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Synthesis and characterization of divalent transition metal complexes of Schiff bases derived from benzoin and 4-amino benzoic acid

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ABSTRACT

The Schiff base (4-(2-hydroxy-1,2-diphenylethylideneamino) benzoic acid) was prepared from benzoin and 4-amino benzoic acid and the complexes of divalent metals of Co (II), Ni (II) and Cu (II) were synthesized. The ligand and metal complexes were characterized by elemental analysis, ultraviolet-visible spectroscopy, infrared spectroscopy, nuclear magnetic resonance spectroscopy, thermogravimetric analysis, mass spectroscopy and magnetic susceptibility measurement. The ligand (HL) was synthesized by condensation of benzoin (H) and 4-amino benzoic acid (L). The geometrical structures of synthesized complexes were identified. Magnetic susceptibility and electronic spectral study of the complexes showed the octahedral geometry. The antimicrobial activity of Schiff base and the metal complexes were studied. The results were compared with standard antibiotic. Surprisingly, the ligand (HL), the cobalt complex (HL-Co) and the nickel complex (HL-Ni) have shown to be more active against the fungi *Candida albicans* and *Aspergillus niger*. The cobalt complex is active against the microorganism *Staphylococcus aureus*. The *Pseudomonas aeruginosa* is resistant to the ligand and all the metal complexes. © 2010 Trade Science Inc. - INDIA

KEYWORDS

Transition metal complexes;
Schiff bases benzoin;
Amino phenol.

INTRODUCTION

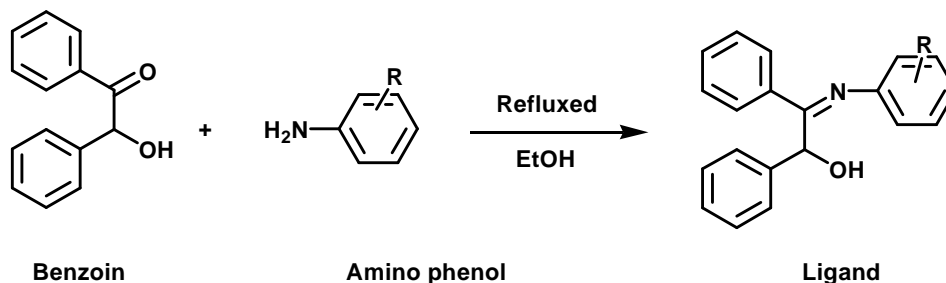
Werner's coordination theory brought out in 1893 was the first attempt at explaining the bonding in coordination complexes^[1]. Thus, since 19th century, the coordination compounds started to be identified. This theory not only gave insight in to the stereochemical aspects of coordination complexes but also initiated more research work in the preparation of a variety of complexes. Coordination chemistry is one of the vast areas which incorporates innumerable applications in science and technology, viz Material science, Analytical chemistry, Biochem-

istry, Medicinal chemistry, Industrial chemistry etc. Thus, the characteristic of metal complexes mainly depends upon metal ions, the donor atom, the structure of ligand and the metal-ligand interactions^[2]. The complexes formed of ligands derived from groups with amines and imidazole are seen to act as an active site of metalloenzymes^[3]. Transition metal complexes with various donor groups have been used in organometallic chemistry^[4]. Numerous metal complexes of Schiff base derivatives having nitrogen and sulphur as donors were studied^[5]. A large number of Schiff base compounds have been synthesized and structurally characterized^[6-13]. The various

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classes of Schiff bases that can be prepared by condensation of different types of amines and carbonyl compounds are very popular due to diverse chelating ability. A number of organic heterocyclic compounds have been used as antimicrobial agents, whose biological activity depends upon size, shape and structure of molecules^[14]. Several transition metal complexes have also been screened for their medicinal properties^[8,15-18].

In this paper we report the synthesis of ligand (HL) (4-(2-hydroxy-1,2-diphenylethylideneamino) benzoic acid) and its Co (II), Ni (II) and Cu (II) metal complexes. The synthesized ligand and metal complexes were characterized by ultra violet-visible, IR, ¹HNMR, Mass spectroscopy, TG-DTG, magnetic susceptibility and also screened for their biological activity.



Scheme 1 : Synthesis Schiff bases.

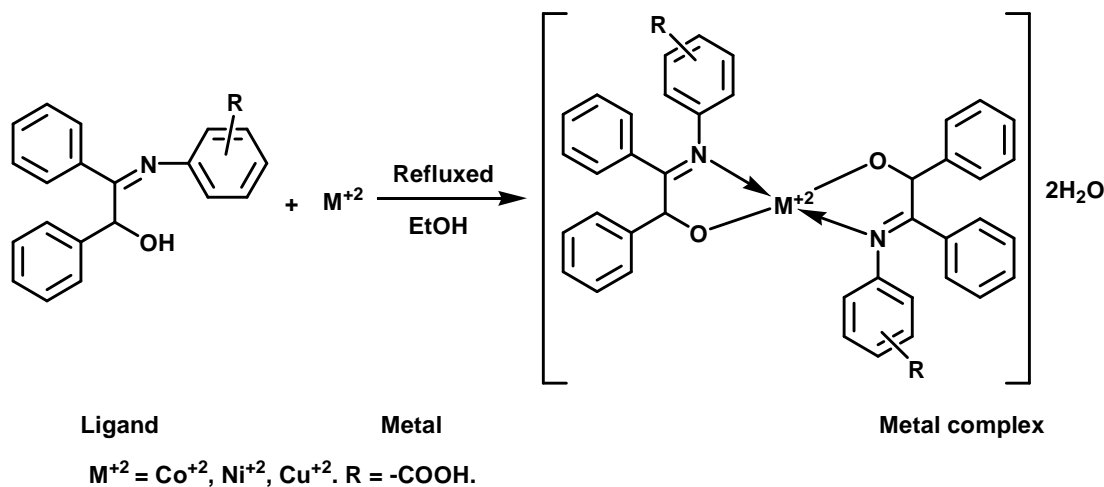
cooling, a crystalline complex was separated by filtration and the crystals were washed with ethanol and anhydrous Et₂O and dried over anhydrous CaCl₂^[19-22].

Synthesis of metal complexes

Scheme 2

A ligand (3.31 gm) [HL] was dissolved in (30 cm³)

ethanol and added to a metal salt [Nickel chloride (2.37gm), Copper chloride (1.70gm) and Cobalt chloride (2.37gm)] ethanolic solution (30 cm³). The metal-ligand molar ratio was (1:1). The mixture was refluxed for 2hrs. On cooling, a crystalline complex was separated by filtration and the crystals were washed and dried as above^[19-22].



Scheme 2 : Synthesis of metal complexes.

EXPERIMENTAL

Materials

All reagents used were pure AR grade such as benzoin, 4-amino benzoic acid, Copper chloride (CuCl₂·2H₂O), Nickel chloride (NiCl₂·6H₂O), and Cobalt chloride (CoCl₂·6H₂O). The solvents used are ethanol, petroleum ether, ethyl acetate etc.

Synthesis of Schiff base ligand

Scheme 1

The benzoin (2.12gm) and 4- benzoic acid (1.37gm) were dissolved in ethanol (30cm³) separately in 1:1 molar ratio. The ethanolic solutions were mixed together. The mixture was refluxed on water bath for 3 hrs. On

RESULT AND DISCUSSIONS

The ligand and the metal complexes synthesized were stable at room temperature and are yellow, yellowish brown and Grey coloured. The ligand and the metal complexes are soluble in common polar solvents like methanol, ethanol and chloroform. They are soluble even in DMF and acetone. The synthesized ligand and the metal complexes were characterized by elemental analysis and spectral analysis. Biological activity of the

ligand and the metal complexes were also studied. Based on their elemental and spectral studies the geometry of the synthesized compounds has been elucidated.

Elemental study

By the elemental analysis, the stoichiometry of ligand and their metal complexes is confirmed. The elemental analysis of ligand and the metal complexes are found in agreement with the proposed structure of ligand and the metal complexes are listed in the TABLE 1.

TABLE 1 : Analytical and physical data of the compounds studied.

Compounds	Molecular Formula	Formula Wt.	Colour	M.P. 0°C	Observed (Theoretical) %		
					C	H	N
HL	C ₂₁ H ₁₇ NO ₃	331	Faint Yellow	148	77.06 (76.12)	4.83 (5.17)	4.73 (4.23)
HL-Co	C ₄₂ H ₃₆ N ₂ O ₈ Co.2H ₂ O	755.68	Yellowish Brown	>250	67.38 (66.70)	5.12 (4.80)	4.09 (3.70)
HL-Cu	C ₄₂ H ₃₆ N ₂ O ₈ Cu.2H ₂ O	760	Grey	>250	66.04 (66.30)	5.39 (4.74)	4.16 (3.68)

Electronic spectra

The electronic spectra and magnetic moment are very useful in the evaluation of results obtained by other methods of structural investigation. Information regarding the geometry of the complexes around the Co (II), Ni

(II) and Cu (II) ions was obtained from electronic spectral studies and magnetic moments. The electronic spectra of ligand and their metal complexes were recorded at room temperature using methanol as a solvent. The assignment of the band of the electronic spectra of ligand

TABLE 2 : Electronic spectral and magnetic moment data

Complex	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	$d \rightarrow d$	Assignment	μ_{eff} B.M.	Geometry
HL	206	248	-	-	-	-
HL-Co	207	251	450 545 734	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ ${}^4T_{1g} \rightarrow {}^4A_{2g}$ ${}^4T_{1g} \rightarrow {}^4T_{2g}$	4.94	Octahedral
HL-Ni	204	250	288 517 655	Charge transfer ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$	3.04	Octahedral
HL-Cu	206	263	465 532	Typical octahedral transition Typical octahedral transition	1.728	Octahedral

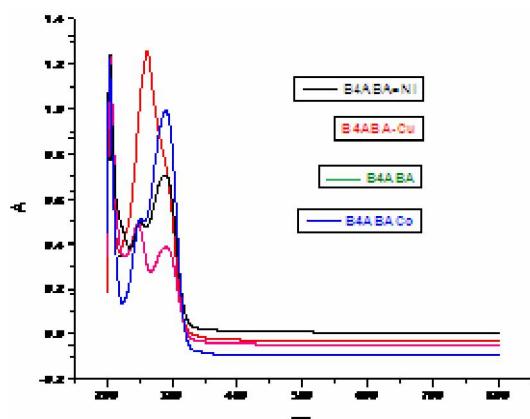


Figure 1 : Electronic spectra of ligand and metal complexes.

and complexes is listed in TABLE 2 and the spectra are presented in Figure 1

The electronic spectra of ligand show bands in the region of about 204-206 nm but in the complexes they are slightly shifted to higher frequencies. The band between 248 -263 can be assigned to $n \rightarrow \pi^*$ of transition of azomethine group. In the spectra of complexes the bands of azomethine chromophore $\pi \rightarrow \pi^*$ transition are shifted to lower frequencies indicates that imine nitrogen is involved in the co-ordination of metal ion. A very weak low intensity absorption band associated with d-d transition for Cu (II) complexes at 465, 532 (typi-

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cal octahedral transition) Co (II) complexes at 450,525 and 734nm and for Ni (II) complexes at 288 (Charge transfer), 517, 655.nm respectively supports the octahedral geometry of metal complexes^[23].

Magnetic moment

The magnetic moments obtained at room temperature are as shown in TABLE 2 The magnetic moment obtained at room temperature indicates paramagnetism. The Co (II) complex shows magnetic moment of 4.94 B.M., the spin free octahedral complex of Co (II) are reported to exhibit magnetic moment in the range of 4.46-5.53 BM^[24-27]. Hence, the observed magnetic moment for the Co (II) complex under study indicates that it has an octahedral configuration The Ni (II) complex shows magnetic moment of 3.04 B.M. The magnetic moment of octahedral Ni (II) complexes are reported to exhibit magnetic moment in the range of 2.80 -3.40 B.M.^[25-28] indicating spin orbital coupling contribution from $^3A_{2g}$ and higher $^3T_{2g}$ states. Hence, the observed magnetic moment for the Ni (II) complex suggests that it may have octahedral geometry. The observed magnetic moment of Cu (II) complex is 1.728 B.M. indicates octahedral geometry^[26-29]. Thus the electronic spectral data and magnetic moment data support the octahedral geometry of the complexes.

IR spectra

The IR data of spectra of Schiff base (HL) and their metal complexes are presented in TABLE 3. The valuable information regarding the nature of group attached to the metal atom can be obtained by IR spectra. The IR spectra of complexes are compared with those of ligand in order to determine the coordination sites that may be involved in chelation. Guide peaks in the spectra of ligand were helpful in achieving this goal. The position and / or intensities of these peaks are changing upon chelation. New peaks are guide peaks, as is water in chelation. The IR spectra of the complexes are shown in Figure 2. In the spectra of ligand (HL) $\nu(C=N)$ azomethine stretching vibration is found at 1620 cm^{-1} indicates clearly the formation of ligand. In the spectra of complexes, $\nu(C=N)$ stretching vibrations was shifted to lower frequencies 1603-1612 cm^{-1} , indicating the participation of azomethine nitrogen in coordination (M-N)^[30-32]. The assignment of the proposed coordination sites is further supported by appearance of band at 506-

516 cm^{-1} suggesting the $\nu(M-N)$ bond. The presence of $\nu(M-O)$ stretching vibration at 629-648 cm^{-1} supports the involvement of oxygen atom in complexation with metal ions. The ligand and metal complexes were characterized mainly using the azomethine and '-OH' bands. The band at the range of 3379-3385 cm^{-1} is attributed to the presence of water molecules. Therefore, from the IR spectra, it is concluded, that the ligand coordinated to the metal ions via azomethine nitrogen and deprotonated oxygen atom of benzoin.

TABLE 3 : IR spectral data

Complex	ν (C=O)	ν (C=N)	ν (C-O)	ν (M-N)	ν (M-O)	ν (C-OH)	ν (H ₂ O)
Benzoin	1679	-	-	-	-	-	-
HL	-	1620	1090	-	-	1093	3379
HL-Co	-	1612	1112	516	629	1314	3385
HL-Ni	-	1600	1112	506	645	1315	3383
HL-Cu	-	1603	1111	511	648	1318	3385

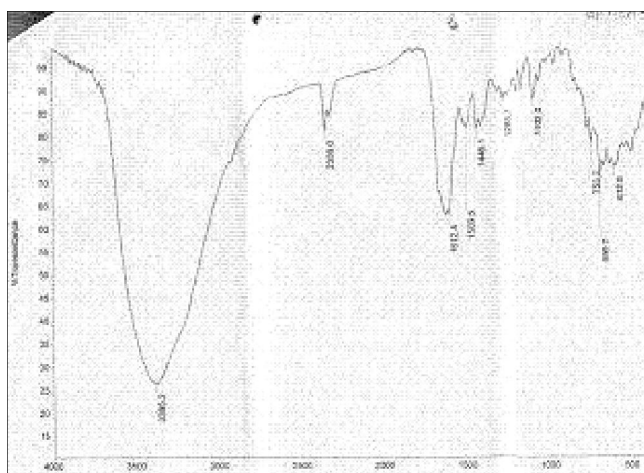


Figure 2 : IR spectra of metal complexes

¹H NMR spectra

The review of literature revealed that NMR spectroscopy has been proved to be useful in establishing the nature and structure of many Schiff bases. The NMR spectra of Schiff base is recorded in CDCl₃, using Tetramethylsilane (TMS) as an internal standard. The ¹H NMR spectra of benzoin show signals at 6.03 ppm assignable to -OH group, 6.09 ppm assignable to -CH- group and 7.06.-8.01 ppm assignable to aromatic protons. In the NMR spectra of ligand, the signal due to -OH shifts to 5.960 ppm^[33] moreover, addition of D₂O results in diminishing the signal due to -OH group supports the involvement of -OH group in the complex formation. Since, Co⁺², Ni⁺² and Cu⁺² complexes are

paramagnetic; their $^1\text{H NMR}$ spectra could not be obtained.^[28]

Mass spectra of the Schiff base

The mass spectra of Schiff base show a base peak m/e at 331 which is due to original molecular weight of the prepared compound (Schiff base) (Figure 3). This means that the condensation of the reactants gave pure compound.

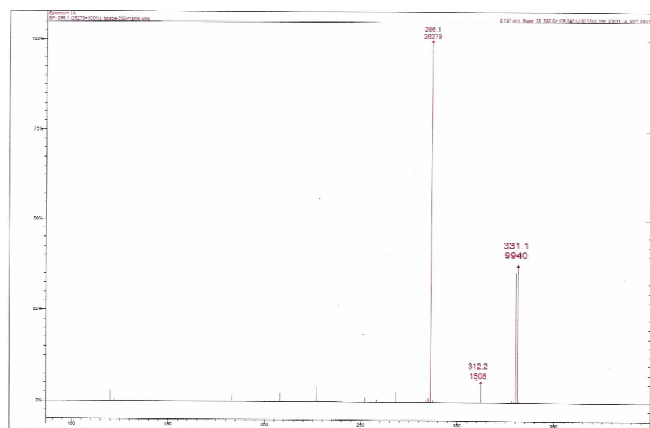


Figure 3 : Mass spectra of (HL) ligand

Thermal analysis

The thermogram of Nickel complex is as shown in Figure 4. Thermal decomposition of Co(II), Ni(II) and Cu(II) metal complexes have been studied as a function of temperature by TGA and DTG. It exhibited two step decomposition for the Schiff base metal complexes. First decomposition takes place around 200 °C due to total cleavage of the base metal complex along with hydroxide to oxide transformation followed by concomitant release of water molecules. The second decomposition takes place at 400 °C attributed to the release of intermediate organic moiety. The second slow and broad decomposition around 500 °C can be attributed to total

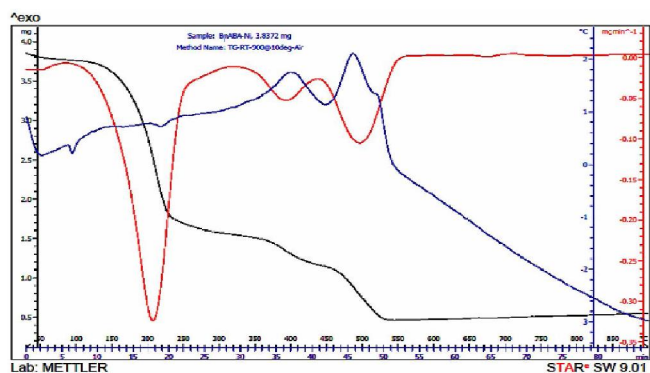


Figure 4 : Thermal analysis of HL-Co

decomposition of organic moiety into carbon dioxide and other gases. The remaining 20 % weight is totally due to presence of inorganic metal oxide^[24,34].

Biological Activity

The antibacterial and antifungal activity of the Schiff bases and their metal complexes was tested on *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Aspergillus niger* and *Candida albicans*. The method used for antibacterial activity was Agar Well-Diffusion method and for antifungal activity was Agar-Ditch method^[35]. The bacteria and fungi were sub-cultured in Nutrient agar and Sabouraud's agar respectively. The stock solution 1mg/ml was prepared and was used to prepare concentrations of 0.8, 0.6, 0.4 and 0.2 mg/ml. The plates were incubated at room temperature for 24h. In order to clarify the effect of DMF on the biological screening, separate studies were carried out with DMF and showed no activity against any bacteria and fungi. The results are as shown in the TABLE 4. The ligand shows activity against the microorganism *Staphylococcus aureus* and the fungi *Aspergillus niger* and *Candida albicans*. HL-Co and HL-Ni complexes

TABLE 4 : Biological activity of complexes.

Name	Concentration mg / lit.	Staphylococcus Aureus	Pseudomonas Aeruginosa	Aspergillus niger	Candida albicans
HL	200	+ ve	- ve	+ ve	+ ve
	400	+ ve	- ve	+ ve	+ ve
	600	+ ve	- ve	+ ve	+ ve
	800	+ ve	- ve	+ ve	+ ve
	1000	+ ve	- ve	+ ve	++ ve
HL-Co	200	+ ve	- ve	+ ve	+ ve
	400	+ ve	- ve	+ ve	+ ve
	600	+ ve	- ve	+ ve	+ ve
	800	+ ve	- ve	++ ve	+++ve
	1000	+ ve	- ve	++ ve	+++ve
HL-Cu	200	- ve	- ve	- ve	- ve
	400	- ve	- ve	- ve	- ve
	600	- ve	- ve	- ve	- ve
	800	- ve	- ve	- ve	- ve
	1000	- ve	- ve	- ve	- ve
HL-Ni	200	+ ve	- ve	+ ve	+ ve
	400	+ ve	- ve	+ ve	+ ve
	600	+ ve	- ve	+ ve	+ ve
	800	+ ve	- ve	+ ve	+ ve
	1000	+ ve	- ve	+ ve	+ ve

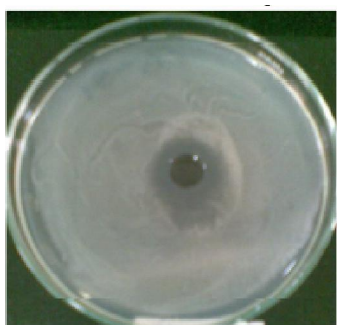
[+= Sensitive -= Resistant]

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show maximum activity against *Aspergillus niger* and *Candida albicans*. The complex HL-Co shows the activity against *Staphylococcus aureus* microorganism. The *Pseudomonas aeruginosa* is found to be resistant. All the organisms are found to be resistant to the HL-Cu complex. (Figure 5(a)-(d)) The results are compared with standard antibiotics like Gentamycin and Streptomycin.



(a) HL ligand against *Aspergillus niger* and *Candida albicans*



(b) HL-Co complex against *Staphylococcus aureus*



(c) HL-Co complex against *Aspergillus niger* and *Candida albicans*



(d) HL-Ni complex against *Aspergillus niger* and *Candida albicans*

Figure 5 : Biological activity of ligand and complexes

CONCLUSION

All the complexes are octahedral geometry and paramagnetic nature. On the basis of the spectral data and magnetic data the structure of the complexes is as shown in Figure 6. Also on the basis of microbial study

the complexes shows remarkable antibacterial and antifungal activity against the *Staphylococcus aureus*, *Aspergillus niger* and *Candida albicans* organisms tested.

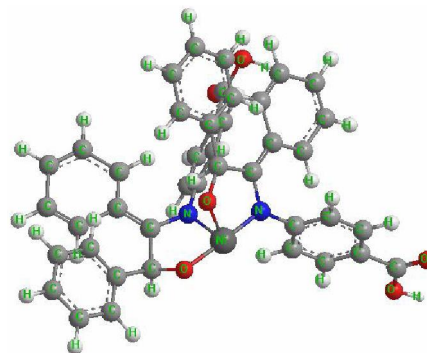


Figure 6 : Structure of metal complex

REFERENCES

- [1] J.D.Lee; Concise Inorganic Chem., 5th Edn.
- [2] A.A.Grinberg; Russ.Chem.Rev., 40 (1961).
- [3] S.S.Singh, D.D.Ansari, M.N.Rana; J.Indian Chem.Soc., 74(6), 448-541 (1997).
- [4] A.R.Sarkar, S.Mandal; Synth.React.Inorg.Met-Org.Chem., 80, 1477 (2008).
- [5] B.L.Shaw, S.D.Parera, M.Thornton-Pett, J.D.Vessey; Inorg.Chem.Acta, 207, 175-178 (1993).
- [6] Offiong E.Offiong; Spectrochimica Acta, 50, 2167 (1994).
- [7] M.T.H.Tarafder, Ali M.Akbar; Can.J.Chem., 56, 2000 (1978).
- [8] F.M.Morad, E.L.M.M.Ajally, S.Ben Gweirif; J.Sci. and Its Appl., 1, 72 (2007).
- [9] S.J.Swamy, A.Dharma Reddy; J.Ind.Chem.Soc., 77, 336-338 (2000).
- [10] B.D.Sharma, J.C.Bailur; J.Amer.Chem.Soc., 77, 5476 (1955).
- [11] F.P.Dwyer, M.S.Gill, E.C.Gyarfas, F.Lion; J.Amer.Chem.Soc., 79, 1269 (1957).
- [12] Salib Kar, S.M.Elsayed, A.M.Elshabiny; Synth.React. Inorg.Met.Org.Chem., 21(10), 1511 (1991).
- [13] B.A.Mahapatra, S.K.Kar; Orient.J.Chem., 10(3), 259 (1954).
- [14] P.P.Hankare, P.H.Bhoite, P.S.Battse, K.M.Garadkar, A.H.Jagtap; Indian J.of Chem., 39A, 1145-1149 (2000).
- [15] H.W.Florey; 'Antibiotics II', Oxford Medical Publications, U.K., 1476 (1949).
- [16] S.G.Shirodkar, P.S.Mane, T.K.Chondhekar; Indian J.of Chem., 40A, 1114-1117 (2001).

- [17] R.Rajavel, M.Senthil, Vadivu, C.Anitha; E.-J.of Chem., **5**, 620 (2008).
- [18] Gangadhar B.Bagihalli, Prakash Gouda Avaji, Prema S.Badami, Sangamesh A.Patil; J.Coord.Chem., **61**, 2793 (2008).
- [19] B.Mahapatra; Ind.Chem.Soc., **59**, 988 (1982).
- [20] B.B.Mahapatra, Debendra Panda; Trans.Met. Chem., **9**, 476-478 (1984).
- [21] T.Narayan, Akinchan et al; Tran.Met.Chem., **19**, 135 (1994).
- [22] P.P.Hankare, A.H.Manikshete et al; J.Indian Chem.Soc., **68**, 557-559 (1991).
- [23] A.A.Ahmed, S.A.BenGuzzi, A.A.Hadi; J.Sci.and Its Appl., **1**, 79 (2007).
- [24] Khlood's Abou-Melha; J.Co-ordination Chem., **61**, 2053 (2008).
- [25] F.A.Cotton, G.Wilkinson; 'Advanced Inorganic Chemistry', 5th Ed., Wiley, New York.
- [26] K.Siddappa, Tukaram Reddy, M.Mallikarjun, C.V.Reddy; E.-Journal of Chem., **5(1)**, 155-162 (2008).
- [27] M.M.Bekhet, K.M.Ibrahim; Synth.React.Inorg.Met. Org.Chem., **16**, 1135 (1986).
- [28] Erdal Canpolat, Mehmet Kaya; Turk.J.Chem., **29**, 409-415 (2005).
- [29] Mohammad Shakir, Mohammad Azam, Shama Parveen, Asad U.Khan, Farha Firdaus; Spectrochimica Acta, **A1**, 1851 (2009).
- [30] M.R.Iskander, L.Ei-Syed, K.Z.Ismail; Trans.Met. Chem., **4**, 225 (1979).
- [31] M.Thankamony, K.Mohanan; Ind.J.Chem., **46A**, 249 (2007).
- [32] Gehad Geindy Mohamed et al; Turk.J.Chem., **30**, 361-382 (2006).
- [33] Wang Bo, Liu Jinxia, Yang Shiyan, Jin Daosen; Polyhedron, **14**, 895 (1995).
- [34] Abdul Hakim, A.Ahmed, Salima A.BenGuzzi, Soad Agumati; J.of Sci.and Its Appl., **2**, 83 (2008).
- [35] C.H.Collins, P.M.Lyne, J.M.Granger, Editors Collins, Lyne's; 'Microbiological Methods', 7th Ed., Oxford: Butterworth-Heinemann, 320 (1995).