



Structural Elucidation of Some Coordination Compounds With Reference To Schiff Base Coordination

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ABSTRACT

This paper reveals that the hexa-coordinated mixed ligand Cu(II), Zn(II), Ni(II) and Co(II) complexes of the type $[MLX]Cl_2$ where X=1,10-phenanthroline and ligand (L) have been synthesised from the condensation of thiophene-2-carboxaldehyde with *o*-phenylenediamine. They were characterised by elemental analysis, molar conductance, magnetic susceptibility, infrared, electronic absorption, proton magnetic resonance and mass spectral studies. An octahedral geometry has been proposed for all these complexes. The high molar conductance studies of the complexes show their electrolytic nature. The infrared spectra of the complexes show that the imine group of the Schiff base coordinate with the metal ion. The electronic absorption spectra of the complexes show the charge transfer, d-d transitions consistent with their proposed geometry. The proton magnetic resonance spectrum of the ligand shows the presence of CH=N group in the ligand. The mass spectral data also confirms the proposed structure of ligand and its complexes. The mixed ligand complexes possess good catalytic activity in the reaction of oxidation of alcohols using H_2O_2 as oxidant. The antibacterial activity of the mixed ligand complexes has been carried out by disc diffusion method. Copper (II) complexes exhibit potent antibacterial activity when compared to the standard drug streptomycin. The above complexes also exhibited DPPH radical scavenging activity.

Keywords: Mixed Ligand Complexes; Catalytic Oxidation; Antibacterial; DPPH radical Scavenging Activity

INTRODUCTION

Schiff bases derived from aromatic amines and aromatic aldehydes or ketones have a wide variety of applications in many fields like biological, inorganic and analytical chemistry^{1,2}. They play important roles in coordination chemistry as they easily form stable complexes with most transition metal ions^{3,4}. Schiff base metal complexes have been widely studied because of their industrial, antifungal, antibacterial⁵, anticancer, antiviral and herbicidal applications⁶⁻¹¹. Transition metal complexes have the ability to mimic the functional properties of natural metalloproteins^{12,13}. The chemistry of metal complexes with multidentate ligands having delocalized π -orbitals has been recently gained more attention because of their use as models in biological systems. The transition metal complexes with tetradentate Schiff base ligands have been studied as catalyst for a number of organic oxidation and reduction reactions^{14,15}. In recent decades, diimino tetradentate Schiff bases and their complexes have been much more attracted because of their potential in the development of biological processes^{16,17}. Insufficient levels of antioxidants or inhibition of the antioxidant enzymes cause oxidative stress and may damage or kill cells. Oxidative stress seems to play a significant role in many human diseases including cancers. Antioxidants are widely used in dietary supplements and have been investigated for the prevention of diseases such as cancer, coronary heart diseases and even altitude sickness. Antioxidants are frequently added to industrial products such as stabilizers in fuels and lubricants to prevent

oxidation and in gasolines to prevent polymerization¹⁸. Bearing these facts in mind, the hexa-coordinated mixed ligand Cu(II), Zn(II), Ni(II) and Co(II) complexes were synthesised from the diimino tetradentate Schiff base which was derived from the condensation of thiophene-2-carboxaldehyde with *o*-phenylenediamine and 1,10-phenanthroline. The complexes possess potent antibacterial and antioxidant activities. These complexes have also been employed as catalyst for the oxidation of alcohols.

MATERIALS AND METHODS

All chemicals used in the present work, viz., thiophene-2-carboxaldehyde, *o*-phenylenediamine, 1, 10-phenanthroline, Copper, Zinc, Cobalt and Nickel chlorides were of analytical reagent grade (Merck, Germany). Common solvents like Ethanol, Methanol, and DMSO used at various stages of this work were purified according to the standard procedures described in Weissenburg series¹⁹ and in quantitative analysis by Vogel²⁰. Elemental analysis (C, H, N and S) were performed using a Carlo Erba 1108 analyzer. The molar conductivity of the complex in DMSO (10^{-3}mol/dm^3) was measured using a Systronic Model-304 digital direct reading conductivity meter. Magnetic susceptibility measurements were carried out by employing the Gouy method at room temperature on powder sample of the complex. Copper sulphate was used as calibrant. Infra-red spectra of the Schiff base and its metal complexes were recorded as KBr discs in the range $400\text{-}4000\text{ cm}^{-1}$ on a Shimadzu spectrophotometer. The electronic absorption spectra of the Schiff base and its metal complexes were recorded on a Shimadzu UV-1601 spectrophotometer. The ¹H NMR spectra of the Schiff base and its zinc complex in DMSO-*d*₆ were recorded using tetramethylsilane as internal standard. Electrospray ionisation mass spectrometry (ESI-MS) analysis was performed in the positive ion mode on a liquid chromatography-ion trap mass spectrometer.

Estimation of metal

The metals were estimated gravimetrically as their oxides²¹ by fusion with AnalaR ammonium oxalate. In a typical experiment, about 0.3g of the dried complex was accurately weighed in a previously weighed silica crucible. AnalaR ammonium oxalate, roughly three parts by weight of the complex, was added and the mixture was incinerated slowly at first and then strongly using a Bunsen burner for 3h. It was then cooled in a desiccator and weighed. The procedure was repeated till the final oxide weight was constant. From the weight, the percentage of metal in the complex was calculated.

Determination of Chloride Content

The chloride present in the complexes was determined gravimetrically as silver nitrate test²².

Synthesis of ligand (L)

An ethanolic solution of thiophene-2-carboxaldehyde (0.04mol, 3.67ml) was added dropwise to an ethanolic solution of *o*-phenylenediamine (0.02mol, 2.163g) with continuous stirring and reaction mixture was refluxed for ca. 5h²³⁻²⁵. The yellow product obtained was filtered and recrystallized from ethanol and dried in desiccator over anhydrous calcium chloride. Yield = 83%. The schematic representation of the Schiff base is given in [figure 1](#).

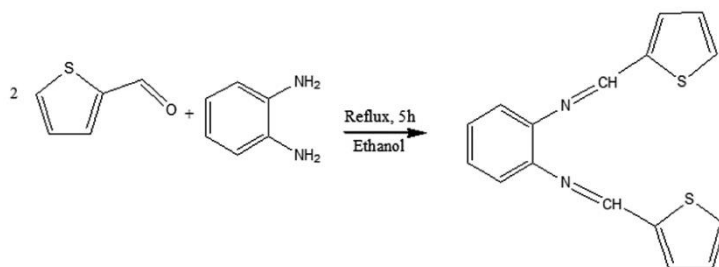


Figure 1 Synthesis of the Schiff base.

Synthesis of metal complexes

An ethanolic solution of the Schiff base (0.002 mol) was added to the ethanolic solution of metal (II) chlorides (0.002 mol) and refluxed for ca. 3 h. To the above mixture an ethanolic solution of 1,10 - phenanthroline (0.002 mol) was added in a 1:1:1 molar ratio and refluxed for about ca.2 h. The solid product formed was filtered and washed with ethanol.

Biological Studies

Antibacterial Studies

The *in vitro* antibacterial screening of the Schiff base and their complexes were evaluated by the disc diffusion method against the human pathogens such as *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli* and *Proteus mirabilis*²⁶. A loop full of bacterial cells from the nutrient agar plates was incubated into a nutrient broth (50 mL) in a 250 mL Erlenmeyer flask and incubated at 37 °C for 18 h with vigorous shaking. Using a sterile L-rod 18 h bacterial cultures (100 µL) were spread on nutrient agar and allowed to dry for 5 minutes. The 5 mm diameter and 1 mm thickness filter-paper discs of uniform size are impregnated with different concentrations of Schiff base and their complexes and then placed on the surface of an agar plate that has been seeded with the organism to be tested. Then the plates were incubated at 37 °C for 24 h. During this period, the test solution diffused and inhibits the growth of the inoculated bacteria. The zone of inhibition, developed on the plate was measured in mm. *Streptomycin* was used as standard.

Antioxidant Studies (DPPH assay):

DPPH scavenging activity was carried out by using the method of Kirby Schmidt (1997) with slight modification. Different concentrations (1000, 500, 250, 125µg/ml) of Schiff base and its complexes were weighed respectively and dissolved in DMSO. Then 5ml of 0.1mM ethanolic solution of DPPH (1, 1, diphenyl – 2 - picrylhydrazyl) was added to each of the test tube containing the sample and the tubes were shaken vigorously. They were then allowed to stand at 35°C for 30 minutes. The control was prepared without any compound and ethanol was used for base line corrections in absorbance (OD) of samples measured at 517 nm. Radical scavenging activities were expressed as % scavenging activity and were calculated by the following formula.

$$\% \text{Radical scavenging activity} = \frac{\text{Control OD} - \text{Sample OD}}{\text{Control OD}} \times 100$$

Catalytic activities

A large number of Schiff base metal complexes exhibit catalytic activities²⁷⁻³⁵. The catalytic oxidation of 1° and 2° alcohols to the corresponding carbonyl compounds have been studied by H₂O₂ as oxidant using the complex [MLX]Cl₂ as catalyst. About 0.1 mol H₂O₂ was added to the mixture of 0.1 mol substrate and 0.001 mol [MLX]Cl₂ in CH₂Cl₂ was stirred for 4-5 hrs at room temperature. The progress of the reaction and completion was checked by TLC. The product was separated and purified by column. The percentage yield of the product was noted.

RESULT AND DISCUSSION

The complexes of the type [MLX]Cl₂ where, M=Cu(II), Zn(II), Ni(II) and Co(II), L=tetradentate Schiff base, X=1,10-phenanthroline were synthesised by the reaction of tetradentate ligand, metal(II)chlorides and 1,10-phenanthroline in a 1:1:1 molar ratio in ethanol. In DMSO the complexes showed high molar conductance value indicates the electrolytic nature. The analytical data for the mixed ligand complexes agreed well with the proposed molecular formula as given in Table 1.

Table 1 Physical characterization, Analytical, Molar conductance, and Magnetic susceptibility data of the ligand and its complexes.

Compound	Yield (%)	Colour	Found (calc)%					Formula Weight	Λ_M/S $cm^2 \cdot mol^{-1}$	μ_{eff}/μ_B
			M	C	H	N	S			
L	83	Yellow	-	64.53 (64.84)	4.01 (4.08)	9.47 (9.45)	21.50 (21.63)	296.4	-	-
[CuLX]Cl ₂	70	Pale green	11.87 (11.76)	63.06 (62.26)	3.67 (3.73)	10.70 (10.37)	11.80 (11.87)	540.2	101.3	1.94
[ZnLX]Cl ₂	68	Yellow	12.45 (12.06)	63.38 (62.05)	3.68 (3.72)	10.54 (10.34)	11.78 (11.83)	542.0	110.4	Diamagnetic
[NiLX]Cl ₂	73	Green	11.40 (10.97)	63.84 (62.82)	3.56 (3.77)	10.79 (10.97)	11.88 (11.98)	535.3	99.5	3.12
[CoLX]Cl ₂	75	Pale brown	11.45 (11.00)	63.26 (62.80)	3.97 (3.76)	10.05 (10.46)	11.65 (11.97)	535.5	105.4	4.78

Infrared Spectral Studies

The IR spectrum of the free ligand shows band at 1660 cm^{-1} is characteristics of the azomethine moiety. This band is shifted to lower frequency in the complexes which indicates the coordination of metal to the azomethine nitrogen. The absorption band at 848 cm^{-1} is due to thiophene ring ν_{C-S-C} . This band shifts to the lower wave number in the complexes. This shows the sulfur in the thiophene is participated in the complexation^{36,37}. The appearance of two new bands in the regions $510-495\text{ cm}^{-1}$ and $421-418\text{ cm}^{-1}$ in the spectra of complexes is due to ν_{M-N} and ν_{M-S} stretching vibrations respectively also confirmed the formation of metal complexes^{38,39}. The FT IR Spectral data are summarized in [Table 2](#).

Table 2 IR Spectral data of the Ligand and its Metal Complexes:

Groups	$\nu(C=N)$ (cm^{-1})	$\nu(C-S-C)$ (cm^{-1})	$\nu(M-N)$ (cm^{-1})	$\nu(M-S)$ (cm^{-1})
Ligand	1660	848	-	-
[CuLX]Cl ₂	1629	825	498	419
[ZnLX]Cl ₂	1629	827	495	421
[NiLX]Cl ₂	1624	805	510	419
[CoLX]Cl ₂	1628	820	506	418

Electronic absorption Spectra and magnetic measurement

The UV-Vis. spectra of the ligand and its mixed ligand metal complexes were recorded in DMSO. The ligand shows the two bands at 42918 and 33113 cm^{-1} assigned for $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ electronic transitions respectively⁴⁰. The extension of the absorption spectra from UV region to visible region is due to ligand to metal charge transfer and d-d transition bands of the metal in the complexes. The electronic spectrum of the Cu(II) complex showed three bands at $18868, 16367$ and 13004 cm^{-1} assigned for ${}^2B_{1g} \rightarrow {}^2B_{2g}$, ${}^2B_{1g} \rightarrow {}^2E_g$, ${}^2B_{1g} \rightarrow {}^2A_{2g}$ electronic transition which suggested the distorted octahedral geometry of the metal complex. It had a magnetic moment value of 1.98 B.M which also confirmed the possibility of an octahedral geometry. Zn(II) complex shows two bands at $32258, 34483\text{ cm}^{-1}$ assigned for $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ electronic transition^{39,41}. Ni(II) complex showed three bands at $20833, 16103$ and 12987 cm^{-1} assigned for ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ electronic transitions suggest the octahedral geometry which was further supported by its magnetic moment value of 3.12 B.M.⁴²⁻⁴⁴. Co(II) complex shows two band at $16667, 14556\text{ cm}^{-1}$ assigned for ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ electronic transitions suggest the octahedral geometry⁴¹. The electronic absorption spectrum of the ligand and its Cobalt complex are given in [figure 2](#) and [3](#).

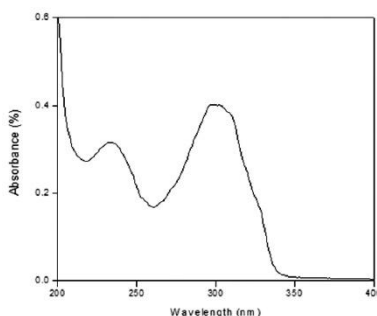


Figure 2 UV Visible spectra of Ligand.

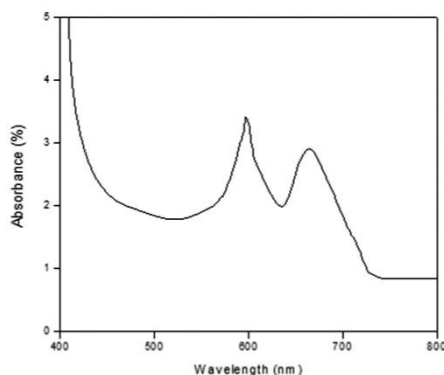


Figure 3 UV Visible spectra of [CoLX]Cl₂

Proton Magnetic Resonance Spectra

The Proton Magnetic Resonance Spectra of ligand and its diamagnetic Zn (II) complex was recorded in DMSO-d₆. The thiophene proton appeared as a singlet at 6.9 ppm. The iminic proton appeared as a singlet at 7.9 ppm and the phenyl multiplet at 7.5-7.7 ppm. In the ¹H-NMR spectrum of Zn (II) complex thiophene proton appeared as a singlet at 6.9-7.2 ppm. The iminic Proton appeared as a singlet at 8.4 ppm and phenyl multiplet at 7.5-7.7 ppm. The singlet at 7.3-7.6 ppm was assigned to phenanthroline proton.

Mass Spectra

The ESI mass spectra of the ligand and its Zn (II) complex were recorded and the obtained molecular ion peak confirmed the proposed formulae. The mass spectrum of the ligand exhibits peak at 296(M⁺) with 100% abundance which was also confirmed by 'nitrogen rule'. The mass spectrum of the inc complex shows peak at 542 (M⁺) with 100% abundance confirms the stoichiometry of metal complexes as [MLX] Cl₂ type.

Based on the elemental analysis, molar conductance, magnetic moments, IR, UV-Vis., proton NMR and Mass spectral data, the proposed structure of the complexes are given in [figure 2](#).

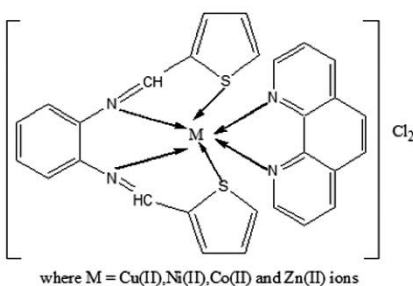


Figure 2 Structure of synthesised complexes.

Biological Studies

Antibacterial Studies

The ligand and its metal complexes have been screened *in-vitro* against Gram positive bacteria *Bacillus subtilis*, *Staphylococcus aureus* and Gram negative bacteria *Escherichia coli* and *Proteus mirabilis* species and the results are given in Table 3. As expected, overall ligand showed weak activity, whereas the metal complexes had the higher antimicrobial activities against both Gram-positive and Gram-negative bacteria. Since chelation of the central metal atom could enhance the lipophilic character which subsequently favors its permeation through the lipid layers of the cell membrane and blocking the metal binding sites on enzymes of microorganism. It is observed that copper (II) complexes are effective against all the bacteria examined except *Bacillus subtilis* when compared to standard drug streptomycin. Cobalt (II) complexes are found to be effective against *Bacillus subtilis*. Zinc (II) and Nickel (II) complexes exhibit moderate antibacterial activities against *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli* and *Proteus mirabilis*.

Table 3 Antibacterial activity of ligand and its metal (II) complexes (Zone of inhibition in mm)

Compound	Gram (+ve) Bacteria						Gram (-ve) Bacteria					
	<i>B. subtilis</i>			<i>S. aureus</i>			<i>E. coli</i>			<i>P. mirabilis</i>		
	25 (µg)	50 (µg)	75 (µg)	25 (µg)	50 (µg)	75 (µg)	25 (µg)	50 (µg)	75 (µg)	25 (µg)	50 (µg)	75 (µg)
L	6	8	9	9	10	12	10	11	12	8	9	11
[CuLX]Cl ₂	14	16	22	17	23	26	25	27	29	15	19	21
[ZnLX]Cl ₂	8	10	12	10	11	12	12	13	16	9	11	13
[NiLX]Cl ₂	7	9	12	11	12	14	11	12	16	9	10	12
[CoLX]Cl ₂	15	17	23	16	20	21	19	20	22	14	16	18
Streptomycin	13	15	20	18	22	24	22	23	26	15	18	20

Antioxidant Studies

DPPH (2,2-diphenyl-1-picrylhydrazyl) is a stable radical in organic solvents; in alcoholic solution it appears purple and has a single electron. This radical is able to react with any compound that releases a hydrogen atom or an electron, resulting in a color change from purple to yellow. The degree of discoloration indicates the scavenging potential of the samples in terms of hydrogen donating ability. Figure 3 shows the comparative effect of metal complexes on DPPH radical. From the IC₅₀ value (table 4) it is inferred that Cobalt (II) complexes (IC₅₀ = 0.601 µM) exhibit potent antioxidant activity when compared to other complexes. The increased activity of the complexes can be attributed to the electron withdrawing effect of Zn (II), Co (II), Ni(II) and Cu (II) ions which facilitate the release of hydrogen to reduce the DPPH radical.

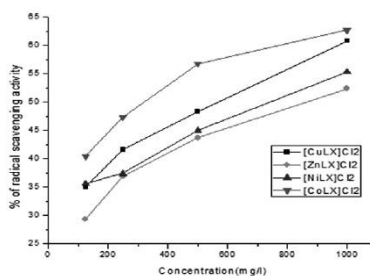


Figure 3 Antioxidant activity of mixed ligand complexes

Table 4 Antioxidant activity of [MLX]Cl₂

Concentration	% of radical scavenging activity			
	[CuLX] Cl ₂	[ZnLX] Cl ₂	[NiLX] Cl ₂	[CoLX] Cl ₂
1000 µg/ml	60.8	52.4	55.3	62.7
500 µg/ml	48.3	43.7	45.0	56.8
250 µg/ml	41.6	36.9	37.4	47.3
125 µg/ml	35.0	29.3	35.6	40.4
IC₅₀ (µM)	1.061	1.601	1.401	0.601

Catalytic Activities

The catalytic oxidation of 1° and 2° alcohols with H₂O₂ was carried out in CH₂Cl₂ in the presence of mixed ligand complex as catalyst⁴⁵. During the course of the reaction water is produced only as a byproduct. The result shows that the metal complexes effectively catalyse the oxidation of alcohols using H₂O₂ as oxidant and is evident from Table 6.

Table 6 Catalytic oxidation of alcohols by [MLX]Cl₂

Compound	Substrate	Product	Yield (%)
[CuLX]Cl ₂	Benzylalcohol	Benzaldehyde	73
	Propan-2-ol	Propanone	78
	Butane-2-ol	Butanone	74
[ZnLX]Cl ₂	Benzylalcohol	Benzaldehyde	80
	Propan-2-ol	Propanone	79
	Butane-2-ol	Butanone	76
[NiLX]Cl ₂	Benzylalcohol	Benzaldehyde	83
	Propan-2-ol	Propanone	78
	Butane-2-ol	Butanone	75
[CoLX]Cl ₂	Benzylalcohol	Benzaldehyde	86
	Propan-2-ol	Propanone	85
	Butane-2-ol	Butanone	79

CONCLUSION

On the basis of above experimental facts, this paper concludes that we synthesised novel mixed ligand Cu(II), Zn(II), Ni(II) and Co(II) complexes of [MLX]Cl₂ type derived from thiophene-2-carboxaldehyde, 1,10-phenanthroline and *o*-phenylenediamine. The UV-Vis., IR, Proton NMR, Mass spectral studies showed the complexes are in octahedral structure. The high conductance showed the complexes are in electrolytic nature. They exhibited antibacterial activities against the Gram positive bacteria *Bacillus subtilis*, *Staphylococcus aureus* and Gram negative bacteria *Escherichia coli* and *Proteus mirabilis*. The results showed that the Cu (II) complexes exhibit higher antibacterial activities against *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli* and *Proteus mirabilis* when compared to the standard drug streptomycin. The other complexes showed moderate activity. The synthesised complexes were tested for catalytic activity of the synthesised metal complexes for the oxidation of alcohols to the corresponding carbonyl compounds. The above reactions in presence of cobalt complex gave good yield than other compounds. All the complexes demonstrated antioxidant properties and could be useful in combating the free radicals which exist in close relationship with cancerous cells. It was notable that the [CoLX]Cl₂ complex exhibited stronger antioxidant effects than others.

REFERENCES

- 1 P. Krishnamoorthy, P. Sathyadevi, A.H. Cowley, R.R. Butorac and N. Dharmaraj, *Eur. J. Med. Chem.*, 46, 3376, (2011).
- 2 D. Lahiri, R. Majumdar, D. Mallick, T.K. Goswami, R.R. Dighe and A.R. Chakravarty, *J. Inorg. Biochem.*, 105, 1086, (2011).
- 3 C. Spinu, M. Pleniceanu and C. Tigae, *Turk. J. Chem.*, 32, 487, (2008).
- 4 B. Clarke, N. Clarke, D. Cunningham, T. Higgins, P. McArdle, M. Ni Cholchu and M. O’Gara, *J. Organometallic Chem.*, 559, 55, (1998).
- 5 D. Sathis Kumar and Ibrahim Sheriff A.K., *Res. J. Chem. Sci.*, 6, 1, (2016).
- 6 K. Singh, M.S. Barwa and P. Tyagi, *Eur. J. Med. Chem.*, 42, 394, (2007).
- 7 P.G. Cozzi, *Chem. Soc. Rev.*, 33, 410, (2004).
- 8 S. Chandra and J. Sangeetika, *J. Indian Chem. Soc.*, 81, 203, (2004).
- 9 F. Arjmand, F. Sayeed and M. Muddassir, *J. Photochem. Photobiol. B*, 103 (2011) 166.
- 10 E. Canpolat and M. Kaya, *J. Coord. Chem.*, 57, 1217, (2004).
- 11 M. Yildiz, B. Dulger, S.Y. Koyuncu and B.M. Yapici, *J. Indian Chem. Soc.*, 81 (2004) 7.
- 12 Z. Lu and L. Yang, *J. Inorg. Biochem.*, 95, 31, (2003).
- 13 J.Z. Wu, H.Li, J.G. Zhang and H. Xu Ju, *Inorg. Chem. Commun.*, 5, 71, (2002).
- 14 L. Canali and D.C. Sherrington, *Chem. Soc. Rev.*, 28, 85, (1999).
- 15 A.A. Isse, A. Gennara and E. Viane, *J. Electroanalytical Chem.*, 444, 241, (1998).
- 16 R. Atkins, G. Brewer, E. Kokot, G.M. Mockler and E. Sinn, *J. Inorg. Chem.*, 24, 127, (1985).
- 17 J.P. Costes, G. Cros, M.H. Darbieu and J.P. Laurent, *J. Inorg. Chim. Acta*, 60, 111, (1982).
- 18 E. Charles, S. George, E. Chester, N. Jyotirindra, *J. American Chem. Soc.*, 12, 3233, (1955).
- 19 A. Weissenberger, E.S. Proskauer, J.A. Riddick and E.E. Toops, *Organic Solvents: Physical Properties and Methods of Purification, Techniques of Organic Chemistry*, 3rd edn., Interscience, New York, 1955.
- 20 A.I. Vogel, *Practical Organic Chemistry*, 4th edn., Longmann, 1978.
- 21 R.J. Angellici, *Synthesis and Techniques in Inorganic Chemistry*, W.B. Saunders Company, 1969.
- 22 A.I. Vogel, *Text Book of Quantitative Chemical Analysis*, 5th edn., Longmann, 1989.
- 23 G. Qin, L. D. Fan, R. Zhang and S. K. Cao, *Advanced Materials Research*, 287-290, 1761, (2011).
- 24 Corrado Crotti, Sergio Cenini, Fabio Ragaini, Francesca Porta and Stefano Tollari, *J. Mol. Catal.*, 72, 283, (1992).

- 25 Gopalakrishnan Karthikeyan and Ponnuchamy Pitchaimani, *Transition Met. Chem.*, 28, 482, (2003).
- 26 N.Raman, A.Kulandaisamy and K.Jeyasubramaniaan, *Indian J. Chem.*, 41, 942, (2002).
- 27 K. Sarkar, M. Nandi, M. Islam, M. Mubarak, A. Bhaumik, *Appl. Catal., A* 81, 352, (2009).
- 28 K.C. Gupta, A.K. Sutar, C.C. Lin, *Coord. Chem. Rev.*, 253, 1926, (2009).
- 29 B. Bahramian, F.D. Ardejani, V. Mirkhani, K. Badii, *Appl. Catal., A* 97, 345, (2008).
- 30 M. Salavati-Niasari, S.N. Mirsattari, *J. Mol. Catal.A: Chem.* 50, 268, (2007).
- 31 M. Salavati-Niasari, M. Hassani-Kabutarhkhani, F. Davar, *Catal. Commun.* 7, 955, (2006).
- 32 M. Salavati-Niasari, P. Salemi, F. Davar, *J. Mol. Catal.A: Chem.* 215, 238, (2005).
- 33 W.S. Kim, Y.-K. Choi, *Appl. Catal., A* 163, 252, (2003).
- 34 C. Baleizo, H. Garcia, *Chem. Rev.*, 106, 3987, (2006).
- 35 T.C.O.M. Leod, D.F.C. Guedes, M.R. Lelo, R.A. Rocha, B.L. Caetano, K.J. Ciuffi, M.D Assis, *J. Mol. Catal. A: Chem.*, 259, 319, (2006).
- 36 C.Spinu, A.Kriza, *Acta Chim. Slov.*, 47, 179, (2000).
- 37 M.Hossain, S.K.Chattopadhyay, S.Ghosh, *Polyhedron*, 16, 1793, (1997).
- 38 Mohammad Nasir Uddin, Didarul Alam Chowdhury, Md. Moniruzzman Rony and Md. Ershad Halim, *Modern Chemistry*, 2, 6, (2014).
- 39 S. Chandra and R. Kumar, *Transition Met. Chem.*, 29, 269, (2004).
- 40 M.A.Neelakantan, S.S.Marriappan, J.Dharmaraja, T.Jeyakumar, K.Muthukumar, *Spectra Chim. Acta Part A.*, 71, 628, (2008).
- 41 B.J. Hathway, M. Duggan, A. Murphy, J. Mullane, C. Power, A. Walsh and B. Walsh, *Coord. Chem. Rev.*, 36, 267, (1981).
- 42 A.B.P. Lever, *Inorganic Electronic Spectroscopy*, 2nd edn, Elsevier, Amsterdam, 1984.
- 43 F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn, Wiley, New York, 1988.
- 44 D.Sathis Kumar, S.Rajiv Gandhi and Ibrahim sheriff, *J.Chem. and Pharm. Research*, 7(1), 416, (2015).
- 45 D. Sathis Kumar and A. K. Ibrahim Sheriff, *Der Pharma Chemica*, 7, 79, (2015).