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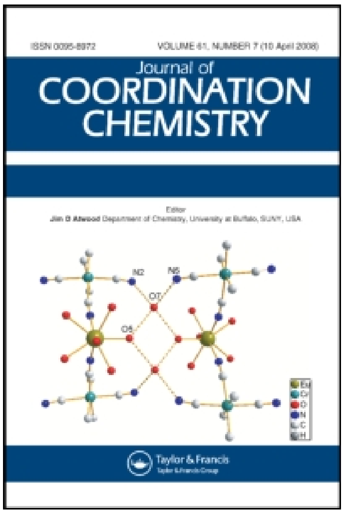

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Structural and Antimicrobial Studies of Some Divalent Transition Metal Complexes with Some New Symmetrical Bis (7-Formylanil Substituted-Sulfoxine) Schiff Base Ligands

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STRUCTURAL AND ANTIMICROBIAL STUDIES OF SOME DIVALENT TRANSITION METAL COMPLEXES WITH SOME NEW SYMMETRICAL BIS (7-FORMYLANIL SUBSTITUTED-SULFOXINE) SCHIFF BASE LIGANDS

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Symmetrical bis (7-formyanil substituted-8-hydroxyquinoline-5-sulfonic acid), Schiff bases, react with Co(II), Ni(II) and Cu(II) ions to give M_nL ($n = 1, 2$) complexes as established by conductometric titration in 1 : 1 DMF : H_2O. The complexes were identified by elemental analyses, molecular weight determination, thermal analysis, infrared, magnetic moments, electronic absorption, and electron spin resonance spectra.

The suggested general geometry for these complexes may have a tetrahedral crystal structure and the general formula is $[M_2L(OH_2)_4]$, where M(II) = Co, Ni and Cu and $L = 7\text{—X—}H_2L$ (—X— = dimethyl, *p*-phenyl, *o*-phenyl), while for the, trimethyl, ligand the tetrahedral crystal structure has the general formula $[M_2L(OH_2)_2]$.

Antimicrobial activity of these ligands and their transition metal complexes has been investigated on some common fungi and bacteria. A considerable increase in the biocide activity of these ligands has been observed on coordination with transition metal ions, therefore, these complexes can be used in the chemotherapy of candidiaces and other fungal skin diseases.

Keywords: Transition metal; Candidiaces; Fungal; Schiff base; Microbial

INTRODUCTION

Schiff-base complexes have received much attention as biomimic model compounds [1]. The [Fe(salen)] complex is a model for the natural iron

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protein, hemerythrin, and has the ability to bind molecular oxygen reversibly [2]. Schiff-base complexes incorporating two similar or different metal ions are of special interest. They are similar to those found in living organisms, *e.g.*, enzymes and proteins, and develop their activity in the presence of two or more metal ions [3, 4]. These complexes are also useful in catalysis [5]. The chemistry of quinoline and its derivatives has attracted special attention due to its therapeutic properties *e.g.*, quinoline sulfonamides have been used to treat cancer [6], and malaria [7]. Some drugs, when administered as metal complexes show increased activity as compared to the ligand involved [8]. Metal complexes of 7-formyl-8-hydroxquinoline (FHQ) have been prepared and characterized [9]. A series of mixed ligand complexes of the type [ML_2] and [MLL^*], [M = Cu(II), L = Schiff base derived from 2-hydroxy-propiophenone and L^* = Schiff base derived from salicylaldehyde or 2-hydroxy-naphthaldehyde] were prepared by Jani *et al.* [10]. Issa and coworker [11, 12] prepared a series of potentially tetradentate Schiff bases containing a tetrahedral N_2O_2 donor ligand. The effect of substituent groups on the thermal stability and volatility of fifteen-tetradentate β-ketoneamines and various metal ions was studied by Dilli *et al.* [13].

The object of the present study is to systematically investigate the complexes formed by reacting transition metal ions with a new series of symmetrical Schiff-base ligands. Thus 7-formyl-8-hydroxyquinoline-5-sulfonic acid, *i.e.*, 7-formyl-sulfoxine (FHQS), was reacted with ethylenediamines, 1,3-propylenediamines, *p*-phenylenediamines, and *o*-phenylenediamines in ratio 1 : 2 (diamine : aldehyde) was investigated. Further insight into the bonding and possible geometrical structure was made by conductometric titration, elemental analyses, molecular weight determination, thermal analysis, infrared, magnetic moment measurements, electronic absorption, and electron spin resonance of the metal complexes. The microbial activity of the above ligands and their metal complexes towards some common bacteria and fungi was investigated.

EXPERIMENTAL

Materials

Cobalt(II), nickel(II), and copper(II) perchlorates (AR grade) were dissolved in carbonate-free, doubly distilled water. Formylation of 8-hydroxyquinoline-5-sulfonic acid was carried out according to the method of Sein *et al.* [14], and the symmetrical Schiff-base ligands were prepared according to Diehi *et al.* [15]. Solid complexes were prepared as follows: 1 mL of 4×10^{-3} M NaOH solution was added to 10^{-3} M of the ligand dissolved in 10 mL of ethanol to convert it to the ionic form. After stirring for 30 minutes, 2×10^{-3} M solution of the metal salt were added. The reaction mixture was stirred for about 1 hour at room temperature, during that time the solid complex precipitated. It was filtered off, washed several times with water then with a small amount of ethanol and diethyl ether, and then dried under vacuum. (Yield ca. 80–92%). Elemental analyses of C, N, H and S were made using a Perkin-Elmer 2400 CHNS Analyzer at the Microchemical Analysis Center, Ain Shams University, Cairo, Egypt. The metal ion content was estimated by complexo-metric titration after destruction of the complex in the conventional manner [16].

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Physical Measurements

The **molecular weights** of metal complexes were determined by freezing point depression using H_2O as a solvent [17]. **Magnetic susceptibility** measurements were carried out at 25 ± 0.2°C by Gouy's method using a magnetic susceptibility balance [Johnson Matthew Alfa Product, Model No. MKI], with $Hg[Co(SCN)_4]$ as calibrant. The values were corrected for diamagnetism by applying Pascal's constants. **Conductometric titrations** were carried out in duplicate at 25.0 ± 0.2°C using a YSI model 32 M conductometer [Yellow Spring Co., USA]. The measured range was from 0.0 to 200.0 microsiemens with maximum errors ± 0.2%. A Model YSI 3417 cell was used with a cell constant K = 100/m. This bridge has a limiting accuracy of $\pm 0.1 \times 10^{-6}\,\mathrm{Ohm}^{-1}$. **Thermal studies** of the metal complexes were made using a TGA-50 derivatograph [Shimadzu Corp., Japan]. Measurements were taken at sensitivity ± 1% of each range for the ± 20-mg sample under nitrogen atmosphere to 1000.0°C at a heating rate 10.0°C min^{-1}. **The ESR spectra** were recorded on the JE01 microwave unit, JES-FE2XG spectrometer at the Central Laboratories, Tanta University, Egypt. The magnetic field was calibrated with 2,2-diphenyl-1-picrylhydrazyl [Aldrich]. The **infrared spectra** were recorded using a MATTSON 1000 FT-IR spectrometer (4000–400 cm^{-1}) with (KBr disc technique) at room temperature. The infrared absorption spectrum of 7-formyl-8-hydroxyquinoline-5-sulfonic acid (FHQS) was assigned by careful comparison with 8-hydroxyquinoline-5-sulfonic acid, and showed bands at 3100, 1625, 1605, 1585, 1570 cm^{-1} assigned to $\nu_{(OH)}$, $\nu_{(C{=}O)}$ free, $\nu_{(C{=}O)}$ bonded, $\nu_{(C{=}N)}$ free,

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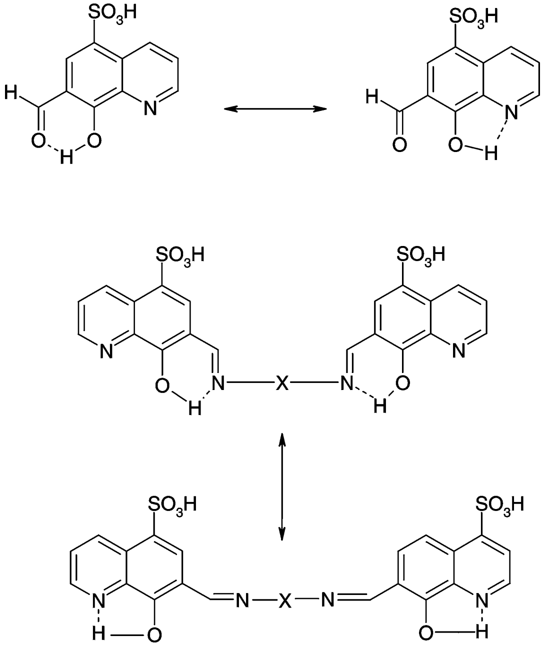
and $\nu_{(C{=}N)}$ bonded. The weak band at 3090 and 3000 cm^{-1} may be due to O···H—O and O—H···N stretching vibrations [18]. Other bands such as $\nu_{4(C{-}S)}$ showed in the region 770 cm^{-1} and $\nu_{1(C{-}S)}$ in the region 840 cm^{-1} for $—SO_3^-$ groups. The infrared absorption spectra of symmetrical Schiff base ligands under investigation:

Bis (7-formyanil-8-hydroxyquinoline-5-sulfo-dimethylenyl), (BFHQSD),
Bis (7-formyanil-8-hydroxyquinoline-5-sulfo-trimethylenyl), (BFHQST),
Bis (7-formyanil-8-hydroxyquinoline-5-sulfo-*p*-phenylene), (BFHQS-*p*-Ph) and
Bis (7-formyanil-8-hydroxyquinoline-5-sulfo-*o*-phenylene), (BFHQS-*o*-Ph), (Tab. I).

The band assignments of the important infrared absorption bands were carried out by applying a method similar to that suggested by Looker [19]. The ^{1}**H NMR spectra** were obtained using a Spectrospin Brucker AC 200 MHz NMR spectrometer. The samples were prepared by dissolution in DMSO (d^6), the chemical shifts were reported with respect to TMS ($\delta = 0.00$ ppm). The ^{1}H NMR spectra of the symmetrical Schiff bases, (BFHQSD) and (BFHQST) show a signal at (8.75 – 8.85) ppm, which can be assigned to the proton of the phenolic —OH group with integration, equivalent to one proton. The compounds show a group of signals corresponding to the aromatic and hetero aromatic protons at (7.28 – 7.45) ppm and (8.15 – 8.25) ppm, respectively. Also, the spectra contain one signal at 3.12 ppm and at 3.57 ppm with integration equivalent to 4H, due to $—CH_2N—$. The ligands show a hydrogen bond at 10.35 ppm and at 10.90 ppm respectively. This can be attributed to the formation of an intramolecular hydrogen bond between the quinoline ring in (FHQS) or the azomethine group of (BFHQSD) and (DBFHQST) with —OH group, the assignments of the main signals in the ^{1}H NMR spectra of both ligands (defined in Scheme 1) are given in Table II.

TABLE I Frequencies and band assignments for various symmetrical Schiff-base ligands (cm^{-1})

Ligand	$\nu_{(O{-}H)}$ *bonded phenolic*	$\nu_{(C{-}H)}$ *aliphatic*	$\nu_{(C{=}N)}$ *free*	$\nu_{(C{=}N)}$ *bonded*	$\nu_{(C{=}N)}$ *aromatic*	$\nu_{(C{-}N)}$	$\nu_{1(C{-}S)}$ $(—SO_3^-)$	$\nu_{4(C{-}S)}$ $(—SO_3^-)$	$\nu_{(C{-}H)}$ *aromatic*
BFHQSD	3220	2310	1620	1605	1580	1225	840	770	750
BFHQST	3235	2305	1625	1610	1582	1228	843	772	745
BFHQS-*p*-ph	3215	2300	1615	1603	1575	1220	845	775	740
BFHQS-*o*-ph	3195	2303	1618	1605	1580	1225	840	773	743



Where: X = $(CH_2)_2$ (BFHQSD)
$(CH_2)_3$ (BFHQST)
(-p-ph-) (BFHQS-p-ph)
(-o-ph-) (BFHQS-o-ph)

SCHEME 1

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TABLE II The main ^1H NMR signals of some Schiff base ligands in DMSO (d^6)

Ligand	δ_{CH_2N} *azomethine*	$\delta_{C\text{—}H}$ *aromatic*	$\delta_{C\text{—}H}$ *hetero*	δ_{OH} *phenolic*	$\delta_{O\cdots H\text{—}O}$ *H-bonded*
BFHQSD	3.12	7.45	8.15	8.75	10.35
BFHQST	3.57	7.28	8.25	8.85	10.90

RESULTS AND DISCUSSION

Studies of Schiff Base Transition Metal Complexes in Solution

In the 1950's and 60's many conductance experiments were developed [20–22], but few conductometric titrations of metal chelates in non-aqueous media [23], with 8-hydroxyquinoline as ligand [24] are found in the literature. In the present investigation the disodium salt of (BFHQSD),

$[Na_2^+(H_2L)^{2-}]$ ligand, was used as a chelating agent for the conductometric determination of the molar ratio of ligand to the three divalent metal ions under investigation. The titration was carried out in 1:1 dimethylformamide: water. The conductometric titration of 10^{-3} M (metal perchlorate salt, where M(II) = Co, Ni and Cu) with 10^{-2} M ligand $[Na_2^+(H_2L)^{2-}]$ show a break in the conductance curve at a M : L ratio of 2 : 1. The reaction can be represented by the following equation, where the electrically neutral transition metal complex is formed $[M_2L(OH_2)_4]$:

$$2[M^{2+}(ClO_4^-)_2] + [Na_2^+(H_2L)^{2-}] \longrightarrow 2[H-(\text{solvated})]^+ + [M_2L(OH_2)_4] + 2Na^+ + 4ClO_4^-$$

The second break was observed at a M : L ratio 1 : 1. The reaction may be represented by the following equation, where the negatively charged transition metal complex is formed $[ML(OH_2)_2]^{2-}$:

$$M^{2+}(ClO_4^-)_2] + [Na_2^+(H_2L)^{2-}] \longrightarrow 2[H-(\text{solvated})]^+ + [ML(OH_2)_2]^{2-} + 2Na^+ + 2ClO_4^-$$

These two complexes were found for all metal ions used, where the (BFHQSD) ligand exhibits breaks at (2 : 1) and (1 : 1) [M : L].

The conductance values slightly increase after the equivalence point due to the partial dissociation of the ligand solution added.

$$[Na_2^+(H_2L)^{2-}] \longrightarrow [H-(\text{solvated})]^+ + 2Na^+ + [HL]^{3-}$$

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Studies of the Solid Schiff Base Transition Metal Complexes

Elemental analyses of the synthesized solid complexes are given in Table III, where the composition of the solid complexes produced from the symmetrical Schiff bases, (BFHQSD), (BFHQST), (BFHQS-*p*-Ph), (BFHQS-*o*-Ph), with Co(II), Ni(II) and Cu(II) metal ions can be represented by the general formula:

$[M_2L(OH_2)_4]$, L = 7—X—H_2L, (—X— = $(CH_2)_2$, *p*-C_6H_4, *o*-C_6H_4), while for the, $(CH_2)_3$, ligand the general formula $[M_2L(OH_2)_2]$. The results of analyses indicate that the stoichiometry of the solid complexes isolated under the prevailing experimental conditions are of the (2 : 1) [M : L] type, with the formation of electrically neutral binuclear complexes in which the Schiff base ligands behave as tetradentate donors (N_2O_2) towards the two metal ions. These results support the data of the conductometric titration

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TABLE III Molecular weight, analytical data, melting points, magnetic moments and percentage yield for different Schiff base ligands and their transition metal complexes

Ligand/complex		*Elemental analysis found (Calcd.)%*					*M.p.*	μ_{eff}	*ESR*	*Yield*
M. wt. found (calcd.)	*Color*	*C*	*H*	*N*	*S*	M^{2+}	(°*C*)	(*B.M*)	g_{eff}	(%)
[BFHQSD] 533.0 (530.0)	Buff	49.9 (49.8)	3.4 (3.4)	10.6 (10.6)	12.1 (12.1)	–	190	–	–	83
$[Co_2(BFHQSD)(OH_2)_4]$ 720.0 (716.0)	Red–Brown	36.9 (36.9)	3.1 (3.1)	7.9 (7.8)	9.0 (8.9)	16.5 (16.5)	> 210 dec.	3.50	1.85	80
$[Ni_2(BFHQSD)(OH_2)_4]$ 721.0 (716.0)	Green	36.9 (36.9)	3.1 (3.1)	7.9 (7.8)	9.0 (8.9)	16.5 (16.5)	> 205 dec.	2.85	–	85
$[Cu_2(BFHQSD)(OH_2)_4]$ 730.0 (725.0)	Brown	36.4 (36.4)	2.8 (2.8)	7.8 (7.7)	8.9 (8.8)	17.6 (17.5)	> 200 dec.	1.65	1.95	88
[BFHQST] 548.0 (544.0)	Brown	50.8 (50.7)	3.7 (3.7)	10.3 (10.3)	11.8 (11.8)	–	195	–	–	82
$[Co_2(BFHQST)(OH_2)_2]$ 700.0 (694.0)	Red–Brown	38.1 (38.0)	2.6 (2.6)	8.1 (8.1)	9.3 (9.2)	16.9 (16.9)	> 200 dec.	3.52	1.84	90
$[Ni_2(BFHQST)(OH_2)_2]$ 701.0 (696.0)	Pale brown	38.1 (38.1)	2.6 (2.6)	8.1 (8.1)	9.3 (9.2)	17.0 (17.0)	> 200 dec.	2.87	–	92
$[Cu_2(BFHQST)(OH_2)_2]$ 708.0 (703.0)	Brown	37.6 (37.6)	2.4 (2.4)	8.0 (8.0)	9.1 (9.1)	18.1 (18.1)	> 195 dec.	1.67	1.92	88
[BFHQS-*o*-Ph] 580.0 (578.0)	Buff	54.0 (54.0)	3.2 (3.1)	9.8 (9.7)	11.1 (11.1)	–	198	–	–	94
$[Co_2(BFHQS\text{-}o\text{-}Ph)(OH_2)_4]$ 770.0 (764.0)	Orange	40.9 (40.8)	2.4 (2.4)	7.3 (7.3)	8.4 (8.4)	15.4 (15.4)	> 210 dec.	3.55	1.82	90
$[Ni_2(BFHQS\text{-}o\text{-}Ph)(OH_2)_4]$ 771.0 (764.0)	Pale brown	 (40.8)	2.4 (2.4)	7.4 (7.3)	8.4 (8.4)	15.5 (15.5)	> 215 dec.	2.88	–	88
$[Cu_2(BFHQS\text{-}o\text{-}Ph)(OH_2)_4]$ 778.0 (773.0)	Brown	40.4 (40.5)	2.4 (2.3)	7.3 (7.2)	8.3 (8.3)	16.5 (16.4)	> 220 dec.	1.70	1.90	85
[BFHQS-*p*-Ph] 582.0 (578.0)	Pale brown	54.0 (54.0)	3.2 (3.1)	9.7 (9.7)	11.0 (11.1)	–	195	–	–	87

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TABLE III (Continued)

Ligand/complex		*Elemental analysis found (Calcd.)%*					*M.p.*	μ_{eff}	*ESR*	*Yield*
M. wt. found (calcd.)	*Color*	*C*	*H*	*N*	*S*	M^{2+}	(°*C*)	(*B.M*)	g_{eff}	(%)
[Co_2(BFHQS-*p*-Ph)$(OH_2)_4$] 768.0 (764.0)	Brown	40.8 (40.8)	2.3 (2.4)	7.3 (7.3)	8.4 (8.4)	15.4 (15.4)	> 205 dec.	3.60	1.81	88
[Ni_2(BFHQS-*p*-Ph)$(OH_2)_4$] 770.0 (764.0)	Brown	40.9 (40.8)	2.4 (2.4)	7.4 (7.3)	8.4 (8.4)	15.5 (15.5)	> 210 dec.	2.95	–	88
[Cu_2(BFHQS-*p*-Ph)$(OH_2)_4$] 777.0 (773.0)	Green – Brown	40.3 (40.4)	2.3 (2.3)	7.2 (7.2)	8.2 (8.3)	16.4 (16.4)	> 215 dec.	1.75	1.88	88

and suggest that complex formation takes place through proton displacement from the phenolic —OH of quinoline and from the lone pair electrons from —N= of the azomethine part of the ligands under investigation.

Thermogravimetric analysis (TGA) of the complexes $[M_2L(OH_2)_4]$, where L = (BFHQSD), M(II) = Co, Ni and Cu, and the pyrolysis steps are given in Table IV. Water and metal oxide contents agree with the data obtained from elemental analyses; water eliminated above 120°C is coordinated water. The complexes decompose in three steps, where the ligand fragmentation has the sequence: sulfonic acid groups, $(—CH{=}N—CH_2—)_2$ fragments, followed by quinoline fragments at the temperature range (200 – 470°C). The decomposition of the whole complex takes place to form the metal oxide at temperatures above 470°C. The thermal stability of the three complexes is in the order Cu > Ni > Co, following the increasing ionic character of the M—O and M—N bonds, which leads to an increase in the thermal stability of the complexes from copper to cobalt [25].

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Infrared spectra (FTIR) and band assignments of the twelve complexes under investigation are given in Table V. The infrared absorption spectra of the solid complexes, in comparison to the free ligands indicates: (1) the infrared spectra of all solid metal complexes under investigation exhibit a broad band around ($3300 - 3410\,cm^{-1}$) which is attributed to $\nu_{(OH)}$ of water associated with complex formation. (2) The new bands observed in the regions ($930 - 950\,cm^{-1}$) and ($630 - 650\,cm^{-1}$) which were absent in the spectra of the free ligands are attributed to $\rho_r(OH_2)$ and $\rho_w(OH_2)$ of the coordinated water molecules. (3) The infrared spectra of $[M_2L(OH_2)_2]$ complexes, where L = (BFHQST) and M(II) = Co, Ni, Cu, show a weak band at ($850 - 860\,cm^{-1}$) which may be assigned to $\nu_{(M—O—M)}(OH_2)$, *i.e.*, out of plane deformation of water molecules acting as bridges between two metal atoms [26]. (4) Other bands such as $\nu_{4(C—S)}$ show a blue shift in the region $730\,cm^{-1}$ and a red shift for $\nu_{1(C—S)}$ in the $820\,cm^{-1}$ region, this is attributed to the effect of complexation on the molecule, although the $—SO_3^-$ group does not take part. (5) The bands at ($1615 - 1625\,cm^{-1}$) corresponding to azomethine, $\nu_{C{=}N}$ of the free ligands shift to lower frequency on complex formation by ($5 - 10\,cm^{-1}$) showing that the nitrogen atom contributes to coordination in all complexes under investigation. (6) New bands in the infrared spectra of all complexes at ($495 - 520\,cm^{-1}$) and at ($470 - 480\,cm^{-1}$) are assigned to $\nu_{M—O}$ and $\nu_{M—N}$, respectively. (7) The $\nu_{C{=}N}$ aromatic of the quinoline ring which is located at ($1575 - 1582\,cm^{-1}$) in the infrared spectra of all ligands under investigation still lies at the same position in the infrared spectra of the metal complexes. This indicates that the $—HC{=}N—CH_2—$ group of the aromatic ring is not involved in complex formation.

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TABLE IV Thermal analysis (TGA) for $[M_2L(OH_2)_4]$ Schiff base transition metal complexes, where, L = (BFHQSD) and M(II) = Co, Ni and Cu

Complex	*M. wt calcd.*	*Temp. range (°C)*	*% Total loss*	*% Difference loss found (calcd.)*	*Representation*	*Assignment*
$[Cu_2(BFHQSD)(OH_2)_4]$	725.0	120 – 200	10.0	10.0 (9.9)	$4H_2O$	Coordinated water molecules
		200 – 240	32.1	22.1 (22.0)	$2{-}SO_3^-$	Sulphonic acid groups
		240 – 350	43.3	11.2 (11.3)	$(-CH{=}N-CH_2-)_2$	$C_4H_6N_2$ fragments
		350 – 470	77.9	34.6 (34.8)	$(-C_9H_4N-)_2$	Quinoline fragments
		470 – 600	**99.7**	21.8 (21.9)	**2CuO**	**Copper(II) oxide**
			(100.0)			
$[Ni_2(BFHQSD)(OH_2)_4]$	716.0	130 – 220	10.0	10.0 (10.0)	$4H_2O$	Coordinated water molecules
		220 – 250	32.1	22.1 (22.3)	$2{-}SO_3^-$	Sulphonic acid groups
		250 – 385	43.5	11.4 (11.5)	$(-CH{=}N-CH_2-)_2$	$C_4H_6N_2$ fragments
		385 – 455	78.9	35.4 (35.3)	$(-C_9H_4N-)_2$	Quinoline fragments
		455 – 600	**99.9**	21.0 (20.9)	**2NiO**	**Nickel(II) oxide**
			(100.0)			
$[Co_2(BFHQSD)(OH_2)_4]$	716.0	135 – 265	10.1	10.00 (10.0)	$4H_2O$	Coordinated water molecules
		265 – 290	32.2	22.1 (22.3)	$2{-}SO_3^-$	Sulphonic acid groups
		290 – 400	43.7	11.5 (11.4)	$(-CH{=}N-CH_2-)_2$	$C_4H_6N_2$ fragments
		400 – 430	79.1	35.4 (35.3)	$(-C_9H_4N-)_2$	Quinoline fragments
		430 – 600	**99.8**	20.7 (21.0)	**2CoO**	**Cobalt(II) oxide**
			(100.0)			

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TABLE V Frequencies and band assignments for symmetrical Schiff base transition metal complexes (cm^{-1})

Complex	$\nu_{(O-H)}$ (H_2O)	$\nu_{(C=N)}$ *azomethine*	$\nu_{(C=N)}$ *aromatic*	ρ_r H_2O	$\nu_{4(C-S)}$ $(-SO_3^-)$	$\nu_{1(C-S)}$ $(-SO_3^-)$	$\nu_{(M-O-M)}$ $H\ H$	ρ_w (H_2O)	$\nu_{(M-O)}$	$\nu_{(M-N)}$
$[Co_2(BFHQSD)(OH_2)_4]$	3300	1610	1580	940	730	830	–	630	500	460
$[Ni_2(BFHQSD)(OH_2)_4]$	3405	1615	1580	930	732	825	–	635	510	470
$[Cu_2(BFHQSD)(OH_2)_4]$	3410	1620	1580	935	735	820	–	640	520	480
$[Co_2(BFHQST)(OH_2)_2]$	3350	1610	1582	–	730	828	850	645	505	470
$[Ni_2(BFHQST)(OH_2)_2]$	3370	1615	1582	–	735	825	855	647	510	475
$[Cu_2(BFHQST)(OH_2)_2]$	3400	1620	1582	–	740	820	860	649	513	478
$[Co_2(BFHQS\text{-}o\text{-}Ph)(OH_2)_4]$	3390	1610	1580	950	740	840	–	635	500	472
$[Ni_2(BFHQS\text{-}o\text{-}Ph)(OH_2)_4]$	3400	1612	1580	945	738	836	–	640	508	475
$[Cu_2(BFHQS\text{-}o\text{-}Ph)(OH_2)_4]$	3410	1615	1580	940	735	835	–	642	510	480
$[Co_2(BFHQS\text{-}p\text{-}Ph)(OH_2)_4]$	3350	1615	1575	940	735	835	–	650	495	470
$[Ni_2(BFHQS\text{-}p\text{-}Ph)(OH_2)_4]$	3380	1618	1575	935	730	830	–	645	500	475
$[Cu_2(BFHQS\text{-}p\text{-}Ph)(OH_2)_4]$	3400	1620	1575	930	725	825	–	640	505	480

The Geometry of the Schiff-base Metal Complexes

Magnetic moments (μ_{eff}) of the complexes were calculated from the corrected magnetic susceptibility measurements (Tab. III). The magnetic moment values of the binuclear cobalt(II) complexes, [d^7], are (3.50 – 3.60) μ_B, the binuclear nickel(II) complexes, [d^8], are (2.85 – 2.95) μ_B, and the binuclear copper(II) complexes, [d^9], are (1.65 – 1.75) μ_B. These values are slightly lower than the proper spin only values for a tetrahedral structure, perhaps due to the presence of two adjacent metal ions in the binuclear complex and subsequent antiferromagnetic exchange between the two neighboring M(II) ions [27].

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Electronic absorption spectra (UV/Visible) of the investigated complexes are measured in DMF solution, Table VI. The electronic spectra of (d^7) cobalt(II) complexes of symmetrical Schiff base ligands exhibit five bands having $\lambda_{\max}$ within the ranges (270 – 285), (408 – 415), (480 – 485), (585 – 590) and (635 – 638) nm, and $\varepsilon_{\max}$ at (0.03 – 0.08), (0.14 – 0.34), (0.12 – 0.18), (0.08 – 0.15) and (0.06 – 0.15) $\text{dm}^{-3}\,\text{mole}^{-1}\,\text{cm}^{-1}$, respectively. The first three bands are assigned to the $\pi-\pi^*$ transition within the organic molecules, the $\pi-\pi^*$ of —C=N—, and a ligand to metal ion charge transfer band (L→Co) as a result of complex formation [28]. The last two bands represent one transition split to two broad bands and assigned to the $^4A_2 \rightarrow {}^4T_1(P)$ transition which indicates tetrahedral geometry of the ligated group around Co(II).

The electronic spectra of (d^8) nickel(II) complexes of symmetrical Schiff base ligands exhibit four bands having $\lambda_{\max}$ within the ranges (275 – 300), (408 – 410), (482 – 485) and (628 – 640) nm and $\varepsilon_{\max}$ at (0.07 – 0.13), (0.30 – 0.40), (0.13 – 0.22) and (0.07 – 0.14) $\text{dm}^{-3}\,\text{mole}^{-1}\,\text{cm}^{-1}$ respectively. The first three bands are assigned to the $\pi-\pi^*$ transition within the organic molecules, the $\pi-\pi^*$ of —C=N—, and a ligand to metal ion charge transfer band (L→Ni) as a result of complex formation [28]. The last broad and is assigned to the $^3T_1 \rightarrow {}^3T_1(P)$ transition which indicates tetrahedral geometry of the ligated group around Ni(II).

The electronic spectra of (d^9) copper(II) complexes of symmetrical Schiff base ligands exhibit four bands having $\lambda_{\max}$ within the ranges (410 – 415), (480 – 490), (620 – 625) and (710 – 715) nm and $\varepsilon_{\max}$ at (0.10 – 0.16), (0.07 – 0.14), (0.03 – 0.08) and (0.02 – 0.05) dm^{-3} mole^{-1} cm^{-1}, respectively. The first two bands are assigned to the $\pi-\pi^*$ of —C=N—, and a ligand to metal ion charge transfer band (L→Cu) as a result of complex formation [28]. The last two band are assigned to the $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions in the energy level diagram of Cu(II), showing highly distorted octahedral arrangements through tetragonal elongation, which finally leads to a situation

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TABLE VI Electronic absorption spectra for various symmetrical Schiff base transition metal complexes in DMF solvent (5×10^{-4} M)

		$\lambda_{max}(nm)$						*Band assignment due to d–d transition*					
Complex	*Color*	$\pi-\pi^*$ *aromatic*	ε $mol^{-1}cm^{-1}$	$\pi-\pi^*$ —C═N—	ε $mol^{-1}cm^{-1}$	*C.T* $L \rightarrow M$	ε $mol^{-1}cm^{-1}$	λ_{max} *nm*	ε $mol^{-1}cm^{-1}$	*d–d transition*	λ_{max} *nm*	ε $mol^{-1}cm^{-1}$	*d–d transition*
$[Co_2(BFHQSD)(OH_2)_4]$	Red–Brown	270	0.08	415	0.30	485	0.15	590	0.12	$^4A_2 \rightarrow {}^4T_1(P)$	638	0.12	$^4A_2 \rightarrow {}^4T_1(P)$
$[Co_2(BFHQST)(OH_2)_2]$	Red–Brown	280	0.07	410	0.32	482	0.16	585	0.11	$^4A_2 \rightarrow {}^4T_1(P)$	635	0.10	$^4A_2 \rightarrow {}^4T_1(P)$
$[Co_2(BFHQS\text{-}o\text{-}Ph)(OH_2)_4]$	Orange	285	0.08	408	0.34	480	0.18	585	0.15	$^4A_2 \rightarrow {}^4T_1(P)$	636	0.15	$^4A_2 \rightarrow {}^4T_1(P)$
$[Co_2(BFHQS\text{-}p\text{-}Ph)(OH_2)_4]$	Brown	285	0.03	408	0.14	480	0.12	585	0.08	$^4A_2 \rightarrow {}^4T_1(P)$	636	0.08	$^4A_2 \rightarrow {}^4T_1(P)$
$[Ni_2(BFHQSD)(OH_2)_4]$	Green	275	0.10	410	0.37	485	0.22	640	0.13	$^3T_1 \rightarrow {}^3T_1(P)$	–	–	–
$[Ni_2(BFHQST)(OH_2)_2]$	Pale brown	295	0.07	410	0.30	483	0.13	635	0.07	$^3T_1 \rightarrow {}^3T_1(P)$	–	–	–
$[Ni_2(BFHQS\text{-}o\text{-}Ph)(OH_2)_4]$	Pale brown	300	0.12	408	0.38	482	0.16	628	0.11	$^3T_1 \rightarrow {}^3T_1(P)$	–	–	–
$[Ni_2(BFHQS\text{-}p\text{-}Ph)(OH_2)_4]$	Brown	300	0.13	408	0.40	482	0.20	628	0.14	$^3T_1 \rightarrow {}^3T_1(P)$	–	–	–
$[Cu_2(BFHQSD)(OH_2)_4]$	Brown	–	–	415	0.14	480	0.11	625	0.05	$^2B_{1g} \rightarrow {}^2E_g$	715	0.04	$^2B_{1g} \rightarrow {}^2B_{2g}$
$[Cu_2(BFHQST)(OH_2)_2]$	Brown	–	–	415	0.16	485	0.14	623	0.08	$^2B_{1g} \rightarrow {}^2E_g$	712	0.05	$^2B_{1g} \rightarrow {}^2B_{2g}$
$[Cu_2(BFHQS\text{-}o\text{-}Ph)(OH_2)_4]$	Brown	–	–	410	0.10	490	0.07	620	0.04	$^2B_{1g} \rightarrow {}^2E_g$	710	0.03	$^2B_{1g} \rightarrow {}^2B_{2g}$
$[Cu_2(BFHQS\text{-}p\text{-}Ph)(OH_2)_4]$	Green brown	–	–	410	0.12	490	0.08	620	0.03	$^2B_{1g} \rightarrow {}^2E_g$	710	0.02	$^2B_{1g} \rightarrow {}^2B_{2g}$

similar to square planar. This is due to the strong splitting of the Jahn-Teller unstable term $^2B_{1g}$, and consequently an overlapping with ^2E_g into a spectral pattern that is characteristic of square planar coordination in DMF solution [29].

Electron spin resonance spectra (ESR) of cobalt complexes solution in which the cobalt(II) coordination is tetrahedral, normally consist of eight lines arising from hyperfine coupling to ^{58}Co nuclei, with a coupling constant of 8 – 10 mT, (Fig. 1). The pattern of the g_{eff} values for cobalt complexes indicate low spin cobalt (II) complexes. The negative contribution in the g_{eff} value (1.81 – 1.85) over that of the free electron, 2.0023, indicates a decrease in the covalent nature of the bonding between Co(II) and ligand molecule [29]. It was found that the ESR spectra of copper(II) complexes show a sharp signal (Fig. 2). The observed g_{eff} values (1.88 – 1.95) are recorded in Table III, confirming a tetrahedral geometry around Cu(II) ion. The negative contribution in the g_{eff} value over that of the free electron indicates

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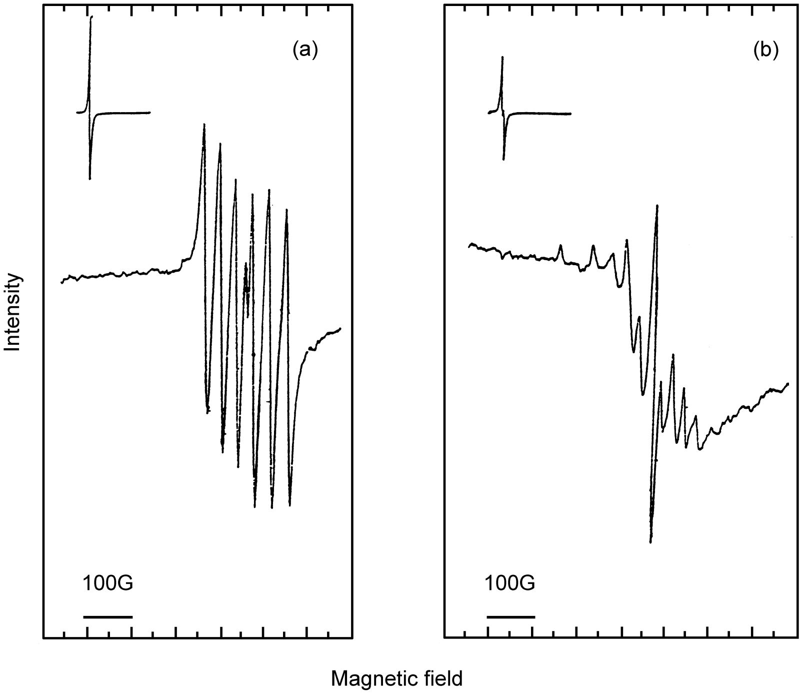

FIGURE 1 ESR spectra of (a) $[Co_2(BFHQSD)(H_2O)_4]$ complex, and (b) $[Co_2(BFHQST)(H_2O)_4]$ complex.

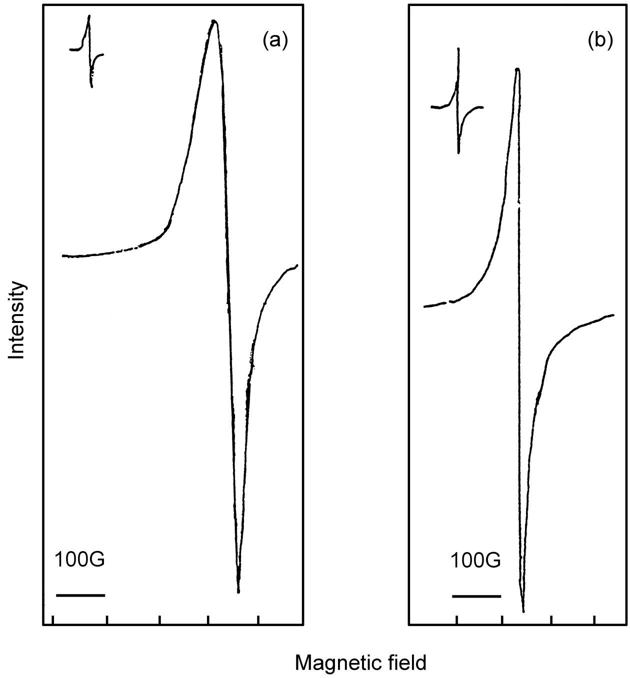

FIGURE 2 ESR spectra of (a) [Cu_2(BFHQSD)(H_2O)$_4$] complex, and (b) [Cu_2(BFHQST)(H_2O)$_4$] complex.

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a decrease in the covalent nature of the bonding between Cu(II) and ligand molecule [29].

Microbial Activity of Schiff-base Ligands and their Metal Complexes

The synthesized binuclear complexes (2 : 1), free metal ions, and the symmetrical Schiff base ligands [7—X—H_2L], were screened for their antimicrobial activity. This was done on *Sarcina lutea* (gram-positive) and *Escherichia coli* (gram-negative) bacteria at 37°C and two common fungi, *Aspergillus niger* and *Candida albicans*, at 30°C by the serial dilution method [30]. A comparative study of the minimum inhibitory concentration values indicates that the ligands [7—X—H_2L] and their corresponding metal complexes are active against the bacteria and fungi used in this study. The proper temperature, pH and the necessary nutrients and growth media free from other microorganisms have been provided for the preparation of cultures of pathogenic bacteria and fungi, using aseptic technique [31]. The

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culture media used were sterilized by the moist heat sterilization method [32]. The incubation period for the bacteria was 24 hours at 37°C while for the fungi it was 48 hours at 30°C. From comparative study of the results in Table VII, it was concluded that the antimicrobial activity of all ligands is enhanced when they are chelated with metal ion (complex formation). It was found [33] that 8-hydroxyquinoline [HL] is a strong inhibitor of copper(II) containing cresolase enzyme present in a wide variety of fungi. It was indicated [34], that (1 : 2) (M : L) chelate penetrates the cell and dissociates into 1 : 1 half-chelate that would become a toxic entity by combining and blocking the metal substances on the enzymes. Other workers [35, 36] also support this mechanism.

The growth inhibition capacity of complexes follow the order: Cu(II) $>$ Ni(II) $>$ Co(II) which is same order as the thermal stability. The growth inhibition capacity of ligands [7—X—H_2L] follows the order: —X—= $(CH_2)_3 > (CH_2)_2 > o\text{-}C_6H_4 \geq p\text{-}C_6H_4$, *i.e.*, (BFHQST) $>$ (BFHQSD) $>$ (BFHQS-*o*-Ph) $\geq$ (BFHQS-*p*-Ph), therefore, longer chains and hence a decrease of steric crowding lead to an increase in the inhibition capacity of the ligand. The highest activity was observed for *Aspergillus niger* fungi which may be attributed to the increased polar character of —SO_3^- groups in

TABLE VII Antimicrobial activity of the free transition metal ions, bis (7-formyanil substituted-8-hydroxyquinoline-5-sulphonic acid) Schiff base ligands, and metal complexes against different bacteria and fungi*

	Bacteria		*Fungi*	
Ligand/complex	*S. lutea*	*E. coli*	*A. niger*	*C. albicaus*
(BFHQSD)	308.0	302.0	307.0	295.0
$[Co_2(BFHQSD)(OH_2)_4]$	50.0	66.0	42.0	44.0
$[Ni_2(BFHQSD)(OH_2)_4]$	40.0	41.0	25.0	28.0
$[Cu_2(BFHQSD)(OH_2)_4]$	30.0	25.0	20.0	22.0
(BFHQST)	300.0	298.0	300.0	290.0
$[Co_2(BFHQST)(OH_2)_2]$	29.0	30.0	25.0	27.0
$[Ni_2(BFHQST)(OH_2)_2]$	26.0	26.0	13.0	15.0
$[Cu_2(BFHQST)(OH_2)_2]$	15.0	15.0	10.0	10.0
(BFHQS-*o*-Ph)	400.0	401.0	410.0	312.0
$[Co_2(BFHQS\text{-}o\text{-}Ph)(OH_2)_4]$	135.0	142.0	130.0	133.0
$[Ni_2(BFHQS\text{-}o\text{-}Ph)(OH_2)_4]$	125.0	128.0	80.0	105.0
$[Cu_2(BFHQS\text{-}o\text{-}Ph)(OH_2)_4]$	100.0	80.0	72.0	82.0
(BFHQS-*p*-Ph)	405.0	402.0	415.0	315.0
$[Co_2(BFHQS\text{-}p\text{-}Ph)(OH_2)_4]$	140.0	150.0	106.0	137.0
$[Ni_2(BFHQS\text{-}p\text{-}Ph)(OH_2)_4]$	130.0	135.0	85.0	110.0
$[Cu_2(BFHQS\text{-}p\text{-}Ph)(OH_2)_4]$	103.0	85.0	73.0	86.0
$Co(ClO_4)_2 \cdot 6H_2O$	1010.0	1005.0	1008.0	995.0
$Ni(ClO_4)_2 \cdot 4H_2O$	1006.0	998.0	1005.0	990.0
$Cu(ClO_4)_2 \cdot 2H_2O$	1000.0	992.0	1002.0	985.0

* Values are minimum inhibitory concentration in $\mu mol\,l^{-1}$.

the ligands and metal complexes. These groups help in its easy distribution in the affected colonies therefore giving ample opportunity for the compounds to react with the microorganisms. From the present work, it is clear that a considerable increase in the biocide activity of these studied ligands has been observed on coordination with metal ions, therefore, these compounds can be recommended for use in the chemotherapy of candidiaces and other fungal skin diseases.

CONCLUSION

From the growth inhibition capacity of Schiff-base ligands and metal complexes on *Sarcina lutea* (gram-positive) and *Escherichia coli* (gram-negative) bacteria and two common fungi, *Aspergillus niger* and *Candida*

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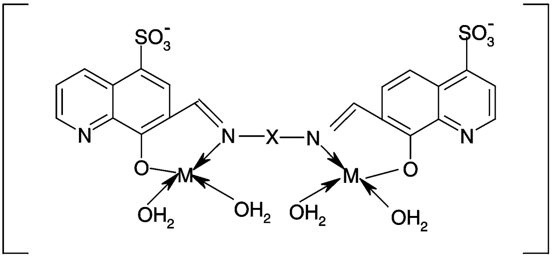
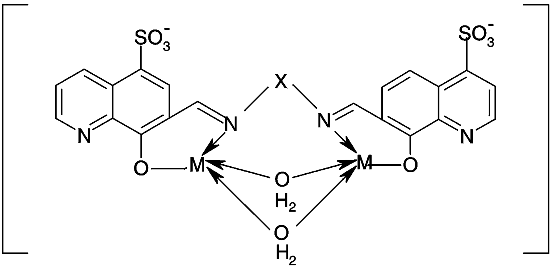


Where X = $(\text{-}CH_2\text{-})_2$ (BFHQSD) ligand
(-p-ph-) (BFHQ-p-ph) ligand
(-o-ph-) (BFHQ-o-ph) ligand
and M(II) = Co, Ni, Cu



Where X = $(\text{-}CH_2\text{-})_3$ (BFHQST) ligand and M(II) = Co, Ni, Cu

SCHEME 2

albicans, one can conclude that: (1) The growth inhibition capacity of metal complexes follows the order Cu(II) > Ni(II) > Co(II). (2) The growth inhibition capacity of ligands [7—X—H_2L] follows the order (BFHQST) > (BFHQSD) > (BFHQS-*o*-Ph) ≥ (BFHQS-*p*-Ph). (3) The highest antibacterial activity was observed in case of *Aspergillus niger* fungi, therefore, these complexes can be recommended for use in the chemotherapy of candidiaces and other fungal skin diseases.

From the studies of conductometric titration, elemental analyses, molecular weight determination, thermogravimetric analysis, infrared, magnetic susceptibility measurements, electronic absorption, and electron spin resonance spectra, one can assign, the following structures for all metal complexes (Scheme 2).

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References

[1] R. D. Jones, D. A. Summerville and F. Basolo, *Chem. Rev.* **79**, 139 (1979).
[2] R. H. Niswander and A. E. Martell, *Inorg. Chem.* **17**, 2341 (1978).
[3] R. R. Gagne, C. I. Spiro, T. J. Smith, W. R. Hamann, W. R. Thies and K. Shiemke, *J. Am. Chem. Soc.* **103**, 4073 (1981).
[4] U. Casellato, D. Fregona, S. Sitran, S. Tamburini, P. A. Vigato and P. Zanelli, *Inorg. Chim. Acta* **95**, 279 (1984).
[5] G. Cross and J. P. Costs, *Acad. C. R. S. C. Paris* **294**, 173 (1982).
[6] L. R. Hoffman, *Swiss Paten, 416648* (1967).
[7] L. H. Schmidt, *Ann. Rev. Microbial.* **427**, 23 (1969).
[8] D. R. Williams, *Chem. Rev.* **72**, 203 (1972).
[9] A. A. El-Asmy, Z. A. El-Sonbati and A. A. Issa, *Transition Metal Chem.* **15**, 222 (1990).
[10] B. Jani and P. K. Bhatta Charya, *Indian J. Chem.* **15A**, 750 (1977).
[11] S. M. Abu-El-Wafa, M. El-Behairy and R. M. Issa, *Bull. Soc. Chem. Fr.*, p. 245 (1987).
[12] F. M. Ashmawy, R. M. Issa, S. A. Amer, C. A. McAuliffe and R. V. Parish, *J. Chem. Soc., Dalton* **2**, 421 (1986).
[13] S. Dilli and E. Patsalides, *Aust. J. Chem.* **7**, 670 (1972).
[14] R. N. Sein and S. K. Ray, *J. Chem. Soc.* (*A*), p. 1658 (1932).
[15] H. Diehi and C. C. Hach, *Inorg. Synth.* **3**, 196 (1950).
[16] R. Pribil, *Applied Complexometry*, Vol. 5, Pergamon Press Ltd., UK, 1982.
[17] W. L. Jolly, The Synthesis and Characterization of Inorganic Compounds, Prentice-Hall, Inc., Englewood Cliffs, N.J., 1970.
[18] J. I. Bullock and H. A. Tajmir-Riahi, *J. Chem. Soc. Dalton Trans.* **4** (1978).
[19] H. Lokker, *J. Org. Chem.* **27**, 361 (1982).
[20] J. L. Hall, P. R. Gibson Jr., P. R. Wilkinson and H. O. Philips, *Anal. Chem.* **26**, 1484 (1954).
[21] F. Vydra and M. Karlik, *Chem. Listy* **50**, 1749 (1957).
[22] I. M. Kolthoff and P. J. Elving, *Treatise on Analytical Chemistry*, Part I, Vol. 4 Interscience, New York, 1963.
[23] C. Yoshimura and T. Huzino; T. Ohnishi and K. Bunseki, **37**,169 (1988) (Jpn.), *Chem. Abst.* **109**, 182596y (1988).
[24] M. T. M. Zaki, W. G. Hanna and M. H. Fawzy, *Bull. Chem. Soc. Jpn.* **61**, 1761 (1988).
[25] T. Hatakeyama and L. Zhenhai, Handbook of thermal analysis, John Wiley & Sons Ltd., Chichester, England, 1998.
[26] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 3rd edn. John Wiely & Sons, New York, 1977.

[27] S. M. Abu-El Wafa, K. A. R. Salib, G. Inany and T. M. Ismail, *Synth. React. Inorg. Met. Org. Chem.* **20**, 1332 (1990).
[28] A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1984.
[29] B. S. Hathaway and D. E. Billing, *Coord. Chem. Rev.* **5**, 143 (1970).
[30] G. C. Donald and A. R. Williams, Assay Methods of Antibiotics, A Laboratory Manual, Medical Encyclopedia Inc., 1955.
[31] E. R. Rawlins, Bentley's Test Book of Pharmaceutics, 8th edn., Bailliere Tindall, London, 1977.
[32] R. Cruichank, Medical Microbiology, The Practice of Microbiology, 12th edn. Chuchill Livingstone, Edinburgh, 1975.
[33] D. Guber and S. S. Block, Inhibition of Cresolan Activity by Fungicidal Chemicals, *Am. Chem.*, Mentin, Miniator, 1953.
[34] A. Albert, Selective Toxicity, Chapman and Hall, London, 1979.
[35] R. Nagar, *J. Inorg. Biochem.* **37**, 193 (1989).
[36] W. G. Hanna and M. M. Moawad, *J. Coord. Chem.* **53**(00), 2000, In press.

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