



Synthesis Characterization and Antimicrobial Activity of Cobalt (II) Complexes with Schiff Base Ligands

M. Shilpa¹, C. Ramalechume², S. Abinaya³

¹Malla Reddy Engineering College for Women Hyderabad, Telangana, INDIA.

²Post Graduate Department of Chemistry, Women's Christian College, Chennai, Tamil Nadu, INDIA.

³II M.Sc Chemistry, post Graduate Department of Chemistry, Women's Christian College, Chennai, Tamil Nadu, INDIA.

Email: shilpamynam@gmail.com

ABSTRACT

Schiff base ligands are easily prepared by the condensation between aldehydes and amines. These compounds are also known as anils, imines or azomethines. Lone pair of nitrogen atom of the azomethine group is of considerable chemical and biological importance. Schiff base ligands are able to coordinate with various transition metal and to stabilize them in various oxidation states. They have been playing an important part in the development of coordination chemistry. These metal complexes have been studied extensively because of their attractive chemical and physical properties and their wide range of applications in numerous scientific areas. Various researchers are aggressively focusing on synthesis of various Schiff bases with different metal complexes and try to identify their unique properties.

Keywords: Schiff base, Transition metal, Cobalt complex, antimicrobial activity biological studies.

Introduction:

The most important simplest compound of class arenes is naphthalene in which two benzene rings are fused in ortho positions [1,2]. The naphthalene-based derivatives are pharmaceutically more important due to their diverse and interesting antimicrobial nature [1,2]. Naphthalene major part containing drugs which play a vital role in the control of microbial infection [1]. Naphthalene containing FAD approved some of the marketed drugs are Nafcillin (Gram positive bacterial infection) [3,5], naftifine (topical antifungal agent) [3,6], terbinafine (antifungal drug) [3,7], tolnaftate (antifungal cream) [1], rifampicin (antitubercular drug)[3], Bedaquiline(multidrug resistance tuberculosis along with other drugs)[3] etc.

On the other side, the imine or azomethine groups containing organic ligands which shows more biological properties, including antimicrobial, anti-inflammatory, analgesic, anti-tubercular, antimycobacterial, antioxidant, antiviral, inhibitory, cytotoxic, anticonvulsant, anti-proliferative, anticancer and antifungal activities [8-10].

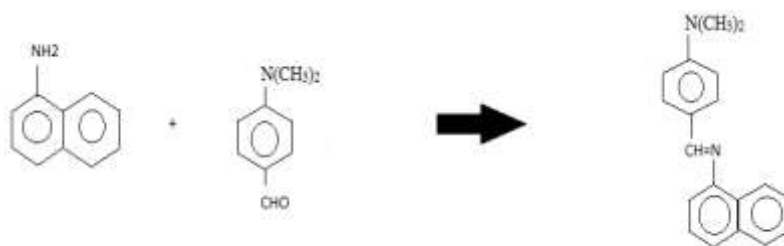
In biological systems, azomethine nitrogen of Schiff bases provides a binding site for metal ions to be attached with various bio-molecules like proteins and amino acids for anti-germ activities. Schiff bases generally catalyze many metabolic reactions in the form of enzymes that show activities against various microbes. Biofunctions of Schiff bases and their metal complexes have been improved by various researches. They exhibit various biological activities depending upon the different transition metal ions with various Schiff bases [10,11]. A large number of reports on the antibacterial properties of cobalt complexes have appeared in the literature, with Co(II) complexes being the most studied, presumably due to their aqueous stability, availability, and ease of synthesis. However a number of examples of stable Co(II) complexes have also been reported [12-21]. The main objective is to synthesize two different Schiff based Co(II) complexes derived from two different aldehydes 4-aminodimethylbenzaldehyde and furfuraldehyde with 1-naphthyl amine. The synthesised complexes were characterized by using characterisation techniques such as UV-Visible and FTIR Spectrometer. The two metal complexes were also screened for their antibacterial activity against bacterial species, Escherichia coli and Staphylococcus aureus.

Experimental Section

All reagents were commercially available and used without any purification. They are cobalt(II) chloride (Paxmy Speciality chemicals), 4-amino dimethyl benzaldehyde, 1-naphthyl amine, furfuraldehyde (Sigma Aldrich), and absolute ethyl alcohol. Solvents were distilled from appropriate drying agents immediately prior to use. Electronic spectra of the prepared compounds were measured in the region 200–800 nm for 10⁻³ M solutions in ethanol at 25°C using a Shimadzu 160 spectrophotometer. IR spectra were recorded using KBr pellet on FTIR spectrum on Shimadzu instrument from 400 to 4000cm⁻¹.

Synthesis of complex 1

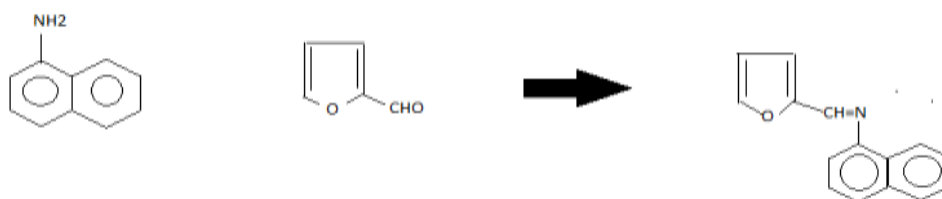
4-aminodimethylbenzaldehyde (0.1mmol) was added to 1-naphthyl amine (0.1mmol) in 1:1 molar ratio in ethanol (0.25 cm³) was refluxed for an hour. Then a solution of 0.01g of cobalt(II) chloride dissolved in ethanol solution was poured in the round bottom flask. Add a porcelain bit to the condenser. The above mixture is refluxed for 2 hours. After cooling the reaction mixture to an ambient temperature, the formed solid was filtered, washed and finally dried. The structure of ligand was shown in scheme 1.



Scheme 1. Structure of ligand -1

Synthesis of complex 2

Procedure is as above complex -1 by using 1-naphthyl amine (0.1mmol) and furfuraldehyde (0.1 mmol). The structure of ligand was shown in scheme 2.



Scheme 2. Structure of ligand -2

Results and Discussion

UV-Visible Spectroscopy

UV-Visible spectrum of the complexes was recorded in ethanol and the spectrum of complex-1, 2 is shown in figure. The peaks for complex-1 are 207 nm, 240 nm, 294 nm and 309 to 353 nm and complex -2 peaks are 219 nm, 236 nm, 272 nm and 321nm respectively. These peaks shows that various types of transition take place in the complex-1 and complex -2. The peak appeared at 207nm, 240nm complex -1 and 219nm, 236nm is due to $\pi \rightarrow \pi^*$ transitions. The peaks around 294nm and 309 nm and 353nm in complex-1 and 272nm, 321nm in complex -2 is due to $n \rightarrow \pi^*$ transition was occurred localized within the imine chromophore and the LMCT (ligand to metal charge transfer bands) transition. Based on these data we can conclude that complex formation occurs between metal and ligand.

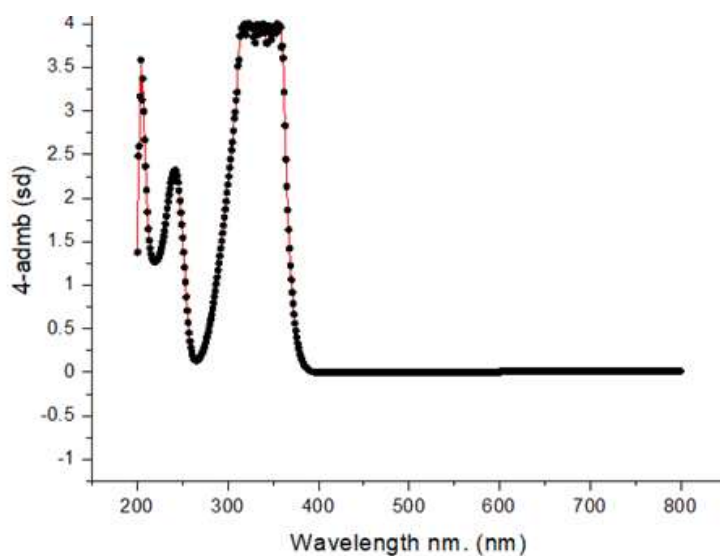


Fig 1. UV-Visible spectrum of complex-1

FTIR Spectroscopy

The FTIR spectra of complex-1 shows in figure 2. Complex -1 IR spectrum shows two bands at 3514 and 3010 cm^{-1} assignable to $\nu(\text{OH})$ phenolic and $\nu(\text{N-H})$ respectively. The IR spectrum of the complex showed a shoulder peak at 1631 cm^{-1} assigned to $\nu(\text{C}=\text{N})$ of the azomethine stretching vibration. This group has occurred from the condensation reaction between (NH_2) and carbonyl $(\text{C}=\text{O})$ group. M-N band appears at $605\text{-}610\text{ cm}^{-1}$. The presence of M-L band at $605\text{-}750\text{ cm}^{-1}$ support the complex formation. In complex-2 shows in figure 3. IR spectrum shows two bands at 3504 and 3103 cm^{-1} assignable to $\nu(\text{OH})$ phenolic and $\nu(\text{N-H})$ respectively. The IR spectrum of the complex showed a shoulder peak at 1629 cm^{-1} assigned to $\nu(\text{C}=\text{N})$ of the azomethine stretching vibration. This group has occurred from the condensation reaction between (NH_2) and carbonyl $(\text{C}=\text{O})$ group. M-N band appears at 615 cm^{-1} . The presence of M-L band at $605\text{-}750\text{ cm}^{-1}$ supports the complex formation.

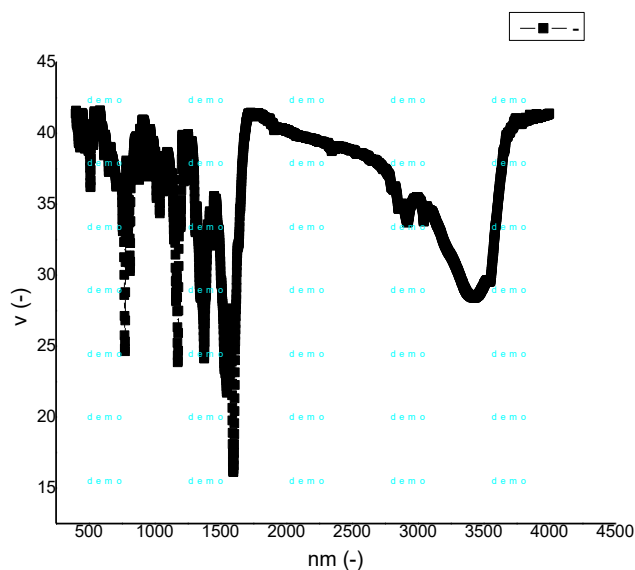


Fig 2. FTIR spectrum of complex-1

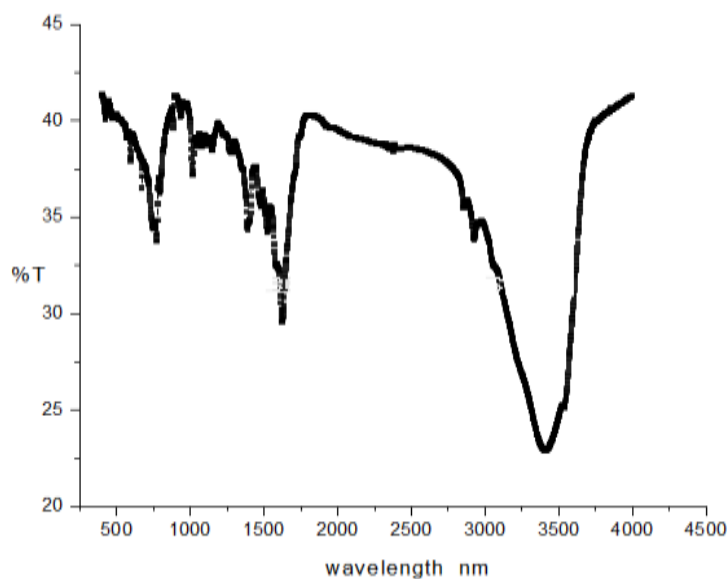


Fig 3. FTIR spectrum of complex-2

Mass spectra

The molecular formula of complex-I is $\text{Co C}_{38}\text{N}_4\text{H}_{38}\text{ClO}$ and theoretical molecular weight is 659. The proposed molecular formula of this complex was confirmed by FAB mass spectroscopy. From this data the complex shows a major peak at 660 (Fig 4) experimental value which is closely related to theoretical value. From this data we can confirm the structure of complex -I structure is central metal cobalt is surrounded by 2 Schiff base ligands and one chlorine and one water molecule. The confirmed complex coordination number is 4.

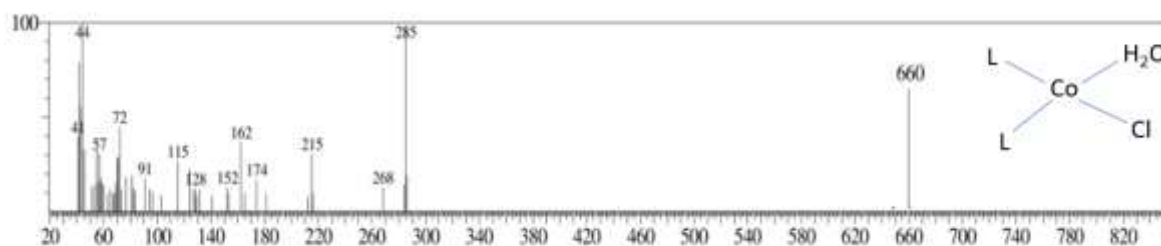


Fig 4. Mass Spectroscopy of Cobalt (II) complex-1

The molecular formula of complex-2 is $\text{Co C}_{30}\text{N}_2\text{H}_{24}\text{ClO}_3$ and theoretical molecular weight is 552. The proposed molecular formula of this complex was confirmed by FAB mass spectroscopy. From this data the complex shows a major peak at 550 (Fig 5) experimental value which is closely related to theoretical value. From this data we can confirm the structure of complex -2 structure is central metal cobalt is surrounded by 2 Schiff base ligands and one chlorine and one water molecule. The confirmed complex coordination number is 4.

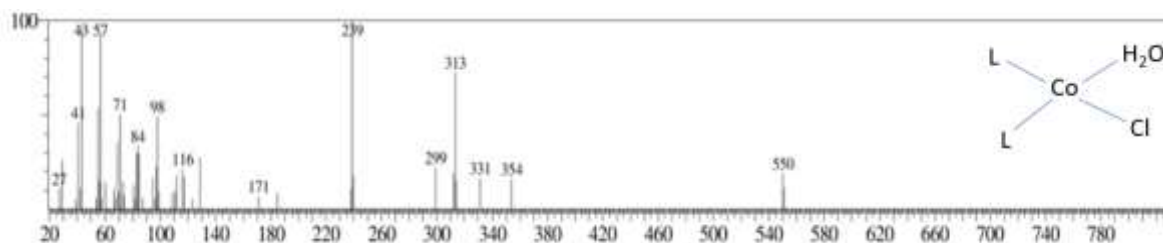


Fig 5. Mass Spectroscopy of Cobalt (II) complex-2

Anti-bacterial activity

The antimicrobial activity done by using the metal complex at different concentration 10% to 40% in ethanol solution. The above two bacteria's E.Coli (gram negative bacteria) and Staphylococcus aureus (gram positive bacteria) show biological activity towards complex-1 and complex-2. In these two complexes complex-2 which shows more antibacterial activity than the complex-1. The antibacterial activity of complex 1 with two different

bacteria's shown in fig 6 & 7 for complex 2 shown in 8 & 9 and zone of inhibition measured in mm for different concentrations shown in table 1 respectively.

Results can also be explained on the basis of chelation therapy and /or may be due to overtones concept [22]. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups and possible π electron delocalization on the whole chelate ring. The lipids and polysaccharides are some important constituents of cell walls and membranes, which cell wall also contains many amino phosphates, carbonyl and cysteinyl ligands, which maintain the integrates of the membrane by acting as a diffusion barrier and also provide suitable sites for binding. Chelation can considerably reduce the polarity of the metal ion and increase the lipophilic character of the chelate. Thus, interaction between metal ion and lipid is favoured. This may lead to the breakdown of the permeability barrier of the cell, resulting in interference with the normal cell process. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organism. Other important factors that contribute to the activity are the nature of the metal ion, nature of the ligand, coordinating site and geometry of the complex, concentration, hydrophobicity, lipophilicity and the presence of co-ligands. Steric factor plays a decisive role in deciding the potency of an antimicrobial agent. The presence of lipophilic and polar substituent is expected to enhance antimicrobial activity. Heterocyclic ligands with multi functionality have a greater chance of interaction either with nucleoside bases or with biologically essential metal ions present in the biosystem and can be promising candidates as bactericides since they always look to enact especially with some enzymatic functional groups to achieve a higher coordination number. Thus, antimicrobial property of metal complexes cannot be described to chelation alone but it is an intricate blend of all the above contributions. The Antibacterial activity of complex-1 and 2 with *Staphylococcus aureus* and *E.Coli*.

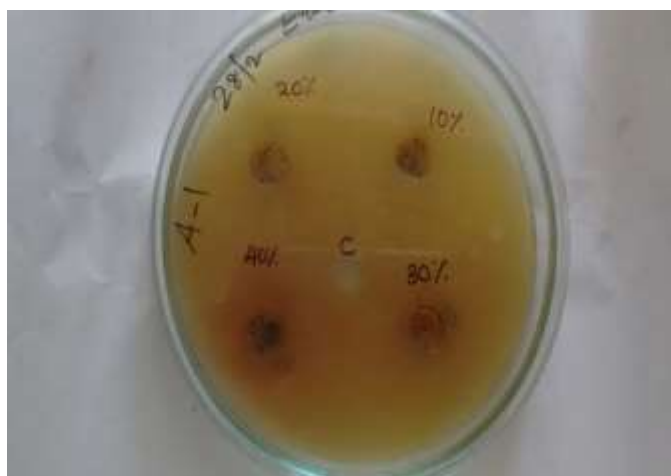


Fig. 6 Antibacterial activity of complex-1 with E.Coli

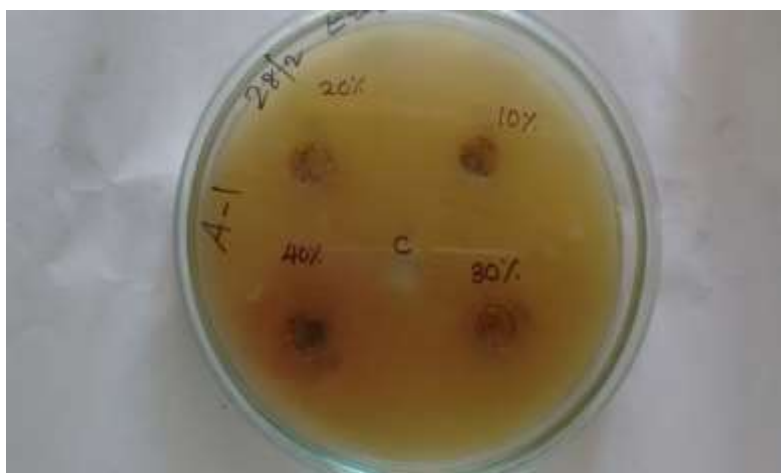


Fig. 7 Antibacterial activity of Complex-1 with Staphylococcus aureus

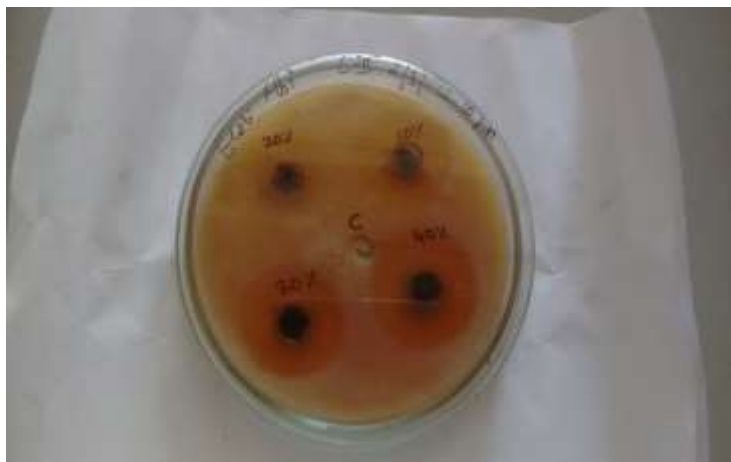


Fig. 8 Antibacterial activity Complex-2 with E.Coli

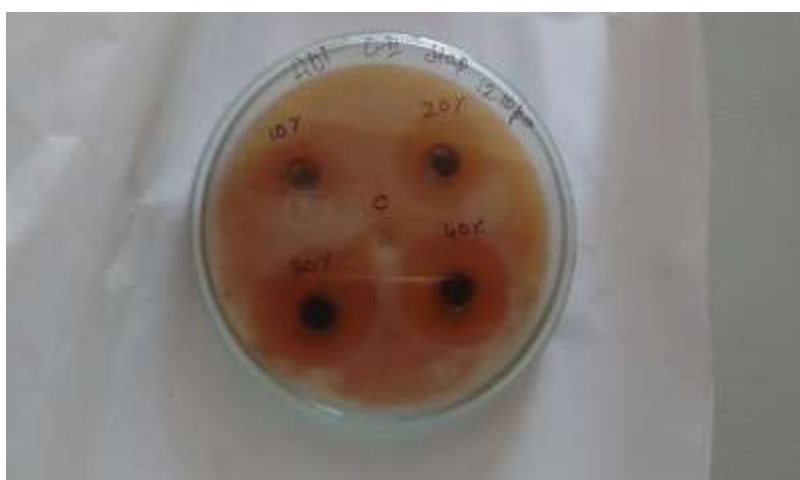


Fig. 9 Antibacterial activity of Complex-2 with Staphylococcus aureus

Table 1 Antibacterial activity of complex 1 and complex 2 with different concentrations

BACTERIA		10%	20%	30%	40%
E.COLI	Complex-1	2mm	5mm	7mm	10mm
	Complex-2	5mm	8mm	10mm	12mm
S.AUREAS	Complex-1	3mm	5mm	8mm	10mm
	Complex-2	10mm	13mm	15mm	18mm

SUMMARY

A novel Co(II) Schiff based metal complexes have been synthesized and characterized by using UV-Visible IR and mass spectroscopy. Based on the spectral studies strongly explained the complex formation take place between Schiff based ligand and metal. By mass spectroscopy confirmed the metal complex with coordination number 4. These two complexes which shows biological activity towards E.Coli and Staphylococcus aureus. In these two complexes complex-2 which shows more anti bacterial activity than the complex-1 on comparing between ligand 1 & 2, ligand 1 is more bulky than ligand 2. The biological activity may also depend upon the ligand structure including planarity of ligand and bulky group attached. In future we can study the DNA interaction for these complexes.

References:

1. Bhawna Chopra, Ashwani K. Dhingra, Ram P. Kapoor And Deo N. Parsad Journal Of Xploratory Research In Pharmacology 2017 Vol. 2 ,105–112.
2. Naphthalene Derivatives Rasayan J. Chem Vol.2, No.4 (2009), 972-980.

3. Naphthalene, A Versatile Platform In Medicinal Chemistry: Sky-High Perspective
4. [Subhajt makartanmay sahasushil K.Singh](#) [European Journal Of Medicinal Chemistry](#) [Volume 161](#), 1 January 2019, Pages 252-276
5. L. Iversen, S. Gibbons, R. Treble, V. Setola, X.-P. Huang, B.L. Roth, Eur. J. Pharmacol. 700 (2013) 147-151.
6. J.M. Mühlbacher, Naftifine: A Topical Allylamine Antifungal Agent, Clin. Dermatol. 9 (1991) 479-485.
7. N. Ryder, I. Frank, M. Dupont, Antimicrob. Agents Chemother. 29 (1986)855-860.
8. F. K. Ommenya, E. A. Nyawade, I D. M. Andala, And J. Kinyua Journal Of Chemistry Volume 2020, Article Id 1745236, 8 Pages
9. Sham M. Sondhi,A,* Nirupma Singh,A Ashok Kumar,B Olivier Lozachc And Laurent Meijerc Bioorganic & Medicinal Chemistry 14 (2006) 3758–3765.
10. Mohammad Nasir Uddin , Sayeda Samina Ahmed And S. M. Rahatul Alam [Journal Of Coordination Chemistry](#) Volume 73, 2020 - [Issue 23](#) Pages 3109-3149.
11. D. Chaturvedi, M. Kamboj. Chem. Sci. J., 7, 1000(2016).
12. Sadeghi, S., Eslahi, M., Naseri, M.A., Naeimi, H., Sharghi, H., Shameli, A., 2003,Electroanalysis, 15 (1327-1333).
13. Mashhadizadeh, M. H., Sheikhshoei, I., Saeid-Nia, S., 2003, Sensors and Actuators B chemical, 94, (241-246).
14. Mahajan, R.K., Kaur, I., Kumar, M., 2003,Sensors and Actuators B chemical, 91 pp(26-31).
15. Mashhadizadeh, M.H., Sheikhshoei, I., 2003, Analytical and Bioanalytical Chemistry, 375: (51).
16. Singh, L. P., Bhatnagar, J. M., Talanta, 2004, J. Chemical Reviews , 64pp (313-319).
17. Fakhari, A.R., Raji, T.A., Naeimi, V., Sensors and Actuators B chemical, 104 (2005) 317-323.
18. Jeong, T., Lee, H.K., Jeong, D.C. Jeon, S., Talanta, 2005:65 (543-548).
19. Shamsipur, M., Yousefi, M. Hosseini, M.R. Ganjali, H. Sharghi, H. Naeimi. 2001 Analytical Chemistry, 73 (2869-2874).
20. Ganjali, M.R., Poursaberi, T., Hosseini, M., Salavati-Niasari, M., Yousefi, M., Shamsipur, M., 2002,Analytical Sciences, 18 (289-292).
21. Ganjali, M.R., Pourjavid, M.R., Rezapour, M., Poursaberi, T., Daftari, A., Salavati-Niasari, M., 2004, Electroanalysis, 16 (922-927).
22. Sigman, D.S., Graham, D.R., Marshall, L.E., Reich, K.A. 1980 J. Am Chem Soc, 102:99(5419).