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Synthesis, Spectral and Cyclic Voltammetric Studies of Some Ru(III) Complexes of Azo Dyes Derived from 4-Aminoantipyrine

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Some novel complexes of an azo dye 2,3-dimethyl-1-phenyl-4-(2-hydroxynaphthylazo)pyrazol-5-one (naphtholazoantipyrine NAAPH) derived from 4-aminoantipyrine with Ru(III) have been prepared and characterized using elemental analysis, magnetic moment and conductance measurements and infrared, electronic and ESR spectroscopic techniques. The electrochemical behaviour of the complex is followed using cyclic voltammetry and it is seen that the metal-ligand linkage is more covalent in nature. The ESR spectrum of the complex [$RuCl_3(PPh_3)$NAAPH) exhibited a single line with 'g' value of 2.39, indicating high symmetry around ruthenium ion. The complexes are found to be neutral with an octahedral geometry.

Key Words: 4-Aminoantipyrine, ESR, Cyclic voltammetry, Octahedral.

INTRODUCTION

Ru(III) forms a large number of complexes which are more numerous than those formed by trivalent osmium. There has been considerable interest in ruthenium complexes now-a-days because of their redox stability, excited state lifetime and excited state reactivities[1]. Metal complexes of ruthenium, containing nitrogen and oxygen donor ligands are found to be very effective catalysts for oxidation, reduction and other organic transformations. The use of ruthenium complex to effect catalytic regioselective homogeneous oxidations has became increasingly important[2]. A survey of the literature shows that no complexes of azo dyes, derived from 4-aminoantipyrine, have been reported. In view of the importance of Ru(III) complexes, we have isolated and characterized some new complexes of the potential multiden-

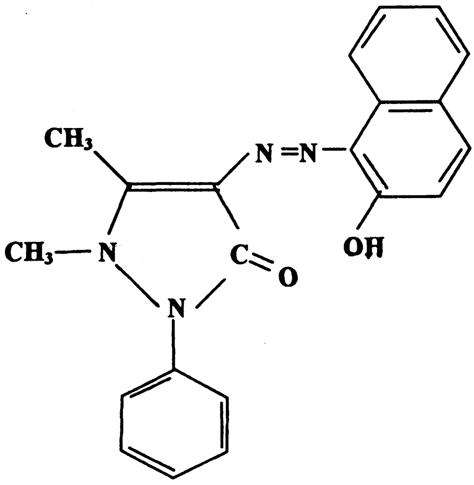

Fig. 1. NAAPH

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tate ligand, 2,3-dimethyl-1-phenyl-4-(2-hydroxy naphthylazo) pyrazol-5-one (naphtholazoantipyrine NAAPH) derived from biologically active molecule; 4-aminoantipyrine[3, 4]. NAAPH is a potential tridentate monobasic ligand (Fig. 1).

EXPERIMENTAL

4-Aminoantipyrine (Fluka, Switzerland), β-naphthol (Loba Chemie, Mumbai), $RuCl_3 \cdot 3H_2O$ (AR grade) were used as supplied and all other chemicals used were of BDH AR grade.

The starting material $RuCl_3(PPh_3)_3$ for the synthesis of complexes was prepared by the following reported procedure[5]. Hydrated ruthenium(III) chloride (0.2 g) was taken in 20 mL of ethanol and 2 mL of concentrated HCl was added to the solution. Triphenylphosphine (0.8 g) was then added and the solution was heated under reflux for about 5 min and then cooled. The resulting reddish brown solid that separated was filtered, washed with ether and dried.

Synthesis of the ligand: The ligand was synthesized from 4-aminoantipyrine and β-naphthol by diazotization and coupling as described in literature[6].

Synthesis of the complexes: To a solution of $RuCl_3(PPh_3)_3$ (2.5 mmol) in benzene, a solution of the ligand (2.5 mmol) in chloroform was added. Colour change was noticed on addition of the ligand, due to the formation of complexes. The contents were refluxed for 5–6 h. The resulting solution was concentrated and the product separated on adding a small amount of petroleum ether. The complex that separated was filtered, washed with benzene followed by ether and then dried *in vacuo* over P_4O_{10}.

For the preparation of thiocyanate and nitrate complexes, an ethanolic solution of $NH_4CNS/LiNO_3$ (*ca.* 0.3 g) as the case may be, was added to a solution of $RuCl_3(PPh_3)$ in benzene (2.5 mmol) and refluxed with a solution of the ligand (2.5 mmol) in chloroform for 5–6 h. The resulting solution was concentrated and the complex was separated by adding a small amount of petroleum ether. It was then filtered, washed with benzene, chloroform and finally with ether and then dried *in vacuo* over P_4O_{10}.

All the complexes are dark brown coloured and are non-hygroscopic. They are soluble in methanol, ethanol but insoluble in ether. CHN analysis of the samples was done by microanalytical technique at RSIC, CDRI, Lucknow. Halide and sulphur in the complexes were estimated by standard methods[7]. The IR spectra of the ligand and complexes were recorded in the region 4000–400 cm^{-1} on a Jasco FTIR 430 spectrophotometer, using KBr pellets. The electronic spectra of the ligand and complexes in the solution state (CH_3OH) were recorded on Jasco V-550 UV-Vis spectrophotometer. ESR spectrum of the complex was run on a Varian E-112 X-Q band spectrometer with DPPH as reference material. Cyclic voltammetric profile of the complex $[RuCl_3(PPh_3)NAAPH]$ was run on a BAS-CV-50W-voltammetric analyzer, using glassy carbon as the working electrode. The molar conductance of complexes in $C_6H_5NO_2$, CH_3OH and CH_3CN (*ca.* 10^{-3} M) were measured at 300 ± 2 K using an Elico conductivity bridge type CM 82T with a dip type cell (ec-03) fitted with platinum electrodes (cell constant is 0.94 cm^{-1}). The magnetic susceptibilities at room temperature (300 ± 2 K) were measured on a Gouy balance using $Hg[Co(NCS)_4]$ as the calibrant[8]. Diamagnetic corrections for various atoms and structural units were computed using Pascal's constants[9].

RESULTS AND DISCUSSION

The analytical data of the complexes (Table-1) correspond to the composition $[RuX_3(PPh_3)L]$ where X = Cl, NO_3 or NCS and L = NAAPH. In some complexes, mixed anions are present. The molar conductance values indicate that all the complexes are non-electrolytes. The effective magnetic moments of the complexes (Table-1) fall in the range 1.94–2.02 BM, corresponding to a single unpaired electron in a low spin $4d^5$configuration[10].

In the IR spectra of the ligand, a broad band of medium intensity observed at *ca.* 2900 cm^{-1} is assigned to hydrogen bonded —OH group[11]. This band disappears in the spectra of all the complexes. Instead, a broad band of medium intensity is observed at *ca.* 3400 cm^{-1}, indicating the presence of free —OH group and its non-involvement in coordination to the metal ion. The ν(C═O) found at 1650 cm^{-1} in the spectrum of the free ligand shows a downward shift by 60 cm^{-1} in the spectra of all the complexes confirming the involvement of the C═O group in complexation[12]. The vibrational band observed at 1455 cm^{-1}, assigned to ν(—N═N—) group in the ligand is shifted by 20 cm^{-1} in the spectra of all the complexes suggesting the participation of the azo group in coordination with the metal ion[13, 14]. Thus the ligand is coordinated to the metal ion through the carbonyl oxygen and one of the azo group nitrogens only, showing a bidentate behaviour during complexation. The band due to coordinated PPh_3 group, usually observed in the range 1436–1434 cm^{-1} could not be located in the spectra of the complexes due to its overlapping with the azo group vibrations.

The infrared spectrum of $[RuCl_2(NO_3)(PPh_3)NAAPH]$ does not exhibit any bands assignable to ionic nitrate, which is in agreement with the conductance data (Table-1). The strong bands occurring at *ca.* 1500, 1350 and 1000 cm^{-1} correspond to the ν_4, ν_1 and ν_2 vibrations of coordinated nitrate group. Separation between the two bands ν_4 and ν_1 (*ca.* 150 cm^{-1}) indicates the monodentate nature of nitrate group. The combination bands for nitrate group *ca.* 1800 cm^{-1} are not seen in the spectrum of the complex under the present studies. The IR spectrum of $[RuCl_2(NCS)(PPh_3)NAAPH]$ shows a very srong band at 2080 cm^{-1}, which can be assigned to the N-coordinated thiocyanate group. A medium intensity band observed at 760 cm^{-1}, attributed to ν(C—S) and another medium intensity band observed at 480 cm^{-1} assigned to δ(NCS) confirms the N-coordinated nature of the thiocynate group[15].

The electronic absorption spectral bands of the complexes in methanol together with the tentative assignments are discussed in detail[16, 17]. The ground state of Ru(III) is $^2T_{2g}$ and the first excited doublet levels in the order of increasing energy are $^2A_{2g}$ and $^2T_{1g}$, which arise from $^4T_{2g} \rightarrow {}^1E_g$ configuration. The electronic spectra of Ru(III) complexes usually show two or three bands in the region 575–345 nm. But in most of the Ru(III) complexes, only charge transfer bands are observed[16] . The electronic spectra of all the complexes under the present study show a band appearing in the *ca.* 575–490 nm, which can be assigned to

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

Complex (Colour)	Analysis, %: Found (Calculated)			μ_{eff} (BM)	Molar conductance (ohm^{-1} cm^{2} mol^{-1})*			λ_{max} (nm)		
	C	H	N		Nitrobenzne	Acetonitrile	Methanol	$\pi \rightarrow \pi^*$	Charge transfer	$^2T_{2g} \rightarrow {}^2A_{2g}$
[$RuCl_3(PPh_3)$NAAP] (Dark brown)	56.52 (56.59)	3.92 (3.99)	6.70 (6.77)	1.96	3.9	21.9	44.1	280	350	490
[$Ru(NO_3)Cl_2(PPh_3)$NAAP] (Dark brown)	54.78 (54.83)	3.82 (3.86)	8.15 (8.20)	1.94	4.0	25.2	48.3	280	345	515
[$Ru(NCS)Cl_2(PPh_3)$NAAP] (Dark brown)	56.46 (56.50)	3.85 (3.88)	8.19 (8.24)	2.02	4.3	27.1	51.4	280	410	575

*$\times 10^{-3}$

$^2T_{2g} \rightarrow {}^2A_{2g}$ transition. The bands *ca.* 425–345 nm are charge transfer bands. Thus the electronic spectra of all these Ru(III) complexes are characteristic of an octahedral environment around Ru(III) ions.

The X-band ESR spectrum of the complex [$RuCl_3(PPh_3)$NAAPH] recorded in the polycrystalline form exhibited only one signal with 'g' value 2.39, indicating high symmetry around ruthenium ion[17]. Such isotropic lines are due to the results of either intermolecular spin exchange which can broaden the lines or due to occupancy of unpaired electron in a degenerate orbital[18]. The value of 'g' is also in agreement with a low spin symmetry of the ligand field, similar to g-values reported for O,N-coordinated Ru(III) complexes[19, 20].

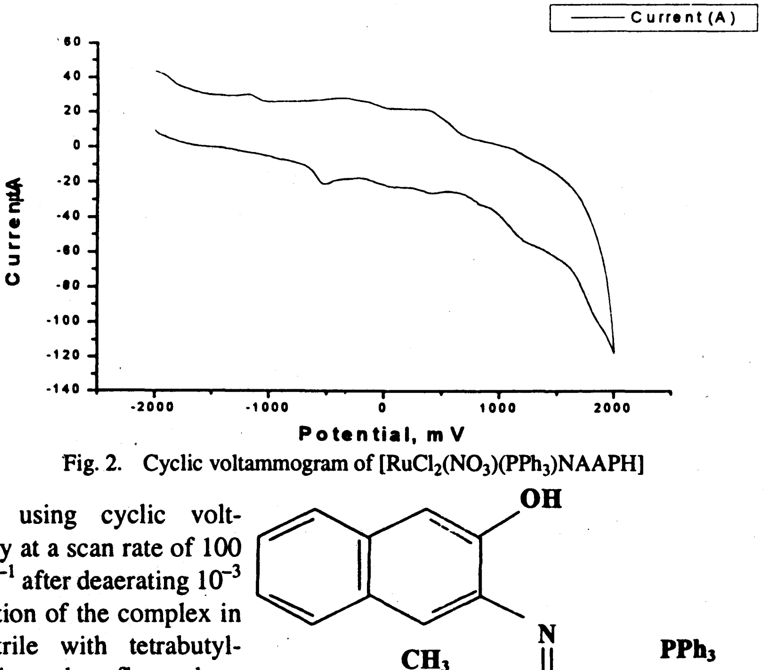

Fig. 2. Cyclic voltammogram of [$RuCl_2(NO_3)(PPh_3)$NAAPH]

The electrochemical behaviour of the complex [$RuCl_3(PPh_3)$NAAPH] was studied using cyclic voltammetry at a scan rate of 100 mV sec^{-1} after deaerating 10^{-3} M solution of the complex in acetonitrile with tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The cyclic voltammogram (Fig. 2) of the complex shows that the oxidation and reduction of Ru(III) in the complex is characterized by a well defined peak at 0.5 V and the redox processes are Ru(IV)-Ru(III)/Ru(III)-Ru(II) with quasi reversible peaks[19–21].

Based on these observations, an octahedral geometry

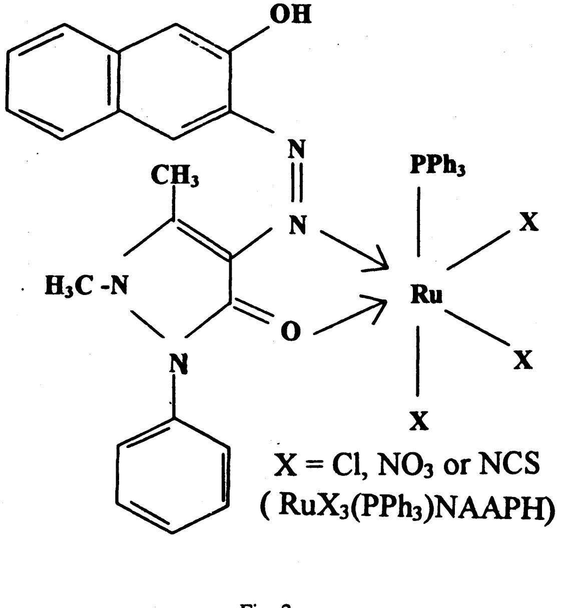

Fig. 3

is proposed for the complexes and a coordination number 6 is shown by Ru(III) in these complexes (Fig. 3).

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