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Research Article

SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITY OF METAL COMPLEX OF FUROIC ACID

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ABSTRACT

The Rhodium tris carboxylate of the type, RhL3 was prepared by the reaction of Rhodium trichloride with sodium salt of furoic acid in 1:3 stoichiometry. The complexes obtained were characterized by elemental analysis, IR and 1H, 13C NMR spectroscopic techniques. Based on spectroscopic data ligand coordination through oxygen atoms of the carboxylate group has been suggested. The metal complex has also been tested in vitro for their antibacterial and anti fungal activity. The experimental results suggest that metal complex is more potent in anti bacterial and anti fungal activities.

Keywords: *Furoic Acid, Carboxylates, Antibacterial Activity; Antifungal Activity*

INTRODUCTION

During the past decades, much attention has been given to the synthesis of new transition metal complexes and their evaluation for antibacterial and antifungal activities. This revival interest was generated by the discovery of the antibacterial and antifungal activity of several transition metal complexes.

In the last few years so many studies has been done on the structure and chemical behaviour of several metal complexes to find out an alternative against the drugs.

The chemistry of rhodium has been an active area of research for more than four decades. Rhodium complexes with variety of ligands viz. xanthates, dithiocarbamates, phosphorous based acids have been studied extensively (Garje and Jain, 2003).

Biological activities such as antibacterial, antimalarial, fungicidal of these complexes have been correlated with their specific structures (Padhye and Kaufman, 1985; Klayman *et al.*, 1983; Casas *et al.*, 2000; Diemer *et al.*, 1995).

It has been reported that metal complexes show enhanced biological activity as compared to free ligands due to reduction in polarity of metal after complexation. Though many structure-activity correlation studies of transition metals have been reported (Agarwal and Singh, 2006; Ibrahim *et al.*, 2002; Ibrahim *et al.*, 1999; Kiran *et al.*, 1986; Nath *et al.*, 1989; Garcıá *et al.*, 2002; West *et al.*, 1996), very few reports are available on rhodium complexes (Singh and Tandon, 1992; Singh and Tandon, 1992; Phor, 1995; Dalvi *et al.*, 2004; Sawant and Garje, 2005; Holmes, 1989).

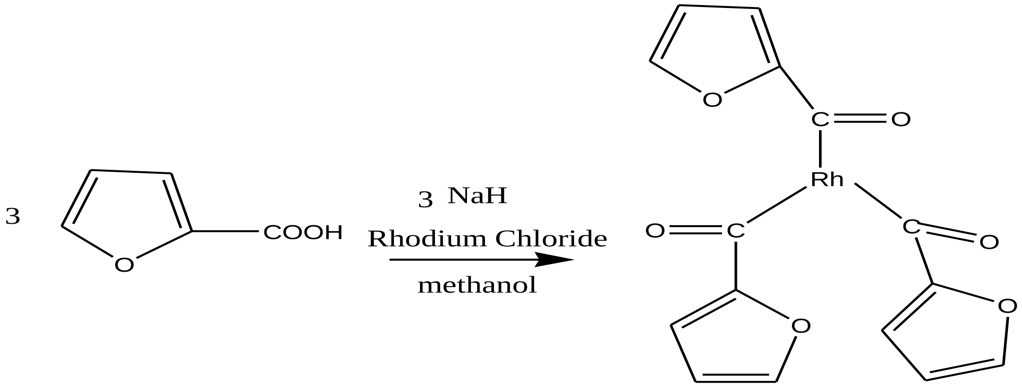
Carboxylic acid is another ligand system which has been widely studied and a variety of metal carboxylate complexes have been reported. In view of this, we thought it worthwhile to synthesize and characterize rhodium carboxylates, where ligand has additional coordination site along with carboxylate moiety.

The metal complex of rhodium with furoic acid was prepared and characterized in the present study. Further, the structure of the complex was predicted from the spectroscopic data.

MATERIALS AND METHODS

The elemental analysis was carried out in the microanalytical laboratory of this department. IR spectra were recorded on Perkin- Elmer spectrum One FT-IR spectrophotometer using KBr pellets from 4000 to 400 cm-1. 1H and 13C NMR spectra were recorded in DMSO-d6 or CDCl3 on a Bruker Avance II 300 MHz FT-NMR spectrometer. The chemical shifts are relative to internal standard tetramethylsilane.

Synthesis of Antimony Furoic Acid Metal Complex



To a weighed quantity of sodium hydride emulsion (0.4747g) dissolved in 30 mL dry methanol, 0.7790 g (6.95 mmol) of furoic acid was added with constant stirring under nitrogen atmosphere and the stirring was continued for thirty minutes. To this sodium furoate salt, rhodium (III) chloride (0.5013 g, 2.19 mmol) was added and the reaction mixture was refluxed in an oil bath for 10 h. Then it was cooled and filtered through G-3 crucible under inert atmosphere. The filtrate was evaporated under reduced pressure. The product obtained was recrystallized from dry methanol (yield: 0.705 g, 70.50%) melting point: 214-215^{O} C

RESULTS AND DISCUSSION

The reaction of antimony trichloride with sodium salt of furoic acid in 1:3 stoichiometry in dry methanol gave antimony tris carboxylate of the type RhL3

The resulting compound was white solid. They were further characterized by elemental analysis, IR and multinuclear 1H and 13C NMR spectroscopic techniques.

Elemental analysis of these compounds is given in Table 1.

Table 1

Compound	**Molecular formula**	**Melting point**	**Elemental analysis % found calculated**		
			Carbon	**Hydrogen**	**Antimony (Sb)**
RHL3	Rh[C15H9O9]	215^{O} C	26.00	39.61	2.10
			25.89	39.55	2.08

It is observed that the stoichiometry between metal and ligand is 1:3.

IR Interpretation

In order to establish the coordination modes of the furoic acid ligand with rhodium metal centre, the IR spectra of complexes were compared with the IR spectrum of the ligand.

IR spectrum of furoic acid showed a strong broad band at 3406 cm-1 which was assigned to √OH of the –COOH group. However, this band disappeared in the IR spectrum of tris complex. Bands observed at 1691 cm-1 and 1585 cm-1 are due to –COO asymmetric and symmetric stretchings, respectively. These bands showed shift to lower frequencies compared to free acid indicating participation of the carboxylate group in the bonding. The asymmetric -COO and symmetric -COO for RhL3 were observed in the region 1580-1610 and 1330- 1360 cm-1 respectively. The magnitude of √ (asym COO - √sym COO) is found to be 217 cm-1. It is comparable to corresponding sodium salt which indicates presence of bidentate carboxylate group (Bohra and Mehrotra, 1983). The bands due to √Rh-C and √Rh-O appear between 459-484 cm-1 and 561 – 585 cm-1 range, respectively. These values are consistent with the literature values (Ma *et al.*, 2001; Yahyi and Et-touhami, 2010; Ma *et al.*, 2002). An additional new band at ~ 522 cm-1 was also observed in the compounds which could be assigned to √Rh-O. Similar observations have been reported in the literature (Bahfenne and Frost, 2010).

NMR Interpretation

The 1H and 13C NMR data of ligand as well as complexes is summarized in Table 2 and the spectra are given in Figures 1-4. The 1H NMR spectrum of 2-furan carboxylic acid showed expected integration and peak multiplicities. The aromatic protons of 2-furan carboxylic acid appeared in the region 6.55- 7.60 ppm. The hydroxyl proton appeared at 11.28 ppm. In the 1H NMR spectrum of tris derivative, RhL3, the deprotonation of ligand is clearly seen from the disappearance of the peak present at 11.28 ppm in the spectrum of the ligand (Figure 1 and 2). This indicates coordination of the ligand through carboxylate group. The presence of ring protons in tris derivative is observed in 6.37-7.48 ppm range,

In the 13C NMR of ligand, the presence of all the carbon atoms could be detected (Figure 3). The signals due to carbons present in the heterocyclic ring of the ligand are observed at 147.45, 143.73, 120.19 and 112.26 ppm. In case of tris derivative these signals are observed at 154.03, 141.88, 110.62 and 110.51 ppm (Figure 4).

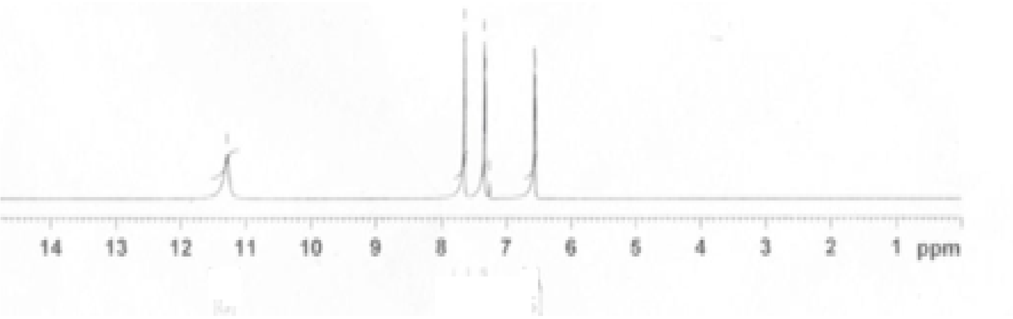


Figure 1: 1H NMR of furoic acid ligand in CDCl3

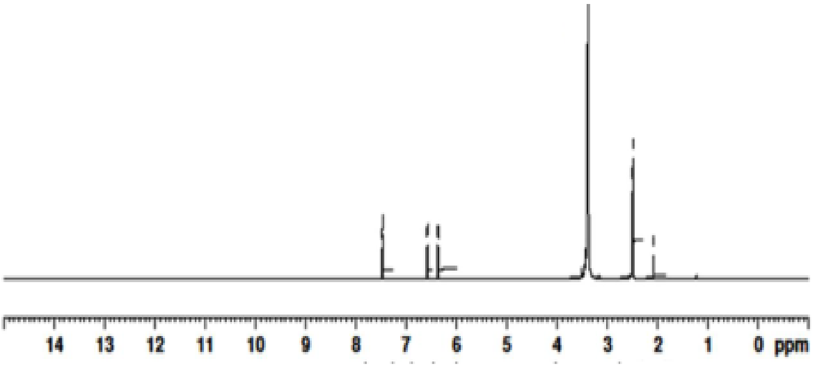


Figure 2: 1H NMR of RhL3 complex in dmso-d6

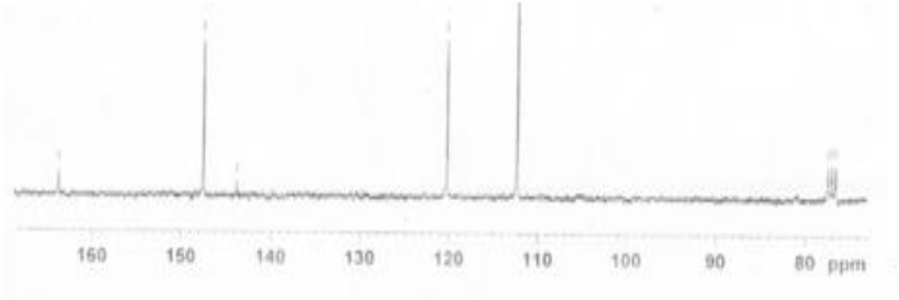


Figure 3: 13C NMR of furoic acid ligand in CDCl3

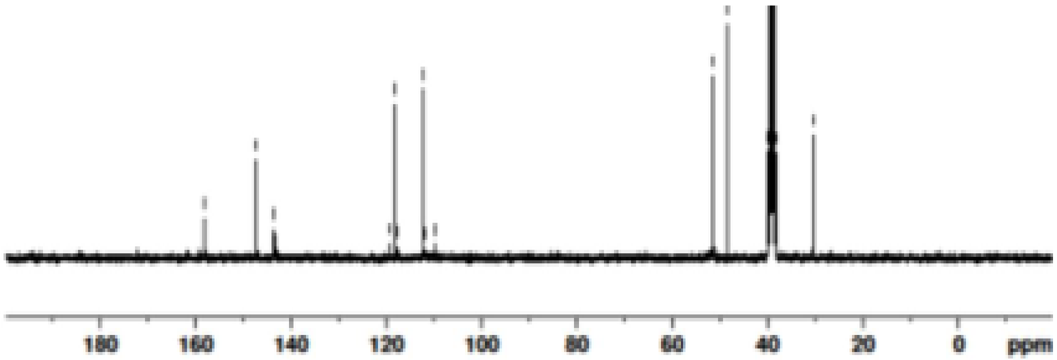
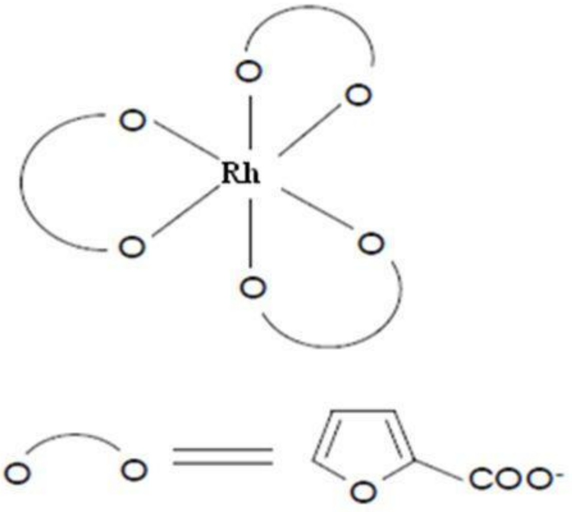


Figure 4: 13C NMR of RhCl3(LH) in dmso-d6

Table 2: 1H NMR Data for furoic acid and Rhodium complex

Compound	1H NMR data	13 C NMR data
Furoic acid	6.6 (dd, H (d), 7.35(dd H (c) 7.7(dd,H9b), 11.3(s,H(a)	164(-COO), 148(C-5) 144 (C-2),122(C-3), 113 (C-4)
RhL3	6.38(m,H(d),6.6(m, H (C), 7.5(m,H(b)	163(-COO),155(C-5),142(C-2),110 (C-4)

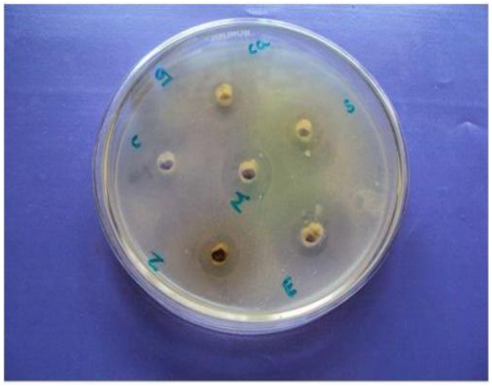
Based on the above observations the presence of a six coordinated rhodium with three bidentate chelating carboxylate ligands in tris derivative can be suggested.



Biological Activity

Antibacterial

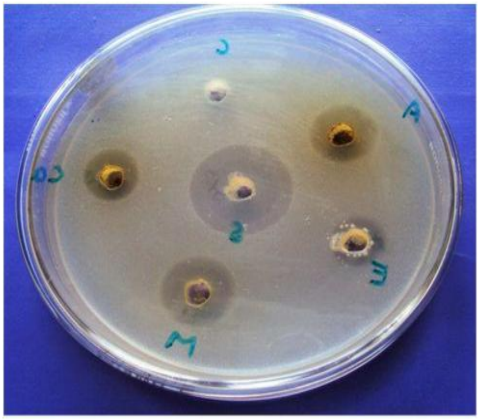
The in vitro biological screening effects of the investigated compounds were tested against the bacteria Bacillus subtilis. Paper discs of Whatman filter paper no. 1 were cut and sterilized in an autoclave. The paper discs were saturated with 10 µl of the compounds dissolved in DMSO solution or DMSO as negative control and was placed aseptically in the Petri dishes containing Nutrient agar media inoculated with the above mentioned two bacteria separately. The petridishes were incubated at 37^0C and the inhibition zones were recorded after 24 h of incubation. Antibiotic disc of gentamycin (100 µg/disc) was used as positive control, while DMSO used as negative control.



Ca: standard drug gentamycin C: control S: 60mg in DMSO M: 40mg in DMSO E: 20mg in DMSO N: 10mg in DMSO

Antifungal

The Schiff base complexes were screened for their antifungal activity against fungi viz. candida. Filter paper discs of 5 mm in size, prepared by using Whatman filter paper no. 1 (sterilized in an autoclave) was saturated with 10 µl of the compounds dissolved in DMSO solution . The fungal culture plates were inoculated and incubated at 25± 2^0C for 48 h. Antibiotic discs of and fluconazole (100 µg/disc) was used as positive control, while DMSO used as negative control. The plates were then observed and the diameters of the inhibition zones (in mm) were measured and tabulated.



Ca: standard drug fluconazole C:control S: 60mg in DMSO M:40mg in DMSO E: 20mg in DMSO A: 10mg in DMSO

Conclusion

The spectral studies of the Rhodium metal of furioc acid complex suggest that the carboxylate group of antimony acts as a bidentate chelating ligand with deprotonation of tris derivative (RhL3).

The synthesized compounds therefore, present a new scaffold that can be used to yield potent antimicrobial compounds. It can be concluded that these compounds certainly holds great promise towards good active leads in medicinal chemistry.

Hence, further study of a synthesized Rhodium III metal complex with furoic acid (RHL3) in antimicrobial and anti fungal activities may become fruitful.

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