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Synthesis and Spectral Studies of Ruthenium(III) Complexes with Amide Group Ligands

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Ru(III) Complexes of a few amide group ligands such as 2-(acetylamino)benzoic acid, 2-(benzoylamino) benzoic acid, 2-(2-aminobenzoylamino)benzoic acid, 2-(aminobenzanilide), 2-(aminocarbonyl)benzoic acid, 2-[2-aminophenylamino)carbonyl]-benzoic acid, maleanilic acid, malea-1-naphthalanilic acid, 2-[(phenylamino)carbonyl] benzoic acid and 2-[(2-naphthalenyl-amino)carbonyl] benzoic acid have been synthesized and characterized by physico-chemical data.

INTRODUCTION

Amide group containing ligands are biologically potent and there are numerous examples of *in vivo* interactions of transition metal ions with these ligand systems[1,2]. In continuation of our earlier work on the transition metal complexes of amide group containing ligands[3–6], we report here the synthesis of Ru(III) complexes of 2-(acetylamino)benzoic acid (AABA), 2-(benzoylamino)benzoic acid (BABA), 2-(2-aminobenzoylamino)benzoic acid (ABABA), 2-aminobenzanilide (ABn), 2-(aminocarbonyl)benzoic acid (ACBA), 2-[(2-minophenylamino)carbonyl]-benzoic acid (APACBA), maleanilic acid (MA), malea-1-naphthanilic acid (MNA), 2-[(phenylamino)carbonyl]benzoic acid (PACBA)] and 2-[2-naphthalenylamino) carbonyl]benzoic acid (NACBA) and their characterization based on analytical, conductance, thermal, magnetic and infrared and electronic spectral data.

EXPERIMENTAL

All the chemicals used were of AR grade. AABA, BABA, ABABA, ABn, ACBA, APACBA, MA, MNA, PACBA and NACBA were prepared by literature methods[7].

The complexes were prepared by mixing a solution of $RuCl_3 \cdot 3H_2O$ (0.02 mol) in 0.1 N HCl with methanolic solutions of the ligands (0.06 mol) and heating the mixture on a hot water bath for about 30 min. The crystalline complexes formed were suction filtered, washed with hot water and methanol and dried in *vacuo* over anhydrous $CaCl_2$.

The Ru(III) complexes wre analysed for C, H and N at the Microanalytical Laboratory, Calcutta University, Calcutta, India. The conductance of the com-

plexes in DMF at the concentration 10^{-3} M was measured using a Digisun Digital Conductivity Meter, Model DI 909. The thermal data of the complexes were obtained employing Stanton thermobalance available at Indian Institute of Chemical Technology, Hyderabad. The IR spectra of the ligands and the metal complexes (4000–200 cm^{-1}) in Nujol mulls and in KBr pellets (using CsI plates in far infrared region) wre recorded on a Perkin-Elmer 283 spectrophotometer. The electronic spectra of the complexes in DMF were obtained with Shimadzu MPS 5000 spectrometer.

RESULTS AND DISCUSSION

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

The analytical, thermal, conductance and magnetic data obtained for the Ru(III) complexes are presented in Table-1. It is clear from the table that the experimental elemental analysis data are in good agreement with the calculated ones for the composition given for each of them. The complexes may, therefore, be formulated accordingly.

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

Complex (Colour)	% Analysis, Found (Calcd)			Initial decomp. temp (°C)	Molar Conductance (mhos cm^2 mol^{-1})	μ_{eff} (B.M.)
	C	H	N			
$[Ru(AABA)_3]$ (Pale yellow)	50.75 (50.78)	3.72 (3.76)	6.55 (6.58)	230	22	1.80
$[Ru(BABA)_3]$ (Brown)	60.76 (60.80)	3.60 (3.64)	5.04 (5.09)	230	20	1.75
$[Ru(ABABA)_2]Cl$ (Yellow)	51.64 (51.69)	3.64 (3.69)	8.58 (8.61)	240	75	1.74
$[Ru(ABn)_3]Cl_3$ (Pale yellow)	55.95 (55.98)	4.25 (4.30)	10.00 (10.06)	235	180	1.77
$[Ru(ACBA)_3]$ (Light Brown)	48.28 (48.32)	3.25 (3.18)	7.15 (7.04)	220	25	1.78
$[Ru(APACBA)_2]Cl$ (Dark yellow)	51.80 (51.85)	3.28 (3.39)	8.59 (8.64)	245	68	1.81
$[Ru(MA)_3]$ (Snuff)	53.60 (53.65)	3.50 (3.57)	6.20 (6.25)	225	20	1.72
$[Ru(MNA)_3]$ (Light yellow)	61.35 (61.38)	3.60 (3.65)	5.08 (5.11)	230	22	1.80
$[Ru(PACBA)_3]$ (Yellow)	61.34 (61.38)	3.62 (3.65)	5.05 (5.11)	220	15	1.73
$Ru(NACBA)_3$ (Light Brown)	66.70 (66.73)	3.65 (3.70)	4.30 (4.32)	240	20	1.82

The complexes are thermally stable up to 220°C and are not hydrated which is confirmed by the absence of endothermic peak in their DTA curves within this temperature. The initial decomposition temperature values associated with the complexes lie in the range 220–245°C and the final product of decomposition above 550°C corresponds, in each case, to ruthenium(III) oxide.

The Ru(III) complexes of AABA, BABA, ACBA, MA, MNA, PACBA and NACBA show only residual molar conductance values (15–25 mhos cm^2 mol^{-1}) suggesting that they are non-electrolytes. The complexes of ABABA and APACBA exhibit values of 75 and 68 mhos cm^2 mol^{-1} respectively that correspond to 1 : 1 electrolyte and that of ABn with a value of 180 mhos cm^2 mol^{-1} to 1 : 3 electrolyte[8].

The ν(C=O) and ν(C—O) frequencies at 1700 and 1330 cm^{-1} in the uncomplexed ligands possessing carboxylic groups are shifted to 1550 and 1380 cm^{-1} in their complexes and are assigned to ν_{asym}(COO) and ν_{sym}(COO) respectively[9]. The ν(O—H) of the carboxylic group appearing at 2600 cm^{-1} in these ligands disappears in the spectra of their complexes. The ν(N—H) frequency in AABA, BABA and ABABA shifts to lower frequency by 100–120 cm^{-1} in their complexes, indicating that the nitrogen of the amide group is coordinated to the metal ion[5]. However, a band at 1650 cm^{-1} in these ligands attributable to ν(C=O) of the amide group shows no shift in their complexes suggesting non-involvement of oxygen of this group in coordination. In the Abn, ACBA, APACBA, MA, MNA, PACBA and NACBA complexes, the ν(N—H) frequency shifts to higher side as compared to the ligand spectra, indicating non-participation of nitrogen of this group in coordination[10]. On the other hand, the ν(C=O) (Amide-I) frequency in this set of ligands undergoes a negative shift (by 40 cm^{-1}) in their complexes suggesting the involvement of oxygen of this group in coordination[10]. Further, the amine ν(N—H) frequency in ABABA, ABn and APACBA undergoes a negative shift in their complexes showing that nitrogen of this group is coordinating. These assignments are further supported by the presence of non-ligand bands in the complexes around 480 and 370 cm^{-1} corresponding to ν(Ru—O) and ν(Ru—N) respectively[11].

Thus, it may be concluded that AABA, BABA, ACBA, MA, MNA, PACBA and NACBA act as mononegative, bidentate ligands, the first two coordinating through carboxylate oxygen and amide nitrogen and the remaining through carboxylate oxygen and amide oxygen. ABABA and APACBA are mononegative, tridentate bonding through carboxylate oxygen and amine nitrogen and the former additionally through amide nitrogen and the latter through amide oxygen. ABn functions as a neutral, bidentate ligand coordinating through amide oxygen and amine nitrogen.

The magnetic moment values observed for the present complexes are in the range 1.72–1.82 B.M. that correspond to the presence of one unpaired electron, thereby indicating the low-spin nature of the complexes. However, the values observed are somewhat lower than the expected value of 2.10 B.M. for a Ru(III) low-spin complex[12]. The lowering in μ_{eff} values in the present cases may be due to the presence of lower symmetry ligand fields and/or electron delocalization[13]

The electronic spectral frequencies observed for the present Ru(III) complexes are presented in Table-2.

TABLE-2
ELECTRONIC SPECTRAL DATA OF THE Ru(III) COMPLEXES

Complex	Frequency (cm^{-1})			
$[Ru(AABA)_3]$	16350	19220	32260	36040
$[Ru(BABA)_3]$	18100	21900	37500	43500
$[Ru(ABABA)_2]Cl$	16200	20200	31740	36350
$[Ru(ABn)_3]Cl_3$	18080	22500	28500	33000
$[Ru(ACBA)_3]$	17000	21000	29200	38300
$[Ru(APACBA)_2]Cl$	18400	22700	—	43000
$[Ru(MA)_3]$	18500	21200	33000	36750
$[Ru(MNA)_3]$	17800	21780	27730	35900
$[Ru(PACBA)_3]$	17890	21700	—	42000
$[Ru(NACBA)_3]$	18120	22020	28200	35700

The electronic spectra of the complexes show either three or four peaks. The first two 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[14] and the other to charge transfer.

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

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