

Studies on rhodium(III) complexes with ligands containing amide group

G Dayakar* & P Lingaiah

Department of Chemistry, University Arts & Science College,
Kakatiya University, Warangal 506 001

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Complexes of Rh(III) with 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-naphthalenylamino)carbonyl]benzoic acid have been prepared and characterized by elemental analysis, conductance, thermal, magnetic, infrared, NMR and electronic spectral data. The above data suggest that the complexes are octahedral in geometry.

There are numerous examples of *in vivo* interactions of transition metal ions with ligands containing amide group and such complexes have been found to be of biological importance^{1,2}. Aminopterin, D-penicillamine, 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^{3,4}. In the present note we report the synthesis and structural characterization of the complexes of Rh(III) with 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-aminophenylamino)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).

Experimental

All the chemicals used were of AR grade. The ligands AABA, BABA, ABABA, ABn, ACBA, APACBA, MA, MNA, PACBA and NACBA were prepared by literature methods⁵. The purity of these compounds was checked by TLC and melting point determination.

Preparation of complexes

The complexes were prepared by mixing a solution of RhCl₃ (0.02 mol) in 0.1 N HCl methanolic solutions 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 CaCl₂.

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 IICT, Hyderabad. The IR spectra of the ligands and the complexes (4000-200 cm⁻¹) in nujol mull and KBr pellet (using CaCl₂ 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. 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 I) indicate that all the Rh(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 (4.8-12.5 ohm⁻¹·cm²·mol⁻¹) in 1×10^{-3} 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 ohm⁻¹·cm²·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 Rh(III) complexes are thermally stable upto 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 com-

Table 1—Analytical and physical data of Rh(III) complexes

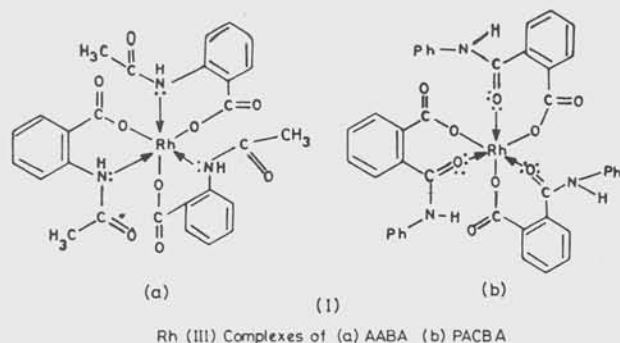
Complex colour	Initial Decomp temp. °C	Found (Calcd), %			Λ_M ohm ⁻¹ mol ⁻¹ cm ²
		C	H	N	
[Rh(AABA) ₃] Brown	268	50.66 (50.70)	3.71 (3.75)	6.51 (6.57)	11.0
[Rh(BABA) ₃] Dark brown	290	61.28 (61.31)	3.25 (3.28)	5.06 (5.10)	9.5
[Rh(ABABA) ₂ Cl] Brown	263	48.20 (48.20)	3.00 (3.01)	7.00 (7.03)	75.0
[Rh(ABn) ₃]Cl ₃ Dirty yellow	260	53.90 (53.77)	4.90 (4.91)	11.40 (11.47)	180.0
[Rh(ACBA) ₃] Yellow	285	54.50 (54.54)	3.87 (3.89)	9.03 (9.09)	6.2
[Rh(APACBA) ₂ Cl] Light yellow	263	54.68 (54.72)	3.56 (3.58)	9.07 (9.12)	65.0
[Rh(MA) ₃] Light yellow	260	53.52 (53.57)	3.52 (3.57)	6.21 (6.25)	6.0
[Rh(MNA) ₃] Black	260	61.26 (61.31)	3.24 (3.28)	5.05 (5.10)	4.8
[Rh(PACBA) ₃] Light yellow	270	61.27 (61.31)	2.26 (2.28)	5.04 (5.10)	12.5
[Rh(NACBA) ₃] Cream	263	66.62 (66.66)	3.64 (3.70)	4.30 (4.32)	5.2

plexes 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 stability order of the complexes formed with different ligands is MNA ~ MA ~ ABn < APACBA ~ ABABA ~ NACBA < AABA < PACBA < ACBA < BABA. All the complexes have been found to be diamagnetic in nature.

In the IR spectra, the $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$ frequencies at 1700 and 1330 cm^{-1} in the free ligands containing carboxylic groups are shifted to 1550 and 1380 cm^{-1} and are assigned to $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ modes respectively⁶. 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 $\nu(\text{N}-\text{H})$ frequency in AABA and BABA shifts to lower side by 100-120 cm^{-1} in their complexes indicating that nitrogen of the amide group of these ligands is coordinating⁷. However, a band at 1650 cm^{-1} in these ligands assignable to $\nu(\text{C}=\text{O})$ of the 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 coordination⁸. On the other hand, the $\nu(\text{C}=\text{O})$ (amide I) 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 coordinating⁸. 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 $\nu(\text{M}-\text{N})$ vibrations⁹.

Thus, it may be concluded that all the carboxylic group containing ligands, (AABA, BABA, ABABA, ACBA, APACBA, MA, MNA, PACBA and NACBA) bond to the metal through carboxylate oxygen. In addition, AABA and BABA coordinate through amide nitrogen, ACBA, MA, MNA, PACBA and NACBA through amide oxygen and ABABA and APACBA 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 the assignment of signals 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 a resonance signal due to NH proton at 6.4 ppm which 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 bonding^{10,11} (Structure Ia). 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-involvement of nitrogen of NH group in coordination. This behaviour of ni-

trogen 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 bonding¹⁰ (Structure Ib).

The electronic spectra of all the Rh(III) complexes exhibit two peaks in the ranges 24390-24920 and 31250-32430 cm^{-1} assignable respectively to the spin-allowed transitions $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$ of octahedral field¹².

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