SYNTHESIS, SPECTRAL, STRUCTURAL DETERMINATION AND ELECTROCHEMISTRY OF NEW N_2O_2DONOR SCHIFF BASE OF TRANSITION METAL COMPLEXES DERIVED FROM [1-(5-CHLORO-2-HYDROXY-4-METHYLPHENYL)ETHANONE AND 4-CHLORO(-3-TRIFLUROMETHYL)ANILINE]

Jaishri N. Bavane, Rahul B. Mohod,
P.G. Department of Chemistry, Shri Shivaji College of Arts, Commerce and Science, Akola-444003 (Maharashtra)
Email:jaishrisonawne@gmail.com Mobile No. : 09011028107

Abstract

A novel bidentate Schiff base ligand [1-(5-chloro-2-hydroxy-4-methyl phenyl)ethanone-4 chloro(-3-trifluromethyl)aniline] was synthesized by the reaction of 1-(5-chloro-2-hydroxy-4-methylphenyl)ethanone and 4-chloro(-3-trifluromethyl)aniline. The structure of the ligand was elucidated by elemental analysis, IR, H^1NMR.The cyclic voltammograms of the Mn(II)/Co(II)/Cu(II) complexes investigated in DMSO solution exhibit metal centered electroactivity in the potential range −1.02 to +0.7V. All the complexes showed one electron quasi-reversible redox waves in the voltammogram. The reduction oxidation potential depends on the structure and confirmation of the central metal atom in the co-ordination compounds.

Keywords : Schiff base, elemental analysis, cyclic voltammetry etc.

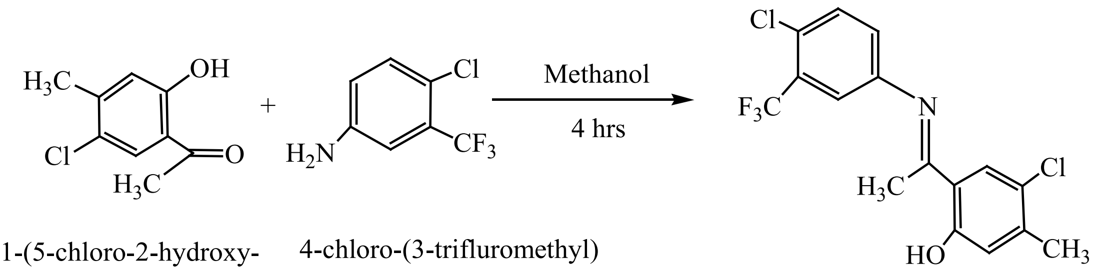
Introduction

Schiff bases have been playing very important role in the development of coordination chemistry. They are prepared by condensing an aldehyde or a ketone and an amine generally in alcohol. Schiff bases have characteristic quality which can stabilize many metals in different oxidation state. Another area of application of these Schiff bases is analytical chemistry where some of these compounds are used as ligand in complexometry topic [1].The coordination sites of ligands depends on the bonding ability of it, nature of atoms,their electronegativity and steric factor.The lone pair of electrons in either π or sp^2 hybridized nitrogen in the C=N group having the fundamental chemical and biological importanceCyclic voltammetry has the further attraction of providing information not only on the thermodynamics of redox processes but also on the kinetics of heterogeneous electron-transfer reactions and coupled chemical reactions. The characteristic shapes of the voltammetric waves and their unequivocal position on the potential scale virtually fingerprint the individual electrochemical properties of redox systems. For this reason the method has been labelled “electrochemical spectroscopy” [2].

Experimental Section

Preparation of [1-(5-chloro-2-hydroxy-4-methyl phenyl) ethanone-4-chloro (-3-trifluro methyl) aniline] (CHMECFA).

The Schiff base was synthesized by adding a methanolic solution of 1-(5-chloro-2-hydroxy-4-methylphenyl)ethanone (CHME) (1.84gm,0.01M) to a methanolic solution of 4-chloro(-3-trifluro methyl) aniline (CFA) (1.95ml,0.01M) with 1 ml of acetic acid. The obtained mixture was refluxed for four hours and then allowed to cool at ambient temperature, filtered and recrystallized from ethanol. The productwas dried under vacuum to get light yellow precipitate. Yield 67.7%,m.pt.150°C.



1-(5-chloro-2-hydroxy-4-methyl-phenyl)ethanone

4-chloro-(3-trifluromethyl) aniline

Ligand II CHMECFA

The newly prepared ligand II was characterized by elemental analysis, IR and ^{1}HNMR spectral studies.The elemental analysis for carbon, hydrogen, nitrogen and chlorine is given as follows

S.N.	Compound	Colour	Time of Reflux(hrs.)	Elemental analysis % found (calcd.)			
				C	H	N	Cl
1.	CHMECFA	Pale yellow	4	53.03 (52.89)	3.31 (3.15)	7.73 (7.55)	39.22 (39.19)

On the basis elemental analysis the ligand CHMECFA has suggested the empirical formula $C_{16}H_{12}ONCl_2F_3$.

^{1}HNMR spectrum of CHMECFA (300MHz,CDCl$_3$δ in ppm)

The ^{1}HNMR spectrum of ligand CHMECFAhas been recorded in CDCl$_3$and is depicted in Fig.2.2 which indicated that different non-equivalent proton resonates at different values of applied field[3-6]. The δ-values in ppm are given below

δ8.24(1H,s, -OH), 7.69 (1H, s, Ar-H), 7.46(1H,s,Ar-H),7.26-6.94(3H,m,Ar-H),2.61(3H,s, -CH$_3$), 2.12 (3H, s, -CH$_3$).

Synthesis of Metal Complexes

The metal complexes were complexes by mixing both solution of Schiff base and Metal (II) acetate in DMF-ethanol in molar ratio 2: 1. The resulting solution was refluxed for 4 to 9 hours onwater bath. Colored complexes formed have been filtered and then dried in *vacuum*.

All metal complexes are colored, stable in air. The solids do not melt sharply and undergo decomposition. These are insoluble in water and soluble in organic solvent such as DMF and

DMSO giving respective colors to the solution.

Results And Discussion

All compounds gave satisfactory elemental analysis. Values are in the close agreement with the

values calculated for expected molecular formulae assigned to these complexes, suggesting 1:2

(M:L) stoichiometry. The physical data of ligand and metal complexes are given. (Table 1)

Table No.1:Analytical Data, Color and Synthetic Condition of Complexes of CHMECFA

S. N.	Compound	Color	Solvent	Time (hrs.)	Elemental analysis % found (calcd.)				
					M	C	H	N	Cl
1.	[Mn(CHMECFA)$_2$(H$_2$O)$_2$]	Off brown	DMF+ Ethanol	4	7.56(7.07)	49.67 (49.42)	2.90 (2.83)	7.85 (7.20)	18.35 (18.01)
2.	[Co(CHMECFA)$_2$].2H$_2$O	Pink	Ethanol	5	7.89 (7.55)	49.85 (49.16)	2.87 (2.81)	7.35 (7.17)	18.09 (17.92)
3.	[Ni(CHMECFA)$_2$(H$_2$	Light	Ethano	4	8.53	49.67	2.96	7.25	18.18

	$O)_2]$. $2H_2O$	green	1		(8.31)	(49.29)	(2.82)	(7.18)	(17.97)
4.	$[Cu(CHMECFA)_2]$	Pale yellow	DMF+ Ethanol	4	8.51(8.14)	49.09 (48.85)	2.98 (2.79)	7.39 (7.12)	17.98 (17.81)
5.	$[Zn(CHMECFA)_2].2H_2O$	Fawn Beige	Ethanol	6	8.45(8.28)	49.26 (48.91)	2.89 (2.80)	7.67 (7.13)	18.14 (17.83)
6.	$[Cd(CHMECFA)_2]$	Royal Ivory	Ethanol	5	13.85(13.42)	46.21 (45.98)	2.78 (2.63)	6.89 (6.71)	16.81 (16.78)

The IR spectrum of CHMECFA and its metal complexes are found to be comparable with each other. In the IR spectrum of ligand CHMECFA, the absorption peak assigned to azomethine (– CH = N –) as a functional group is appeared at 1654 cm^{-1}. This is uncoordinated stretching vibrations occurs as coupled bands are shifted to 1637 – 1610 cm^{-1} on coordination to the metal ions, indicative of the involvement of N and O donor atoms of C = N and enol groups respectively [7,8].

The IR spectra Schiff base ligand showed characteristic broad band at 3219 cm^{-1} υ (–OH) [9,10]. On complexation this banddisappears indicating deprotonation of the phenolic –OH by metal ion [11]. The medium band observed at 1224 cm^{-1} in the ligand is indicating to – C – O stretching vibration and on chelation this shows marked shift showing the metal oxygen bonding. The band at 1654 cm^{-1} in the ligand may assigned to υ (C = N) stretching vibration of the azomethine group which already shifted to lower frequencies in most of the complexes suggesting that this group is involved in the coordination with metal [12]. The hydrated complexes exhibited on IR band approximately by 3420 – 3320 cm^{-1} in range due υ(H_2O) suggesting the coordination of water molecules in some complexes. The Mn(II) and Ni(II) complexes exhibit medium sharp bands in the range 1508-1506 cm-1 and 790-804 cm^{-1} (coordinated water) suggesting six coordinated structure [13], which is further confirmed by TGA analysis. Thus it may be concluded that Schiff base CHMECFA acts as a dibasic tetradentate ligand. In addition, the appearance of some new bands showing the involvement of M – N and M – O band in the complex formation. The Schiff base with metal ion was shown by the appearance of low frequency new bands during 578– 519 cm^{-1} range due to metal oxygen υ(M – O) stretching vibration [14,15] confirming the involvement of oxygen and metal band in the coordination. Further formation of coordination bonding between metal and azomethine nitrogen is confirmed by new bands in the range of 459 – 426 cm^{-1}due to υ(M – N) stretching vibrations [16].

Table 2: Infrared Spectral Data (cm^{-1}) of CHMECFA and its Metal Complexes

S. N.	Compound	υ(O-H)	υ(C=N)	υ(C-O)	υ(M-O)	υ(M-N)	υ(H_2O)
01	CHMECFA	3219	1654	1224	--	--	--
02	$[Mn(CHMECFA)_2(H_2O)_2]$	--	1637	1351	521	459	3320, 1508, 790
03	$[Co(CHMECFA_2)].2H_2O$	--	1610	1332	519	426	3390
04	$[Ni(CHMECFA)_2(H_2O)_2].2H_2O$	--	1537	1369	521	448	3420, 1506, 804

05	[Cu(CHMECFA)$_2$]	--	1629	1367	523	468	
06	[Zn(CHMECFA)$_2$].2H$_2$O	--	1629	1369	569	463	3441
07	[Cd (CHMECFA)$_2$]	--	1628	1369	578	480	

The magnetic moment was recorded at room temperature and is shown in Table No. 3 Magnetic

studies also help to look into the structure of the complexes. The observed magnetic moment of Co(II) and Cu(II) found to be 4.70 B.M and 1.80 B. M. indicating tetrahedral and square planar environment around central metal ion respectively [17-18]. The magnetic moment value of Mn(II) and Ni(II) complexes is found to be 6.30 and 2.80 B. M. respectively, which is well within the expected range of octahedral complexes.

The electronic spectrum of Co(II) complex exhibited three bands at 13422 cm-1, 16694 cm-1 and 26178cm-1 assignable to $^4A_2 \rightarrow {}^4T_1{}^4A_2 \rightarrow {}^4T_1$ (F) and charge transfer transition respectively for a tetrahedral geometry.

The Cu(II) complex exhibited bands at 13888cm-1,17064cm-1 and 19157 cm-1 respectively which indicate square planner geometry.

The electronic spectrum ofMn(II) complex shows absorption bands at 17761cm^{-1},24271cm^{-1}and 26666 cm^{-1}corresponding to the $^6A_{1g} \rightarrow {}^4T_{1g}$ (4G), $^6A_{1g} \rightarrow {}^4T_{2g}$ (4G) and $^6A_{1g} \rightarrow {}^4E_g$ transition supporting square planar structure of the complex [19].

The electronic spectrum of Ni(II) complex exhibited bands at 11933 cm^{-1},13605 cm^{-1} and 23809cm^{-1}corresponding,$^3A_2$g (F) →^{3}T1g (F), $^3A_2$g →$^3T_2$g and $^3A_2$g (F) →$^3T_1$g (F) respective transition. The other high intensity band at 23881cm-1 give charge transfer transition15 exhibite square planar complex [20].(Table 3)

Table 3: Electronic and Magnetic spectral data of complexes of CHMECFA

Sr. No.	Ligan1d	μeff B.M.	Absorption band		Assignments
			(nm)	(cm^{-1})	
1	[Mn (CHMECFA)$_2$]	6.30	563 412 375	17761 24271 26666	$^6A_{1g} \rightarrow {}^4T_{1g}$ (4G) $^6A_{1g} \rightarrow {}^4T_{2g}$ (4G) $^6A_{1g} \rightarrow {}^4E_g$
2	[Co (CHMECFA)$_2$]	4.70	745 599 382	13422 16694 26178	$^4A_2 \rightarrow {}^4T_1$ $^4A_2 \rightarrow {}^4T_1$ (F) C.T.
3	[Ni (CHMECFA)$_2$]	2.80	838 785 420	11933 13605 23809	$^3A_2$g (F) →^{3}T1g (F) $^3A_2$g →$^3T_2$g $^3A_2$g (F) →$^3T_1$g (F)
4	[Cu (CHMECFA)$_2$]	1.80	720 586 522	13888 17064 19157	$^2B_{2g} \rightarrow {}^2A_{1g}$ $^2B_{1g} \rightarrow {}^2E_g$ C.T.
5	[Zn (CHMECFA)$_2$]	Diamagnetic	-	-	-
6	[Cd (CHMECFA)$_2$]	Diamagnetic	-	-	-

Cyclic Voltammetry

Cyclic voltammetric analysis of metal complexes of CHMECFA:

The literature data observed with a diversity of redox potential for Mn(II) →Mn(III) and Mn(III) →Mn(IV) couple. For example the value reported by Chandra *et al* [21] and for manganese complex with salen type ligand vary between – 0.3 and – 0.8 V for Mn(III) →Mn(IV) couple and also those for Mn(III) →Mn(IV) couple range between 0.01 and + 0.6 V Vs SEC. Nevas*et al* [22] reported the values of + 0.20 and + 0.57 V vs SEC for Mn (II) →Mn (III) and Mn (III) →Mn(IV) couples respectively.

From the above literature value the waves at 0.115 V and 0.079 V Vs Ag/AgCl for manganese complex of CHMECFA can be assigned to the oxidation of Mn(II) to Mn(III), and reduction of Mn(II) to Mn(I). At second redox potential region the reduction potential wave E_{pc} = – 0.61 V is associated with oxidation potential waveE_{pa}= – 0.502 V and having peak to peak separation(ΔE) near about 0.108 V which suggest that reversible one electron transfer process, which is ligand based reversible process.

In case of Co(II)–CHMECFA complex the first reduction peak was observed at about E_{pc} = 0.181 V is associated with oxidation peak was observed at about E_{pa} = 0.328 V. This is quasi-reversible to cathodic peak currents (i_{pa}/i_{pc}), corresponding to the simple one electron process Co(II) → Co(I).

The second quasi-reversible process at second reduction peak was observed at about E_{pc} = – 1.348 V gives Co(II) → Co(I) are corresponding second oxidation peak was observed at about E_{pa} = -1.252 V give Co (I) → Co(II) and also one electron process also [23]. The potential difference ΔE in Co complex exceeds the Nerstian requirement of 59/n mV (n = no of electron involved in oxidation – reduction). Which suggest quasi-reversible character of the electron transfer reaction [24].

The cyclic voltammogram of Cu(II)–CHMECFA complex showed new redox couple located at reduction and oxidation potential range for thefirst peak is E_{pc} = 0.648 V and E_{pa} = 0.701 respectively. First reduction is Cu(II) → Cu(I) and second is Cu(I) → Cu(0), from the peak current ratio it is two electron transfer redox process. Second redox potential occurs at reduction peak at E_{pc} = – 0.16 V associated with E_{pa} = 0.043 V oxidation potential. The voltammetric data showed that Cu(II) was first reduced to Cu(I) and then decomposed copper metal at the cathodic region and at the anodic peak potentials was oxidized to give Cu(0) → Cu(I) and Cu(II) ions, respecting indicating that processes took place on the metal center of the complex respectively [25].

Table 4: Electrochemical data of Metal complexes of CHMECFA

Complexes of CHMECFA	E^1_{pc} (V)	E^1_{pa} (V)	$E_{½}$(V)	ΔE (V)	E^2_{pc} (V)	E^2_{pa} (V)	$E_{½}$(V)	ΔE (V)
Mn(II)	0.079	0.115	0.097	0.036	-0.61	-0.502	-0.556	0.108
Co(II)	0.181	0.328	0.254	0.147	-1.348	-1.252	-1.3	0.097
Cu(II)	0.648	0.701	0.674	0.053	-0.16	0.043	-0.117	0.202

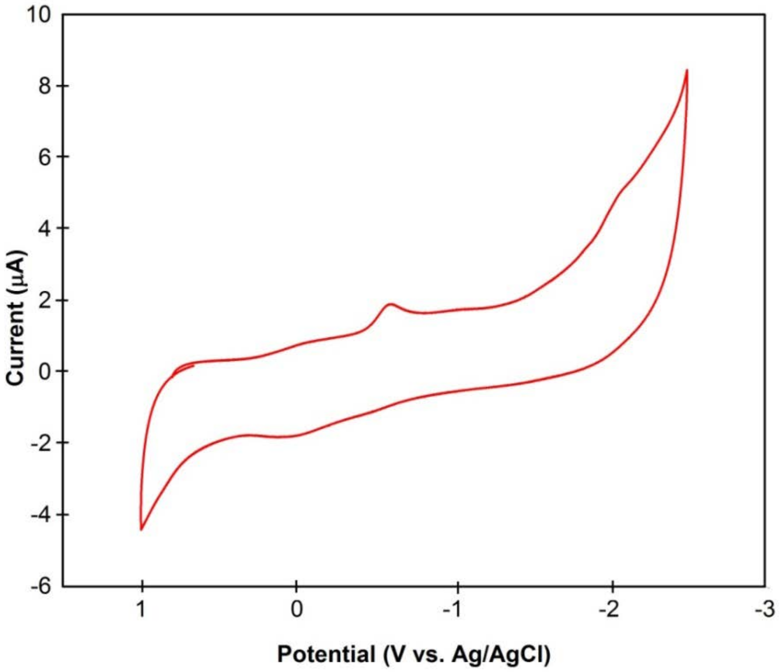


Fig. 1 : Cyclic Voltammogram of Mn(II) complex of CHMECFA

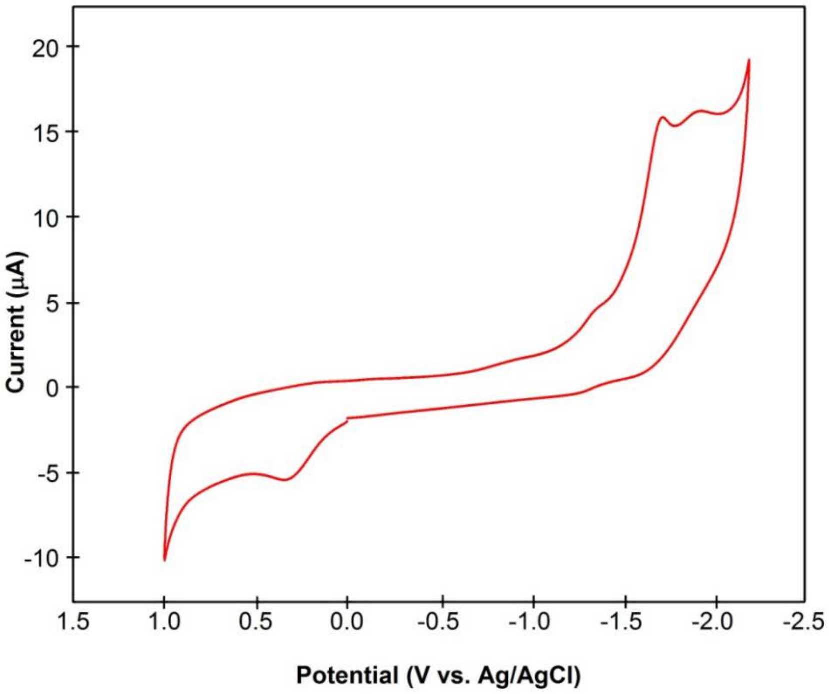


Fig. 2 : Cyclic Voltammogram of Co(II) complex of CHMECFA

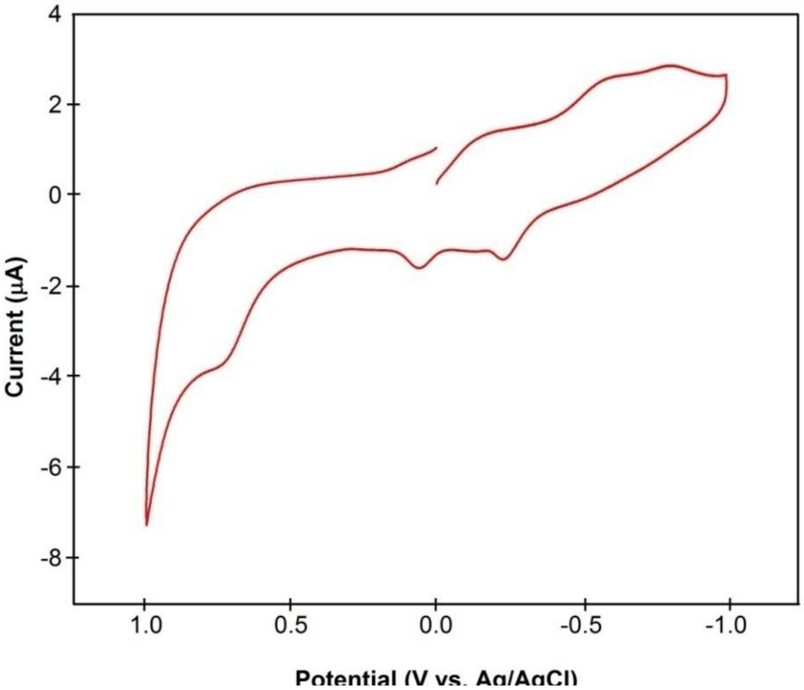


Fig. 3 : Cyclic Voltammogram of Cu(II) complex of CHMECFA

CONCLUSION

The cyclic voltametry is usually employed to study the redox behaviour of metal complexes of Mn(II), Co(II) and Cu(II) with Schiff base ligand. In the present course of study reduction and oxidation potentials were measured from the voltamammogram. The values of ΔE and E½ (Potential difference and half potential respectively) calculated from their respective voltamammogram. The values are obtained by plotting a graph current against potential [26].

The metal complexes of Mn(II), Co(II) and Ni(II) were studied by using this property because of these complexes showed variable valences due to this we could observed the redox property clearly (more than one electron transferred). From this study oxidation states of metals were confirmed also. Some of the metal ions showed with different ligand the redox behaviour such as weather it may be reversible, quasi reversible and irreversible.

ACKNOWLEDGEMENT

The authors are greatly thankful to SAIF, CDRI Lucknow and SAIF, Cochin (Kerla) for providinganalytical and spectral data. Authors are also thankful to Head, Department of Chemistryand Dr. S. G. Bhadange, Principal, Shri Shivaji College, Akola for providing necessary facilities also Head, Department of Chemistry, Pune University for analysis of Cyclic Voltammetry.

References

1. S. Anbu, M. Kandaswamy, P. Suthakaran, V. Murugan,Babu Varghese,Structural, magnetic, electrochemical, catalytic, DNA binding and cleavage studies of new macrocyclic binuclear copper(II) complexes, *Journal of Inorganic Biochemistry*,2009, **103**, 401.
2. JiirgenHeinze, Agnewandte Chemie, *Cyclic Voltammetry-"Electrochemical Spectroscopy". New Analytical Methods (25)".* International Edition Volume 23 Number 11 November 1984 Pages 831 - 91 8
3. J. R. Dyer, “ Application of Absorption Spectroscopy of Organic Compounds”, 8th ed., Prentice Hall, P(a) 36, (b) 37, (c) 84, (d) 88, 1991.
4. R. M. Silverstein and F. X. Wenster, “Spectromwtric Identification of Organic Compounds”, 6th ed., John Wiley and Sons, Inc. New York, P(a) 83, (b) 86, (c) 97, (d) 98, (e) 102, (f) 103, (g) 104, (h) 106, 2004.
5. J. D. Joshi, N. P. Patel, S. D. Patel, *J. Indian Poly.*, 2006, **15**(3), 219.
6. M. Kidwai,P. R. Poddar, K. Singhal, *Indian J. Chem.*,2009, **48B**, 886.

7. A. A. Osowole, G.A. kolawole and O.E.Fagade, *React. Inorg. synth. Met. Org. Chem and Nano-Met. Chemistry*, 2005, **35**, 829.
8. M. M. Omar, G. G. Mohamed, A. M. M. Hindy, *J. Therm. Anal. Cal.*, 2006, **86**, 315.
9. Sonmez, M. S., Ekerci, M.,*Synth. React. Inorg. Met.-Org. Chem.*,2004, **34**, 485-498.
10. Abd El-Wahab, Z. H. *J. Coord. Chem.*,2008, **61**, 1696-1709.
11. Thaker, B. T., Lekkhadia, J. Patel, A. and Thaker, *P. Trans. Met. Chem.*, 1994, **19**, 623.
12. Bhave, N. S. and Aswar, A. S., *Asian J. Chem.*, 1992, **4**(1), 65.
13. Patel, B. S. and Patel, S. R., *Macromol. Chem.,* 1979, **180**, 1159.
14. V. D. Bhatt and A. Ray, *Synthetic Metals*, 1998, **92**(2), 115–120.
15. D. Prakash, C. Kumar, S. Prakash, A. K. Gupta, and K. R. R.P. Singh, *Journal of the Indian Chemical Society*, 2009, **86**(12) 1257–1261.
16. N. Raman, S. Esthar, and C. Thangaraja, *Journal of Chemical Sciences*, 2004, **116**(4) : 209–213,.
17. A.B.P.Lever, Inorganic Electronic Spectroscopy., Elsevier, Amsterdam,New York (1984).
18. Aswar, A.S.; Bhave, N.S., *Asian J. Chem.*, 1994, **6**, 472.
19. Reddy K.H., and Reddy M.R., *J. Ind. Chem. Soc.*, 2002, **79**, 219.
20. PulimamidiSaritha Reddy, P. V. Anantha Lakshmi and V. JayatyagaRaju, *International Journal of Chem. Tech. Research,* 2010, 2(**3**), 1494-1500.
21. S.K. Chandra, D. Ray, S. Pal, A. Chakravorty, *Inorg. Chem.*, 1990, **29**, 2423.
22. A.Neves, S.M.D.Erthal, I.Vencato, A.S.Ceccato,Y.P.Mascarenhas,O.R.Nascimento, M. Ho¨rner, A.A. Batista, *Inorg. Chem.,* 1992, **31**, 47-49.
23. Ali Hossein Kianfar, Maryam Sedighipoor, Gholam Hossein, Mohammad Nezhad, Helmar Görls, Winfried Plass, Mahmoud Roushani, *Iranian Chemical Society,* 2016.
24. Usha S., Palaniandavar M., *J. Chem. Soc. Dalton. Trans.*, 1994,**15**, 2277-2283.
25. Mehmet Sonmez, Metin C¸ Elebi, AbdulkadirLevent, Ismet Berber And ZuhreS. Enturk, *Journal of Coordination Chemistry,* **63**(11), 2010, 1986–2001
26. Mohammad Hossein Habibi,Elahe Shojaee Yuki, Yamane Takayoshi Suzuki,*J. Iran. Chem. Soc.,*2012, **22**(1), 190–195.