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Spectroscopic Properties of Gallium(III) Complexes with Acetylferrocene Semicarboxamide

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ABSTRACT

The coordination chemistry of gallium (III) is of great current research activity from several viewpoints, including materials science and biomedical developments Biological important complexes of gallium(III) derived from biologically active sulfur donor ligand 1-acetylferrocene hydrazinecarboxamide (LH) have been prepared and investigated using a combination of micro analytical analysis, melting point, electronic, IR, 1H NMR and 13C NMR spectral studies,. Aluminium and gallium isopropoxide interacts with the ligand in 1:1, 1:2 and 1:3 molar ratios (metal: ligand) resulting in the formation of coloured products. On the basis of conductance and spectral evidences, a penta coordinated structure for gallium(III) complexes have been assigned. The ligand are coordinated to the gallium (III) via the azomethine nitrogen atom and the enolic oxygen atom.

KEYWORDS: *Schiff bases, isopropoxide, azomethine, 1-acetylferrocene hydrazinecarboxamide.*

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1. INTRODUCTION

Inorganic Medicinal Chemistry is currently a growing field of research that offers the great diversity of metal coordination chemistry to the development of novel bioactive compounds for therapeutic or diagnostic medicinal purposes. The most significant part of this research has been directed to the development of drugs active against different kinds of cancer. In particular, the interest in gallium(III) coordination chemistry has evolved from this approach. The anti-neoplastic activity of simple Ga(III) salts was discovered in the 1970s and much work has been performed since then to elucidate their mechanism of action[1] Gallium plays an important role in pharmaceuticals[2] and as antitumor[3], antiviral[4] and anticoagulant agents and thallium as a probe for K^+ in biological systems[5].

2. EXPERIMENTAL

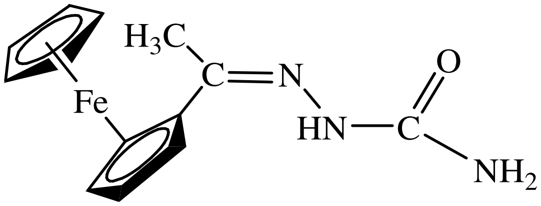
All the chemicals used in the synthesis of the complexes were of A.R. grade. All the solvents were dried and distilled before use.

2.1. Analytical Methods and Physical Measurements

The molecular weights were determined by the Rast camphor method. IR spectra of the ligand and their metal complexes were recorded with the help of Nicolet Megna FT IR 550 spectrophotometer using KBr pellets. The purity of these ligand and their metal complexes was checked by the TLC on silica Gel-G using anhydrous dimethylsulphoxide and benzene (1:1) as solvent. ^1H NMR and ^{13}C NMR spectra were recorded in deuterated dimethylsulphoxide (DMSO-d_6) using tetramethylsilane (TMS) as standard on a JEOL AL 300 FT NMR spectrometer. Electronic spectra of the complexes were recorded in DMF on a UV-160 a Shimadzu spectrophotometer in the range 200-600 nm. X-Ray powder diffractograms of the compounds were obtained on a Philip Model PW 1840 automatic diffractogram using Cu(Kα) target with Mg filter. The wavelength used was 1.540598 Å. Nitrogen and sulfur were estimated by the Kjeldahl's and Messenger's methods, respectively[6]. Carbon and hydrogen analyses were performed at the CDRI, Lucknow.

2.2. Preparation of the Ligand

The ligand (LH) by the condensation of 1-acetylferrocene with hydrazinecarboxamide hydrochloride in presence of sodium acetate in equimolar ratio (1:1:1) in ethanol. as reported earlier[7].



1-Acetylferrocene hydrazinecarboxamide

2.3. Preparation of gallium (III) complexes

Gallium (III) isopropoxide and ligand were dissolved in dry benzene in 1:1 and 2:3 molar ratios. The resulting mixture was refluxed for 16-20 hours. The progress of the reaction was checked by measuring the amount of isopropanol in the azeotrope. After completion of the reaction the excess of the solvent was removed under reduced pressure and dried in vacuo. The physical properties and analytical data of these complexes are enlisted in **Table 1**.

Table 1; Synthetic and analytical data of of the ligand and their gallium (III) complexes of 1-Acetylferrocene hydrazinecarboxamide

S. No	Reactants (g)		Molar ratio	Product and Colour	M.P. (°C)	Analyses (%) Found/ (Calcd)					Mol. Wt. Found/ (Calcd.)
	Metal	Ligand				C	H	N	S	M	
1.	-	$C_{13}H_{15}N_3OFe$ (LH)		Brown	185	54.68 (54.76)	5.26 (5.30)	14.63 (14.74)			271.39 (285.13)
4.	$Ga(OPr^i)_3$	LH	1:1	$\{Ga(OPr^i)_2(L)\}_2$ Sandy brown	120-122			8.82 (8.91)	-	14.68 (14.77)	952.78 (944.01)
5.	$Ga(OPr^i)_3$	LH	1:2	$\{Ga(OPr^i)(L)_2\}_2$ Brown	116-118			11.98 (12.06)	-	9.90 (10.00)	1399.87 (1394.06)
6	$Ga(OPr^i)_3$	LH	1:3	$\{Ga(L)_3\}$ Brown	112-114			13.56 (13.67)	-	7.42 (7.56)	934.58 (922.11)

3. RESULTS AND DISCUSSION

3.1. Reactions of gallium(III) isopropoxide with various N⌒O and N⌒S donor ligand of 1-acetylferrocene

The reactions of gallium(III) isopropoxide with monofunctional bidentate ligand of 1-acetylferrocene (LH) refluxing in benzene in 1:1, 1:2and 1:3 molar ratios have resulted in the successive replacement of isopropoxy groups according to the following equations:

$$2[Ga(OPr^i)_3] + 2N^\frown OH \xrightarrow[\text{Dry benzene}]{1:1} [(OPr^i)_2Ga(N^\frown O)]_2 + 2Pr^iOH$$

$$2[Ga(OPr^i)_3] + 4N^\frown OH \xrightarrow[\text{Dry Benzene}]{1:2} [(OPr^i)\,Ga(N^\frown O))_2]_2 + 4Pr^iOH$$

$$[Ga(OPr^i)_3] + 3\,N^\frown OH \xrightarrow[\text{Dry benzene}]{1:3} [Ga(N^\frown O)_3] + 3Pr^iOH$$

These reactions are quite facile and the resulting complexes are coloured solids and soluble in methanol, $CHCl_3$, DMF, THF and DMSO but insoluble in common organic solvents. All these newly synthesized complexes are monomeric in nature as indicated by their molecular weight determinations by the Rast Camphor method. The complexes are non electrolytes in nature, because they have low molar conductance values (8-14 $ohm^{-1}\,cm^2\,mol^{-1}$).

3.2. Electronic Spectra

The electronic spectra of the ligand (LH) show broad maxima in the range 370-360 nm due to the n-π* electronic transitions of the azomethine group, which undergoes a blue shift in the gallium(III) complexes, due to the polarisation within the >C=N chromophore caused by the metal ligand interactions.The bands in the region 285-280 nm due to π-π* electronic transitions of the ligand, undergoes a bathochromic shift in the complexes. In the ligand L_9H two broad bands at 255 nm and 315 nm due to ϕ-ϕ and π-π* (benzenoid) transitions, respectively, confirm its cyclic nature. A band around 395 nm due to n-π* transitions of the azomethine group is observed in the spectra of the complexes which remains absent in the free ligand.

3.3. Infrared Spectra

The infrared spectra of the ligand (LH) show strong band in the region 1620-1590 cm^{-1} due to the >C=N group, which shifts to the higher wave number in the complexes thus showing the coordination of the azomethine nitrogen to the metal atom. The absorption bands at 3410-3140 cm^{-1}, 1610-1580 cm^{-1}, 1010-1015/ 1680-1660 cm^{-1} and 950-940 cm^{-1} are assigned to ν(N-H), ν(C=S)/ν(C=O) and ν(N-N), respectively[8]. The ν(N-H), δ(N-H), ν(C=S) and ν(C=O) bands are absent in the complexes, indicating the enolization of the ligand followed by deprotonation during the complexation. The new bands at 1170-960 cm^{-1} and 935-920 cm^{-1} in 1:1 complexes are ascribable to νC–O vibrations of terminal[9] and bridging[10] isopropoxy groups, respectively. Whereas, the bands at 960-925 cm^{-1} in the spectra of 1:2 complexes are assignable to ν C–O vibrations of bridging isopropoxy groups. The complexes exhibit new bands in the region 660–600 cm^{-1},480–350 cm^{-1} and 320–280 cm^{-1} which may be attributed to the different vibrational modes of Ga– O, Ga←N and Ga-S frequencies, respectively. Two sharp bands at 3485-3455 and 3365-3345 cm^{-1} due to the asymmetric and symmetric vibrations of (NH_2) group remain unchanged in the spectra of the complexes showing the non-involvement of this group in coordination. The characteristic bands of the ferrocenyl group[11] appears at 3080-3070 cm^{-1}, 1450-1445 cm^{-1}, 1120-1110 cm^{-1}, 829-825 cm^{-1} and 480-470 cm^{-1} arising from ν(C-H), ν(C=C), δ(C-H), π(C-H) and (Fe-ring), respectively.

3.4. ^{1}H NMR Spectra

The proposed bonding pattern in the newly synthesized complexes is further supported by the ^{1}H NMR spectral studies. The ^{1}H NMR spectra of the ligand and their gallium complexes were recorded in DMSO-d_6 and the chemical shift values (δ, ppm) are listed in **Table 2.** The methyl proton signal (δ 2.10-2.35 ppm) of the azomethine moiety in the spectra of the ligand gets shifted towards downfield in the complexes. The disappearance of the -NH proton signal (δ 8.34- 8.96 ppm) of the ligand (LH) in their respective metal complexes indicates the removal of a proton from the -NH group and the coordination of nitrogen with simultaneous covalent bond formation by sulfur or oxygen with the metal. The NH_2 proton signal (δ 2.21-2.42 ppm) remains almost at the same position in the ligand (LH) and their complexes, indicating the non-involvement of NH_2 group in the complexes. In addition, there appears a sharp singlet (δ 6.22-6.62 ppm) giving evidences for the presence of η-C_5H_5 group in all the complexes.

Table 2 : ^{1}H NMR Spectral data (δ, ppm) of the ligand and their gallium(III) complexes.

Compound	-NH (s)	-NH_2 (s)	-S-CH_2 (s)	-CH_3 (s)	Isopropoxy groups	
					Gem-dimethyl (d)	Methine (septet)
LH	8.34	2.21	-	2.12	-	-
$\{Ga(OPr^i)_2(L)\}_2$	-	2.22	-	2.43	1.04 (terminal) 1.23 (bridging)	4.16 (terminal) 4.52 (bridging)
$\{Ga(OPr^i)(L)_2\}_2$	-	2.24	-	2.46	1.25 (bridging)	4.56 (bridging)
$\{Ga(L)_3\}$	-	2.28	-	2.42	-	-

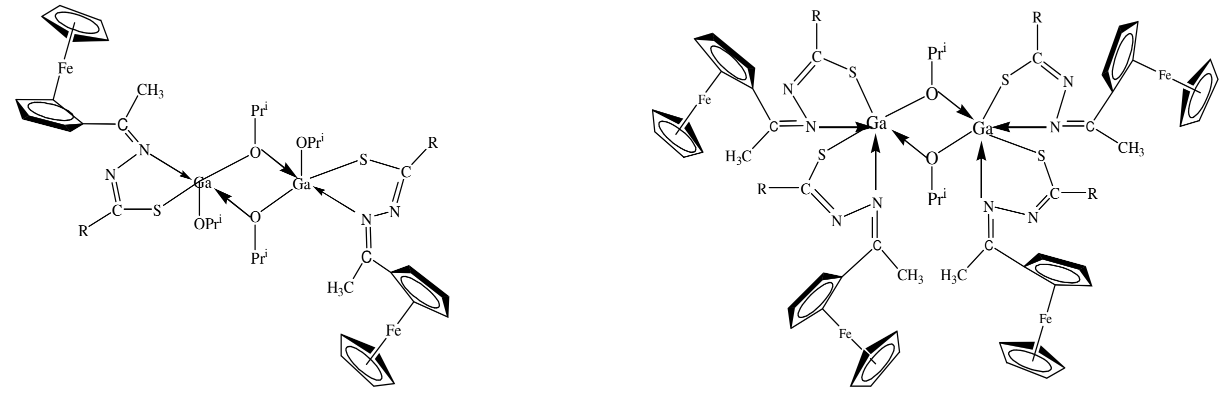
3.5. ^{13}C NMR Spectra

The ^{13}C NMR spectra of the ligand and their corresponding metal complexes have also been recorded in DMSO-d_6 (**Table 3).** The chemical shift values of the carbon atoms attached to the azomethine nitrogen, thiolic sulfur and amido oxygen, show considerable shift which further support the proposed coordination in the complexes.35-38

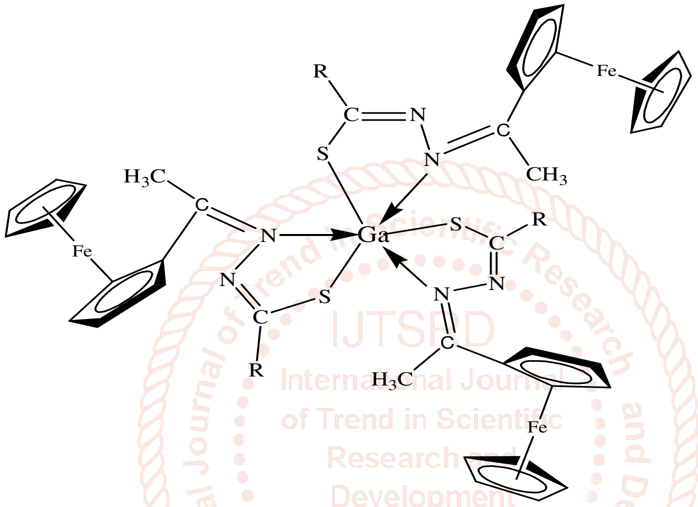
Table 3 : ^{13}C NMR Spectral data (δ, ppm) of ligand and their gallium (III) complexes.

Compound	Chemical shift values				Isopropoxy group	
	>C=O / >C=S	>C=N	-CH_3	Ferrocenyl carbons	α-carbon	β-carbon
LH	189.42	185.59	11.13	69.91, 71.18, 72.99, 77.45	-	-
$\{Ga(OPr^i)_2(L)\}_2$	190.18	186.81	11.20	69.93, 71.17, 73.94, 77.41	71.94 terminal) 73.79(bridging)	22.82(terminal) 23.38(bridging)
$\{Ga(OPr^i)(L)_2\}_2$	191.92	188.53	11.18	69.92, 71.24, 73.04, 77.82	73.19(bridging)	23.06(bridging)
$\{Ga(L)_3\}$	193.20	189.75	11.16	70.01, 71.22, 73.12, 77.74	-	-

On the basis of the UV, IR, ^{1}H and ^{13}C NMR spectral data, the following penta and hexa coordinated structures for the derivatives of monobasic bidentate ligand have been suggested.



1:1 Complex **1:2 Complex**



1:3 Complex

Fig. 1. Structure of the gallium(III) complexes.Where R=NH_2

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