

Studies on Iridium(III) Complexes with Ligands Containing Amide Group

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A new series of complexes of iridium(III) with 2-(acetylamino) benzoic acid, 2-(benzoylamino) benzoic acid, 2-(amino benzoylamino) benzoic acid, 2-[(2-aminophenyl amino) carbonyl] benzoic acid, maleanilic acid, malea-1-naphthalanilic acid, 2-[(phenylamino) carbonyl] benzoic acid have been synthesised and characterised 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 ligands.^{1,2} In continuation of our earlier work on these transition metal complexes of amide group containing ligands,³⁻⁶ we report here the synthesis of iridium(III) complexes of 2-(acetylamino) benzoic acid (AABA), 2-(benzoylamino) benzoic acid (BABA), 2-(amino benzoylamino) benzoic acid (ABABA), 2-(amino benzoni- lide) (ABn), 2-(amino carbonyl) benzoic acid (ACBA), 2-[(2-aminophenyl amino) carbonyl] benzoic acid (APACBA), maleanilic acid (MA), malea-1-naphthalanilic acid (MNA), 2-[(phenylamino) carbonyl] benzoic acid (PACBA) and 2-(2-naphthalenylamino) carbonyl] benzoic acid (NACBA) and their characterisation based on analytical, conductance, thermal, infrared, NMR 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 IrCl_3 (0.02 mol) in 0.1 N HCl methanolic solution of the ligands (0.06 mol) and heating the mixture on a hot water bath for 2 h. The crystalline complexes formed were suction filtered, washed with hot water and methanol and dried *in vacuo* over anhydrous CaCl_2 .

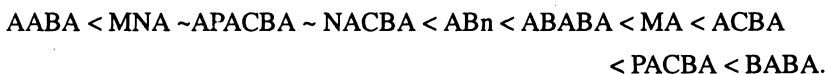
The complexes were analysed for C, H and N at the Microanalytical Laboratory, Calcutta University, Calcutta. Molar conductances of the complexes in DMF at 1×10^{-3} M concentration were measured using a Digisun Digital conductivity meter, Model DI-909. The thermal data for the complexes were obtained on a stanton thermobalance available at the ICT, Hyderabad. The IR spectra of the ligands and the complexes ($4000\text{--}200\text{ cm}^{-1}$) in nujol mull and KBr pellets (using CaCl_2 plates in FTIR 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. The ^1H NMR spectra of the ligands and their complexes in DMSO-d_6 were recorded using a Jeol JNM-FX 100 NMR 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 data of the complexes (Table-1) indicate that all the Ir(III) complexes except those of ABABA and APACBA have 1 : 3 (metal : ligand) stoichiometry. The complexes of ABABA and APACBA are of 1 : 2 type. All the complexes except those of ABABA, ABn and APACBA exhibit low molar conductance ($4.8\text{--}12.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) in $1 \times 10^{-3} \text{ M}$ DMF solution suggesting that they are non-electrolytes. The complexes of ABABA, ABn and APACBA have, on the other hand, molar conductances of 75, 180 and $65 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ indicating that they are 1 : 1, 1 : 3 and 1 : 1 electrolytes respectively.

The initial decomposition temperatures of the complexes are listed in Table-1. All the Ir(III) complexes are thermally stable up to 250°C and are not hydrated. This fact is confirmed by their DTA curves which do not show an endothermic peak in the above temperature range. All the complexes undergo sharp decomposition with the loss of ligand above 250°C and the final product of decomposition above 560°C corresponds, in each case, to metal oxide. The initial decomposition temperatures of the complexes vary within a narrow range and based on the values observed. The solubility order of the complexes formed with different ligands is:



In the IR spectra the $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$ frequencies at $1700\text{--}1330 \text{ cm}^{-1}$ in the free amide ligand containing carboxylic groups⁸ are shifted to $1550\text{--}1380 \text{ cm}^{-1}$ and are assigned to $\nu_{\text{asym}}(\text{COO})$ and $\nu_{\text{sym}}(\text{COO})$ modes respectively.⁹ The $\nu(\text{O}-\text{H})$ of the carboxylic group appearing at 2600 cm^{-1} in free ligands disappear in the spectra of their complexes. The $\nu(\text{N}-\text{H})$ frequencies in AABA and BABA shift to lower side by $100\text{--}120 \text{ cm}^{-1}$ in their complexes indicating that nitrogen of the amide group of these ligands is coordinating. However, a band at 1650 cm^{-1} in these ligands assignable to $\nu(\text{C}-\text{O})$ of amide group shows no significant shift in their complexes suggesting non-involvement of amide oxygen in coordination. In the ABABA, ABn, ACBA, APACBA, MA, MNA, PACBA and NACBA complexes the $\nu(\text{N}-\text{H})$ frequency shifts towards higher side as compared to the ligand spectra indicating non-participation of the nitrogen in coordination.¹⁰ On the other hand, the $\nu(\text{C}=\text{O})$ (amide) frequency in the above set of ligands undergoes a negative shift (40 cm^{-1}) in their complexes pointing out that the oxygen of this group is coordinating¹⁰. Further, amine $\nu(\text{N}-\text{H})$ frequency in ABABA, ABn and APACBA undergoes a lower 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 corresponding to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ vibrations.¹¹

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

Complex (Colour)	Decomp. Temp (°C)	Found (Calcd.) %			Λ_m (ohm ⁻¹ cm ² mol ⁻¹)
		C	H	N	
[Ir(AABA) ₃] (Brown)	225	44.40 (44.44)	3.26 (3.29)	5.72 (5.76)	10.5
[Ir(BABA) ₃] (Snuff)	300	55.21 (55.26)	2.92 (2.96)	4.55 (4.60)	9.0
[Ir(ACBA) ₃] (Brown)	280	41.86 (41.92)	2.60 (2.62)	6.08 (6.11)	6.0
[Ir(PACBA) ₃] (Black)	290	55.23 (55.26)	2.93 (2.96)	4.56 (4.60)	12.0
[Ir(ABABA) ₂]Cl (Light brown)	270	47.54 (47.59)	4.37 (3.39)	7.90 (7.93)	65.5
[Ir(ABn) ₃]Cl ₃ (Gray)	270	56.90 (56.93)	4.35 (4.37)	10.18 (10.21)	185.0
[Ir(MA) ₃] (Brown)	275	47.20 (47.24)	3.12 (3.14)	5.46 (5.51)	6.0
[Ir(MNA) ₃] (Light brown)	260	55.24 (55.26)	2.94 (2.96)	4.54 (4.60)	4.8
[Ir(APACBA) ₂]Cl (Snuff)	260	47.60 (47.65)	3.10 (3.12)	7.91 (7.94)	70.5
[Ir(NACBA) ₃] (Brown)	265	61.00 (61.01)	3.08 (3.10)	3.91 (3.95)	5.5

Thus, it may be concluded that all the carboxylic group containing ligands (AABA, BABA, ABABA, ACBA, APCBA, MA, MNA, PACBA and NACBA) bond to the metal through carboxylate oxygen. In addition, AABA and BABA coordinate through amide nitrogen and ACBA, MA, MNA, PACBA and NACBA through amide oxygen and amine nitrogen. ABn bonds through amide oxygen and amine nitrogen.

The ¹H NMR spectra of AABA and PACBA and deuterium exchange studies on AABA and PACBA confirm that the assignment of signals is at 6.4 and 3.2 ppm to NH protons and at 12.2 and 10.3 ppm to COOH protons in these compounds respectively.

The spectrum of AABA shows that a resonance signal due to NH proton at 6.4 ppm is not observed in its complex in the range (0–15 ppm) studied, implying a large downfield shift of this proton. However, there is no measurable change in the position of methyl protons. This gives ample evidence in favour of nitrogen atom, but not the amide carbonyl group oxygen atom, as the site of coordination. In addition, a signal at 12.2 ppm in the AABA spectrum assignable to carboxylic proton disappears in the spectrum of its complex indicating the involvement of the carboxylate ion oxygen in bonding¹² (figure 1a). A similar comparison of the NMR spectrum of PACBA with that of its complex shows that the proton of the amide group undergoes an insignificant downfield shift indicating the non-in-

volvement of nitrogen of NH group in coordination. This behaviour of nitrogen can be accounted for by the presence of bulky phenyl group attached to it which hinders the nitrogen from coordination. The signal at 10.3 ppm in the free ligand assignable to carboxylic group proton disappears in the complex confirming the participation of this group in bonding¹² (Fig. 1b).

The electronic spectra of Ir(III) complexes exhibiting the d-d bonds located at 25750–23250 cm^{-1} in the absorption spectra are respectively assigned to ${}^1T_{1g} \leftarrow {}^1A_{1g}$ and ${}^1T_{1g} \leftarrow {}^1A_{1g}$ transitions of an octahedral geometry. The weaker band at 21550 cm^{-1} can arise due to transition from a singlet-ground state to triplet excited state.¹³

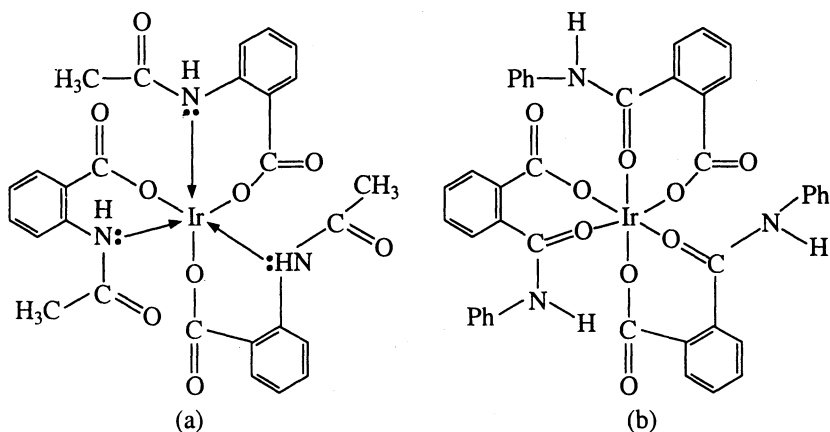


Fig. 1 Ir(III) complexes of (a) AABA; (b) PACBA

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