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SYNTHESIS AND APPLICATIONS OF COMPLEXES OF CHROMIUM METAL WITH HYDRAZINECARBOTHIOAMIDES LIGANDS

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Abstract: - This paper incorporates the preparation, characterization and biochemical screening of the biologically potent ligands and their complexes with chromium (III). The ligands used in these studies are hydrazinecarbothioamides. These ligands and their corresponding metal complexes were synthesized by two synthetic procedures, i.e., microwave as well as the conventional heating. A comparison has been made between these two synthetic methods on the basis of the yield of the products, refluxing time and the solvent consumed. The structural deductions were made on the basis of magnetic measurements, electronic, infrared, ESR, and NMR spectral studies. The Four complexes of Chromium (III) with hydrazinecarbothioamides have been synthesized. The bonding pattern of the ligands and the geometry of their Chromium (III) complexes have been deduced on the basis of UV, IR, ^{1}H NMR, ^{13}C NMR spectral and X-ray diffraction studies. Some selected metal complexes and their parent ligands have been screened for their antifungal activities and the observed results have been explained.

Introduction

This chapter incorporates the coordination behavior and characterization of several azomethine ligands and their chromium (III) complexes. The ligands and their metal complexes were prepared by the conventional method as well as by microwave method[1]. Green synthesis under solvent free and less solvent conditions are attractive offering reduced pollution, low cost and offer high yields together with simplicity in processing and handling. The authenticity of the ligands and their complexes has been established by elemental analyses, melting point determinations, molecular weight determinations, and various spectroscopic techniques like, EPR, IR, ^{1}H NMR, ^{13}C NMR, UV-Visible and X-ray powder diffraction studies.

Experimental

The present research work incorporates the synthesis of a variety of fluoroimine complexes of chromium (III) by using different methods and apparatus, which have been discussed in this section. The details of these techniques are given in the following pages:

1. APPARATUS

The well cleaned apparatus was rinsed with rectified spirit and then dried at 110-120 ºC in an electric oven for few hours and cooled at the room temperature by keeping them in desiccators.

MATERIALS

(a) **Methanol** (B.D.H., B.P.: 65 ^{o}C) was refluxed over magnesium methoxide (prepared from magnesium ribbon and methanol in presence of iodine) and then distilled.

(b) **Dimethylformamide** (E. Merck, B.P.: 66 ^{o}C/35 mm) was distilled after storing it over anhydrous sodium carbonate and further redistilled under reduced pressure.

(c) ***n*-Hexane** (B.P.: 69 ^{o}C) was dried by refluxing over sodium wire.

(d) **Cyclohexane** (B.P.: 80 ^{o}C) was dried by refluxing over sodium wire

(e) **Ether** (B.P.: 34.6 ^{o}C) was kept over calcium chloride (anhydrous) for 3-4 days and then distilled. It was then refluxed and distilled over sodium wire.

(f) **Tetrahydrofuran** (SISCO, B.P.: 66.5 ^{o}C) was dried by distilling it over sodium wire and then tested it with benzophenone.

(g) **Benzene** (B.D.H., B.P: 80 ^{o}C) was dried by storing and refluxing over sodium wire for 2-3 days, followed by azeotropic distillation with ethanol

(h) **Chloroform** (B.D.H., B.P.: 61.2 ^{o}C) was collected after storing it for two days over barium oxide.

2. ANALYTICAL METHODS

The analyses of synthesized azomethines and their metal complexes were performed by the following methods.

(I) **Estimation of Carbon and Hydrogen:-** Carbon and hydrogen analyses of the complexes as well as the ligands were performed at the *Micro analytical Laboratory, Chandigarh*.

(II) **Estimation of Nitrogen** [1-2]:- Nitrogen was estimated by the Kjeldahl's method.

(III) **Estimation of Sulphur**[3-4] **:-** Sulphur was estimated as $BaSO_4$ by the Messenger's method.

(IV) **Estimation of Chlorine**[5]**:-** Chloride was estimated volumetrically by Volhard's method.

Estimation of Metals

a) Chromium Estimation [6]

The chromium metal was determined as Cr_2O_3 gravimetrically. The weighed amount of the compound was placed in a 500 mL beaker and decomposed with concentrated nitric acid. It was then diluted with 200 mL of distilled water. To this solution, ammonium chloride was added followed by heating just to boiling. Diluted ammonia solution (1:1) was added drop wise from a burette till the solution was alkaline. The precipitate obtained was filtered through a whatmam filter paper. It was washed with 2 % ammonium chloride solution, dried and ignited in a silica crucible. It was finally weighed as Cr_2O_3.

3. INSTRUMENTAL METHODS

The instrumental methods adopted during these studies are as follows:

(I) **Thin Layer Chromatography:-** To test the purity of the synthesized compounds, T.L.C. was employed on silica gel G using various solvents.

(II) Molecular Weight Determinations[8-9]**:-** The molecular weights were determined by the Rast Camphor method using resublimed camphor (M.P. 178°C).

(III) **Ultraviolet Spectra:-** Ultraviolet spectra were recorded on a Perkin-Elmer model spectrophotometer.

(IV) **Infrared Spectra:-** IR spectra were recorded on a Perkin-Elmer model spectrophotometer, in the range 4000–200 cm^{-1} in KBr optics as well as in Nujol mulls.

(V) **EPR Spectra:-** ESR spectra of the complexes were monitored on Varian E- 4X band spectrometer at SAIF, IIT, Madras, Chennai.

(VI) **Magnetic Measurements:-** Magnetic measurements were recorded at vibrating sample magnetometer Model 155 room temperature at SAIF, IIT, Madras, Chennai.

(VII) **Molar Conductance Measurements:-** The molar Conductivity of the resulting compounds was determined on Century Digital Conductivity Meter Model CC 601 at room temperature. The solutions of the order of 10^{-3}M concentration were employed for the conductivity measurements.

(VIII) **X-Ray Powder Diffraction:-** X-Ray powder diffractograms of the compounds were obtained on a RIGAKU miniFlex automatic diffractogram using Cu (Kα) target with Mg filter. The wavelength used was 1.540 Å.

Preparation:

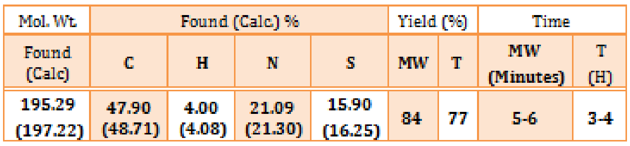
4. SYNTHETIC METHODS

Preparation of the Ligands

⇒ ***Preparation of hydrazinecarbothioamides*** **(L^1H and L^2H)**

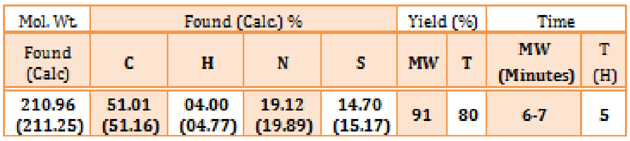
The hydrazinecarbothioamides of o-fluorobenzaldehyde, o-fluoroacetophenone and 3-acetyl coumarin were prepared by the condensation of o-fluorobenzaldehyde, o-fluoroacetophenone and 3-acetyl coumarin with thiosemicarbazide in 1:1 molar ratio in the medium of ethanol. The contents were refluxed for about 4-5 hours in thermal method and about 5-6 minutes in microwave method. After refluxing, the contents were separated out as crystalline solids. These were dried and purified by recrystallisation from the same solvent. Analysis of the above ligands is as follows:

(a) **[2-(2-fluorophenyl)methylene] hydrazinecarbothioamide (L^1H):-_ ($C_8H_8N_3SF$) Colour, White, M. P., 190°C**



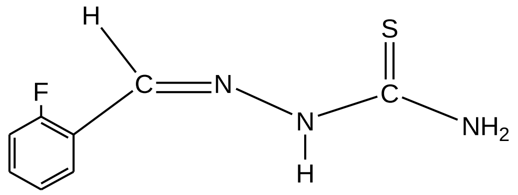
Mol. Wt.	Found (Calc) %				Yield (%)		Time	
Found (Calc)	C	H	N	S	MW	T	MW (Minutes)	T (H)
195.29 (197.22)	47.90 (48.71)	4.00 (4.08)	21.09 (21.30)	15.90 (16.25)	84	77	5-6	3-4

(b)[2-{1-(2-fluorophenyl) ethyledene}] hydrazinecarbothioamide (L^2H):- ($C_9H_{10}N_3SF$) Colour, White, M. P., 121°C

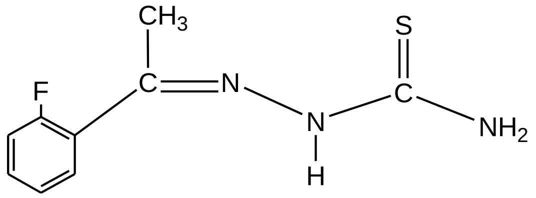


Mol. Wt.	Found (Calc) %				Yield (%)		Time	
Found (Calc)	C	H	N	S	MW	T	MW (Minutes)	T (H)
210.96 (211.25)	51.01 (51.16)	04.00 (04.77)	19.12 (19.89)	14.70 (15.17)	91	80	6-7	5

Structure of Schiff Base ligands: (**L^1H – L^2H*****)***



[2-(2-fluorophenyl) methylene] hydrazinecarbothioamide (L



1H)

[2-{1-(2-fluorophenyl) ethyledene}] hydrazinecarbothioamide (L^2H)

SYNTHESIS OF CHROMIUM (III) COMPLEXES

1. Preparation of the Chromium (III) Complexes

➢ ***Preparation of the chromium(III) complexes of hydrazinecarbothioamides: (L^1H-L^2H)***

The weighed amount of hydrated chromium trichloride ($CrCl_3.6H_2O$) in dry methanol was added to the methanolic solution of ligands (L^1H and L^2H) in 1:1 and 1:2 molar ratios using NaOH in appropriate stoichiometric proportions. The reaction mixture was subjected under both energy sources, thermal as well as microwave. The physical properties and analytical data of these complexes were reported as follows:

Chromium(III) complex with L^1H (monofunctional bidentate N∩S)	
(1:1) **$[CrCl_2(L^1)(H_2O)_2]$** **Green**	Mol. Wt., 353.64 (355.14), C, 26.45 (27.05), H, 03.00 (03.12), N, 10.92 (11.83), Cl, 19.08 (19.96), Cr, 13.61(14.64), S, 09.00 (09.02), $\mu_{eff.}$ (B.M.), 3.81, M.P., 211°C(d)
(1:2) **$[CrCl(L^1)_2(H_2O)]$** **Green**	Mol. Wt., 495.90 (497.89), C, 36.90 (38.59), H, 02.91 (03.23), N, 16.80 (16.87), Cl, 07.01 (07.12), Cr, 10.01(10.44), S, 12.48 (12.87), $\mu_{eff.}$ (B.M.), 3.79,

	M.P., 208°C(d)
Chromium(III) complex with L^2H (monofunctional bidentate N⌒S)	
(1:1) **$[CrCl_2(L^2)(H_2O)_2]$** **Green**	Mol. Wt., 368.31 (369.16), C, 27.11 (28.28), H, 03.17 (03.52), N, 10.50 (11.38), Cl, 19.00 (19.20), Cr, 13.84(14.08), S, 07.60 (08.68), $\mu_{eff.}$ (B.M.), 3.78, M.P., 179°C,
(1:2) **$[CrCl(L^2)_2(H_2O)]$,** **Dark green**	Mol. Wt., 523.86 (525.94), C, 39.91 (41.12), H, 03.54 (03.82), N, 14.92 (15.97), Cl, 05.53 (06.74), Cr, 09.19(09.81), S, 11.93 (12.19), $\mu_{eff.}$ (B.M.), 3.82, M.P., 146°C,

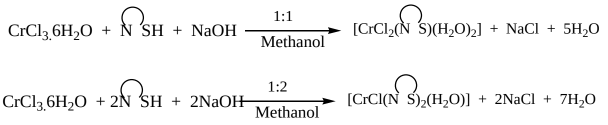
Result and Discussion:

(1) **CHROMIUM(III) FLUOROIMINE COMPLEXES:-** This section deals with characterization of chromium (III) azomethine complexes which have been synthesized during the present investigations and can be discussed under the following sections:

(1.1) Hydrazinecarbothioamide complexes

(i) $[CrCl_2(L^1)(H_2O)_2]$ and $[CrCl(L^1)_2(H_2O)]$
Where,L^1H:[2-(2-fluorophenyl)methylene]hydrazinecarbothioamide
(ii) $[CrCl_2(L^2)(H_2O)_2]$ and $[CrCl(L^2)_2(H_2O)]$
Where,L^2H:[2-{1-(2-fluorophenyl)ethyledene}]hydrazinecarbothioamide

The chromium (III) complexes of monofunctional bidentate ligands (L^1H and L^2H) were prepared by dissolving a calculated amount of metal chloride ($CrCl_3.6H_2O$) in methanol and then adding a methanolic solution of the ligand. The reactions were carried out in 1:1 and 1:2 molar ratios using stoichiometric amount of NaOH. Overall reaction of 1:1 and 1:2 chromium (III) complexes with hydrazinecarbothioamide are as follows:



$$CrCl_{3.}6H_2O + \overset{\frown}{N\ \ S}H + NaOH \xrightarrow[\text{Methanol}]{1:1} [CrCl_2(\overset{\frown}{N\ \ S})(H_2O)_2] + NaCl + 5H_2O$$

$$CrCl_{3.}6H_2O + 2\overset{\frown}{N\ \ S}H + 2NaOH \xrightarrow[\text{Methanol}]{1:2} [CrCl(\overset{\frown}{N\ \ S})_2(H_2O)] + 2NaCl + 7H_2O$$

(Where, $\overset{\frown}{N\ \ S}$ is the donor system of the hydrazinecarbothioamides (L^1H-L^2H))

The resulting complexes have been obtained as coloured solids and are insoluble in most of the common organic solvents but soluble in methanol, ethanol dimethylformamide and dimethylsulfoxide. The bonding pattern and the geometry of these complexes have been deduced on the basis of IR, ESR, UV-Vis and X-ray powder diffraction studies. The electronic spectra of the hydrazinecarbothioamides (L^1H and L^2H) and their chromium (III) complexes have been recorded in methanol. In the electronic spectra, organic moieties show broad band at 27000–30303 cm^{-1} due to the n-π* transitions of the azomethine group, which undergo a blue shift on complexation which confirms the coordination of nitrogen atom to the central metal atom. The electronic spectra of chromium complexes in the visible range show three spin allowed d-d transitions at 16456–17413 cm^{-1}, 22880–24138 cm^{-1} and 30221–32480cm^{-1} may be assign to ${}^4A_{2g}\rightarrow{}^4T_{2g}$, ${}^4A_{2g}\rightarrow{}^4T_{1g}$ and ${}^4A_{2g}\rightarrow{}^4T_1$ transitions respectively , suggesting an octahedral geometry around the Cr^{+3} ion in the complexes. Several parameters, which are often used to characterize the electronic properties of transition-element complexes, can be derived from the energies of these transitions. The most important ones are the crystal field parameter 10Dq, if the octahedral approximation is considered, energy of the first spin allowed transition $[{}^4A_{2g}(F)\rightarrow{}^4T_{2g}(F)]$ directly gives the value of 10Dq and the Racah parameters B which are calculated by the formula:

$$B = \frac{(2\nu_1 - \nu_2)(\nu_2 - \nu_1)}{3(9\nu_1 - 5\nu_2)}$$

$$\beta = B/B^0$$

The ligand field spectral parameters for chromium (III) complexes are found to be *Dq*=1645-1741 cm^{-1}, *B* = 630-666 cm^{-1} and β = 0.68-0.72. The reduction of the Racah parameter (B^0) from the free ion value of 918 cm^{-1} and the value of β indicates the covalent nature of the chromium (III) complexes. Various ligand field parameters like Dq, B and β have been calculated and given in Table 2.10.

Table 1: Electronic spectral data of chromium (III) complexes

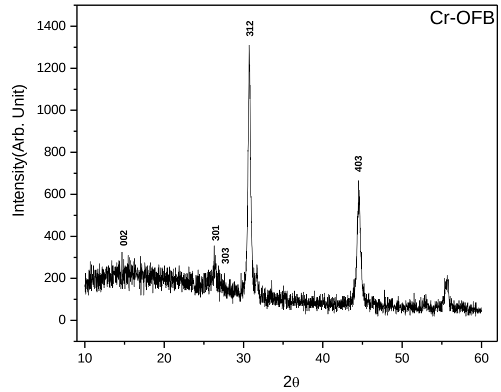
Compounds	**Transitions**	**Spectral bands cm^{-1}**	**Dq**	**B**	**$\beta = B/B^o$**	**ν_2/ν_1**
$[CrCl_2(L^1)(H_2O)_2]$	${}^4A_{2g}(F)\rightarrow{}^4T_{2g}(F)$ ${}^4A_{2g}(F)\rightarrow{}^4T_{1g}(F)$ ${}^4A_{2g}(F)\rightarrow{}^4T_{1g}(P)$	16456 22880 31372	1645	637	0.69	1.39
$[CrCl(L^1)_2(H_2O)]$	${}^4A_{2g}(F)\rightarrow{}^4T_{2g}(F)$ ${}^4A_{2g}(F)\rightarrow{}^4T_{1g}(F)$ ${}^4A_{2g}(F)\rightarrow{}^4T_{1g}(P)$	17381 23852 32010	1738	633	0.68	1.37
$[CrCl_2(L^2)(H_2O)_2]$	${}^4A_{2g}(F)\rightarrow{}^4T_{2g}(F)$ ${}^4A_{2g}(F)\rightarrow{}^4T_{1g}(F)$ ${}^4A_{2g}(F)\rightarrow{}^4T_{1g}(P)$	16935 23629 32480	1693	666	0.72	1.39
$[CrCl(L^2)_2(H_2O)]$	${}^4A_{2g}(F)\rightarrow{}^4T_{2g}(F)$ ${}^4A_{2g}(F)\rightarrow{}^4T_{1g}(F)$ ${}^4A_{2g}(F)\rightarrow{}^4T_{1g}(P)$	17413 24138 30221	1741	665	0.71	1.38

In the IR spectra of the hydrazinecarbothioamides (L^1H and L^2H) two common sharp bands observed around 3360 and 3420 cm^{-1} due to $\nu_{sym.}$ and $\nu_{asym.}$ vibrations of NH_2 group, respectively. The broad band due to ν(NH) vibrations at 3100-3280 cm^{-1} disappears in the spectra of the metal complexes indicating the deprotonation of this group on coordination with the metal atom (Table 2.11). The band due to ν(>C=S) modes in the spectra of the ligands is observed at 1030–1040cm^{-1} which shifted to lower frequency in the spectra of the chromium (III) complexes suggesting tautomerization of the ligands and their chelation through the thiolic sulfur. A sharp band in the range 1605-1610 cm^{-1} due to ν(>C=N) group shifts towards the lower frequency (15-20 cm^{-1}) and occurrence of the ν(N–N) band at higher frequency in the spectra of chromium(III) complexes, The mode of coordination is further supported by the appearance of new bands in the spectra of chromium(III) complexes at 512-528 cm^{-1}, 330-350 cm^{-1} and 315-320 cm^{-1} due to ν(Cr←N), ν(Cr-S) and ν(Cr-Cl), respectively. In the spectra of chromium (III) complexes a band is observed in the range 870-880 cm^{-1} which may be attributed to the coordinated water molecule. Further, a broad band around 3540-3450 cm^{-1} may be due to ν(O-H) of water molecule.

Table2: IR (cm^{-1}) Spectral data of the ligands and their chromium (III) complexes

Compound	IR Spectral data (cm^{-1})					
	ν(C=N)	ν(NH)	ν(OH) (water molecule)	ν(Cr←N)	ν(Cr-S)	ν(Cr-Cl)
L^1H	1615	3280	-	-	-	-
L^2H	1610	3100	-	-	-	-
$[CrCl_2(L^1)(H_2O)_2]$	1593	-	3450	520	344	319
$[CrCl(L^1)_2(H_2O)]$	1604	-	3500	522	350	315
$[CrCl_2(L^2)(H_2O)_2]$	1601	-	3522	512	330	320
$[CrCl(L^2)_2(H_2O)]$	1590	-	3540	528	345	320

The significant ^1H NMR and ^{13}C NMR spectral data of hydrazinecarbothioamides (L^1H and L^2H) have been recorded in $CDCl_3$ using TMS as an internal standard. The ^1H NMR spectra of the thiosemicarbazones show a signal at δ10.24-11.27 ppm which is due to NH proton. A signal due to NH_2 proton appears at δ2.16-3.16 ppm. The aromatic proton signals were appeared in the range δ6.70-8.28 ppm in the spectra of the ligands. The spectra of free ligands exhibit the signals due to the azomethine proton and methyl protons at δ8.33 and δ1.80-2.30 ppm respectively. In the ^{19}F NMR spectra of free ligands L^1H and L^2H, the signals arise at δ122.34 and 109.00 ppm respectively. In the ^{13}C NMR spectra of the ligands a signal observed at δ147.52-157.38 ppm due to the azomethine carbon. The ^{13}C NMR spectra of the ligands (L^1H and L^2H) show a signal at δ178.45-179.52 ppm due to the thiolo carbon. The signals due to the methyl carbon attached to the azomethine group appear at δ17.34 ppm. The possible lattice dynamics of the finely powdered chromium (III) complex, *$[CrCl(L^1)_2(H_2O)]$* has been deduced on the basis of X-ray powder diffraction studies. The observed interplanar spacing values ('d' in Å) have been measured from the diffractogram of the compound *$[CrCl(L^1)_2(H_2O)]$* (Graph1) and the Miller indices h, k and l have been assigned to each d value and 2-theta angles are reported in Table 2.12. The results show that the compound belongs to 'orthorhombic' crystal system having unit cell parameters as a=9.1000, b=17.3000, c=21.0100, maximum deviation of 2-theta 0.2 and Alpha= 90, Beta= 90, Gama=90 at the wavelength = 1.54 A^0.

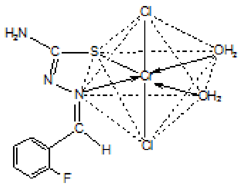


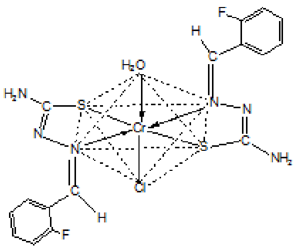
Graph 1: X-ray powder diffraction pattern for $[CrCl(L^1)_2(H_2O)]$

Table- 3: X-ray diffraction data of $[CrCl(L^1)_2(H_2O)]$

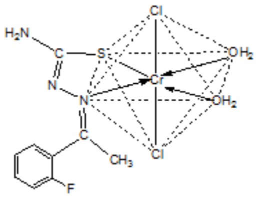
H	K	l	2-theta (Exp.)	2-theta (Calc.)	2-theta (Diff.)	d (Exp.)	d (Calc.)	Intensity (Exp.)
0	0	2	15.02	15.52	-0.5	6.3863	6.3685	11.45
3	0	1	26.72	26.37	-0.35	3.8411	3.8364	8.12
3	0	3	27.21	27.93	-0.72	2.9862	2.9203	11.25
3	1	2	28.12	28.45	-0.33	2.9681	2.9166	91.23
4	0	3	43.92	44.60	-0.68	2.4933	2.4595	7.21

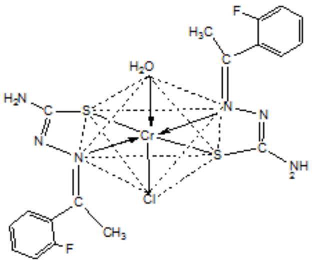
Thus, on the basis of the above discussion, it becomes clear that hexa-coordinated octahedral structures are most suitable for the 1:1 and 1:2 chromium (III) complexes (Figs.1-4)





$[CrCl_2(L^1)(H_2O)_2]$Complex $[CrCl(L^1)_2(H_2O)]$ Complex (1:1) (1:2) (Fig.1) (Fig.2)





$[CrCl_2(L^2)(H_2O)_2]$Complex $[CrCl(L^2)_2(H_2O)]$ Complex (1:1) (1:2) (Fig.3)(Fig.4)

REFERENCES

[1]. A. I. Vogel, *"A Text Book of Quantitative Inorganic Analysis",* Longmans Green ELBS, London **(1962).**

[2]. A.I. Vogel, *"A Textbook of Quantitative Chemical Analysis", Sixth edition*, Pearson Education Ltd. U.K., 387 **(2006).**

[3]. S. P. Mittal, R.V. Singh and J.P. Tandon, *Indian J. Chem.*, **20A**, 199 **(1981)**.

[4]. A.I. Vogel, *"A Textbook of Quantitative Chemical Analysis", Sixth edition*, Pearson Education Ltd. U.K., 498 **(2006).**

[5]. J. Volhard, *J. Prakt. Chem*., **9**, 217 **(1874).**

[6]. A. I. Vogel *"A Text Book of Quantitative Inorganic Analysis", Third Edition,* Longmans Green ELBS, London **(1968)**.

[7]. N. Fahmi, D.K. Sharma and R.V. Singh, *Synth. React. Inorg. Met.-Org. Chem*., **25**, 1345 **(1995)**

[8]. K. Rast, *Ber. Chem. Ges*., *Iv B*, **1051**, 3727 **(1922).**

[9]. A.I. Vogel, *"A Textbook of Organic Quantitative Analysis", Fifth edition*, Pearson Education Ltd. U.K., 243 **(2004).**

[10]. J.S. Bonadies and C.J. Carrano, *J. Am. Chem. Soc.* **108,** 4088 **(1986).**

[11]. M. Thankamony and K. Mohanan, *Indian J. Chem.,* **46A**, 249 **(2007).**

[12]. P. B. Sreeja and M. R. P. Kurup, *Spectrochim Acta,* **61(A),** 331 **(2005).**

[13]. A. P. Mishra and L. R. Pandey *Indian J. Chem,* **44A,** 1800 **(2005).**

[14]. R.Rajavel, M. S. Vadivu and C. Anitha, *E-J. Chem*., **5 (3),** 620 **(2008).**

[15]. K. Nakamoto, *Infrared and Raman Spectra of inorganic and coordination, Compounds,* 3rd Ed., New York: Wiley, (**1997).**

[16]. R.B. Von Dreele and R.C. Fay, *J. Am. Chem. Soc*.**, 94,** 7935 **(1972).**

[17]. N. Sharma, M. Thakur and S.C. Chaudhry, *J. Coord. Chem.,* **63 (6),** 1071 **(2010).**