

**SYNTHESIS, CHARACTERIZATION AND PHYSIC-CHEMICAL INVESTIGATION OF Cu (II) COMPLEXES WITH NEWLY PREPARED MANNICH BASE LIGANDS DERIVED FROM HETROCYCLES WITH SULPHACETAMIDE/SULPHANILAMIDE**

**MAHENDRA PRATAP SINGH**

*Department of Chemistry, Shri Sadguru Saibaba Science College, Ashti, Gadchiroli-442707 (M.S.), India*

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In this study, I have synthesized Mannich base ligands MB<sub>1</sub> or 2-FAMSA (2-furfuryl-1-anilinomethyl-4-sulphacetamide) and MB<sub>2</sub> or 2-FAMSN (2-furfuryl-1-anilinomethyl-4-sulphanilamide) by refluxing sulphacetamide with 2-furfuraldehyde and sulphanilamide with 2-furfuraldehyde respectively. A complex of the above ligands also prepared with CuCl<sub>2</sub>/CuSO<sub>4</sub> in ethanol/methanol. Structures of the newly synthesized compounds were confirmed and characterized by physico-chemical methods, magnetic susceptibility measurements, electronic spectra, IR, ESR and elemental analysis.

**KEYWORDS:** MB<sub>1</sub> (2-FAMSA), MB<sub>2</sub> (FAMSN), Cu (II) metal complexes, ESR, IR, Mannich base, Schiff base, Hetrocycles.

## **INTRODUCTION**

The chemistry of transition metal complexes of hetrocyclic ring containing Schiff bases and Mannich bases ligand utilizes in drug design and synthesis is an essential aspect of bioinorganic and medicinal chemistry, and having high degree of binding affinity to biological system [1] and have been reported to exhibit pronounced pharmacological, analytical and industrial applications [2]. A lot of aminomethylated Mannich base have biological activities like anticancer, cytotoxic, analgesic and antimicrobial activities [3-8] and complexation properties with divalent transition metals [9-11], further the complexation of Mannich bases with metal ions may enhance their microbial properties and metal complexes also used as protect drugs in the treatment of infectious diseases [12-14]. Several workers have synthesized Cu (II) complexes with Mannich base ligands having various bridging and nonbridging units [15], which having antimicrobial and biological action [16-17]. The present studies have been completed by the reduction of synthesized Schiff base ligands through the reaction of furfuraldehyde and sulphadiazine drugs like sulphacetamide and sulphanilamide, and resulting Cu (II) complexes of Mannich bases with chloride/sulphate salt.

## **EXPERIMENTAL: MATERIAL AND METHODS**

All the chemical used were of analytical and G.R. grade (BDH, E-Merk, S.D. Fine's and Sisco Chemical Industries Bombay). The solvent and liquid reagents were carefully purified

by distillation, while the solid reagents and metal salts were used as such. Elemental analysis were carried out by microanalysis of element on at RSIC Chandigarh. The metal percentage in metal complexes were determined by standard methods [36-40] using pyridine and ammonium thiocyanate as precipitants for Cu (II). Estimation of sulphur in ligands and complexes were determined by standard method [32] and estimate of halogen was estimation by volhard's method to form the chloride in the ionized form as silver chloride [33] gravimetrically. Conductivities of the prepared metal complexes were carried out at room temperature on EG & G model 155 VSM. IR spectra of ligands and their complexes were recorded on Perkin Elmer Spectrometer in the FT-IR region using KBr pellets. Electronic spectra in solution ethanol/DMF were recorded on ELICOSL 171 Spectrophotometer at room temperature. Mass spectra of the ligands were taken on MASPEC System (MSW/9629) using 200°C inlet temperature. The ESR spectra of Cu (II) complexes were recorded on a varian x-band spectrometer E<sub>4</sub>.

#### Synthesis of MB<sub>1</sub> and MB<sub>2</sub>:

The titled Mannich base were prepared by refluxing sulphacetamide/sulphanilamide (10mmol in 25 ml ethanol/methanol) and 2-furfuraldehyde on water bath for 3-4 hours with stirring. The resulted Schiff base product then cooled to 0°C and reduced the obtaining product by sodiumborohydride (10mmol, 0.39 gm for each) over a period of two hours. Slowly the temperature was raised to room temperature and kept it for 15-16 hour for evaporated the solvent and then recrystallised with ethanol/acetone and dried in air. Deep yellow/Radish yellow crystals were found.

The analytical and spectral data obtained for the ligand MB<sub>1</sub>/MB<sub>2</sub> are furnished below.

Analysis calculated for C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>S/C<sub>11</sub>H<sub>12</sub>O<sub>3</sub>N<sub>2</sub>S: C 53.04/52.36, H 4.79/4.79, N 9.51/19.02, S 10.89/12.70% Found; C 52.86/52.26, H 4.86/4.68, N 9.48/19.13, S 10.96/12.74: IR (KBr cm<sup>-1</sup>) 3380/3350 (-CH<sub>2</sub>-NH<), 1268 (C-O-C), 3269 (-SO<sub>2</sub>-NH<): Mass (m/z) 304/254

#### Synthesis of complexes:

The metal chloride/sulphate (5 mmol) in 25 ml ethanol was added slowly to a solution of the ligand MB<sub>1</sub>/MB<sub>2</sub> (10 mmol) in 25 ml ethanol. The resulting mixture was stirred for thirty minutes and then refluxed for 2-3 hours on a water bath. The product were cooled and solvent was slowly evaporated then washed with ethanol, acetone and ether, dried in air. The different coloured crystal of different complexes with different metal salts and liquids in 1 : 2 metal:ligand molar ratio have been isolated as. These complexes were subjected to physico-chemical studies.

## RESULTS AND DISCUSSION:

The newly prepared Cu (II) complexes were characterized with the help of magnetic susceptibility measurements, Electronic spectra, IR, ESR and elemental analysis. The analytical data shows 1 : 2 metal-ligand stoichiometry for all the complexes, and having distorted octahedral geometry.

#### Magnetic Moments and Electronic Spectra:-

The magnetic moment values of Cu (II) complexes are found in the range 1.80-1.95 BM at room temperature pointing to the distorted octahedral geometry [19] around Cu (II) as well as the presence of one unpaired electron on the metal ion. The geometry of these complexes further substantiated on the basis of spectral studies.

**Table 1. Analytical, Electronic Spectral and Magnetic data of the metal complexes of Mannich bases MB<sub>1</sub>/MB<sub>2</sub>**

Compound	Colour	Eff (B.M)	Analytical (%) of elements (found /Calculated)							Electronic Absorption(cm <sup>-1</sup> )
			C%	H%	O%	N%	S%	Cl%	M%	
Cu(MB <sub>1</sub> )Cl <sub>2</sub>	Bluish Brown	1.90	43.15	3.95	17.75	7.72	8.82	9.78	8.79	11800, 13100
			43.04	3.90	17.7	7.74	8.86	9.85	8.78	15440, 17300
Cu(MB <sub>1</sub> )SO <sub>4</sub>	Bluish Black	1.85	41.70	3.80	25.58	7.53	12.83	-	8.53	12340, 14320
			41.73	3.70	25.65	7.48	12.85	-	8.49	25400, 27800
Cu(MB <sub>2</sub> )Cl <sub>2</sub>	Bluish Brown	1.80	41.32	3.78	15.04	8.70	10.06	11.12	9.94	11880, 13240
			41.34	3.78	15.00	8.76	10.00	11.09	9.64	15680, 17520
Cu(MB <sub>2</sub> )SO <sub>4</sub>	Dark Brown	1.95	39.86	3.60	24.00	8.40	14.52	-	9.59	12400, 14200
			39.78	3.64	24.08	8.43	14.38	-	9.39	25640, 27720

**Table 2. Electronic Spectral Data for the Cu II Complexes (cm<sup>-1</sup>)**

S.No.	Parameters	Complexes			
		Cu (MB <sub>1</sub> )Cl <sub>2</sub>	Cu (MB <sub>1</sub> )SO <sub>4</sub>	Cu (MB <sub>2</sub> )Cl <sub>2</sub>	Cu (MB <sub>2</sub> )SO <sub>4</sub>
1	Peak Position				
	v <sub>1</sub>	11800	12340	11880	12400
	v <sub>2</sub>	13100	14320	13240	14200
	v <sub>3</sub>	15440	25400	15680	25640
	v <sub>4</sub>	17300	27800	17520	27720
2	Cristal field parameters 10Dq	13100	14320	13240	14200
3	Tetragonal distortion Parameters D <sub>s</sub>	2197	3574	2223	3604
	Dt	602	-391.6	597.8	-402.8
4	Spin orbit coupling constant λ	-1240	-1600	-1227	-1386
5	Energy of Seperation v <sub>4</sub> -v <sub>3</sub>	1860	2400	1840	2080

Six iacoordinated Cu (II) complexes possess two or more bands, which may be assigned to the transition  ${}^2E_g \rightarrow {}^2T_{2g}$ , a characteristic of the distorted octahedral Cu (II) complexes [20]. The broadening may be due to Jahn Teller Effect, since the  ${}^2E_g$  state is susceptible to Jahn Teller distortion.

The experimental and resolved optical absorption spectra of the present four Cu (II) complexes with MB<sub>1</sub> and MB<sub>2</sub> containing overlapping bands, Each of the resolved spectra of the Cu (II) complexes show four bands given in **table-2**. On the basis of coloured and peak positions, these complexes show the octahedral coordinated geometry. The results are broadning with the report Cu (II) complexes [21-22]. The broadening in the observed bands reflects the distortion in these complexes. Which cannot be attributed to Jahn Teller Effect [20]. Hence, the interpretation of the spectrum was carried out assuming that Cu (II) is tetragonally distorted in D<sub>4</sub><sup>th</sup> symmetry. The band assignment was carried out considering the spin orbit interaction, considering the electronic spectra of the synthesized on [Cu(MB<sub>1</sub>)Cl<sub>2</sub>

complex exhibited band at 15440  $\text{cm}^{-1}$  and 17300  $\text{cm}^{-1}$  respectively, may be due to the transitions.

$$\Gamma = 7^a ({}^2E_g) \rightarrow \Gamma 6b ({}^2T_{2g}) \quad \text{and} \quad \Gamma 7^a ({}^2E_g) \rightarrow \Gamma 7^c ({}^2T_{2g})$$

According to conventional theory, the spin orbit splitting of these bands should amount to about  $3/2\lambda$  in first order [23]. The energy separation between the  ${}^2T_{2g}$  state bands 1858  $\text{cm}^{-1}$  is higher than that of the free ion value 1245  $\text{cm}^{-1}$ . The large value of  $\lambda$  indicate the slight molecular distortion [31] in the complex formation, besides the spin orbit coupling. Two other bands appear at 11800  $\text{cm}^{-1}$  and 13100  $\text{cm}^{-1}$  were correspond to transitions as follows.

$$\Gamma 7^a ({}^2E_g) \rightarrow \Gamma 6a ({}^2E_g) \quad \text{and} \quad \Gamma 7^a ({}^2E_g) \rightarrow \Gamma 7^b ({}^2T_{2g})$$

Hence, the root for  $d^9$  complexes in first order becomes as

$$E [\Gamma 7^a ({}^2E_g)] = -6 Dq - 2DS + Dt \quad \dots (1)$$

$$E [\Gamma 6^a ({}^2E_g)] = -6 Dq + 2DS + 6Dt \quad \dots (2)$$

$$E [\Gamma 7^b ({}^2T_{2g})] = 4Dq - 2DS + Dt \quad \dots (3)$$

$$E [\Gamma 6^b ({}^2T_{2g})] = 4Dq + 2DS - 4Dt + \lambda \quad \dots (4)$$

$$[\Gamma 7^c ({}^2T_{2g})] = 4Dq + DS - 4Dt - \lambda/2 \quad \dots (5)$$

Here equation (3) corresponds to  $10 Dq$ . From this equation  $\lambda$  can easily calculate. The other parameters ( $Dq$ ,  $DS$  and  $Dt$ ) were determined by using  $\lambda = -1240$  (table 2). The spectroscopic analysis of other synthesized complexes have been carried out similarly. All the above information indicated the distorted octahedral [20] geometry around Cu (II) metal ion in all Cu (II) complexes. The analytical data and magnetic moment values are given in **table-1**.

#### Infrared Spectra:

The IR spectra of  $MB_1/MB_2$  ligand and their Cu (II) complexes were quite informative and the important IR frequencies are given in **table-4**. A broad absorption band of  $MB_1$  and  $MB_2$  observed at 3380  $\text{cm}^{-1}$  and 3350  $\text{cm}^{-1}$  respectively [25], due to  $\nu_{N-H}$  stretching vibration. On complexation these bands are observed at higher frequencies 3407-3411  $\text{cm}^{-1}$  and 3405-3384  $\text{cm}^{-1}$ , indicating the participation of nitrogen of  $MB_1/MB_2$  ligand linkage  $-CH_2-NH-$  in coordination. This is also confirmed with the appearance of peaks at 340  $\text{cm}^{-1}$  and 325  $\text{cm}^{-1}$ .  $MB_1$  corresponding to Cu-N vibrations [34] as other band in  $MB_2$  ligand appeared at 3269  $\text{cm}^{-1}$  due to sulphonamide ( $-SO_2-NH$ ) group, which disappeared in complexation, involvement of nitrogen of sulphonamide group in coordination, It gets further support by the presence of new bands at 420-425  $\text{cm}^{-1}$  in the metal complexes due to  $\nu(M-N)$  [24] respectively. The band observed at 1268  $\text{cm}^{-1}$ , 1040  $\text{cm}^{-1}$  in free  $MB_1$  and  $MB_2$  ligand is attributed to furyl oxygen. On complexation, this band get shifted towards lower frequency region 122 1245  $\text{cm}^{-1}$  in  $MB_1$  and not in  $MB_2$  indicating participation of oxygen in coordination in  $MB_1$  and not in  $MB_2$ . Both ligands and these four complexes showed bands in between 1337-1310  $\text{cm}^{-1}$  and 1150-1154  $\text{cm}^{-1}$  due to  $-SO_2$  group. These bands in complexes were obtained, are unchanged or negligible change, which indicating the non-participation in coordination.

The another band at 1090  $\text{cm}^{-1}$  and 628  $\text{cm}^{-1}$  in  $MB_1$  sulphato complexes and 1097  $\text{cm}^{-1}$  and 620  $\text{cm}^{-1}$  in  $MB_2$  sulphato complex, indicating the bidentate sulphato moiety in Cu (II) complexes. The non ligand band at 435  $\text{cm}^{-1}$  corresponds to the co-ordination through sulphur with Cu (II) ion. The peak moderate intensity at 420-440  $\text{cm}^{-1}$ , 374  $\text{cm}^{-1}$  in  $[Cu(MB_1)SO_4]$  and 290  $\text{cm}^{-1}$  in  $[Cu(MB_1)Cl_2]$ , may be attributed to  $\nu(M-O)$ ,  $\nu(M-S)$  [25] and  $\nu M-Cl$  vibration respectively. All the above observation suggests that both the ligands show bidentate nature

and coordinates through NN in  $[\text{Cu}(\text{MB}_2)\text{Cl}_2]$  and  $[\text{Cu}(\text{MB}_2)\text{SO}_4]$  ON in  $[\text{Cu}(\text{MB}_1)\text{Cl}_2]$  and  $[\text{Cu}(\text{MB}_1)\text{SO}_4]$  sides respectively.

**Table 3. ESR Values of Cu (II) Complexes**

S. No.	Parameters	Complexes			
		$\text{Cu}(\text{MB}_1)\text{Cl}_2$	$\text{Cu}(\text{MB}_1)\text{SO}_4$	$\text{Cu}(\text{MB}_2)\text{Cl}_2$	$\text{Cu}(\text{MB}_2)\text{SO}_4$
1	g	2.11	2.09	2.09	2.10
2	$g_{\text{II}}$	2.25	2.27	2.23	2.29
3	$g_{\text{I}}$	2.16	2.12	2.15	2.16
4	gav	2.19	2.17	2.28	2.20
5	G	1.562	2.25	1.533	1.812
6	A <sub>II</sub>	208	256	208	272
7	A <sub>I</sub>	80	48	88	88
8	A <sub>av</sub>	122.66	116.13	134.66	149.33
9	$\lambda/\Delta_{\text{II}}$	0.0309	0.0334	0.0284	0.0359
10	$\lambda/\Delta_{\text{I}}$	0.0788	0.0588	0.0738	0.0788
11	$\mu_{\text{eff}}$	1.896	1.879	1.97	1.90

#### ESR Spectra:

All four Cu (II) complexes of MB<sub>1</sub> and MB<sub>2</sub> ligand and their ESR spectra have been recorded at room temperature with two “g” values computed by Piesach and Blumberg’s method<sup>30</sup>. All complexes show a broad signal with similar pattern. The different values of g,  $g_{\text{II}}$  and  $g_{\text{I}}$  of each complexes have been calculated by the ESR spectrum in the following expression.

$$g = \nu h / \beta h \quad \dots (6)$$

The  $g_{\text{II}}$  and  $g_{\text{I}}$  values were also calculated by using  $H_{\text{II}}$  and  $H_{\text{I}}$  in Gauss respectively.

The magnetic moment ( $\mu$ ) for Cu (II) ion in a crystal field, was calculated by the first approximation method<sup>26</sup>

$$\mu_{\text{eff}} = g [S(S+1)]^{1/2} \quad \dots (7)$$

Here S = Spin Quantum Number

$$\mu_{\text{eff}}^2 = 3/2 g^2 \nu \quad \dots (8)$$

$$g^2 \nu = 1/3 (g_1^2 + g_2^2 + g_3^2) = 1/3 (g_{\text{II}}^2 + g_{\text{I}}^2) \quad \dots (9)$$

$$g \nu = 1/3 (g_{\text{II}} + 2g_{\text{I}}) \quad \dots (10)$$

in D<sub>4</sub><sup>h</sup> field,  $g_{\text{I}} = g_{\text{II}}$ ,  $g_2 = g_3 = g_{\text{I}}$ , thus the equation (9) would be equation (10) by substituting, the g value obtained from ESR Spectra into the above equation. It is seen from the **table-3** that  $g_{\text{II}} > g_{\text{I}} > g_e$  for all the Cu (II) complexes of Mannich bases of sulphacetamide or sulphanylamide, which implies 3d-unpaired electrons of Cu (II) ion occupied the  $dx^2 - y^2$  orbital as the ground state, it would be characteristic of axial symmetry [27] *i.e.* tetragonal distorted octahedral conformation [28, 29]. The g’s in a D<sub>4</sub><sup>h</sup> symmetry should be,

$$g_{\text{II}} = g_e + 8\lambda/\Delta_{\text{II}} \quad \dots (11)$$

$$g_{\text{I}} = g_e + 2\lambda/\Delta_{\text{I}} \quad \dots (12)$$

where  $g_e$  is the  $g$  value of free electron ( $g_e = 2.0023$ ) and  $\lambda$  is the spin coupling constant, the value of  $\lambda$  for Cu (II) ion is given as  $-830 \text{ cm}^{-1}$ .

**Table 4. InfraRed Spectral Data (in  $\text{cm}^{-1}$ ) of Mannich Base and their Cu (II) Metal Complexes**

S. N.	Ligand	Complex	$\nu\text{-CH}_2\text{-NH-}$	$\nu\text{-C=O-NH-}$	$\nu_{\text{asy}}\text{-SO}_2$	$\nu\text{-SO}_2\text{-NH}$	$\nu_{\text{sym}}\text{-SO}_2$	$\nu\text{C-O-C}$	$\nu\text{M-N}$	$\nu\text{M-O}$	$\nu\text{Cl}$	$\nu\text{M-S}$
1	MB <sub>1</sub>		3380b	1705w	1334m	-	1150m	1268s	-	-	-	-
		Cu(MB <sub>1</sub> )Cl <sub>2</sub>	3407b	1708m	1334m	-	1154s	1225m	340s	420w	290w	-
		Cu(MB <sub>1</sub> )SO <sub>4</sub>	3411s	1706s	1323s	-	1153s	1245s	325vw	440b	-	374w
2	MB <sub>2</sub>		3350 b	-	1339w	3269w	1152s	1047m	-	-	-	-
		Cu(MB <sub>2</sub> )Cl <sub>2</sub>	3405b	-	1337b	-	1153m	1042w	471w	-	280m	-
		Cu(MB <sub>2</sub> )SO <sub>4</sub>	3384b	-	1310m	-	1152m	1042m	425w	-	-	435m

The various  $g$  and  $A$  values were obtained from ESR spectral data, when the  $g$  value were putted into the equation (6) and (7), the corresponding  $\lambda/\Delta$  values were determined, are given in **table-3**.

$A_{\text{av}}$  values were also calculated by using the following equation.

$$A_{\text{av}} = 1/3 (A_{\text{II}} + 2A_1) \quad \dots (13)$$

The constant  $A_{\text{II}}$  and  $A_1$  were founded from ESR spectrum. It has been reported that for a Cu (II) complexes,  $g_{\text{II}}$  can be a parameter sensitive enough to indicate covalence. If the value of  $g_{\text{II}}$  is normally equal or more than 2.3, the environment is essentially ionic and whether the value of  $g_{\text{II}}$  is less than 2.3, indicate a covalent environment in the tetragonal field, the  $g$  values are related by the following equation.

$$G = (g_{\text{II}} - 2)/(g_1 - 2)$$

where  $G$  measure the exchange of interaction between Cu (II) centre in the solid state. If  $G < 4$  than it indicates no exchange coupling [34] in complexes. The value of ' $G$ ' in the present complexes lies in the range 1.53-2.25.

From table-3, that for these complexes  $\lambda/\lambda_{\text{II}} < \lambda/\Delta_1$  indicating the  ${}^2\text{Eg}$  level lies below the  ${}^2\text{B}_2\text{g}$  level. An essential feature for interpreting the ESR spectra of these Cu (II) complexes, is the magnitude of parameters  $\Delta g_{\text{II}}$  ( $\Delta g_{\text{II}} = g_{\text{II}} - g_e$ ). From equations (9), (11) and (12). It is seen that reduction in  $\Delta g_{\text{II}}$  values may be due to an increase in  $\Delta$  or a decrease in  $\lambda$  or a combination of both. An increase  $\Delta g_{\text{II}}$ ,  $\Delta$  and (or) a decrease in  $\lambda$  will lead to decrease in  $\Delta g_{\text{II}}$ ,  $\Delta g_1$  and  $\Delta g_{\text{av}}$  and increase in covalency of the coordination bonding [30] from metal to ligand and opposite it, shows increasing ionic character of the co-ordination bonding [35]. Therefore, from the ESR spectra of these complexes. We can concluded that they show covalent character of the metal ligand bond.

## REFERENCES

1. Rajiv, D., Suman, S., Sonmane, S.K., Shrivastava, S.K., Pharmacological Significance of Synthetic Heterocycles Scaffold, *A Review, Advances in Biological Research*, **5(3)**, 120-144 (2016).
2. Aderoju, A.O., Chioma, F., *Journal of Chemical Biological and Physical Sciences, An International Peer Review E-3 Journal Of Sciences*, **6(1)**, 80-89 (2016).
3. Mittal, P., Uma, V., *Der Chemica Sinica*, **1(3)**, 124 (2010).
4. Gul, H.I., Ojanen, T., Vespalainen, I., Gul, M., Erciyas, E., Hanninen, O., *Arzneimittelforschung*, **52(1)**, 72 (2001).
5. Gul, H.I., Gul, M., Henninen, O., *Arzneimittelforschung*, **52(11)**, 840 (2002).
6. Satr-Papastaikoudi, T., Tsotinis, A., Chinou, I., Roussakis, C., *Farmaco*, **49(3)**, 221 (1994).

7. Sabastiyani, A., Suvaikin, M.Y., *Adv. in App. Sci. Res.*, **3(1)**, 45 (2012).
8. Koechel, D.A., Rankin, G.O., *J. Med. Chem.*, **21(8)**, 764 (1978).
9. Weaver, W., *J. Am. Chem. Soc.*, **66**, 2241 (1944).
10. Sabastiyani, A., Venkappayya, D., *J. Indian Chem. Soc.*, **61**, 16 (1984).
11. Sabastiyani, A., "Metal Complexes of Some Aminomethyl Substituted Urea and Thiourea," *Ph.D. Thesis*, Bharathidarsan Univ. Trichurappalli (1987).
12. Sabastiyani, A., Yosuva, M.S., *Adv. Appl. Sci. Res.*, **3(1)**, 45-50 (2012).
13. Ramesh, M., Sabastiyani, A., *Der Chimica Sinica*, **3(3)**, 534-542 (2012).
14. Yosuva, M.S., Sabastiyani, A., *Int. J. Chem. Tech. Res.*, **4(2)**, 805-815 (2012).
15. Sujata, S., Rajendran, T.M., Kennapan, R., Venkatesa, R., Rao, P.S., *Proc. Ind. Acad. Sci. (Chem. Sci.)*, **112(6)**, 559 (2000).
16. Prabhu, G.V., Venkappayya, D., *J. Indian Chem. Soc.*, **72**, 681 (1995).
17. Donopoulos, A.A., Paraskewas, S.M., *Inorg. Chem. Acta*, **55**, 141 (1981).
18. Drown, D.H., Nuttall, R.H., McAvoy, J., Sharp, D.W.A., *J. Chem. Soc.*, **A**, 892 (1966).
19. Figgis, B.N., Lewis, J., in "Modern Co-ordination Chemistry", J. edLewis, R.G. Wilkins, Interscience, Newyork (1960).
20. Lever, A.B.P., "Inorganic Electronic Spectroscopy", Elsevier Amesterdum (1968).
21. Vogel, A.I., Ref. 1, *ibid*, 816 (1978).
22. Vogel, A.I., "A Text Book Of Practical Organic Chemistry", **4<sup>th</sup> ed**, Longmann, London, 811 (1978).
23. Liehr, A.D., *J. Phys. Chem.*, **64**, 43 (1963).
24. Prabhu, V., Venkappaya, D., *J. Indian Chem. Soc.*, **72**, 681 (1995).
25. Mylonas, S., *Ph.D. Thesis Athens* (1976).
26. Jorgenson, C.K., *Adv. Chem. Phys.*, **5**, 33 (1963).
27. Hathway, B.J., Tomlinson, A.A.G., *Coord Chem. Rev.*, **5**, 1 (1970).
28. Bai, L.J., Wng, Z.F., Chen, Y.T., *J. Indian Chem. Soc.*, **59**, 1280 (1982).
29. Nohria, L., Gupta, M., Mathur, P., *Indian J. Chem.*, **40(A)**, 316 (2001).
30. Piesach, J., Blumberg, W.E., "EPR of Metal Complexes", edited by Ten Fu Yen, Adam Higher Ltd, London, 71 (1961).
31. Ortolano, T.R., Selbin, J., McGlynn, S.P., *J. Chem. Phys.*, **41**, 262 (1964).
32. Well, F.P. Trade, "Analytical Chemistry", John Wiley and Sons Inc., London (1968).
33. Vogel, A.I., "A Text Book Of Quantitative Analysis", **3rd ed.**, Longmans, London (1961).
34. Procter, I.M., Hathway, B.J., Nicollas, P., *J. Chem. Soc.*, **A**, 1678 (1968).
35. Kivelson, D., Neimann, R., *J. Chem. Phys.*, **35**, 147 (1961).
36. Weicher, F. J., "Organic Analytical Reagent", D. Von Nostrand, Newyork (1965).
37. Weicher, F. J., "The Analytical Role Of EDTA", D. Von Nostrand, Newyork (1965).
38. Khalthof, J.M., Erving, P.I., "Treatise on Analytical Chemistry," **2<sup>nd</sup> ed.**, Interscience, Newyork (1963).
39. Wathrich, K., *Halv. Chem. Acta*, **48**, 779 (1965).
40. Foscupe, H., *Micro Chem. Acta*, **5**, 361 (1954).



