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Synthesis and Spectral Analysis of Some Ru(III) Complexes of Azodyes Derived from 1-Phenyl-2,3-dimethyl-4-amino pyrazol-5-one

M.L. HARIKUMARAN NAIR* and A.T. MARIAMMA
Department of Chemistry, University College, Thiruvananthapuram-695 034, India
E-mail: drmlhnair@gmail.com

Eight novel complexes of the azodyes 2,3-dimethyl-1-phenyl-4-(2-hydroxy-5-methyl phenyl azo)-pyrazol-5-one (cresol azo antipyrine CAAP) and 2,3-dimethyl-1-phenyl-4-(2,4-dihydroxyphenylazo) pyrazol-5-one (resorcinol azo antipyrine RAAP) have been synthesised and characterized by elemental analysis, IR, electronic, ESR and NMR spectra, magnetic, conductance measurements and cyclic voltammetric studies. The ligands are found to behave in a neutral bidentate manner. All the complexes are non electrolytes with octahedral geometry having general formulae [$RuCl_2X(PPh_3)$ (CAAP)] and [$RuCl_2X(PPh_3)$ (RAAP)] where X = Cl, NCS, NO_3 or ClO_4. The X-ray powder diffraction patterns of one of the complexes has also been examined and found to be orthorhombic with unit cell dimensions a = 16.0189 Å, b = 11.4826 Å and c = 7.6652 Å. The electrochemical behaviour of one of the complexes is followed using cyclic voltammetry.

Key Words: Ru(III) Complexes, Azodyes, 1-Phenyl-2,3-dimethyl-4-amino pyrazol-5-one.

INTRODUCTION

Ruthenium complexes play vital roles in industrial endeavors as well as biological organisms[1-3]. Ru(III) complexes were reported to be effective catalysts in the oxidation of primary alcohols to their corresponding aldehydes in the presence of N-methyl morpholine-N-oxide(NMO) as co-oxidant[4]. Complexes of Ru containing nitrogen and oxygen donor ligands are found to be very effective catalysts for oxidation reduction and other organic transformations. The use of Ru(III) complexes to effect catalytic regioselective homogenous oxidations have been increasingly important[5,6]. A survey of literature shows that very few Ru(III) complexes of azodyes derived from 4-aminoantipyrine have been reported[7]. In view of the importance of Ru(III) complexes, the synthesis and characterization of some complexes of Ru(III), with potentially tridentate ligands 2,3-dimethyl-1-phenyl-4-(2-hydroxy-5-methyl phenyl azo)pyrazol-5-one (cresol azo antipyrine CAAP) and 2,3-dimethyl-1-phenyl-4-(2, 4-dihydroxy phenylazo) pyrazol-5-one (resorcinol azo antipyrine RAAP) derived from biologically active molecule 4-aminoantipyrine[8-10] have been reported.

EXPERIMENTAL

4-Aminoantipyrine (Fluka) was used as such. All other chemicals used were of BDH analar grade.

Synthesis of ligands: The ligands CAAP and RAAP were synthesized from 4-amino antipyrine and *p*-cresol/resorcinol as the case may be by diazotisation and coupling as reported earlier[11].

Synthesis of the complexes: The starting complex $RuCl_3(PPh_3)_3$ was prepared by reported procedure[12]. The following method was adopted for the preparation of $[RuCl_3(PPh_3)(CAAP)]$ and $[RuCl_3(PPh_3)(RAAP)]$. To a solution of $RuCl_3(PPh_3)_3$ (2 m mol) in benzene, a methanolic solution of the ligand (2 m mol) was added. The contents were refluxed on a water bath for 5-6 h. The resulting solution was concentrated. On adding a small amount of petroleum ether, the solid separated was filtered washed with benzene followed by ether and dried *in vacuo* over P_4O_{10}.

$[RuCl_2NO_3(PPh_3)L]$, $[RuCl_2PPh_3(NCS)L]$, $[RuCl_2PPh_3(ClO_4)L]$ (L = CAAP/RAAP) were prepared by adding a methanolic solution of the starting complex (2 m mol) containing $LiNO_3/NH_4CNS/LiClO_4$ (0.3 mg) as the case may be to methanolic solution of CAAP or RAAP (2 mmol) respectively. It was then refluxed on a water bath for 5-6 h. The volume was reduced to 3 mL and the complexes were separated by the addition of petroleum ether. The complexes were filtered, washed with benzene followed by ether and dried *in vacuo* over P_4O_{10}.

Micro analysis (CHN) were performed at RSIC, CDRI, Lucknow. Halogen, sulphur and perchlorate in the complexes were estimated by standard methods[13]. The IR spectra were recorded on a Jasco/FTIR 430 spectrophotometer using KBr pellets. The electronic spectra in the solution state (CH_3OH) were recorded on Jasco V-550 UV-Vis spectrophotometer. ESR spectra of two complexes were run on a Varian E 112X-Q band spectrometer with DPPH as the reference material. ^1H NMR spectra of the ligands were recorded in $CDCl_3$ on a 300 MHz FT NMR instrument using TMS as reference. The X-ray powder diffraction patterns of one of the complexes were recorded using Philips X-ray PW 1710 diffractometer. Cyclic voltammetric profile of one of the complexes was run on BAS-CV-50 W voltammetric analyser, using glassy carbon as the working electrode. The molar conductance of the complexes in $C_6H_5NO_2$, CH_3OH and CH_3CN (*ca.* $\times 10^{-3}$ 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 const 0.995 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[14]. Diamagnetic corrections for various atoms and structural units were computed using Pascal's constants[15].

RESULTS AND DISCUSSION

All the complexes are brown coloured non-hygroscopic solids, soluble in hot $C_6H_5NO_2$, CH_3OH and CH_3CN and sparingly soluble in benzene and insoluble in ether. The analytical data of the complexes (Table-1) corresponds to the composition $[RuCl_2X(PPh_3)L]$ where X = Cl, NO_3, NCS or ClO_4 and L = CAAP/RAAP. Molar conductances show that all the complexes are non electrolytes[16,17].

The ^{1}H NMR spectrum[18] of the ligand CAAP shows three singlets which corresponds to methyl protons and are observed at δ2.3, δ3.10 and δ3.4. The signal due to five aromatic protons appeared as a multiplet between δ7.04-7.59. The singlet at δ8.1 is assigned to hydrogen bonded phenolic proton. In the ^{1}H NMR spectrum of RAAP, the signals due to two methyl protons were observed as singlets at δ2.7 and δ3.2. The signal due to five aromatic protons of the antipyrine phenyl ring appeared as a multiplet between δ 7.46-d7.55 and due to three protons of the phenol ring appeared as a multiplet between δ 6.9 and δ 7.32. The OH proton signal appears as doublet between δ 8.58-δ8.6.

In the IR spectra of the ligands CAAP and RAAP, a broad medium band observed at 2930 and 2920 cm^{-1}, respectively are assigned to hydrogen bonded OH group[19,20]. In the spectra of their complexes instead of these bands, new broad band appears *ca.* 3400 cm^{-1}, indicating the presence of free OH group and hence its nonparticipation in coordination with the metal ion. The ν(C=O) of the pyrazolone ring observed at 1665 cm^{-1} and 1650 cm^{-1} in CAAP and RAAP, respectively are shifted to a lower frequency *ca.* 1600 cm^{-1} in all the complexes[21,22]. The vibrational bands at 1450 cm^{-1} assigned to ν(N=N) in the spectra of the ligands show a slight downward shift by 20 cm^{-1} in the spectra of all the complexes confirming the coordination through one of the azo group nitrogens[23-25]. Thus the ligands exhibit a neutral bidentate behaviour in all the complexes, coordinating through the C=O and -N=N-groups only.

The bands due to coordinated PPh_3 group usually observed in the range 1436-1430 cm^{-1} could not be located in the spectra of the complexes due to its overlapping with the azo group vibrations[12]. The bands 740, 695 and 520 cm^{-1} are assigned to PPh_3 fragments in the spectra of the complexes[26,27].

In the IR spectra of nitrate complexes of CAAP and RAAP, three additional bands 1495, 1385 and 1025 cm^{-1} which are not present in the spectra of the ligands are attributed to ν_4, ν_1 and ν_3 modes of the coordinated nitrate ions[28]. Since the difference between ν_4 and ν_1 is 110 cm^{-1}, it is suggested that the nitrate ions are coordinated monodentately to the metal ion.

The thiocyanate complexes of CAAP and RAAP showed very strong bands 2070 cm^{-1} which can be assigned to the N-coordinated thiocyanate group. Medium intensity bands observed at 750 cm^{-1} is attributed to

TABLE-1

ANALYTICAL AND PHYSICAL DATA OF Ru(III) COMPLEXES

Complex	Elemental analysis: Found (Calcd.) %					μ_{eff} (BM)	Molar conductance ohm^{-1} cm^{2} mol^{-1} × 10^{-3} M			$^{2}T_{2g} \rightarrow {}^{2}A_{2g}$
	C	H	N	Cl	S/ClO$_4$		C_6H_5OH	CH_3CN	CH_3OH	
[RuCl$_3$(PPh$_3$)(CAAP)]	54.38 (54.57)	4.01 (4.16)	8.11 (8.21)	13.26 (13.43)	–	1.93	3.2	20.8	41.1	510
[RuCl$_2$ (NCS) (PPh$_3$)(CAAP)]	54.41 (54.53)	4.00 (4.05)	8.31 (8.59)	8.56 (8.71)	3.83 (3.92)	1.94	3.8	21.2	43.2	540
[RuCl$_2$(NO$_3$) (PPh$_3$)(CAAP)]	52.51 (52.79)	3.88 (4.03)	8.23 (8.55)	8.51 (8.66)	–	1.96	4.1	28.3	45.1	520
[RuCl$_2$(ClO$_4$) (PPh$_3$)(CAAP)]	50.15 (50.48)	3.62 (3.85)	6.32 (6.54)	8.20 (8.28)	11.41 (11.59)	1.93	5.6	32.1	48.2	495
[RuCl$_3$(PPh$_3$)(RAAP)]	52.78 (52.92)	3.71 (3.90)	6.98 (7.05)	13.11 (13.40)	–	2.01	3.4	25.1	44.2	550
[RuCl$_2$(NCS)(PPh$_3$)(RAAP)]	52.82 (52.93)	3.71 (3.79)	8.52 (8.57)	8.58 (8.70)	3.85 (3.93)	2.16	4.1	22.6	38.9	530
[RuCl$_2$(NO$_3$)(PPh$_3$)(RAAP)]	51.11 (51.20)	3.69 (3.77)	8.27 (8.33)	8.59 (8.64)	–	1.98	3.8	22.6	40.5	570
[RuCl$_2$(ClO$_4$)(PPh$_3$)(RAAP)]	48.73 (48.96)	3.58 (3.61)	6.48 (6.52)	8.13 (8.26)	11.48 (11.62)	1.97	4.8	26.1	44.3	565

TABLE-2
KEY IR SPECTRAL BANDS (cm^{-1}) OF Ru(III) COMPLEXES OF CAAP AND RAAP

CAAP	[$RuCl_3(PPh_3)$(CAAP)]	[$RuCl_2$(NCS)(PPh_3)(CAAP)]	[$RuCl_2(NO_3)(PPh_3)$(CAAP)]	[$RuCl_2(ClO_4)(PPh_3)$(CAAP)]	RAAP	[$RuCl_3(PPh_3)$(RAAP)]	[$RuCl_2$(NCS)(PPh_3)(RAAP)]	[$RuCl_2(NO_3)(PPh_3)$(RAAP)]	[$RuCl_2(ClO_4)(PPh_3)$(RAAP)]	Assignments
–	3400bm	3413bm	3420bm	3410bm	–	3410bm	3420bm	3410bm	3418bm	ν(O-H) free
2930bm	–	–	–	–	2920bm	–	–	–	–	ν(O-H) hydrogen bonded
–	–	2069s	–	–	–	–	2063s	–	–	ν(C=N) of thiocynate
1665s	1630s	1600s	1614s	1610s	1650s	1600s	1595s	1595s	1600s	ν(C=O) pyrazolone
–	–	–	1500s	–	–	–		1495s		$\nu_4NO_3^-$
1450s	1429s	1433s	1434s	1435s	1450s	1425s	1425s	1436s	1430s	ν(N=N)
–	–	–	1384m	–	–	–	–	1385m	–	$\nu_1NO_3^-$
–	–	–	–	1120s	–	–	–	–	1118s	$\nu_4ClO_4^-$
–	–	–	–	1077s	–	–	–		1092s	$\nu_1ClO_4^-$
–	–	–	1028m	–	–	–	–	1026m	–	$\nu_2NO_3^-$
–	–	750m	–	–	–	–	750m	–	–	ν(C-S) of N bonded NCS
–	–	–	–	635w	–	–	–	–	630w	$\nu_3ClO_4^-$
–	–	467m	–	–	–	–	470m	–	–	δ(NCS)

ν(C-S). The medium intensity bands observed at 480 cm^{-1} assigned to δ(NCS) confirms the N-coordinated nature of the thiocyanate group[30].

For the perchlorate complexes, the three bands at 1120, 1077 and 630 cm^{-1} are assigned to ν_4, ν_1 and ν_3 modes of unidentately coordinated perchlorate ion[31] (Table-2).

The electronic absorption spectral bands of the complexes in methanol with tentative assignments are discussed[32,33]. 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 $T_{2g}{}^4E_g{}^1$ configuration[33]. 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[32]. The electronic spectra of all the complexes under the present study show bands appearing 570-495 nm which can be assigned $^2T_{2g} \rightarrow {}^2A_{2g}$ transition. The bands 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 complexes [$RuCl_3(PPh_3)$ (CAAP)] and [$RuCl_3(PPh_3)$(RAAP)] (poly crystalline form) at room temperature exhibited a single line each with g value 2.32, indicating high symmetry around ruthenium ion[33]. Such isotropic lines are due to occupancy of the unpaired electron in a degenerate orbital[34]. The g values are also in agreement with a low spin symmetry of the ligand field, similar to g values reported for O,N-coordinated Ru(III) complexes[5,7,35,36].

The magnetic moment values of the complexes (1.93-2.16 BM) corresponding to the presence of an unpaired electron indicate the paramagnetic nature.

The complex [$RuCl_3(PPh_3)$(CAAP)] is found to be orthorhombic by X-ray powder diffraction method and was indexed using Hesse and Lipson procedure[37-39]. The unit cell dimensions are $a = 16.0189$ Å, $b = 11.4826$ Å and $c = 7.6652$ Å.

The electrochemical behaviour of the complex [$RuCl_3(PPh_3)$(CAAP)] was studied using cyclic voltammetry at a scan rate of 100 mV s^{-1} after deaerating 10^{-3} M solution of the complex in acetonitrile with tetrabutyl ammonium hexafluoro phosphate as the supporting electrolyte. The cyclic voltammogram (Fig. 1) of the complex shows that the oxidation and reduction of Ru(III) in the complex is characterized by a well defined peak and the redox processes are Ru(IV)-Ru(III)/Ru(III)-Ru(II) with quasi reversible peaks[35,36,40].

Based on the analytical, spectral (IR, UV-Visible and ESR) and electrochemcial data, an octahedral structure (Figs. 2 and 3) have been tentatively proposed for all the Ru(III) complexes.

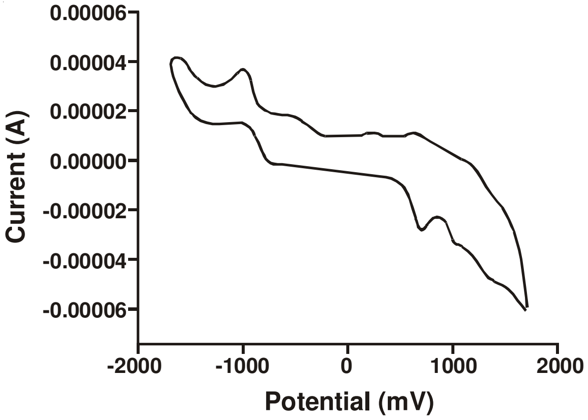

Fig. 1. Cyclic Voltammogram [$RuCl_3(PPh_3)$CAAP]

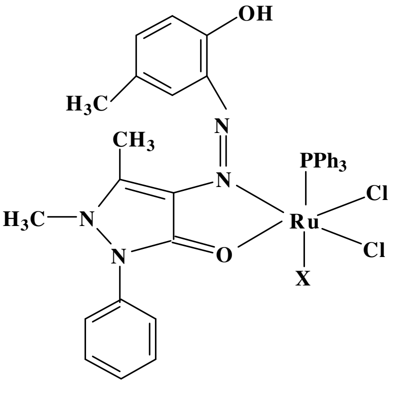

Fig. 2. [$RuCl_2X(PPh_3)$(CAAP)]
X = Cl, NCS, NO_3, ClO_4

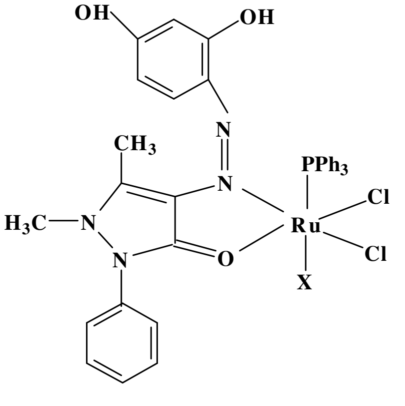

Fig. 3. [$RuCl_2X(PPh_3)$(RAAP)]
X = Cl, NCS, NO_3, ClO_4

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