

STRUCTURAL, CATALYTIC OXIDATION AND ANTIMICROBIAL STUDIES OF A NEW SERIES OF TRANSITION METAL SCHIFF BASE COMPLEXES DERIVED FROM QUINOXALINE-2-CARBOXALDEHYDE

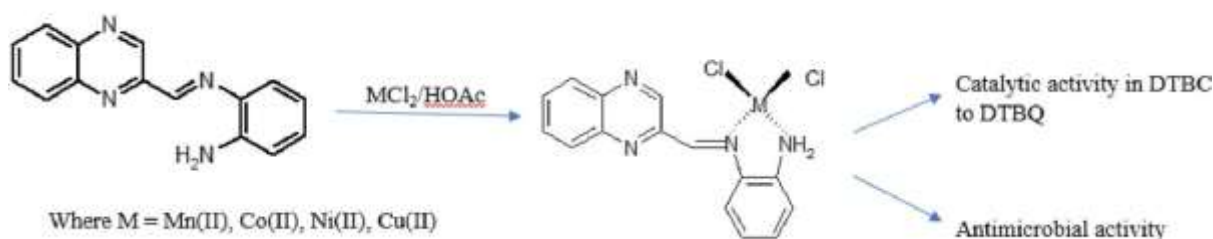
Mayadevi S^{1*} and Basil Baby²

¹Department of Chemistry, NSS College of Engineering, Palakkad-678008, Kerala, India

²Research scholar, Research and Development Centre, Bharathiar University, Coimbatore-641046

*Author for communication: Dr. Mayadevi S

Graphical Abstract



Abstract

The present work focuses on the synthesis, characterization, oxidation catalysis and antimicrobial activity of a series of metal complexes, $[M(QOD)_mCl_n]$, $M = Mn(II), Co(II), Ni(II)$ and $Cu(II)$, of a new ligand, quinoxaline-2-carboxalidene-1,2-phenylenediamine containing a deactivating heterocyclic ring system.. Structural investigations were carried out on the metal complexes by a combination of microanalytical, spectroscopic and magnetic techniques. The results suggested distorted tetrahedral geometry for all the complexes. The catalytic activity of the prepared complexes was determined spectrophotometrically by monitoring the oxidation of di-*tert*-butylcatechol to the corresponding *o*-benzoquinone using molecular oxygen as the oxidant. The oxidation activity of the metal complexes are in the order $Mn(II) \gg Cu(II) > Co(II) > Ni(II)$. To explore the therapeutic potential of a deactivating heterocyclic ring system, all the prepared complexes were checked for their antimicrobial activity against potent bacterial pathogens such as *E.coli*, *Proteus sp* and *Salmonella typhi* and non pathogenic *Lactobacillus*. All the complexes except Mn(II) are found to possess antibacterial activity. Co(II) complex exhibited broad spectral antibacterial effect to all the isolates. A comparative study was made with the antibiogram of antibiotics of known potencies. The present study points to the futuristic aspects of Co(II) and Cu(II) complexes to be utilized as agents for therapy of infectious diseases either individually or as a mixture in combination with pharmaceutical agents.

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Ni(II) and Cu(II)), of a new ligand, quinoxaline-2-carboxaldehyde-1,2-phenylenediamine containing a deactivating heterocyclic ring system.. Structural investigations were carried out on the metal complexes by a combination of microanalytical, spectroscopic and magnetic techniques. The results suggested distorted tetrahedral geometry for all the complexes. The catalytic activity of the prepared complexes was determined spectrophotometrically by monitoring the oxidation of di-*tert*-butylcatechol to the corresponding *o*-benzoquinone using molecular oxygen as the oxidant. The oxidation activity of the metal complexes are in the order Mn(II)>> Cu(II)>Co(II)>Ni(II). To explore the therapeutic potential of a deactivating heterocyclic ring system, all the prepared complexes were checked for their antimicrobial activity against potent bacterial pathogens such as *E.coli*, *Proteus sp* and *Salmonella typhi* and non pathogenic *Lactobacillus*. All the complexes except Mn(II) are found to possess antibacterial activity. Co(II) complex exhibited broad spectral antibacterial effect to all the isolates. The present study points to the futuristic aspects of Co(II) and Cu(II) complexes to be utilized as agents for therapy of infectious diseases either individually or as a mixture in combination with pharmaceutical agents.

Keywords : antimicrobial activity, catalytic activity, 1,2-phenylenediamine, quinoxaline-2-carboxaldehyde, Schiff base, manganese(II), cobalt(II), nickel(II), copper(II) complexes

Introduction

Increasing efforts are set forth in formulating structurally diverse metal complexes of Schiff bases containing nitrogen and other donors. This may be credited by their stability [1] and potential application in many fields such as oxidation catalysis electrochemistry etc [2-5]. Transition metal complexes with heterocyclic ring system are of immense interest in this context as their ligand field strengths are expected to be weaker than the corresponding aromatic ring system. It has been established by Kochi and coworkers that in such complexes the substitution on the ring by an electron withdrawing group enhances catalytic activity due to lowered electron density on the metal ion [6]. The quinoxaline group is promising due to the deactivating ring system. The catalytic as well as cytotoxic activities of certain transition metal complexes of the Schiff bases derived from quinoxaline-2-carboxaldehyde have been reported earlier [7-9]. With this view, herein, we report the synthesis and characterisation of some transition metal complexes of a new Schiff base derived from quinoxaline-2-carboxaldehyde and 1,2-phenylenediamine(QPD) (Fig. 1.). Metal complexes of this ligand have not yet been reported. The prepared complexes were screened for their catalytic activity in the oxidation of 3,5-di-*tert*-butylcatechol (DTBC) to the corresponding *o*-quinone, DTBQ with molecular oxygen.. The complexes were found to exhibit significant antimicrobial activity against certain pathogenic and non-pathogenic bacterial species.

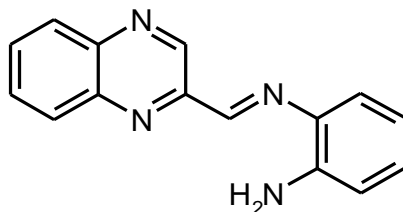


Fig. 1 Quinoxaline-2-carboxalidene-*o*-phenylenediamine

Materials and Methods

Materials

MnCl₂·4H₂O, CoCl₂·6H₂O, NiCl₂·6H₂O, CuCl₂·2H₂O and 1,2-phenylenediamine were used as received from E. Merck. Styrene and all other reagents were purified by reported procedures [27].

Preparation of Ligand

Quinoxaline-2-carboxaldehyde was obtained in the pure form using reported procedure [28,29]. The Schiff base, quinoxaline-2-carboxylidene-1,2-phenylenediamine (QPD) was prepared by condensing the aldehyde (0.01 mol; 1.58 g) with 1,2-phenylenediamine (0.01 mol; 0.54 g) for fifteen minutes in ethanol. The orange coloured solid formed was filtered and washed with ethanol. The ligand was recrystallised twice from ethanol and stored in vacuum over anhydrous calcium chloride after drying. Yield: 70 % , 1.62 g, M. P. :230° C.

Preparation of the Complexes

All the complexes were prepared by the following method: A solution of the Schiff base ligand (0.01 mol; 2.48 g) in acetic acid (100 mL) was refluxed for ten minutes with the corresponding metal salts (0.01 mol; 1.98 g MnCl₂·4H₂O, 2.37 g CoCl₂·6H₂O, 2.37 g NiCl₂·6H₂O or 1.7 g CuCl₂·2H₂O) dissolved in minimum quantity of ethanol. The solid complexes separated out were filtered, washed thoroughly with chloroform and stored in vacuum after recrystallisation from methanol.

Analytical Methods

Both the metal and halide contents were determined by known analytical procedures [30]. Microanalysis for carbon, hydrogen and nitrogen were done on a Heraeus CHN elemental analyzer. Molar conductance of the complexes were determined in methanol at 28 ± 2 ° C using a Century 601 conductometer with a dip type cell and a platinised platinum electrode. The room temperature magnetic susceptibility measurements of the complexes were done on a Gouy type magnetic balance.

The electronic spectra of the complexes were taken in methanolic solution and also in the solid state. The near IR spectra of complexes in the region 2000-1000 nm were recorded with a Hitachi U-3410 spectrophotometer. Infrared spectra of the ligand and the complexes were taken in the region 400-4000 cm^{-1} as KBr discs on a Shimadzu 8101 FTIR spectrophotometer. The X-band EPR spectra of the complexes were taken in DMSO at LNT using Varian E-112 X/Q band spectrophotometer.

Procedure for the catalytic oxidation of DTBC

DMSO was selected as solvent in order to avoid vaporization during the experiment. The solvent was made 0.1 molar with respect to triethylamine (15 mL/L of DMSO) to increase its basicity. The DTBC solution (0.22 g in 90 mL solvent) was prepared afresh before each experiment in order to avoid slow aerial oxidation. The catalyst solution (100 mL) was prepared in the same solvent. The catalyst substrate ratio selected for the present study was 1:10.

The catalytic oxidations were carried out at a temperature of $28 \pm 1^\circ\text{C}$ using atmospheric oxygen as oxidant. The reaction was initiated by the addition of catalyst solution to DTBC solution. The course of the reaction was monitored by measuring the change in absorbance of the product quinone (DTBQ) at 400 nm. A solution of the catalyst with the same concentration as that of the reaction mixture was used as the reference. The rate of conversion was evaluated. The concentration of DTBC undergoing oxidation in moles being derived from the molar extinction coefficient (ϵ) value of DTBQ.

Antibacterial Activity

Kirby-Bauer disc diffusion method [31] was tried to study the antibacterial activity. 18 hour nutrient broth culture of *E.coli*, *Salmonella typhi*, *Proteus* and *Lactobacillus* were swabbed on separate sterile nutrient agar petri plates. Sterile Whatman filter paper discs incorporated with a known concentration of metal complex solutions made in DMSO were placed on the plates at equal distances. On incubation at 37°C for 24 hrs diameter of zone of inhibition was measured. Reference studies were conducted with antibiotic discs of known potency (Hi media) to the same bacteria. All the tests were done in triplicate and an average of the values was reported here.

Results and Discussion

All the complexes are stable in air and non-hygroscopic. The physical and analytical data of the prepared complexes are prearranged in Table I. They are soluble in ethanol, methanol, acetonitrile, DMF and DMSO. The molar conductance values (Table 2) reveal that the complexes are non-electrolytes in methanol.

Complex (Empirical formula)	Yield (%)	C (%) Found (calc)	H (%) Found (calc)	N (%) Found (calc)	M (%) Found (calc)	Cl (%) Found (calc)
[Mn(QPD)Cl ₂] (MnC ₁₅ H ₁₂ N ₄ Cl ₂)	60	47.99 (48.15)	3.07 (3.20)	14.83 (14.90)	14.51 (14.69)	18.91 (18.96)
[Co(QPD)Cl ₂] (CoC ₁₅ H ₁₂ N ₄ Cl ₂)	70	47.44 (47.60)	3.10 (3.17)	14.59 (14.82)	15.30 (15.60)	18.67 (18.80)
[Ni(QPD)Cl ₂] (NiC ₁₅ H ₁₂ N ₄ Cl ₂)	70	47.35 (47.70)	3.10 (3.20)	14.40 (14.83)	15.20 (15.50)	18.50 (18.81)
[Cu(QPD)Cl ₂] (CuC ₁₅ H ₁₂ N ₄ Cl ₂)	70	46.84 (47.10)	3.07 (3.10)	14.51 (14.60)	16.43 (16.60)	18.37 (18.53)

where QPD= quinoxaline-2-carboxalidene-1,2-phenylenediamine

Table I. Physical and analytical data of the Schiff base (QPD) complexes.

Complex	Colour	Magnetic Moment (B. M.)	Molar Conductance (ohm ⁻¹ cm ² mol ⁻¹)
[Mn(QPD)Cl ₂]	Dark yellow	5.7	4.8
[Co(QPD)Cl ₂]	Brick red	4.6	31.7
[Ni(QPD)Cl ₂]	Dark green	4.1	10.8
[Cu(QPD)Cl ₂]	Light brown	2.0	18.7

Table II. Molar conductance and Magnetic moment data

The ¹H NMR spectrum of the ligand QPD shows a singlet at δ 9.7 due to the azomethine proton, a multiplet in the range δ 6.9 to 9.0 due to quinoxaline and phenyl rings and a broad two proton singlet at 10.6 due to the NH₂- group.

IR Spectral Studies

The vibrational spectral data of the ligand and the complexes are given in Table III. The strong sharp band at 3376 cm⁻¹ in the Schiff base may be attributed to ν(N-H) of the amino group. There is a substantial shift for this band to lower regions in all the complexes supporting N coordination of this group to the metal center. The ν(C=N) of the azomethine group in the free ligand appears around 1608 cm⁻¹ and it undergoes a blue shift of the order of 5-55 cm⁻¹ on complexation, supporting the participation of azomethine nitrogen atom in complexation [10]. The band observed at 1580 cm⁻¹ may be assigned to ν(C=N) of the quinoxaline ring of QPD. This band is found to be retained at 1580 cm⁻¹ in all the complexes,

Ligand	[Mn(QPD)Cl ₂]	[Co(QPD)Cl ₂]	[Ni(QPD)Cl ₂]	[Cu(QPD)Cl ₂]	Tentative assignment
3376 (s)	3350 (s)	3346 (s)	3333 (s)	3333 (s)	ν (N-H)
1608 (s)	1625 (m)	1628 (m)	1628 (m)	1613 (m)	ν (C=N) azomethine
1580 (w)	1580 (w)	1585 (w)	1580 (w)	1582 (w)	ν (C=N)

					ring
867 (w)	867 (w)	862 (w)	866 (w)	866 (w)	$\rho(\text{CH})$
759 (s)	758 (s)	759 (s)	760 (s)	760 (s)	$\rho(\text{CH})$ Ph
----	496 (w)	502 (w)	500 (w)	499 (w)	$\nu(\text{M-N})$

abbreviations: s = strong; m = medium; w = weak

Table III. Infrared Spectral Data (in cm^{-1})

showing that N atom of the quinoxaline ring is not coordinated to the metal center in any of the complexes. In the spectra of all the complexes the additional band appearing in the range 495 - 502 cm^{-1} can be assigned to $\nu(\text{M-N})$ vibrations [11]. All these observations suggests that the Schiff base QPD is acting as a bidentate ligand coordinating through the amino and the azomethine groups.

Electronic Spectra

The electronic spectral data of the complexes are given in Table IV. For the manganese(II) complex, there is a very weak band at 22900 cm^{-1} , which can be assigned to d-d transition in tetrahedral environment [12]. The cobalt(II) complex exhibits a band at 18800 cm^{-1} , which may be assigned as the ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ transition of tetrahedral Co(II) species [13]. The band observed in the near IR region at 6890 cm^{-1} , may be attributed to ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$ transition of Co(II) in a tetrahedral environment [14]. The nickel(II) complex exhibits a band at 17630 cm^{-1} , which can be assigned to the ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$ transition, and is characteristic of Ni(II) in tetrahedral geometry [15]. The near IR band which is expected for tetrahedral nickel(II) complexes appears at 6860 cm^{-1} and can be assigned to the ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{A}_2(\text{F})$ transition. Copper(II) complex shows a broad band in the region 21 420 cm^{-1} , which is in agreement with other reported cases of tetrahedral copper(II) complexes [16]. The

Complex	Absorption Maximum (cm^{-1})	Log ϵ	Tentative assignment
[Mn(QPD)Cl ₂]	40350	4.4	$n \rightarrow \pi^*$
	28750	3.7	charge transfer
	22900	1.1	d-d transition
[Co(QPD)Cl ₂]	40940	4.4	$n \rightarrow \pi^*$
	32800	3.8	charge transfer
	28800	3.7	charge transfer
	18800	1.3	${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$
	6890	0.9	${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{F})$
[Ni(QPD)Cl ₂]	41620	4.4	$n \rightarrow \pi^*$
	33000	3.9	charge transfer
	23920	3.4	charge transfer
	17630	1.4	${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$
	6890	0.8	${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{A}_2(\text{F})$
[Cu(QPD)Cl ₂]	40350	4.4	$n \rightarrow \pi^*$

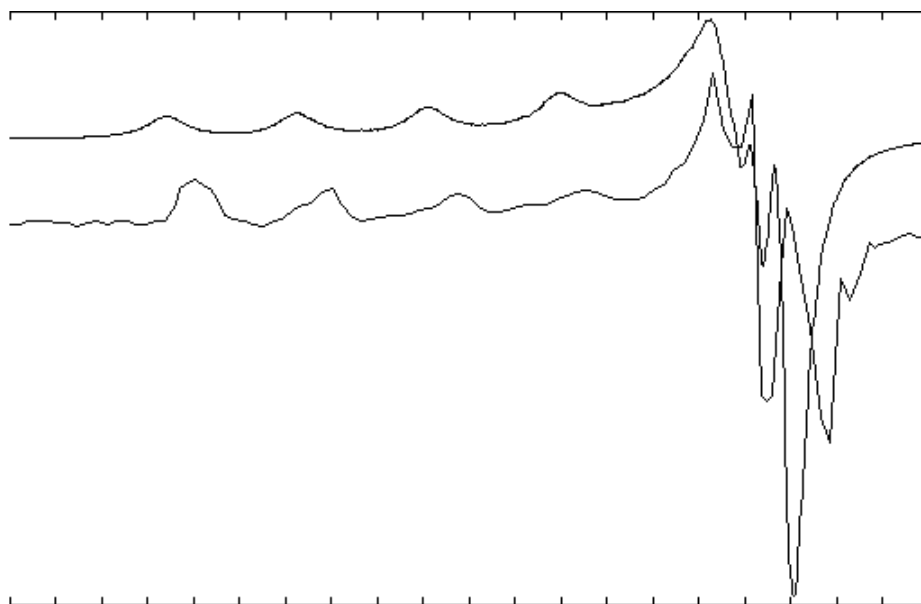
	29300	3.9	charge transfer
	27000	3.3	charge transfer
	21420	1.1	d-d transition

Table IV. Electronic Spectral Data

strong absorptions observed around $40\,000\text{ cm}^{-1}$ in the spectra of all the complexes may be due to the $n \rightarrow \pi^*$ transitions [17]. Further all the complexes exhibit strong bands in the range $33\,000\text{ cm}^{-1}$ and $27\,000\text{ cm}^{-1}$ which can be assigned to charge-transfer transitions.

Magnetic susceptibility measurements

Magnetic moments of the complexes are shown in Table II. The μ_{eff} value of manganese(II) complex is found to be 5.7 B. M which indicates a high spin state for the ion [18]. The μ_{eff} values of 4.6 B. M. and 4.1 B. M. for the cobalt(II) and nickel(II) complexes are in agreement with that expected for tetrahedral structure [19,20]. The magnetic moment of 2.0 B.M. for the present copper(II) complex is indicative of a distorted tetrahedral structure [21].

**Fig. 2 EPR Spectrum of [Cu (QPD)Cl₂]**

$A_{\parallel}(\text{cm}^{-1})$	140
g_{\parallel}	2.37
g_{\perp}	2.08
g_{av}	2.18
α^2	0.44
G	4.65

Table V. EPR spectral data of [Cu(QPD)Cl₂]

The EPR spectrum of [Cu (QPD)Cl₂] was recorded in DMSO at LNT. Simulation was carried out on the experimental spectrum and both the experimental and simulated spectra are given in Fig.2. The EPR parameters corresponding to the best fit between the experimental and simulated spectra are noted and given in Table V. It is found that $g_{//} \gg g_{\perp} > g_e$ (2.0023) which indicates an elongated axial system with a $d_x^2 - y^2$ ground state [22,23]. The splitting in the perpendicular region is due to the slight reduction in symmetry from the axial to the rhombic. The α^2 value of the present complex supports the covalent nature of the complex. Based on the above observations, the structure shown in Figure 3 has been proposed for the complexes.

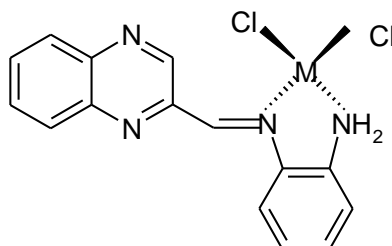


Fig 3 where M = Mn(II), Co(II), Ni(II) and Cu(II)

Catalytic activity studies

The oxidation of DTBC was found to be negligible even in the presence of the metal complex catalyst. However on adding the amine, reactions acquired a measurable rate. Therefore, in all experiments triethylamine was added. DTBC may be partially dissociated in the presence of amine so that it can easily interact with metal complexes. The rate of conversion data indicates that all the complexes are catalytically active in the oxidation DTBC → DTBQ. The catalytic activity of the metal complexes show the following order:

Complex	Weight of Catalyst in 100 mL Solution (g)	Rate of Conversion (mol dm ⁻³ s ⁻¹)
[Mn(QPD)Cl ₂]	0.020	4.9x10 ⁻⁴
[Co(QPD)Cl ₂]	0.023	8.1x10 ⁻⁵
[Ni(QPD)Cl ₂]	0.022	6.6x10 ⁻⁵
[Cu(QPD)Cl ₂]	0.024	9.9x10 ⁻⁵

Table.VI. Rate of Conversion Data of the Complexes in the Oxidation of DTBC to DTBQ

Mn(II) >> Cu(II) > Co(II) > Ni(II). The rates of conversion to benzoquinone are given in Table-VI. It may be proposed that on the approach of a DTBC molecule some of the labile metal ligand bonds dissociate and give way to the formation of a ternary complex. The prerequisite for this is the presence of vacant coordination sites on the catalyst. The reaction mechanism assumed here includes the associative oxygen species adsorbed to metal ions. The

intramolecular electron transfer within the ternary complex (DTBC-ML-O₂) generates the corresponding quinone. In many reactions reported earlier, it has been shown that the dissociation of one or two bonds of the chelate may be the rate determining step in the catalyzed reaction.[24]. The highest activity of the [Mn(QPD)Cl₂] complex shown may be explained by the tetrahedral structure suggested for it from the electronic spectral data. The Ni(II) complex is catalyzing the oxidation due to the tetrahedral structure. The results of the simulation study of the EPR spectrum of the present copper complex show a slight reduction in symmetry from axial to rhombic. The Cu based enzyme, tyrosinase that is accomplishing this oxidation in biological systems is having a rhombic local symmetry around copper [25].

Anti microbial studies

The new metal derivatives reported here were proved to have anti bacterial activity against one or more bacterial species as compared to the uncomplexed Schiff bases. The ligand was found to have no antibacterial activity. The results of the biological studies are exhibited in Table VII. All the complexes except Mn (II) are found to possess antibacterial activity. Co(II) complex exhibited broad spectral antibacterial effect to all the isolates.

Sl. No.	Bacteria	Diameter of zone of inhibition (mm) for			
		Copper	Cobalt	Manganese	Nickel
1	<i>E.coli</i>	-	12	-	-
2	<i>Lactobacillus</i>	37	37	-	10
3	<i>Proteus sp.</i>	18	10	-	-
4	<i>Salmonella typhi</i>	-	15	-	-

The amount of complex per disc = 1000 µg.

Bacteria	Cephalothin (30 µg)	Clindamycin (2 µg)	Co-Trimoxazole (25 µg)	Erythromycin (15 µg)	Gentamycin (10 µg)	Ofloxacin (1µg)	Pencillin (10 µg)
<i>E.coli</i>	7	13	-	-	20	11	-
<i>Lactobacillus</i>	22	18	18	23	26	28	-
<i>Proteus sp</i>	-	-	22	20	-	20	-
<i>Salmonella typhi</i>	12	13	-	-	25	18	-

Table VIII Diameter of zone of inhibition (mm) obtained with antibiotic discs:

Cu(II) Schiff base complex showed significant activity against *Proteus sp* and *Lactobacillus*, whereas Ni(II) showed activity only against *Lactobacillus*. The inclusion of *Lactobacillus sp* in the present study was from the view point of evaluating the antibacterial effect of the afore

mentioned complexes on a non pathogenic bacteria. The pattern of antibacterial activity exhibited by complexes was exponential as follows ; Co(II) > Cu(II) > Ni(II).

A comparative study was made with the antibiotics of known potencies. The activity shown by potent antibiotics are as shown in Table VIII. Another interesting certitude noticed was that none of the antibiotics evaluated in the present study extended antibacterial activity to all the four bacteria, where as Co(II) extended activity against all the afore mentioned bacteria. Also, it was intriguing to note that all the bacteria evaluated in the present study extended resistance to the antibiotic penicillin, underscoring the presence of penicillin resistance factors in them. The exhibition of antibacterial activity by metal complexes compared to the ligands upon coordination can be explained on the basis of Overtone concept and Tweedy's chelation theory [26]. All these results underscore the potential chances of developing metal Schiff base complexes as a skeleton for formulations in antibacterial chemotherapy and disease management.

Conflicts of interest

There are no conflicts of interests to declare

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