(2.50) 2.34	(6.95) 7.25	(16.31) 16.49	146
9	$[Zn_2L_{IIb}(H_2O)_4]Cl_2 \cdot H_2O$	2 : 1	Yellow	317	(46.58) 46.35	(3.88) 3.90	(7.25) 7.05	(16.92) 17.10	150
10	$[Cd_2L_{IIb}(H_2O)_4]Cl_2 \cdot H_2O$	2 : 1	Orange	321	(42.41) 42.30	3.30 (3.41)	(6.60) 6.53	(13.24) 12.92	147

2.2 *Preparation of the ligands*

The Schiff-base ligands in the present investigation were prepared according to procedures of Diehel and Hach [12] by condensation of 1 mole of 1,5-diaminonaphthalene or 1,8-diaminonaphthalene with 2 moles of FHQ in absolute ethanol. The solids were purified by repeated crystallization from 80% EtOH, yield 65–75%. The purity of the Schiff bases prepared was checked by elemental analysis (table 1) and IR spectroscopy (table 3). The structure of Schiff bases Ia and IIb are as follows.



Schiff base (Ia)



Schiff base (IIb)

2.3 *Preparation of complexes*

Complexes were prepared by mixing an ethanolic solution of the organic ligand (1 mole) with 1 or 2 moles of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) chloride. The mixture was refluxed for *ca* 2 h on a water bath, during which time the solid complex precipitated, was filtered off, washed several times with ethanol to remove any traces of metal ions or free ligands, and finally washed with diethyl ether and dried *in vacuo*, yield 65–70%. All the solid complexes were soluble in DMF but insoluble in water and common organic solvents.

2.4 *Apparatus and working procedures*

IR spectra were recorded as KBr disks using the IR Shemadzo model 470 spectrophotometer (400–4000 $\mathrm{cm^{-1}}$). Electronic spectra of solutions of the complexes in DMF were recorded on a Jasco model V.550 UV–VIS spectrophotometer. ESR spectra of the metal complexes were recorded on the Jeol microwave unit JES-FE2XG spectrophotometer at the central laboratories of Tanta University, Tanta, Egypt. The magnetic field was calibrated with 2,2-diphenyl-1-picrylhydrazine purchased from Aldrich. TGA measurements were carried out on a Shimatzu thermogravimetric analyzer in dry nitrogen at a heating rate of 10°C min^{-1} using the TA-50 WSI program. Microanalyses of carbon, hydrogen and nitrogen were carried out at the Microanalytical Center, Cairo University, Giza, Egypt. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a Johnson Matthey Alfa MKI magnetic susceptibility balance, with $Hg[Co(CNS)_4]$ as calibrant. Conductivities were measured for solutions of the complexes in DMF (1×10^{-3} M) using a Model LBR 40A conductivity meter (Wissenschaftlich-Techmische Werkstatten, Weilheim, Germany).

Screening the investigated compounds for antifungal activities was performed in Czpek's agar medium, using the disk diffusion method as follows: filter paper disks (2.5 mm in diameter) were impregnated with 100 ppm of each compound dissolved in DMF, which was used as control. Individual disks were placed aseptically on the surface of Czpek's agar medium for 168 h. The diameter of the inhibition zone was measured and the percentage inhibition was calculated.

The other physical measurements and analyses were as described previously [13,14].

3. Results and discussion

3.1 *Elemental analysis and conductance measurements*

Elemental analyses of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes of Schiff-base ligand Ia (table 1) indicate a $1:1\,M^{2+}:L$ stoichiometry denoting the formation of mononuclear complexes in which Ia behaves as a dibasic tetradentate ligand towards the metal(II) ions. Elemental analysis for complexes of ligand IIb (table 1) indicate the stoichiometry to be $2:1\,M^{2+}:L$, denoting binuclear complexes in which the Schiff-base ligand IIb binds to two metal ions.

The molar conductance values of mononuclear complexes in DMF (1×10^{-3} M) are low (table 1) suggesting the absence of ionic character. The molar conductance values for the binuclear complexes show values of 142–152 $ohm^{-1}\,cm^2\,mol^{-1}$, within the expected range of values for 1 : 2 electrolytes [15], indicating that the Cl^- anion is not coordinated.

The stoichiometry of the complexes formed between Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions and ligands L_{Ia} and L_{IIb} was determined by conductometric titrations in solution. The conductance molar ratio curves are characterized by breaks denoting the formation of 1 : 1 complexes. In addition, ligand L_{IIb} exhibits a break at a mole ratio 2 : 1 (M : L) due to the formation of binuclear complexes. The curves exhibit a gradual increase in conductance with increasing volume of the ligand added, reflecting the displacement of H^+ from the ligand groups by the metal ions through complexation.

3.2 *Thermogravimetric analysis (TGA)*

The TGA data (table 2) for mono- and binuclear Ni(II) and Cu(II) complexes lead to the following conclusions:

1. Crystal lattice water and ethanol molecules volatilize within the temperature range 40–115°C, whereas coordinated water molecules are removed in the range

Table 2. Thermogravimetric analysis of Ni(II) and Cu(II) complexes.

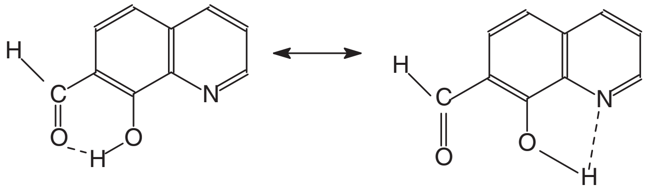
Complex	Temp. range (°C)	% Loss Calcd. (found)	Lost fragments	Residue
$[Ni_2L_{Ia}(H_2O)_4]H_2O$	75–105	2.90 (2.95)	One H_2O lattice	$[NiL_{Ia}(H_2O)_4]$
	130–165	14.49 (14.60)	4 H_2O coordinated	$[NiL_{Ia}]$
	200–300		Thermal stability	
	> 380	24.10 (24.20)		NiO
$[Ni_2L_{IIb}(H_2O)_8]Cl_2 \cdot H_2O$	80–110	2.19 (2.30)	One H_2O lattice	$[Ni_2L_{IIb}(H_2O)_8]Cl_2$
	135–180	19.71 (20.10)	8 H_2O coordinated	
	220–270	28.22 (28.20)	2 Cl^- ions	
			Thermal stability	$[Ni_2L_{IIb}]Cl_2$
	290–400			$[Ni_2L_{IIb}]$
	> 430	42.58 (42.41)		
				2NiO
$[CuL_{Ia}]EtOH \cdot H_2O$	45–85	6.93 (6.95)	One EtOH lattice	$[CuL_{Ia}]H_2O$
	90–115	9.65 (9.50)	One H_2O lattice	$[CuL_{Ia}]$
			Thermal stability	
	220–400			
	> 450	19.22 (19.5)		CuO
$[Cu_2L_{IIb}(H_2O)_4]Cl_2 \cdot H_2O$	80–115	4.63 (4.50)	Two H_2O lattices	$[Cu_2L_{IIb}(H_2O)_4]Cl_2$
	130–180	13.99 (14.00)	4 H_2O lattices	
	230–265	22.91 (23.00)	2 Cl^- ions	
			Thermal stability	$[Cu_2L_{IIb}]Cl_2$
	340–460			$[Cu_2L_{IIb}]$
	> 500			
				2CuO

130–180°C. The number of water molecules determined from the thermograms confirms the data obtained by elemental analysis.

2. The uncoordinated Cl^- ions in the case of binuclear complexes were lost as HCl in the temperature range 220–270°C.
3. The Ni(II) and Cu(II) mononuclear complexes decompose above 380 and 430°C, respectively, while the binuclear Ni(II) and Cu(II) complexes decompose above 450 and 500°C, respectively; that is, the binuclear complex is thermally more stable than the mononuclear. Cu(II) complexes are also more stable than Ni(II) complexes.

3.3 *Infrared spectra*

The most characteristic bands of the IR spectrum of FHQ have been assigned based on careful comparison with 8-hydroxyquinoline. The spectrum of FHQ shows a new band at 1675 cm^{-1} assigned to $\nu_{C=O}$. the broad weak bands centered at 2600, 2100 and 1950 cm^{-1} may be due to O···H–O stretching and bending vibrations [16]. Intramolecular hydrogen bonding in the structure of FHQ can be represented as follows:



IR spectral data for the free ligands L_{Ia} and L_{IIb} and their complexes are listed in table 3. Bonding of the ligands to Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions was investigated by comparing the IR spectra of the solid complexes with those of the free ligands. We can conclude that:

1. The IR spectra of all solid complexes under investigation exhibit a broad band around 3320–3345 cm^{-1}, which is attributed to ν(OH) of water and/or ethanol molecules associated with complex formation. The mono- and binuclear Ni(II)

Table 3. Characteristic IR bands (cm^{-1}) of FHQ and ligands L_{Ia} and L_{IIb} with their complexes.

Compound	ν_{OH} water	ν_{OH} phenolic	$\nu_{C=O}$	$\nu_{C=N}$	$\nu_{C=N}$ ring	ν_{M-O}	ν_{M-N}
FHQ	–	3255	1675	–	1593	–	–
L_{Ia}	–	3310	–	1640	1580	–	–
Co, L_{Ia}	3325	–	–	1623	1580	510	463
Ni, L_{Ia}	3320	–	–	1620	1580	516	460
Cu, L_{Ia}	3325	–	–	1622	1583	522	470
Zn, L_{Ia}	3330	–	–	1625	1580	530	451
Cd, L_{Ia}	3335	–	–	1620	1582	524	458
L_{IIb}	–	3245	–	1650	1590	–	–
Co, L_{IIb}	3330	–	–	1630	1590	528	465
Ni, L_{IIb}	3330	–	–	1632	1592	530	476
Cu, L_{IIb}	3340	–	–	1635	1591	535	485
Zn, L_{IIb}	3340	–	–	1630	1590	532	481
Cd, L_{IIb}	3345	–	–	1631	1593	535	486

complexes and binuclear Co(II), Cu(II), Zn(II) or Cd(II) complexes show new bands in the regions 935–950 and 645–650 cm^{-1}, which are attributed to $\rho(H_2O)$ and $\omega(H_2O)$ of the coordinated water molecules.

2. The IR spectra of the dehydrated metal chelates show the disappearance of the ν(OH) phenolic and ν(C–OH) bands observed at 3210–3245 and 1260–1275 cm^{-1}, respectively, in the IR spectra of the free ligands, indicating proton displacement from the phenolic OH groups by the metal ion. thus, bonding of the metal ions to the ligands under investigation takes place through a covalent link with oxygen of the phenolic group.
3. The bands due to ν(C=N) of the quinoline moiety located at 1580–1590 cm^{-1} in the IR spectra of all ligands under investigation lie at the same position in the IR spectra of the metal complexes indicating that the N atom of the aromatic ring does not participate in complex formation [16–18].
4. The bands at 1640–1660 cm^{-1}, corresponding to the azomethine ν(C=N) of the free ligands, shift by 15–20 cm^{-1}; hence the nitrogen atom of the azomethine group coordinates to the metal(II) ion in all the complexes under investigation. This is supported by the existence of new bands in the IR spectra of the complexes at 510–535 and 460–485 cm^{-1}, which are assigned to ν(M–O) and ν(M–N), respectively.

3.4 *Electronic spectra*

The electronic spectra of Co(II), Ni(II) and Cu(II) complexes were obtained in DMF solutions. The values of λ_{max} are listed in table 4. The electronic spectra of Co(II) complexes have, in general, three bands with λ_{max} in the regions (290, 300), (400, 410) and (480, 485) nm, respectively, which can be assigned to π–π^* transition within the organic molecules, π–π^* of the C=N group and a ligand to Co(II) ion charge transfer ($L \rightarrow Co^{2+}$) as a result of complex formation. In addition, the electronic spectra of Co(II) complexes exhibit one additional band with λ_{max} (560, 570) nm, corresponding to the $^4A_2 \rightarrow {}^4T_1(p)$ transition of the Co(II) ion in tetrahedral geometry [13]. The Cu(II) complexes show four bands located at (270, 280), (390, 395), (450, 460)

Table 4. Electronic spectral and magnetic data for Schiff-base complexes.

		λ_{max} in DMF ($\varepsilon_{max} \times 10^4$ L mol^{-1} cm^{-1})					
No.	Complex	π–π^* aromatic ring	π–π^* C=N	CTL → M	d–d transition	d–d assignment	μ_{eff} (BM/M)
1	Co, L_{Ia}	290 (0.09)	400 (0.35)	480 (0.25)	560 (0.12)	$^4A_2 \rightarrow {}^4T_1(p)$	3.10
2	Ni, L_{Ia}	260 (0.08)	410 (0.37)	475 (0.31)	530 (0.07), 740 (0.06)	$^3A_{2g} \rightarrow {}^3T_{1g}(\nu_2)$ $^3A_{2g} \rightarrow {}^3T_{1g}(\nu_2)$	2.95
3	Cu, L_{Ia}	270 (0.11)	390 (0.42)	450 (0.37)	610 (0.15)	$^2B_{1g} \rightarrow {}^2E_g$	1.68
4	Zn, L_{Ia}	275 (0.07)	395 (0.30)	450 (0.21)			Diamagnetic
5	Cd, L_{Ia}	280 (0.08)	400 (0.33)	455 (0.22)			Diamagnetic
6	Co_2, L_{IIb}	300 (0.13)	410 (0.39)	485 (0.40)	570 (0.18)	$^4A_2 \rightarrow {}^4T_1(p)$	2.98
7	Ni_2, L_{IIb}	260 (0.15)	415 (0.44)	480 (0.43)	540 (0.13), 750 (0.11)	$^3A_{2g} \rightarrow {}^3T_{1g}(\nu_2)$ $^3A_{2g} \rightarrow {}^3T_{1g}(\nu_2)$	2.90
8	Cu_2, L_{IIb}	280 (0.16)	395 (0.49)	460 (0.51)	620 (0.23)	$^2B_{1g} \rightarrow {}^2E_g$	1.62
9	Zn_2, L_{IIb}	295 (0.13)	405 (0.41)	470 (0.33)			Diamagnetic
10	Cd_2, L_{IIb}	290 (0.11)	400 (0.39)	475 (0.27)			Diamagnetic

and (610, 620) nm. The first three bands were assigned to π–π^* transitions within organic molecules, π–π^* of the C=N group and a ligand to Cu(II) ion charge transfer ($L \rightarrow Cu^{2+}$) as a result of complex formation. The last band can be assigned to $^2B_{1g} \rightarrow {}^2E_g$ transition of the Cu(II) ion in tetragonally elongated octahedron or square planar geometry [13]. The electronic spectra of mono- and binuclear Ni(II) complexes have, in general, three bands with λ_{max} in the regions (260), (410, 415) and (475, 480) nm, respectively, which can be assigned to π–π^* transition within the organic molecule, π–π^* of the C=N group and a ligand to metal ion charge transfer ($L \rightarrow Ni^{2+}$) as a result of complex formation. The electronic spectra of these Ni(II) complexes also exhibit two additional bands with λ_{max} at (530, 540) and (740, 750) nm, which can be assigned to the $^3A_{2g} \rightarrow {}^3T_{1g}(\nu_1)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_2)$ transitions, respectively. This indicates octahedral geometry around the Ni(II) ion and is further supported by a ν_2/ν_1 ratio of (1.4, 1.39), which corresponds to an octahedral geometry [19].

The molar absorptivities (ε_{max}) of the complexes under investigation are listed in table 4. The transitions due to the ligands are characterized by their higher ε_{max} values, while those due to d–d transitions of the central transition metal ions are lower. The values of the molar absorptivities of the mononuclear complexes increase in the order $Cu > Co > Ni$; the same trends are observed for binuclear complexes but with higher ε_{max} values.

On the basis of elemental analysis, conductance, TGA and IR spectral data, tetrahedral geometry is proposed for the Zn(II) and Cd(II) complexes.

3.5 *Magnetic properties*

Magnetic moment data for Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes at room temperature are given in table 4. Values of μ_{eff} showed that Zn(II) and Cd(II) are diamagnetic. The effective magnetic moments (1.68 and 3.1 BM) of the mononuclear Cu(II) and Co(II) complexes are fairly close to those observed for complexes with one unpaired electron, confirming tetrahedral geometry of Co(II) complexes and square-planar geometry of Cu(II) complexes [20], in good agreement with the results obtained from the electronic spectra. The value of the magnetic moment of the mononuclear Ni(II) complexes is 2.95 BM, corresponding to the d^8 spin-only value for an octahedral environment [21], in agreement with the results obtained from the electronic spectra. The magnetic moment values for the binuclear complexes are slightly lower than the moment expected, perhaps due to antiferromagnetic exchange interaction between the metal ions of the crystal, suggesting the possibility of spin-coupled system [22,23], or possibly due to intermolecular interaction.

3.6 *EPR spectra*

An X-band EPR spectrum of Complex **8** was measured in the solid state at room temperature (300 K) (see figure 1) to confirm the nature of the coordination around the Cu(II) ion. Complex **8** shows an intense broad band with $g_{eff} = 2.03$. The value of the g_{eff} and the shape of EPR signal of the Cu(II) complex suggest square-planar coordination around the Cu(II) ion [22]. Generally the complex under investigation is not magnetically dilute and therefore exchange [24] and/or dipole

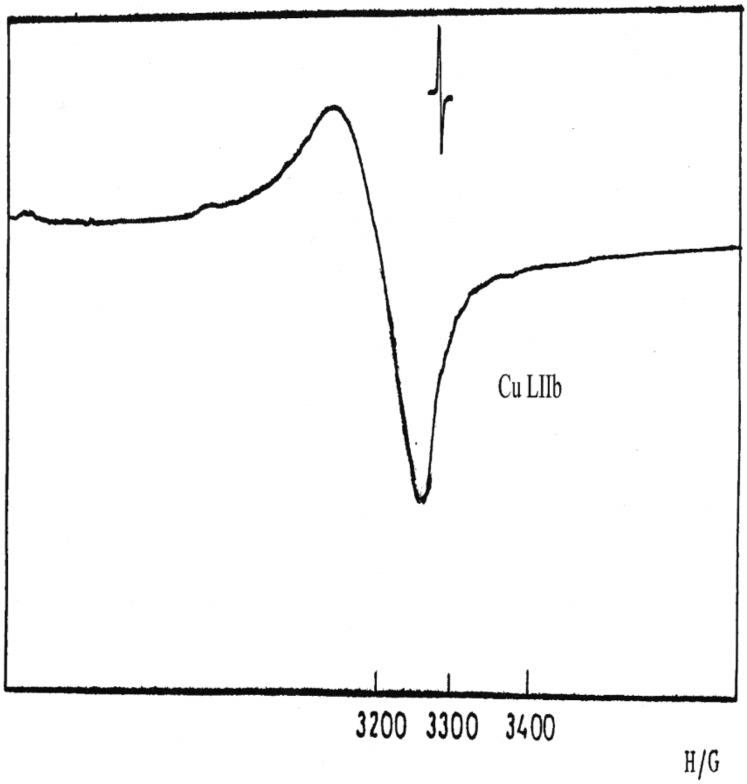


Figure 1. X-band EPR spectrum of Cu L_{IIb} complex at room temperature.

forces are expected to operate. Exchange is indicated by lack of hyperfine structure. According to Fidone and Stevens [25], the positive contribution in the g_{eff} value over the free electron (2.0023) indicates an increase in the covalent nature of the bonding between the Cu(II) ion and the ligand. The EPR spectral data show a covalent link between Cu(II) and the Schiff base in the square-planar complex.

3.7 *Fungicidal studies*

The growth method [26] was used for evaluating the fungitoxic effect against *Curvularia lunata* at different concentrations using Czpek's agar medium. Percentage inhibition [27] was calculated (after 168 h).

Fungicidal screening data are shown in table 5, revealing that all the Schiff bases and their metal complexes were highly active against the fungus. The metal complexes were more active than their corresponding ligands, confirming that chelation of metal to the ligand increases the toxicity of the compound [3]. The fungicidal activity shows a gradual change with change of the metal ion in the complexes in the order Cu(II) > Ni(II) > Co(II) > Cd(II) > Zn(II). Thus the Cu(II) complexes showed maximum fungitoxicity. In general, the mononuclear Schiff-base complexes were found to be less toxic than the binuclear complexes.

Table 5. Fungicidal data for Schiff bases and metal complexes.

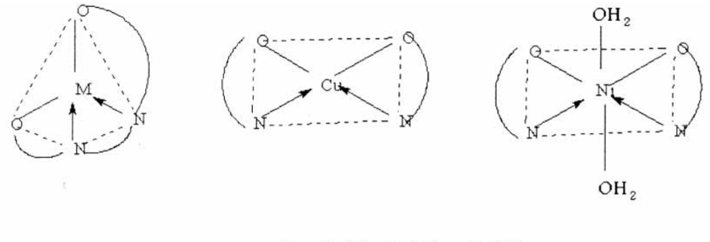
	Average percentage inhibition of Curvularia lunata[a]		
Compound	100 ppm	50 ppm	20 ppm
L_{Ia}	28.56 ± 0.16	18.10 ± 0.13	9.85 ± 0.14
Co, L_{Ia}	30.95 ± 0.32	18.64 ± 0.11	9.88 ± 0.23
Ni, L_{Ia}	31.62 ± 0.40	19.25 ± 0.24	10.46 ± 0.19
Cu, L_{Ia}	32.24 ± 0.22	19.98 ± 0.12	11.72 ± 0.15
Zn, L_{Ia}	30.42 ± 0.25	18.20 ± 0.16	8.98 ± 0.30
Cd, L_{Ia}	30.44 ± 0.21	18.76 ± 0.21	9.22 ± 0.12
L_{IIb}	37.02 ± 0.24	23.24 ± 0.12	12.95 ± 0.19
Co, L_{IIb}	38.12 ± 0.12	24.22 ± 0.13	13.24 ± 0.11
Ni, L_{IIb}	38.40 ± 0.31	25.87 ± 0.23	13.78 ± 0.37
Cu, L_{IIb}	39.95 ± 0.18	26.02 ± 0.14	14.12 ± 0.13
Zn, L_{IIb}	37.46 ± 0.28	24.46 ± 0.10	12.12 ± 0.12
Cd, L_{IIb}	37.82 ± 0.11	24.97 ± 0.32	12.81 ± 0.19

[a] Values are means of three experiments (±SD).

4. Conclusion

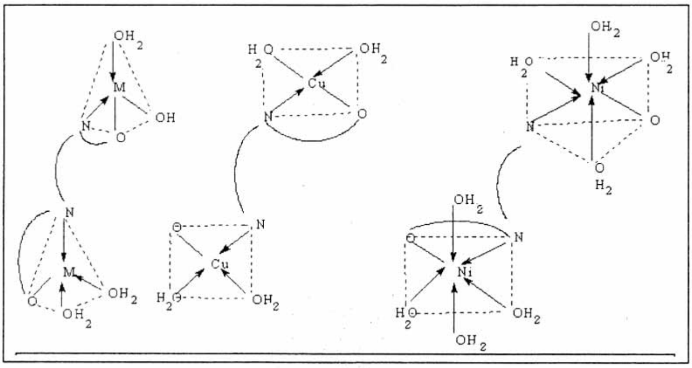
Based on the above results, the structure of the complexes under investigation can be formulated as follows:

(i) Structure of metal complexes of Schiff's base (Ia)



M = Co(II) , Zn(II) or Cd(II)

(ii) Structure of metal complexes of Schiff's base (IIb)



(LIIb) M = Co(II), Zn(II) or Cd(II)

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