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Studies on Ruthenium(III) Complexes of Amide Group Containing Ligands

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Complexes of Ru(III) with 3-phenyl-4-benzamidoethenyl-β-carboxy-5-isoxazolone, β-(3-methyl-4-isoxazolylamido-5-styryl)-benzoic acid, β-(3-methyl-4-isoxazolylamido-5-styryl)acrylic acid, β-(3-methyl-4-isoxazolylamido-5-styryl)propionic acid, β-(5-methyl-3-isoxazolylamido)benzoic acid, β-(5-methyl-3-isoxazolylamido)acrylic acid and β-(5-methyl-3-isoxazolylamido)propionic acid have been synthesized and characterised by elemental analysis, conductance, thermal, magnetic, infrared and electronic spectral data. The above data suggest that the complexes are octahedral in geometry.

Key Words: Characterization, Ruthenium(III) complexes, Amide.

INTRODUCTION

Amide group containing ligands are biologically potent and there are several examples of *in vivo* interactions of transition metal ions with these ligands[1,2]. The metal complexes of amide group ligands serve as models for metalopeptide interactions and metalloenzymes in which the properties of peptides are modified by the fact that the metal ions are attached to them. An amide group offers two potential binding atoms, the oxygen and nitrogen, for complexation with metal ions[3]. Aminopterin, D-penicilamine, phenylalanine mustard and 6-mercaptopurine, all possessing an amide group, show an increased anticancer activity when administered as metal complexes. A series of nickel, palladium and platinum complexes and some of the rhodium and iridium complexes have been reported in this regard[4,5]. In the present investigation, the synthesis and structural characterization of the complexes of Ru(III) with 3-phenyl-4-benzamidoetheneyl-β-carboxy-5-isoxazolone (PBECI), β-(3-methyl-4-isoxazolylamido-5-styryl)benzoic acid (4-MIABA), β-(3-methyl-4-isoxazolylamido-5-styryl)acrylic acid (4-MIAAA), β-(3-methyl-4-isoxazolyl-amido-5-styryl)propionic acid (4-MIAPA), β-(5-methyl-3-isoxazolylamido)benzoic acid (3-MIABA), β-(5-methyl-3-isoxazolylamido)acrylic acid (3-MIAAA) and β-(5-methyl-3-isoxazolylamido)-propionic acid (3-MIAPA) were reported.

EXPERIMENTAL

All the chemicals used were of AR grade. All the seven ligands were prepared by literature methods[6]. The purity of these compounds was checked by TLC and melting point determinations.

The complexes were prepared by mixing a solution of ($RuCl_3$) (0.02 mol) in 0.1 N HCl methanolic solutions of the ligands (0.06 mol) and heating the mixture on hot water bath for 1 h. The crystalline complexes formed were suction filtered, washed with hot water and methanol and dried *in vacuo* over anhydrous $CaCl_2$.

The complexes were analyzed for C, H and N at the microanalytical laboratory, Kolkata University, Kolkata, India. Molar conductances of the complexes in DMF at 1×10^{-3} M concentration were measured using Digisun Digital conductivity Meter Model DI-909. The thermal data for the complexes were obtained on a stanton thermoblance available at the IICT, Hyderabad. The IR spectra of the ligands and the complexes (4000-200 cm^{-1}) in nujol mull and KBr pellet (using $CaCl_2$ plates in FIR region) were recorded on a Perkin-Elmer-283 spectrometer. The electronic spectra of the complexes in DMF were obtained with a Shimadzu MPS 5000 spectrometer.

RESULTS AND DISCUSSION

All the complexes are stable at room temperature and non-hygroscopic. They are slightly soluble in methanol and freely soluble in DMF and DMSO.

The analytical data of the complexes (Table-1) indicate that all the Ru(III) complexes have 1:3 (metal:ligand) stoichiometry. These complexes exhibit low molar conductance (7.5-12.5 ohm^{-1} cm^2 mol^{-1}) in 1×10^3 M DMF solution suggesting that they are non-electrolytes.

The initial decomposition temperatures of the complexes are listed in Table-1. All the Ru(III) complexes were thermally stable upto 220 ºC and are not hydrated. The fact is confirmed by the DTA curves which do not show an endothermic peak in this temperature range. All the complexes undergo sharp decomposition with loss of ligand above 210 ºC and the final product of decomposition above 550 ºC corresponds to metal oxide. The initial decomposition temperatures of the complexes vary within a narrow range and based on the values observed the stability order of the complexes formed with different ligands is PBECI < 3-MIAPA < 3-MIABA < 3-MIAAA < 4-MIAPA < 4-MIABA < 4-MIAAA.

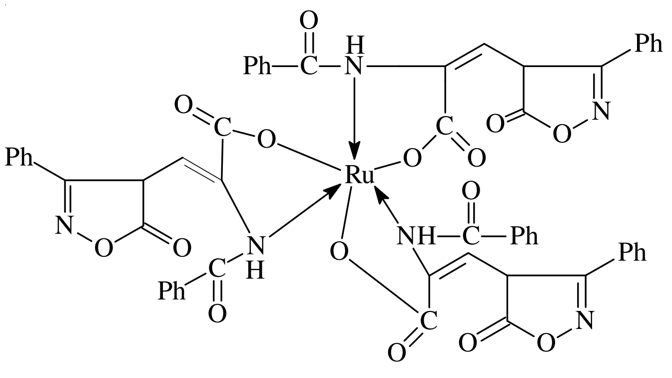
In the IR spectra, the ν(C=O) and ν(C-O) frequencies at 1695 and 1330 cm^{-1}, respectively in the free ligands containing carboxylic groups are shifted to 1545 and 1380 cm^{-1} and are assigned to ν_{as}(COO) and ν_s(COO) modes, respectively[7]. The ν(O-H) of the carboxylic group appearing at 2980 cm^{-1} in free ligands is disappearing in the spectra of their complexes.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF Ru(III) COMPLEXES

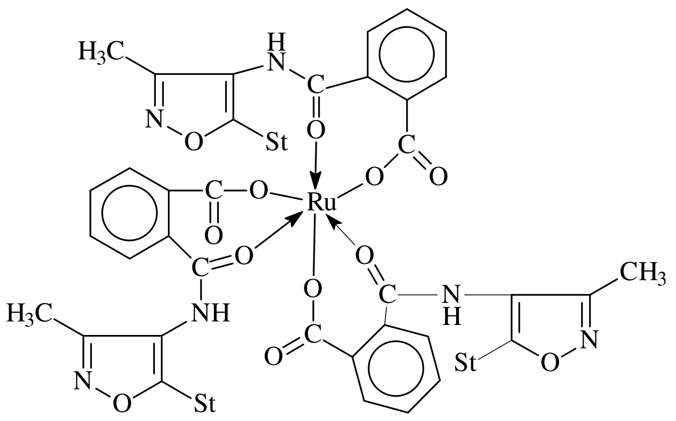
Complex	Elemental analysis %: Found (Calcd.)			Initial decomp. Temp. (°C)	Molar conductance (Ω^{-1} cm^{2} mol^{-1})	μ_{eff} (BM)
	C	H	N			
[Ru(PBECI)$_3$]	60.21	3.40	7.38	220	7.5	1.82
(Pale yellow)	(60.26)	(3.43)	(7.40)			
[Ru(4-MIABA)$_3$]	63.56	3.69	7.40	230	12.5	1.80
(Brown)	(63.60)	(3.41)	(7.42)			
[Ru(4-MIAAA)$_3$]	58.62	4.25	8.52	235	10.0	1.74
(Brown)	(58.65)	(4.27)	(8.55)			
[Ru(4-MIAPA)$_3$]	58.26	4.23	8.48	230	9.01	1.70
(Brown)	(58.29)	(4.25)	(8.50)			
[Ru(3-MIABA)$_3$]	52.28	3.60	10.12	225	9.5	1.75
(Light brown)	(52.30)	(3.63)	(10.16)			
[Ru(3-MIAAA)$_3$]	42.58	3.53	12.40	228	9.0	1.72
(Light brown)	(42.60)	(3.55)	(12.42)			
[Ru(3-MIAPA)$_3$]	42.20	4.36	12.29	224	9.5	1.75
(Light brown)	(42.22)	(4.39)	(12.31)			

The ν(N-H) frequency in PBECI shifts to lower side by 100-110 cm^{-1} in its complexes indicating the nitrogen of the amide group of this ligand is coordinating[8]. However a band at 1670 cm^{-1} in this ligands assignable to ν(C=O) of the amide group shows no significant shift in its complex suggesting non-involvement of amide oxygen in coordination. In the 4-MIABA, 4-MIAAA, 4-MIAPA, 3-MIABA, 3-MIAAA and 3-MIAPA complexes the ν(N-H) frequency almost remain same as in the ligand spectra, indicating non-participation of the nitrogen in coordination[9]. On the other hand, the ν(C=O) (amide I) frequency in the above set of ligands undergo a negative shift (50 cm^{-1}) in their complexes pointing out that the oxygen of this group is coordinating[9]. These assignments are further supported by the presence of non-ligand bands in the complexes corresponding to ν(M-O) and ν(M-N) vibration[10].

Thus, it may be concluded that all the carboxylic group containing ligands (PBECI, 4-MIABA, 4-MIAAA, 4-MIAPA, 3-MIABA, 3-MIAAA and 3-MIAPA) act as mononegative, bidentate ligands bond to the metal through carboxylate oxygen. In addition PBECI coordinate through amide nitrogen (**Ia**) and 4-MIABA, 4-MIAAA, 4-MIAPA, 3-MIABA, 3-MIAAA and 3-MIAPA through amide oxygen (**Ib**).



I(a)



I(b) St = CH=CH-Ph

Ru(III) Complexes of I(a) PBECI I(b) 4-MIABA

The magnetic moment values observed for the present complexes are in the range 1.70-1.82 BM that correspond to the presence of one upaired electron, thereby indicating the low-spin nature of the complexes. However, the values observed are somewhat lower than the expected values of 2.10 BM for a Ru(III) low-spin complex[11]. The lowering in μ_{eff} values in the present cases may be due to the presence of lower symmetry ligand fields and electron delocalization[12].

The electronic spectra of the complexes shows either three or four peaks. The first peaks in the increasing order of frequency may be assigned to $^2T_{2g} \rightarrow {}^4T_{2g}$ and $^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$ transitions of low spin octahedral geometry and the other two to change transfer[13].

Hence, based on all the data obtained, the present Ru(III) complexes have been assigned octahedral geometry.

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