Ultra Chemistry Vol. 10(1), 31-34 (2014).

Synthesis, Characterization and Biochemical studies of some organoruthenium (II) complexes with mixed ligands

R.N. SHARMA, SANJAY SINGH, TAPAN KUMAR[a] and SHREYA MEMON[a]

Department of Chemistry, K.N. Govt. P.G. College, Gyanpur,
S.R.N. Bhadohi (221304) UP (INDIA)
[a]Department of Biotechnology, Manipal Institute of Technology
Manipal (Karnatka) (INDIA)
Email: drramnaresh sharma @ gmail com.

(Acceptance Date 9th February, 2014)

Abstract

Fairly air stable organoruthenium (II) complexes having spectral formula $[RuH(CS)(P\phi_3)_n(APMTH)_n^{I}(Py)_n^{II}Cl]$ (where n=3,2,1,1; n^{I}= 0,1,2,1 and n^{II}=0,0,0, 1 respectively) have been prepared and characterized using various physico-chemical methods. All these complexes are found to be non-electrolytic and diamagnetic in nature. The ligand and its metal complexes are screened for their antifungal activities against A. niger and these may be classified as mixed antifungal agents.

Introduction

Synthesis and characterization of ruthenium complexes have been received considerable attention owing to their interesting photo physical and photo chemical properties related to many biological systems[1-3]. They provide interesting insights into bonding, structure and reactivity of molecules[4]. So, we are reporting here the synthesis, characterization and biological studies of the products obtained by reaction of 4-amino -3 propyl -5 mercapto -S-triazine with $[RuH(CS)((P\phi_3)_3Cl)]$.

Experimental

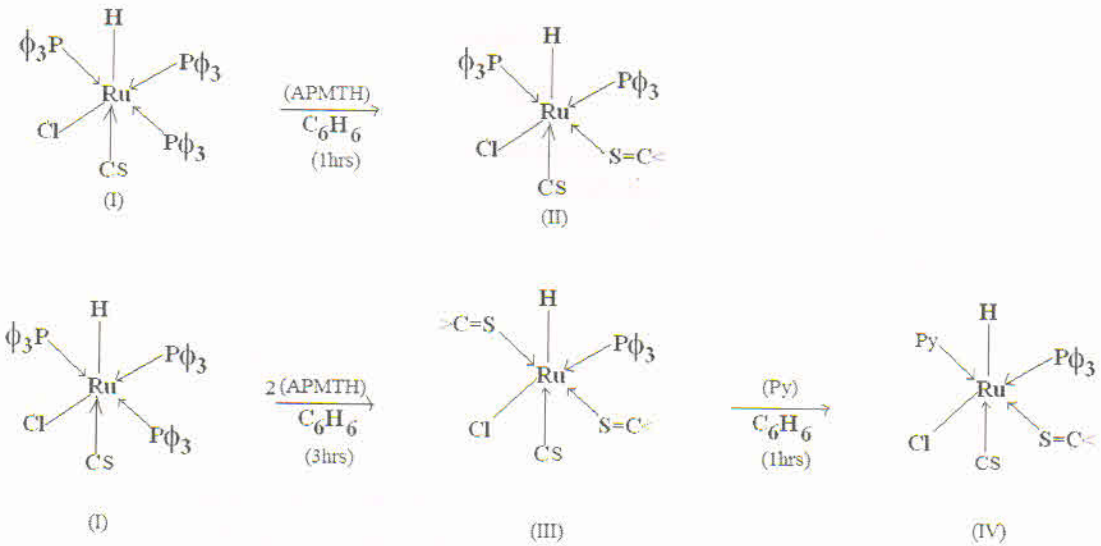
All the chemicals used were of AR or CP grade. Solvents were distilled and dried before use. The complex $[RuH(CS)(P\phi_3)_3Cl]$ was prepared by the method of Agarwala *et. al*[5]. The ligand 4-amino-3 propyl 5-mercapto-S- triazine (APMTH) was prepared by the slightly modified method described in literature[6]. A solution of ligand in dry benzene was added slowly to a continuously stirred solution of $[RuH(CS)(P\phi_3)_3Cl]$ in benzene in ann appropriate ratio. The mixture was refluxed about one to three hours and then allowed to cool in an ice-bath. The compound obtained with different metal ligand ratio were washed with ice-cold benzene and dried under reduced pressure. 10 ml pyridine was mixed in third compound filtrate and refluxed for about one

hour and ice cooled to get pyridyl derivative of complex.

Carbon, hydrogen and nitrogen analysis, infrared and electronic spectra were recorded at CDRI, Lucknow. Magnetic measurements were made by Gouy balance at room temperature (300K). Calibration was done using $Hg[Co(NCS)_4]$ as standard. Analytical and physical data of complexes are given in table 1.

Results and Discussion

The molecular complexes with the general formulation $[RuH(CS)(P\phi_3)_3Cl]$ could easily be prepared in qualitative yield by replacement reaction as shown below:



Single replacement of ϕ_3 occured in generally one hour but further replacement occurs under more vigorous conditions by increasing the time of refluxing to 3 hrs. Bonded hydride ion, chlorine atom and thio carbonyl groups are not replaced. The CS and $P\phi_3$ groups have large trans effect and, the two replaced $P\phi_3$ molecules must have been present in the trans position. This has been found true experimentaly in the present case. All complexes formed quantitatively.

All products obtained after substitution reactions are non-conducting in DMF and diamagnetic, indicating spin pairing in d^6 electronic configuration for Ru(II). So these complexes have similar configuration as the parent compound. Electronic spectra of all, are almost identical with two medium bands at 570-580 and 370-390 nm are assigned to $^1A_{1g} \rightarrow {}^1T_{1g}$ & $^1A_{1g} \rightarrow {}^1T_{2g}$ respectively having octahedral configuration[7]. The band in the region of 255 - 270 nm is assigned as $n \rightarrow \pi^*$ transition.

The I.R. spectrum of $P\Phi_3$ has been interpreted by Deacon and Green[8]. The ligand

Table 1. Analytical, Spectral and Biochemical Activity data of Complexes

S. N.	Compound colour/mp(°C)	Elemental Analysis (cal/exp.)				I. R. Band Position			Antifungal Data (%) Transmittance		
		C	H	N	Ru	νNH	νSH	Tab IV	10	100	1000
1.	APMTH Dirty white	46.12 45.73	7.68 7.09	21.52 21.11	---	3220mb 3110 s 3040 mb	i450 wb	780m	+	+	++
2.	[RuH(CS)($P\Phi_3$)$_3$Cl] Brown (100 °C)	68.16 67.59	4.75 4.51	---	10.50 9.79	---	---	-	+	+	+
3.	[RuH(CS)($P\Phi_3$)$_2$ (APMTH)Cl] Brown (75 °C)	58.30 58.11	4.74 4.67	6.47 5.49	11.76 11.02	3240 mb 3180 s 3050 s		730	+	++	++
4.	[RuH(CS)($P\Phi_3$) (APMTH)^{2}Cl] Pink (92°C)	45.75 45.21	4.73 4.39	14.72 14.62	13.37 12.88	3220 mb 3110 s 3040 m	-	735	+	++	+
5.	(RuH(CS)($P\Phi_3$) (APMTH)(Py)(Cl)] Brown (85 °C)	51.07 50.32	4.54 4.01	10.27 10.01	14.92 13.15	3230 mb 3110 s 3040 m	-	735	+	++	+++

% Transmission: (-) – 1-25, (+) = 26-50, (++) = 51-75, (+++)= 76-100,(++++)>100

(APMTH) contain thio amide moiety (H-N-C=S) give four characteristic bands in i.r. spectra[9-10]. The thio amide band (TAB) I (at 1570 cm^{-1}), II (at 1385 cm^{-1}) and III (at 1035cm^{-1}) of ligand are blue shifted or identical but band IV (at 780cm^{-1}) are red shifted (~30-50cm^{-1}) after complexation showed absence of bonding through imino nitrogen and involvement of thio sulphur atom in coordination[11-12]. These are supported by the blue shifting of νNH band observed at (3220, 3110, 3040) cm^{-1} and disappearance of νSH band of ligand at 2450 cm^{-1} [13-14]. A very strong band at 1360 cm^{-1} in thio carbonyl complexes indicates the presence of terminal coordinated thiocarbonyl[15]. No such band is present in the spectrum of APMTH and other complexes. The medium intence band at (2010-1950) and 710 cm^{-1} in all complexes are assigned[16-17] to νRuH and δ Ru-H. The non- ligand bands at 1635(w), 1390 (w), 970(w), 915 (w), 720(w), 540(w) and 510(w) are assigned as $\nu P\Phi_3$ in all complexes[18]. In plane ring deformation and out of ring deformation bands of pyridine[19] is observed at 604 and 405 cm^{-1} in [RuH(CS) (APMTH)($P\Phi_3$)(Py)Cl]. Far infrared spectra of all complexes display νRuCl stretching mode[20] at 470 cm^{-1}, νRuS[21] at 320 cm^{-1} and νRu–P[22] at 480 cm^{-1} suggesting the involvement of sulphur, phosphorus and chlorine atom in bonding.

Anti biological activities :

All complexes, ligand and reference compound (Salicylic Acid) were screened against A. niger, a typical fungus at 1000, 100, 10 ppm concentration using cup plate method[23]. The results are given in table 1. It is very clear that almost all complexes showed significant antifungal activities. [RuH(CS)(APMTH)

$(P\Phi_3)(Py)Cl]$ showed 79% activity against A.niger. All these may be classified as mixed fungicides.

On the basis of normal co-ordinate analysis, tentative octahedral structures have been suggested for all Ru(II) organometallic compounds.

References

1. A. Singh, A.N. Sahay, D.S. Pandey, M.C. Pureta and P. Valerga; *J. Organometallic Chem.*, 605, 74 (2000).
2. F. Bargiletti and L. Flamigni; *Chem. Soc. Rev.*, 29, 1 (2000).
3. V. Balzani, A. Jursi, M. Venturi, S. Campagan and S. Serroni; *Chem. Rev. 96,* 96 (1996).
4. M. Chandra, A.N.Sahay D.S. Pandey, M.C. Pureta and P. Valerga; J. *Organometallic Chem.*, 648, 39 (2002).
5. R.K. Podar and U. Agarwala; *Indian J. Chem.*, 9, 477 (1977).
6. K.S. Dhaka, J. Mohan, V.K. Chada and H.K. Pujari; *Indian J. Chem., 12,* 288 (1974).
7. T. Singh and J.P. Singh; *J. Indian Chem. Soc.*, 69, 158 (1992).
8. G.B. Deacon and J.H.S. Green; *Spectrochim. Acta, 24A,* 845 (1968).
9. R.N. Sharma and R.N. Pandey; *J. Ultra, Chem.* 392 (2011).
10. U. Agarwala and B. Singh; *Inorg. Chem.* 8, 2341 (1969).
11. Bhaskra N. and Mishra, R.K. Verma and R.N. Sharma, *Asian, J. Chem., 21,* 777 (2009).
12. C.N.R. Rao, R. Vankataraghavan and T.R. Kasturi; *Cand. J.Chem., 42,* 36 (1964).
13. Richa Sharma, D.K. Sharma and R.N. Pandey; *J. Ultra Chem., 7,* 329 (2011).
14. R.N. Pandey and R.N. Sharma; *Oriental J. Chem.*, 21, 580 (2005).
15. J.D. Gilbert, M.C. Bairde and G. Wilkinson *J. Chem Soc.*, A, 2198 (1968).
16. O.S. Sisodiya, A.N. Sahay and D.S. Pandey, *Indian J. Chem.*, 39A, 453 (2000).
17. R.N. Pandey and K.V. Gautam; *Asian J. Chem., 23,* 2785 (2011).
18. G.B. Deacon and J.H.S. Green; *Spectrochim. Acta.*, A 24, 845 (1968).
19. R.J.H. Clark and C. S. Williams; *Inorg. Chem.*, 4, 350 (1965).
20. R.N. Sharma and R.N. Pandey, *Oriental J. Chem., 20,* 186 (2004).
21. K.H. Smith and A. Muller, *Coord. Chem. Rev.*, 19, 41 (1976).
22. M.L. Druce and F.G.A. Stone; *J. Chem. Soc.*, A, 1238 (1967).
23. Pradip V. Tekada, K.N. Patil, P.S. Bodkhe and D.V. Hande, *Acta Ciencia India., 35,* 264 (2009).