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Structural Elucidation and Antibacterial Studies on Half-Sandwich Ruthenium(II) Complexes Incorporating Arene, Phosphine, Arsine and Thioamide Ligands

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The half-sandwich arene complexes of ruthenium(II) incorporating arsine, phosphine and thioamide ligands with formula [Ru(η^6-arene)(ER_3)(AEtT)]$^+BPh_4^-$ η^6-arene = C_6H_6 or *p*-cymene; E = P/As; R = C_6H_5/$C_6H_5CH_2$; AEtT = 4-amino-3-ethyl-5-mercapto-1,2,4-triazole bidentate mononegative anion) are prepared and investigated. The reaction products have been characterized by elemental analyses, conductometric, magnetic, IR, UV-visible and ^{1}H NMR spectra. Antibacterial activities of ligand and complexes are tested against *E. coli*, *B. subtilus* and *S. aureus*. The data revealed that all the complexes are more active than free thioamide ligand.

Keywords: Half-sandwich compounds, Chelating thioamide, Bio-activities, Ruthenium(II).

INTRODUCTION

The half-sandwich ruthenium-arene complexes endowed with anticancer properties[1-4]. A large number of ruthenium complexes with arene ligands have been employed as catalyst in many organic reactions[5-8]. However, less amount of work have been done on arene complexes of ruthenium incorporating chelating (N, S) secondary thioamide ligands. Hence, the present paper is devoted to the synthesis, structural elucidation and biological evaluation of half-Sandwich complexes of ruthenium incorporating the arene, arsine and heterocyclic secondary thioamide ligand following our previous report[9].

EXPERIMENTAL

All the chemicals used were of CP grade or AR grade. Solvents were distilled and dried before use. The precursor complexes [Ru(η^6-arene)Cl_2]$_2$[10,11] (η^6-arene = C_6H_6/P-cymene) and ligand, 4-amino-3-ethyl-5-mercapto-1,2,4-triazole (AEtTH)[12], Tribenzyl phosphine[13] (PBz_3) were prepared by the methods reported in literature. Triphenyl arsine ($As\phi_3$) and triphenyl phosphine ($P\phi_3$) were purchased from either Aldrich or B.D.H. and were used without purification.

All complexes were prepared using a general method by refluxing a mixture containing precursors, tertiary phosphines, $NaBPh_4$, thioamide ligand and Et_3N in MeOH following our previous method reported in literature[9] (**Schemes I** and **II**). The analysis of C, H and N were done at the micro-analytical section of CDRI, Lucknow. The IR spectra of ligand and complexes were recorded with Perkin Elmer model 577 Spectrophotometer in the range of 4000-200 cm^{-1} as KBr pellets. Electronic spectra were recorded with Zeiss (Jena) model and molar conductance of complexes were measured in DMF using Wiss-Werkstatter Weitheim obb type LBR conductivity meter. ^{1}H NMR spectra of ligand and complexes were recorded with 90 MHZ NMR spectrophotometer in $CDCl_3$ solution. The magnetic susceptibility was measured on a gouy balance using $Hg[Co(SCN)_4]$ as calibrant.

RESULTS AND DISCUSSION

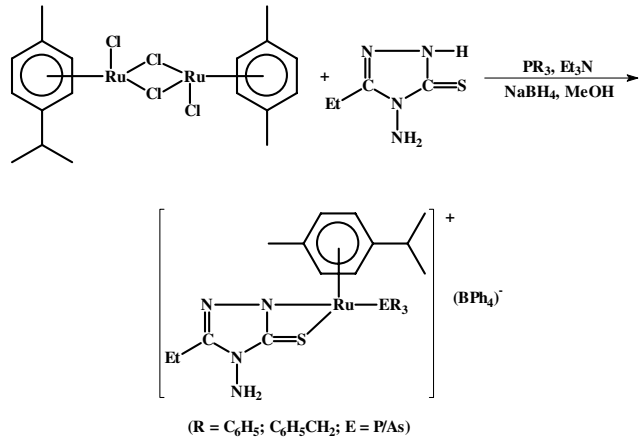
The new arene ruthenium(II) complexes ligated with bidentate thioamide ligand of the type [Ru(η^6-arene)(PR_3)-(AEtT)]$^+BPh_4^-$ (η^6-arene = C_6H_6/or *p*-cymene; R = -C_6H_5/$C_6H_5CH_2$) were isolated as yellow or orange coloured air stable solid. All were highly soluble in polar organic solvents such as CH_2Cl_2, $CHCl_3$, DMF, DMSO and insoluble in EtOEt and petroleum ether. The analytical data are in good agreement with the composition proposed. The molar conductance values were found in the range of 110-115 Λ^{-1} cm^2 mol^{-1} in DMF (10^{-3} M) shows 1:1 electrolytic nature[14,15]. In all reactions, the ligand behaves as monobasic bidentate N and S chelating anion (Table-1).

All complexes were found to be diamagnetic indicating characteristic of low spin d^6 complexes of ruthenium(II)[16-18].

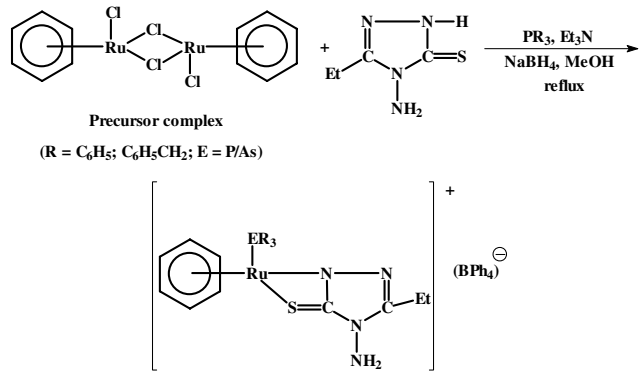
Spectral characterization: Electronic spectra of complexes exhibits three intense transition between 480-215 nm. Two bands around 295-305 nm (n $\rightarrow \pi^*$) and 215-220 nm (n $\rightarrow \pi^*$) and intense band in the range of 330-354 nm (MLCT) are consistent with octahedral structure around ruthenium(II) ion containing thioamides[19-21].

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

Complex/(MF)	Analysis (%) : found/(calcd)			Molar cond. (Λ^{-1} cm^2 mol^{-1})	λ_{max} (nm)/ Assignemnts
	C	H	N		
$[Ru(\eta^6\text{-}C_6H_6)(P\phi_3)(AEtT)]BPh_4$ $(RuC_{52}H_{48}N_4BPS)$	69.01 (69.11)	5.32 (5.31)	6.11 (6.20)	110.0	295 (n→π*) 215 (π→π*) 330 (MLCT)
$[Ru(\eta^6\text{-}C_6H_6)(As\phi_3)(AEtT)]BPh_4$ $(RuC_{52}H_{48}N_4BAsS)$	66.01 (66.04)	5.11 (5.88)	5.93 (5.92)	112.0	298 (n→π*) 220 (π→π*) 335 (MLCT)
$[Ru(\eta^6\text{-}C_6H_6)(PBz_3)(AEtT)]BPh_4$ $(RuC_{55}H_{54}N_4BPS)$	69.98 (69.85)	5.73 (5.71)	6.01 (5.92)	112.6	300 (n→π*) 218 (π→π*) 340 (MLCT)
$[Ru(\eta^6\text{-P-Cymene})(P\phi_3)(AEtT)]BPh_4$ $(RuC_{56}H_{56}N_4BPS)$	70.01 (70.08)	5.92 (5.84)	5.88 (5.84)	115.0	305 (n→π*) 220 (π→π*) 354 (MLCT)
$[Ru(\eta^6\text{-P-Cymene})(As\phi_3)(AEtT)]BPh_4$ $(RuC_{56}H_{56}N_4BPS)$	67.32 (67.01)	5.92 (5.84)	5.85 (5.58)	115.0	307 (n→π*) 222 (π→π*) 350 (MLCT)
$[Ru(\eta^6\text{-P-Cymene})(PBz_3)(AEtT)]BPh_4$ $(RuC_{59}H_{62}N_4BPS)$	70.85 (70.74)	6.32 (6.20)	5.68 (5.60)	112.8	305 (n→π*) 325 (π→π*) 352 (MLCT)



Scheme-I



Scheme-II

The free thioamide ligand (AEtTH) exhibits three bands at 3260, 3210 and 3110 cm^{-1} due to interaction between -NH_2 and -N-H group[22]. These bands are perturbed on complexation with reduction in intensity and observed at 3240 and 3100 cm^{-1} in ruthenium(II) complexes. This is probably due to deprotonation of -NH hydrogen by ruthenium(II) ion and formation of Ru- N bond. The formation of Ru-N bond is further indicated by new band in far IR at 470-460 cm^{-1} assigned to ν(Ru-N). Thioamide band I[23] has major contribution from δNH undergoes red shift of 15-25 cm^{-1} on complexation also support the formation of ruthenium-N bond. The simultaneous Ru-N and Ru-S bonds are confirmed by the change in position and intensity of thioamide bands on complexation. The thioamide band II blue shift and thioamide band III and band IV red shift to lower frequency (Table-2) indicating simultaneous formation of Ru-N and Ru-S bonds considering previous observations[24-26].

Thus, the thioamide ligand acts as chelating N, S-mononegative bidentate nature in all the complexes.

^{1}H NMR spectra: Supplementary data have been obtained by ^{1}H NMR spectroscopy recorded for the ligands and arene complexes to substantiate further metal-ligand bonding and proton chemical shift are given in Table-3.

The free thioamide ligand exhibits signals at δ 2.12, (S, 3H, CH_3) ppm, δ 3.08 (S, 1H, SH) ppm, δ 7.7 (S, 1H, NH) ppm and δ 4.22-4.34 (S, 2H, NH_2) ppm. The resonances due to NH and SH protons are not found in complexes due to deprotonation of imino nitrogen and existence of thione tautomeric form on complexation. The presence of coordinated $P\phi_3$/$As\phi_3$ group is indicated signals at 8.22-8.42 (multiplet) and coordinated tribenzyl phosphine at δ 7.15-7.32 (m, 15H) ppm and at δ2.78 (S, 6H, CH_2) ppm in corresponding ruthenium(II) complexes. The two isopropyl methyl protons of the *p*-cymene appeared as doublet in the region δ 0.70-0.90 ppm and methine proton in the range of δ0.9-2.1 ppm as septet and methyl group of the *p*-cymene comes as singlet around the region of δ1.48-1.75 ppm. The arene protons exhibited down field as compared with that in precursor complex[27]. Thus, ^{1}H NMR spectra of complexes is consistent with IR spectral results.

Antibacterial evaluation: The antibacterial activities of the compounds were determined by disc diffusion method reported in literature[28]. The bacteria were cultured in nutrient agar medium in petriplates and used inoculums for the study. The ligand and complexes were dissolved in DMSO to a final concentration of 0.25, 0.50 and 1 % and soaked in filter paper

TABLE-2
MAJOR INFRARED SPECTRAL BANDS (cm^{-1}) OF LIGAND (AEtTH) AND RUTHENIUM(II) COMPLEXES

Compounds	Thioamide bands				ν(Ru-N)	ν(Ru-S)	ν(SH)
	Band I	Band II	Band III	Band IV			
AEtTH (ligand)	1570 (s)	1390 (ms)	1050 (s)	770 (s)	-	-	2350 (w)
$[Ru(\eta^6\text{-}C_6H_6)(P\phi_3)(AEtT)]BPh_4$	1555 (ms)	1405 (m)	1035 (m)	740 (m)	470 (m)	430 (w)	-
$[Ru(\eta^6\text{-}C_6H_6)(As\phi_3)(AEtT)]BPh_4$	1550 (ms)	1410 (m)	1035 (m)	745 (m)	460 (m)	410 (w)	-
$[Ru(\eta^6\text{-}C_6H_6)(PBz_3)(AEtT)]BPh_4$	1562 (m)	1405 (m)	1030 (m)	740 (m)	465 (m)	435 (m)	-
$[Ru(\eta^6\text{-P-cymene})(P\phi_3)(AEtT)]BPh_4$	1560 (m)	1400 (m)	1040 (m)	735 (m)	485 (m)	415 (m)	-
$[Ru(\eta^6\text{-P-cymene})(As\phi_3)(AEtT)]BPh_4$	1555 (m)	1410 (m)	1045 (m)	730 (m)	480 (m)	420 (w)	-
$[Ru(\eta^6\text{-P-cymene})(PBz_3)(AEtT)]BPh_4$	1550 (m)	1415 (m)	1065 (m	735 (m)	490 (m)	410 (w)	-

TABLE-3
^1H NMR (δ ppm) SPECTRA OF LIGAND (AEtTH) AND RUTHENIUM(II) COMPLEXES

Compounds	*p*-Cymene				AEtTH				$P\phi_3(As\phi_3)$
	Ar-H	$CH(CH_3)_2$	CH_3	CH	N-H	SH	CH_3	NH_3	
AEtTH	-	-	-	-	7.70-7.72	3.08	2.12	4.32-4.34	-
3	5.1-5.72	0.90	1.47	1.9	-	-	2.21	4.40	8.22-8.25
4	5.0-5.82	0.82	1.50	1.9	-	-	2.34	4.50	8.42
5	5.2-5.82	0.91	1.70	1.9	-	-	2.40	4.44	8.20-8.44
6	5.1-5.6	0.92	1.73	2.10	-	-	2.44	4.46	8.34-8.50

TABLE-4
ANTIBACTERIAL BIOASSAY OF LIGAND (AEtTH) AND RUTHENIUM (II) COMPLEXES DIAMETER OF INHIBITION ZONES (mm)

Compounds	*E. coli*			*B. subtilus*			*S. aureus*		
	0.25 %	0.5 %	1 %	0.25 %	0.5 %	1 %	0.25 %	0.5 %	1 %
AEtTH (ligand) 1	10	11	13	9	10	12	10	11	13
2	12	14	16	12	13	15	11	13	13
3	NT	NT	NT	NT	NT	NT	NT	NT	NT
4	12	15	17	11	12	14	12	14	16
5	12	14	16	11	13	15	11	13	15
6	11	13	15	10	12	13	10	12	13
Streptomycin (standard drug)	23	24	28	23	28	29	29	29	26

NT = Not tested; compound serial number is same as in Table-1

disc of 5 mm diameter and 1 mm thickness. The standard drug streptomycin was used as standard. The complexes display higher activity than thioamide ligand but could not reach the effectiveness of the standard drug streptomycin (Table-4). The results showed that the complexes exhibit moderate activity against the bacteria used. The toxicity of ruthenium chelates increases on increasing concentration agreement with our previous observations[29-31] and may be explained in light of Tweedy chelation theory[32].

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