

Synthesis, Characterization and Antimicrobial Properties of Mononuclear Ruthenium (III) Complexes Containing Chelating Secondary Thioamides

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Abstract

Mixed ligand mononuclear six-coordinated octahedral ruthenium (III) complexes of the type $[RuX_2(E\phi_3)L]$ ($E = P$ or As ; $X = Cl$ or Br ; $L =$ monobasic bidentate anion of 1-benzyl tetrazoline-5-thione) have been synthesized and characterized by elemental analysis, magnetic susceptibility measurements, Molar conductance data and spectral analysis (IR, UV-vis & 1H NMR). The new complexes were also exhibited antimicrobial investigations.

Key words : Mixed ligand, chelating secondary thioamide, Ruthenium (III), Low-spin, antimicrobial studies.

Introduction

We present here the synthesis, spectroscopic properties and antimicrobial activities of some new mononuclear phosphine and arsine complexes of ruthenium (III) ligated with N,S-chelating secondary thioamides as a part of going efforts.¹⁻³ The simple displacement reactions with suitable precursors were designed and elucidation of structure and mode of bonding of isolated solid products is reported herein using IR, far-IR, UV-vis and 1H NMR spectra. The antibacterial and

antifungal activities of thioamide ligands and their chelates are also reported in the present communication.

Experimental

All the reagents used were CP grade and of analytical reagent grade. The solvents were dried before use and all the reactions were performed under strictly anhydrous conditions. The ligand 1-benzyl-tetrazoline-5-thione was prepared by the method of Lieber *et al.*⁴ and the precursor complexes

[RuX₃(Eφ₃)₃] (X = Cl/Br; E = P/As) and [RuBr₃(Pφ₃)₂(CH₃OH)] were prepared by the methods reported in literature.⁵⁻⁸ The new complexes were prepared using a general method.

Preparation of new complexes:

Benzene solution of [RuX₃(Eφ₃)₃] (X = Cl/Br, E = P/As) and ligand were mixed in equimolar ratio and stirred on magnetic stirrer for 15 mins and heated on reflux for four hours and initial brown colour changed to yellowish green. The working mixture was concentrated and cooled. Addition of light petroleum ether produced coloured solids which was filtered and dried in vacuo. (yield = 71%) For the preparation of thiocyanate complexes, ethanolic solution of NH₄SCN was added to benzene solution of [RuX₃(Eφ₃)₃] and reflux with solution of ligand using desired molar ratio. The complexes were obtained by concentration of refluxed solution to ~ 5 cm³ and addition of small quantity of ether cooling.

IR Spectra of ligands and complexes were recorded on a Perkin Elmer 577 spectrophotometer and electronic spectra on a Backmann DU-6 spectrophotometer. The ¹H NMR was recorded on Bruker 400 MHz using TMS as reference and molar conductance of complexes (10⁻³ M) were measured in DMF using Wiss-Werkstätten Weihem obb type LBR conductivity meter. Magnetic measurements were made on a Gouy balance using Hg(Co(SCN)₄) as calibrant. The analysis of C, H and N were performed at CDRI, Lucknow, India and chlorine and bromine by

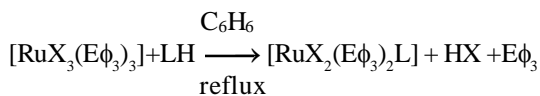
standard methods.

Analysis:

1. [RuCl₂(Pφ₃)₂(L)] (Yellowish green) : **Calculated (%)** for RuC₄₄H₃₇N₄P₂SCl₂ (887) : C = 59.52; H = 4.17; N = 6.31; Cl = 8.00; Ru = 11.38; **Found (%)** : C = 59.61; H = 4.27; N = 6.42; Cl = 8.12; Ru = 11.42;
2. [RuCl₂(Asφ₃)₂L] (Light green) : **Calculated (%)** for RuC₄₄H₃₇N₄As₂SCl₂ (975) : C = 54.15; H = 3.79; N = 5.74; Cl = 7.28; Ru = 10.35; **Found (%)** : C = 54.50; H = 3.82; N = 5.68; Cl = 7.38; Ru = 10.40;
3. [RuBr₂(Pφ₃)₂L] (Greenish brown) : **Calculated (%)** for RuC₄₄H₃₇N₄P₂SBr₂ (976) : C = 54.15; H = 3.79; N = 5.73; Br = 16.39; Ru = 10.34; **Found (%)** : C = 54.35; H = 3.82; N = 5.80; Br = 16.85; Ru = 10.50;
4. [RuBr₂(Asφ₃)₂L] (Greenish brown) : **Calculated (%)** for RuC₄₄H₃₇N₄As₂SBr₂ (1064) : C = 49.62; H = 3.47; N = 5.26; Br = 15.03%; Ru = 9.49; **Found (%)** :
5. [RuBr(Pφ₃)L₂] (Light green) : **Calculated (%)** for RuC₃₄H₂₉N₈S₂PBr (825) : C = 49.45; H = 3.51; N = 13.57; Br = 9.69; Ru = 12.24; **Found (%)** : C = 49.32; H = 3.56; N = 13.62; Br = 9.50; Ru = 12.30;
6. [Ru(NCS)₂(Pφ₃)₂L] (Yellowish green) : **Calculated (%)** for RuC₄₆H₃₇N₆P₂S₃ (952) : C = 57.98; H = 3.88; N = 8.82; Ru = 10.60; **Found (%)** : C = 56.01; H = 3.90; N = 8.88; Ru = 10.72;
7. [Ru(NCS)₂(Asφ₃)₂L] (Light green) : **Calculated (%)** for RuC₄₆H₃₇N₆As₂S₃ (1040) : C = 53.07; H = 4.42; N = 8.00; Ru = 9.71; **Found (%)** : C = 53.11; H = 4.50; N = 8.10; Ru = 9.82;

Results and Discussion

All derivatives of 1-benzyl tetrazoline-5-thione interacts with precursor complexes $[\text{RuX}_3(\text{E}\phi_3)_3]$ ($\text{E} = \text{P/As}$; $\text{X} = \text{Cl/Br}$) in equimolar ratio and ligand acts as mono-negative bidentate anion.



($\text{X} = \text{Cl/Br}$; $\text{E} = \text{P/As}$)

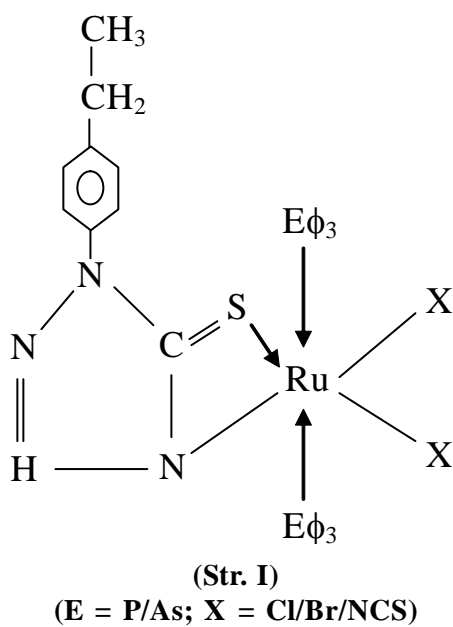
The analytical data are in good agreement with the general molecular formula proposed. The thioamide ligand replaces one triphenyl phosphine or triphenyl arsine molecule and one chloride or bromide ion and one methanol from the precursors. All the complexes are air-stable, non-hygroscopic in nature, in soluble in water and highly soluble in coordinating solvents DMF, DMSO and acetonitrile producing yellow-green solution. The molar conductance in DMF (10^{-3} M) fall in the range $15.66 - 23.60 \text{ } \Lambda^{-1}\text{cm}^2\text{mol}^{-1}$ indicating the non-electrolytic nature of complexes¹⁰ and anions are of coordinated nature and present in the inner sphere of complexes. The magnetic moment at room temperature was found to be $1.92 - 1.86 \text{ BM}$ corresponding to one unpaired electron which support low spin ruthenium (III) having electronic configuration $\text{T}_{2g}^5\text{e}_g^0$ in an octahedral environment.¹¹ The ground state of Ru (III) is $^2\text{T}_{2g}$ and the first excited state doublet levels in the order of increasing

energy are $^2\text{A}_{2g}$ and $^2\text{A}_{1g}$ which arises from $\text{t}_{2g}^4\text{e}_g^1$ configuration.¹² Hence, two bands corresponding to $^2\text{T}_{2g} \rightarrow ^2\text{A}_{2g}$ and $^2\text{T}_{2g} \rightarrow ^2\text{T}_{1g}$ transitions are possible. The electronic spectra of complexes exhibit high intensity bands at 260-265 nm ($\pi \rightarrow \pi^*$), 340-360 nm ($n \rightarrow \pi^*$), 450-461 nm ($\text{T}_{2g} \rightarrow \pi^*$, MLCT) and at a broad band at 540-560 nm ($^2\text{T}_{2g} \rightarrow ^2\text{A}_{2g}$) of low intensity are consistent with octahedral structure of other ruthenium (III) complexes.¹³⁻¹⁵

The characteristics νNH (3185 cm^{-1}), SH (2550 cm^{-1}) bands of free ligand were not found on complexation indicating deprotonation of iminonitrogen and formation of Ru-N and Ru-S bonds. The systematic shift of thioamide bands (table 2) agreement with previous observation¹⁶⁻¹⁸ and normal coordinate analysis (NCA) of thioamide ligand.¹⁹⁻²⁰ Thioamide band II of free ligand (1290 cm^{-1}) blue shift to higher frequency and band I (1510 cm^{-1}), band III (1050 cm^{-1}) and band IV (810 cm^{-1}) red shift to lower frequency (table 2) on coordination which increases CN bond order and decreases CS bond order of thioamide group due to formation of simultaneous Ru-N and Ru-S bond.¹² New bands at $435-460 \text{ cm}^{-1}$ (Ru-N) and at $405-410 \text{ cm}^{-1}$ (Ru-S) due to stretching modes supports these observations. Moreover, the presence of more than one $\nu\text{Ru-X}$ band confirms the two chlorine or bromine atoms are at mutual cis-position in octahedral structure of complexes and two bulky $\text{P}\phi_3$ or $\text{As}\phi_3$ are at Trans-position. (Str. I).

Table 1. Conductivity, Magnetic Susceptibility, UV-vis and ^1H NMR Spectral data of ligand and complexes

Compound	$\mu_{\text{eff.}}$ (BM)	Molar Cond. ($\text{cm}^2\text{mol}^{-1}$)	Electronic Spectra λ_{max} (nm)/ Assignments	^1H NMR (δPPM)		
				-NH Proton	Phenyl Proton	CH_2 Proton
ligand (LH)	—	—	302 ($n \rightarrow \pi^*$) 267 ($\pi \rightarrow \pi^*$)	1.55	7.70–7.96 Multiplet	2.93
$[\text{RuCl}_2(\text{P}\phi_3)_2\text{L}]$	1.91	20.32	560 ($^2\text{T}_{2g} \rightarrow ^2\text{A}_{2g}$) 450 ($\text{T}_{2g} \rightarrow \pi^*$) 360 ($n \rightarrow \pi^*$) 260 ($\pi \rightarrow \pi^*$)	(—)	7.46–7.70 Multiplet	2.32
$[\text{RuCl}_2(\text{As}\phi_3)_2\text{L}]$	1.96	16.32	555 ($^2\text{T}_{2g} \rightarrow ^2\text{A}_{2g}$) 455 ($\text{T}_{2g} \rightarrow \pi^*$) 350 ($n \rightarrow \pi^*$) 265 ($\pi \rightarrow \pi^*$)	(—)	7.85–7.98 Multiplet	2.80
$[\text{RuBr}_2(\text{P}\phi_3)_2\text{L}]$	1.93	15.32	560 ($^2\text{T}_{2g} \rightarrow ^2\text{A}_{2g}$) 460 ($\text{T}_{2g} \rightarrow \pi^*$) 345 ($n \rightarrow \pi^*$) 261 ($\pi \rightarrow \pi^*$)	(—)	7.86–7.98 Multiplet	2.79
$[\text{RuBr}_2(\text{As}\phi_3)_2\text{L}]$	1.96	15.80	565 ($^2\text{T}_{2g} \rightarrow ^2\text{A}_{2g}$) 460 ($\text{T}_{2g} \rightarrow \pi^*$) 340 ($n \rightarrow \pi^*$) 260 ($\pi \rightarrow \pi^*$)	(—)	7.88–7.92 Multiplet	2.78
$[\text{RuBr}(\text{P}\phi_3)\text{L}_2]$	1.92	15.02	540 ($^2\text{T}_{2g} \rightarrow ^2\text{A}_{2g}$) 462 ($\text{T}_{2g} \rightarrow \pi^*$) 342 ($n \rightarrow \pi^*$) 262 ($\pi \rightarrow \pi^*$)	(—)	7.89–8.02 Multiplet	2.90
$[\text{Ru}(\text{NCS})_2(\text{P}\phi_3)_2\text{L}]$	1.96	23.60	544 ($^2\text{T}_{2g} \rightarrow ^2\text{A}_{2g}$) 461 ($\text{T}_{2g} \rightarrow \pi^*$) 340 ($n \rightarrow \pi^*$) 263 ($\pi \rightarrow \pi^*$)	(—)	7.88–8.23 Multiplet	2.76
$[\text{Ru}(\text{NCS})_2(\text{As}\phi_3)_2\text{L}]$	1.98	16.66	545 ($^2\text{T}_{2g} \rightarrow ^2\text{A}_{2g}$) 460 ($\text{T}_{2g} \rightarrow \pi^*$) 342 ($n \rightarrow \pi^*$) 261 ($\pi \rightarrow \pi^*$)	(—)	8.02–8.44 Multiplet	2.77



and 1555 cm^{-1} are attributed to coordinated $\text{P}\phi_3/\text{As}\phi_3$ in complexes²¹ and strong bands of medium intensities at 2080 cm^{-1} , 770 cm^{-1} and 480 cm^{-1} confirms the N-bonded isothiocyanato group and assigned to νNCS , $\nu\text{C}=\text{S}$ and δNCS modes.²²

All complexes exhibit broad multiplet in their ^1H NMR spectra in the region $\delta 7.46\text{--}7.78\text{ PPM}$ due to phenyl protons in complexes. The broad nature of peak may be due to large quadrupole resonances broadening effect of four nitrogen atoms.²³ The resonances due to imino proton in the ligand at $\delta 1.55\text{ PPM}$ is absent in the spectra of complexes suggesting deprotonation and formation of Ru-N bond during complexation. The aromatic protons of $\text{P}\phi_3$ or $\text{As}\phi_3$ were observed in the expected region at $\delta 7.30\text{--}8.46\text{ PPM}$.²⁴

The strong non-ligand bands near 535, 685, 750

Table 2. IR Characterization bands (cm^{-1}) of ligand and complexes

Compounds	νNH	Thioamide Bands ψ				$\nu\text{Ru-N}$	$\nu\text{Ru-S}$
		Band I	Band II	Band III	Band IV		
(LH, ligand)	3180 m	1510 (s)	1290 m	1050 m	810 m	—	—
$[\text{RuCl}_2(\text{P}\phi_3)_2\text{L}]$	—	1490 m	1310 m	1035 m	770 m	460 m	410 w
$[\text{RuCl}_2(\text{As}\phi_3)_2\text{L}]$	—	1485 m	1305 m	1030 m	775 m	441 m	405 w
$[\text{RuBr}_2(\text{P}\phi_3)_2\text{L}]$	—	1480 m	1315 m	1035 m	775 m	435 m	400 w
$[\text{RuBr}_2(\text{As}\phi_3)_2\text{L}]$	—	1482 m	1310 m	1032 m	770 m	438 m	405 w
$[\text{RuBr}(\text{P}_3)\text{L}_2]$		1485 m	1315 m	1040 m	775 m	435 m 440 m	400 w
$[\text{Ru}(\text{NCS})_2(\text{P}\phi_3)_2\text{L}]$	—	1480 m	1310 m	1035 m	775 m	475 m	402 w
$[\text{Ru}(\text{NCS})_2(\text{As}\phi_3)_2\text{L}]$	—	1485 m	1305 m	1025 m	780 m	480 m	410 w

ψ : Mixed bands : Band I = $\delta\text{NH} + \delta\text{CH} + \nu\text{C}=\text{N}$;
 Band II = $\nu\text{C}^{\text{---}}\text{N} + \delta\text{NH} + \delta\text{CH} + \nu\text{C}=\text{S}$;
 Band III = $\nu\text{C}^{\text{---}}\text{N} + \nu\text{C}^{\text{---}}\text{S}$;
 Band IV = $\nu\text{C}^{\text{---}}\text{S}$

Table 3. Antibacterial activity of ligand and Ruthenium (III) complexes

Ligand/Complex	Diameter of inhibition zones (mm)								
	Escherichia coli			S. aureus			B. Subtilis		
	0.25%	0.5%	1%	0.25%	0.5%	1%	0.25%	0.5%	1%
Ligand (LH)	-	-	6	6	7	10	-	5	7
[RuCl ₂ (Pφ ₃) ₂ L]	6	8	8	9	11	12	7	8	10
[RuCl ₂ (Asφ ₃) ₂ L]	8	10	11	11	13	15	10	11	13
[RuBr ₂ (Pφ ₃) ₂ L]	8	10	12	NT	NT	NT	10	13	15
[RuBr ₂ (Asφ ₃) ₂ L]	8	11	12	10	12	14	10	13	14
[RuBr(Pφ ₃)L ₂]	7	9	12	NT	NT	NT	12	13	15
[Ru(NCS) ₂ (Pφ ₃)L]	7	9	11	8	10	12	10	13	14
Streptomycin (stand.)	23	24	30	22	23	29	25	28	30

NT = not tested; (-) inactive

Antibacterial Activity:

The antibacterial activities of the ligand and complexes were determined by disc diffusion method²⁵ using microbials namely *Escherichia coli*, *S. aureus* and *B. subtilis*. The bacteria were cultured in nutrient agar medium in petri plate and used inoculums for the study. The complexes to be tested were dissolved in DMSO to a final concentration of 0.25%, 0.50% and 1% and soaked in filter paper disc of 5 mm diameter and 1 mm thickness and incubated at 35°C for 24 h. The diameter of inhibitory zone around each disc were measured. Streptomycin was used as standard. The results are given in table 3.

The toxicity of complexes increases on increasing the concentration²⁶⁻²⁸ and all complexes have lower activity than streptomycin but higher than ligand. The higher activity of complexes than ligand may be due

to chelation.

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