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# **RESEARCH ARTICLE**

## SYNTHESIS AND APPLICATIONS OF COMPLEXES OF CHROMIUM (III) METAL WITH HYDRAZINECARBOXAMIDES LIGANDS

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# ARTICLE INFO ABSTRACT Article History: This paper incorporates the preparation, characterization and biochemical screening of the biologically

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Key words:

Synthesis, Hydrazinecarboxamides, Biochemical. 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 hydrazinecarboxamides. 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 hydrazincarboxamides 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, <sup>1</sup>H NMR, <sup>13</sup>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.

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# INTRODUCTION

This chapter incorporates the coordination behaviour 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 (Sharma, 2010). 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 melting established by elemental analyses, point determinations, molecular weight determinations, and various spectroscopic techniques like, EPR, IR, <sup>1</sup>H NMR, <sup>13</sup>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:

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### APPARATUS

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

## MATERIALS

The starting materials of metals used for carrying out the reactions were hydrated chromium trichloride and vanadium oxytrichloride. All the chemicals and solvents used were dried and purified by the standerd methods.

- *Methanol* (B.D.H., B.P.: 65 °C) was refluxed over magnesium methoxide (prepared from magnesium ribbon and methanol in presence of iodine) and then distilled.
- *Dimethylformamide* (E. Merck, B.P.: 66 °C/35 mm) was distilled after storing it over anhydrous sodium carbonate and further redistilled under reduced pressure.
- (c) n-Hexane (B.P.: 69 °C) was dried by refluxing over sodium wire.
- *Cyclohexane* (B.P.: 80 °C) was dried by refluxing over sodium wire

- *Ether* (B.P.: 34.6 °C) was kept over calcium chloride (anhydrous) for 3-4 days and then distilled. It was then refluxed and distilled over sodium wire.
- *Tetrahydrofuran* (SISCO, B.P.: 66.5 °C) was dried by distilling it over sodium wire and then tested it with benzophenone.
- *Benzene* (B.D.H., B.P: 80 °C) was dried by storing and refluxing over sodium wire for 2-3 days, followed by azeotropic distillation with ethanol
- *Chloroform* (B.D.H., B.P.: 61.2 °C) was collected after storing it for two days over barium oxide.

### ANALYTICAL METHODS

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

- Estimation of Carbon and Hydrogen
- Carbon and hydrogen analyses of the complexes as well as the ligands were performed at the *Microanalytical Laboratory, Chandigarh*.
- Estimation of Nitrogen<sup>1-2</sup>
- Nitrogen was estimated by the Kjeldahl's method.
- Estimation of Sulphur<sup>3-4</sup>
- $\circ$  Sulphur was estimated as BaSO<sub>4</sub> by the Messenger's method.
- Estimation of Chlorine<sup>5</sup>
- Chloride was estimated volumetrically by Volhard's method.
- Estimation of Metals

## Chromium Estimation<sup>6</sup>

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 dropwise 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 finaly weighet as  $Cr_2O_3$ 

#### **INSTRUMENTAL METHODS**

The instrumental methods adopted during these studies are as follows:

#### Thin Layer Chromatography

To test the purity of the synthesized compounds, T.L.C. was employed on silica gel G using various solvents.

## Molecular Weight Determinations<sup>8-9</sup>

The molecular weights were determined by the Rast Camphor method using resublimed camphor (M.P. 178°C). The depression in freezing point from that of pure camphor was determined with sufficient accuracy and the molecular weight of the compound was calculated by using the formula:

M=

K.w.1000

#### Where,

- M = Molecular weight of the compound
- K = Molecular depression constant for campbor (39.7)
- w = Weight of the compound taken
- W= Weight of the camphor taken

T = Difference of the melting point temperatures of camphor and the mixture of camphor and the compound

#### Ultraviolet Spectra

Ultraviolet spectra were recorded on a Perkin-Elmer model spectrophotometer.

#### Infrared Spectra

IR spectra were recorded on a Perkin-Elmer model spectrophotometer, in the range 4000–200 cm<sup>-1</sup> in KBr optics as well as in Nujol mulls.

### <sup>1</sup>H and <sup>13</sup>C NMR Spectra

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a JEOL-AL-300 FT NMR spectrometer in DMSO-d<sub>6</sub> using TMS as the internal standard.

#### **EPR** Spectra

ESR spectra of the complexes were monitored on Varian E-4X band spectrometer at SAIF, IIT, Madras, Chennai.

#### **Magnetic Measurements**

Magnetic measurements were recorded at vibrating sample magnetometer Model 155 room temperature at SAIF, IIT, Madras, Chennai.

#### **Molar Conductance Measurements**

The molar Conductivity of the resulting compounds were 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.

#### X-Ray Powder Diffraction

X-Ray powder diffractograms of the compounds were obtained on a RIGAKU miniFlex automatic diffractogram using Cu (K $\alpha$ ) target with Mg filter. The wavelength used was 1.540 Å.

#### Preparation

#### SYNTHETIC METHODS

#### **Preparation of the Ligands**

Preparation of hydrazinecarboxamides:  $(L^{3}H \text{ and } L^{4}H)$ The hydrazinecarboxamides of o-fluorobenzaldehyde, ofluoroacetophenone and 3-acetyl coumarin were prepared by the condensation of o-fluorobenzaldehyde, ofluoroacetophenone and 3-acetyl coumarin with semicarbazide hydrochloride (in presence of sodium acetate) in 1:1 molar ratio using ethanol as a solvent. Analyses of the above ligands are as follows:

#### [2-(2-fluorophenyl)methylene]hydrazinecarboxamide (L<sup>3</sup>H):

 $(C_8H_8N_3OF)$  Colour, Off white, M. P., 218°C

[2-{1-(2-fluorophenyl) ethyledene}] hydrazinecar boxamide (L<sup>4</sup>H) (C<sub>9</sub>H<sub>10</sub>N<sub>3</sub>OF) Colour, White, M. P., 195°C Structure of Schiff Base ligands: (L<sup>3</sup>H – L<sup>4</sup>H)



[2-(2-fluorophenyl)methylene]hydrazinecarboxamide (L<sup>3</sup>H) [2-{1-(2-fluorophenyl)ethyledene}]hydrazinecarboxamide (L<sup>4</sup>H)



Preparation of the Chromium (III) Complexes

 Preparation of the chromium(III) complexes of hydrazinecarboxamides: (L<sup>3</sup>H-L<sup>4</sup>H)

The weighed amount of hydrated chromium trichloride  $(CrCl_3.6H_2O)$  in dry methanol was added to the methanolic solution of ligands  $(L^3H \text{ and } L^4H)$  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: Result and Discussion:

#### 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:

#### Hydrazinecarboxamide complexes

 $[CrCl_2(L^3)(H_2O)_2]$  and  $[CrCl(L^3)_2(H_2O)]$  Where,  $L^3H$ : [2-(2-fluorophenyl)methylene]hydrazinecarboxamide

 $[CrCl_2(L^4)(H_2O)_2]$  and  $[CrCl(L^4)_2(H_2O)]$  Where,  $L^4H$ :  $[2-\{1-(2-fluorophenyl)ethyledene\}]$ hydrazinecarboxamide

For the preparation of above complexes, the reactions of  $CrCl_3.6H_2O$  with the ligands (L<sup>3</sup>H and L<sup>4</sup>H) and stoichiometric amount of NaOH, were carried out in equimolar and bimolar ratios using methanol as a solvent. The overall reactions of 1:1 and 1:2 complexes with hydrazinecarboxamides are as follows

$$CrCl_{3}6H_{2}O + NOH + NaOH \xrightarrow{1:1} [CrCl_{2}(NO)(H_{2}O)_{2}] + NaCl + 5H_{2}O$$

$$CrCl_{3}6H_{2}O + 2NOH + 2NaOH \xrightarrow{1:2} [CrCl(NO)_{2}(H_{2}O)] + 2NaCl + 7H_{2}O$$

$$(Where, NO is the donor system of the hydrazine carboxamides (L3H-L4H))$$

The resulting chromium(III) complexes have been obtained as coloured solids and are insoluble in most of the common organic solvents but soluble in ethanol, methanol, dimethylformamide and dimethylsulfoxide. The bonding pattern and the geometry of these complexes have been detected on the basis of UV-Vis, IR, X-Ray and ESR spectral studies.

The of electronic spectra the fluoroimine hydrazinecarboxamides  $(L^{3}H)$ and  $L^{4}H$ and their chromium(III) complexes have been recorded in methanol. Due to the n- $\pi^*$  transitions of the azomethine group, the electronic spectra of the organic moieties show broad band at 27000-30303 cm<sup>-1</sup> and it undergo a hypsochromic shift on complexation due to the coordination of nitrogen atom to the central metal atom. This shift occurs because of the donation of a lone pair of electrons by the nitrogen of the azomethine group of the ligand to the central metal ion. A consistent treatment for the bands is to assign the band at 22900-24140 cm<sup>-1</sup> as the  ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$  transition; the band near 15450–17800 cm<sup>-1</sup> as the  ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$  transition; and that 30070–32780 cm<sup>-1</sup> as the  ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}(P)$  transition. These three transitions provides an octahedral geometry around the Cr<sup>+3</sup> ion.<sup>10</sup> To characterize the electronic properties of transition-element complexes, the most important parameters are the crystal field parameter 10Dq, if the octahedral approximation is considered, Energy of the first spin allowed transition  $[{}^{4}A_{2}g(F) \rightarrow {}^{4}T_{2}g(F)]$ directly gives the value of 10Dq and the Racah parameters B which are calculated by the following formulae which have been discussed in previous section.

The ligand field spectral parameters for chromium(III) complexes are found to be  $Dq=1660-1744 \text{ cm}^{-1}$ , B = 644-678 $cm^{-1}$  and  $\beta = 0.70-0.73$ . The reduction of the Racah parameter  $B^0$  from the free ion value of 918 cm<sup>-1</sup> and the value of  $\beta$ indicates the covalent nature of the chromium(III) complexes. Various ligand field parameters like Dq, B and  $\beta$  have been calculated and given in Table 1 . In the IR spectra of free ligands, two common sharp bands observed around 3360 and 3420 cm<sup>-1</sup> due to  $v_{sym}$  and  $v_{asym}$  vibrations of NH<sub>2</sub> group, respectively in the fluoroimines, which remain unchanged in the spectra of metal complexes and thus indicates the noninvolvement of nitrogen atom of NH<sub>2</sub> group in coordination. Broad and strong bands in the region, 3280-3100 cm<sup>-1</sup> appeared due to v(NH) vibrations, wich disappeared in the spectra of metal complexes providing the evidence of deprotonation due to complexation<sup>11</sup>. The bands at 1690 and 1703 cm<sup>-1</sup> due to v(>C=O) vibrations, in the spectra of free ligands, are shifted towards lower frequency in the spectra of metal complexes, indicating complexation takes place through enolic oxygen atom to the central metal ion. The absorption at ca.1605-1610  $cm^{-1}$  characteristic of azomethine (>C=N) group<sup>17</sup> in the spectra of fluoroimines which shifted to the lower frequency by ca.15-20 cm<sup>-1</sup> in the spectra of chromium complexes indicating the coordination of azomethine nitrogen to the central metal atom (Table 2).

Mol. Wt.	Found (	Found (Calc.) %				6)	Time	
Found (Calc)	C	Н	Ν	S	MW	Т	MW Minutes)	T (H)
180.70	52.11	03.98	22.29	-	87	76	5	4-5
(181.16)	(53.03)	(04.45)	(23.19)					
Mol. Wt. Found (Calc.) %				Yield	d (%)	Time		
Found (Calc)	С	Н	N	S	MW	Т	MW (Minutes)	T (H)
194.13	52.68	05.00	22.74	-	91	87	5	4
(195.19)	(53.37)	(05.16)	(23.15	)				

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Chromium(III) complex with L <sup>3</sup> H (monofunctional bidentate N <sup>O</sup> )						
(1:1) $[CrCl_2(L^3)(H_2O)_2]$ Green	Mol. Wt., 337.45 (339.07), C, 27.34 (28.33), H, 03.00 (03.26), N, 11.47 (12.39), Cl, 19.27 (20.90), Cr, 14.99 (15.33), $\mu_{eff}$ (B.M.), 3.76, M.P.,227°C(d),					
(1:2) $[CrCl(L^3)_2(H_2O)]$ Brownish green	Mol. Wt., 463.67 (465.77), C, 39.90 (41.25), H, 03.19 (03.46), N, 17.47 (18.04), Cl, 07.02 (07.61), Cr, 10.99(11.16), μ <sub>eff</sub> (B.M.), 3.70, M.P., 224°C(d),					
Chromium(III) complex with I	$^{4}$ H (monofunctional bidentate N $^{\circ}$ O)					
(1:1) [CrCl <sub>2</sub> (L <sup>4</sup> )(H <sub>2</sub> O) <sub>2</sub> ] Green	Mol. Wt., 352.54(353.010), C, 29.97(30.61), H, 03.45(03.70), N, 10.11(11.92), Cl, 19.25 (20.07), Cr, 14.08(14.78), μ <sub>eff</sub> (B.M.), 3.77, M.P., 215°C(d),					
(1:2) $[CrCl(L4)2(H2O)]$ Green	Mol. Wt., 490.76(493.82), C, 42.91(43.70), H, 03.99(04.01), N, 16.97(17.01), Cl, 06.98 (07.17), Cr, 10.16(10.52), µ <sub>eff</sub> . (B.M.), 3.78, M.P., 208°C(d)					

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

Compounds	Transitions	Spectral bands cm <sup>-1</sup>	Dq	В	$\beta = B/B^{o}$	$\nu_2$ / $\nu_1$
$[CrCl_2(L^3)(H_2O)_2]$	${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(F)$	16700	1670	644	0.70	1.38
	${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{1g}(F)$	23200				
	${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{1g}(P)$	30070				
$[CrCl_2(L^3)_2(H_2O)]$	$^{4}A_{2g}(F) \rightarrow ^{4}T_{2g}(F)$	17240	1724	678	0.73	1.39
	${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{1g}(F)$	24050				
	${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{1g}(P)$	32040				
$[CrCl_2(L^4)(H_2O)_2]$	${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(F)$	16600	1660	644	0.70	1.39
	${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{1g}(F)$	23095				
	${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{1g}(P)$	30310				
$[CrCl(L^4)_2(H_2O)]$	${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(F)$	17440	1744	661	0.72	1.38
	${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{1g}(F)$	24140				
	${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{1g}(P)$	32350				

Table 2. IR (cm<sup>-1</sup>) Spectral data of the ligands and their chromium(III) complexes

Compound	IR Spectra	IR Spectral data (cm <sup>-1</sup> )						
	v(C=N)	v(NH)	v (OH) (water molecule)	v(Cr←N)	v(Cr-O)	v(Cr-Cl)		
L <sup>3</sup> H	1615	3280	-	-	-	-		
$L^{4}H$	1605	3100	-	-	-	-		
$[CrCl_2(L^3)(H_2O)_2]$	1585	-	3550	504	611	315		
$[CrCl(L^{3})_{2}(H_{2}O)]$	1595	-	3540	533	609	314		
$[CrCl_2(L^4)(H_2O)_2]$	1589	-	3539	507	613	315		
$[CrCl(L^4)_2(H_2O)]$	1586	-	3505	530	597	318		



Graph 1. EPR spectra of [CrCl<sub>2</sub>(L<sup>4</sup>)(H<sub>2</sub>O)<sub>2</sub>]



 Table 3. ESR spectral data of the chromium (III) complexes



 Table- 4: X-ray diffraction data of [CrCl(L<sup>4</sup>)(H<sub>2</sub>O)<sub>2</sub>]

h	K	1	2-theta (Exp.)	2-theta (Calc.)	2-theta (Diff.)	d (Exp.)	d (Calc.)	Intensity (Exp.)
1	0	1	13.03	12.79	0.24	06.5436	6.4963	12.12
0	1	3	22.29	22.19	0.10	04.5210	4.5101	14.65
0	3	-1	26.32	26.27	0.05	03.2554	3.2555	08.45
1	-2	-3	29.71	30.68	-0.97	03.2026	3.1862	92.12
1	2	3	36.41	36.32	0.09	03.2026	3.1862	07.23
3	0	-3	38.87	38.43	0.44	02.2532	2.1654	06.89



[CrCl<sub>2</sub>(L<sup>3</sup>)(H<sub>2</sub>O)<sub>2</sub>]Complex (1:1)



[CrCl(L<sup>3</sup>)<sub>2</sub>(H<sub>2</sub>O)] Complex (1:2)

(Fig.1)



The far IR spectra of these metal complexes exhibited new bands, which are not present in the spectra of the ligands. The single band observed at ca. 314-318 cm<sup>-1</sup> is due to v (Cr-Cl) suggesting thereby that the complexes have a trans structure<sup>12</sup> and the presence of  $v(Cr \leftarrow N)$  and v(Cr - O) vibrations around 504-533 and 597-613 cm<sup>-1</sup>, respectively, indicate that complexation takes place through the azomethine nitrogen and enolic oxygen atoms. In the spectra of chromium (III) complexes the presence of coordinated water is confirmed by a broad band around 3540-3450 cm<sup>-1</sup> may be due to v(O-H) of water molecule. Further, a medium intensity band is observed in the range 870-880 cm<sup>-1</sup> which may be attributed to rocking and wagging modes of vibrations due to coordinated water molecule. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of fluoro substituted ligands (L<sup>3</sup>H and L<sup>4</sup>H) have also been recorded in DMSO-d<sub>6</sub> using TMS as internal standard. In <sup>1</sup>H NMR spectra, the appearance of a signal due to  $NH_2$  group is found at  $\delta 2.35$  and 3.08 ppm . A multiplet appears at  $\delta 6.16-7.68$  ppm due to aromatic protons in the spectra of free ligands. The free ligands exhibit –NH proton resonance signal at  $\delta 10.25$ -11.67 ppm. The <sup>1</sup>H NMR signals due to the azomethine proton and azomethine methyl protons are also observed at  $\delta 8.42$  and 1.56ppm respectively. The <sup>13</sup>C NMR spectra of the ligands (L<sup>3</sup>H and  $L^4H$ ) show the signals at  $\delta 156.51-160.24$  and  $\delta 164.58-$ 175.20 ppm due to the azomethine carbon and the >C=O carbon, respectively. The signal due to the methyl carbon appears at  $\delta 15.88$  ppm.

At room temperature the ESR spectra of 1:1 and 1:2 chromium(III) complexes were recorded. The ESR spectra of  $[CrCl_2(L^4)(H_2O)_2]$  complex consist of a single broad peak (Graph 4) and from which the Lande splitting factor ('g' values) has been calculated (Table2), which lie in the range 1.9350–1.9980, with  $g_{iso}$  (2.0) which is characteristic of octahedral geometry.<sup>13</sup> The effective magnetic moment recorded at room temperature for the chromium(III) complexes are close to the predicted values for three unpaired electrons in the metal ion. The observed magnetic moment<sup>14</sup> value of 3.63-3.78 BM indicates that chromium(III) complexes are paramagnetic in nature<sup>15</sup> and the electronic spectra of the complexes support the octahedral structure of the complexes. The possible lattice dynamics of the finely powdered chromium(III) complex,  $[CrCl(L^4)(H_2O)_2]$  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<sup>16-17</sup> of the compound  $[CrCl(L^4)(H_2O)_2]$ (Graph 2) and the Miller indices h, k and l have been assigned to each d value and 2-theta angles are reported in Table 4.



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 =  $1.54 \text{ A}^0$ . Thus, on the basis of the above spectral and analytical data an octahedral environment around the chromium(III) ion has been established in the complexes. The structures of complexes are shown below (Figs. 1-4)

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