Preparation and Characterization of Ruthenium(II) Porphyrins

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Abstract

The ruthenium complex Ru(TPP)(CO)(EtOH) is prepared by the reaction of $RuCl_3 \cdot 3H_2O$ with HCHO in the presence of H_2TPP. This complex reacts with NOCl, NOBr, $AsPh_3$, $P(OPh)_3$ and $P(OEt)_3$ to afford the complexes Ru(TPP)(NO)X (X = Cl, Br) and Ru(TPP)L_2 (L = $AsPh_3$, $P(OPh)_3$, $P(OEt)_3$). CS_2 reacts with Ru(TPP)(CO)(EtOH) to give Ru(TPP)(CO)(CS). These complexes have been characterized by elemental analysis and spectral studies.

Introduction

The reaction, structure and bonding of small molecules like NO, O_2 and CO with metalloporphyrins and their relationship to the corresponding hemoprotein complexes have been intensively investigated [1–11]. In recent years most interest has been given to the porphyrin complexes of platinum metals. The present work describes the synthesis and characterization of some interesting porphyrin complexes of ruthenium(II). The ruthenium complex Ru(TPP)(CO)(EtOH) was prepared previously either by reaction of the highly poisonous gas carbon monoxide with $RuCl_3 \cdot 3H_2O$ in the presence of H_2TPP [12] or by the reaction of the ruthenium carbonyl complex $Ru_3(CO)_{12}$ with H_2TPP [13–15]. The present work reports a very simple synthetic route for this complex and its reactions with NOCl, NOBr, $AsPh_3$, $P(OPh_3)_3$, $P(OEt)_3$ and CS_2. Reactions of Ru(TPP)(CO) with PPh_3, $P(OMe)_3$ and PEt_3 have been reported previously [16].

Experimental

All the reagents used were AnalaR or chemically pure grade. The solvents were dried by standard procedures and were freshly distilled and degassed before use. Every reaction was carried out under pure dry nitrogen atmosphere. H_2TPP (*meso*-tetraphenylporphyrin), NOCl and NOBr were prepared as previously described [17–19]. A formaldehyde 40 wt.% solution in water was used.

Carbon and hydrogen in the complexes were analysed by the microanalytical section of the Indian Institute of Technology, Kanpur and the Central Drug Research Institute, Lucknow. Infrared spectra of the samples were recorded with a Perkin-Elmer Model 580 spectrometer using KBr pellets. The proton NMR spectrum of Ru(TPP)(NO)Br was recorded in $CDCl_3$ using a Varian EM 360L spectrometer. The electronic spectra of the samples were recorded in CH_2Cl_2 with a Simadzu 160-spectrophotometer. The results are given in Tables 1 and 2.

Preparation of Ruthenium(II) Tetraphenylporphyrins

(a) (meso-Tetraphenylporphyrinato)carbonyl(ethanol)ruthenium(II), Ru(TPP)(CO)(EtOH)

To a solution of $RuCl_3 \cdot 3H_2O$ (1.0 g) in ethyl glycol (20 ml) formaldehyde solution (20 ml) was added and the resulting solution was refluxed until the colour of solution changed to pale yellow. It was reduced to 15 ml and was added dropwise over the course of 1 h to a hot, stirred solution of H_2(TPP) (1.0 g) in ethyl glycol (80 ml). The reaction was monitored by visible spectroscopy and heat was discontinued when the characteristic spectrum of H_2TPP was no longer evident. The reaction was completed in 30 h. It was filtered and distilled water (200 ml) was added to the filtrate. A brown precipitate separated out, which was filtered, washed with water and dried in vacuum.

The crude product was dissolved in dichloromethane (20 ml) and ethanol (80 ml). The solvent was reduced to 30 ml under reduced pressure. On cooling the reddish brown complex Ru(TPP)(CO)(EtOH) separated out, was filtered, washed several times with n-hexane and dried in vacuum (yield 0.9 g, 70%).

(b) Chloro-nitrosyl(meso-tetraphenylporphyrinato)ruthenium(II), Ru(TPP)(NO)Cl

A saturated solution of NOCl (10 ml) in benzene was added to a stirred solution of Ru(TPP)(CO)(EtOH) 0.05 g in benzene (10 ml). The reaction mixture was stirred for 2 h and reduced to 5 ml

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TABLE 1. Analytical data of the metalloporphyrin complexes

Complexes	Melting point (°C)	Elemental analysis (calc.)found (%)				
		C	N	H	Cl/Br	S
Ru(TPP)(CO)(EtOH)	>300	(71.65)	(7.11)	(4.30)		
		71.7	7.1	4.4		
Ru(TPP)(NO)Cl	>300	(67.82)	(8.99)	(3.62)	(4.55)	
		68.0	9.0	3.6	4.6	
Ru(TPP)(NO)Br	>300	(64.16)	(8.50)	(3.42)	(9.70)	
		64.2	8.6	3.6	9.9	
$\mathrm{Ru(TPP)(AsPh_3)_2}$	>300	(72.43)	(4.22)	(4.40)		
		72.6	4.3	4.6		
$\mathrm{Ru(TPP)[P(OPh)_3]_2}$	>300	(72.01)	(4.19)	(4.37)		
		72.1	4.3	4.5		
$\mathrm{Ru(TPP)[P(OEt)_3]_2}$	>300	(64.30)	(5.35)	(5.58)		
		64.4	5.2	5.5		
Ru(TPP)(CO)(CS)	>300	(70.31)	(7.10)	(3.59)		(4.08)
		70.4	7.2	3.6		4.2

TABLE 2. Electronic spectral data and important IR frequencies

Complexes	UV–Vis			IR ($\mathrm{cm^{-1}}$)
	Solvent	λ_{max} (nm)	ϵ_{max} ($\mathrm{M^{-1}\ cm^{-1}}$)	
Ru(TPP)(CO)(EtOH)	$\mathrm{CH_2Cl_2}$	408	1.0×10^5	ν(CO) = 1953
		530	9.7×10^4	
Ru(TPP)(NO)Br	$\mathrm{CH_2Cl_2}$	438	1.0×10^5	ν(NO) = 1884
		590	1.0×10^4	
		655	6.6×10^3	
Ru(TPP)(NO)Cl	$\mathrm{CH_2Cl_2}$	440	1.0×10^5	ν(NO) = 1880
		550	1.0×10^4	
		587	1.0×10^4	
		651	7.0×10^3	
$\mathrm{Ru(TPP)(AsPh_3)_2}$	$\mathrm{CH_2Cl_2}$	410	9.5×10^4	
		530	2.9×10^4	
$\mathrm{Ru(TPP)[P(OPh)_3]_2}$	$\mathrm{CH_2Cl_2}$	404	1.1×10^5	
		420	1.1×10^5	
$\mathrm{Ru(TPP)[P(OEt)_3]_2}$	$\mathrm{CH_2Cl_2}$	405	1.2×10^5	
		425	1.4×10^5	
		527	5.1×10^4	
Ru(TPP)(CO)(CS)	$\mathrm{CH_2Cl_2}$	406	1.4×10^5	ν(CO) = 1955
		529	3.3×10^4	ν(CS) = 1385

under reduced pressure. On addition of n-hexane (25 ml) the greenish brown complex Ru(TPP)(NO)Cl separated out, which was centrifuged, washed with n-hexane and dried in vacuum (yield 0.04 g, 81%).

(c) Bromo-nitrosyl(meso-tetraphenylporphyrinato)ruthenium(II), Ru(TPP)(NO)Br

A solution of NOBr (0.8 mmol) in benzene was added to a stirred solution of Ru(TPP)(CO)(EtOH) (0.05 g) in benzene (10 ml) and the greenish brown complex Ru(TPP)(NO)Br was isolated by a procedure similar to that given in (b), yield 0.038 g, 73%.

(d) (meso-Tetraphenylporphyrinato)bis(triphenylarsine)ruthenium(II), Ru(TPP)(AsPh$_3$)$_2$

Ru(TPP)(CO)(EtOH) (0.05 g) and triphenylarsine (0.1 g) were dissolved in dichloromethane (30 ml). The reaction mixture was stirred for 4 h and reduced to 5 ml. On addition of methanol (30 ml), the brownish violet complex Ru(TPP)(AsPh$_3$)$_2$ separated out, which was centrifuged, washed with methanol and dried under vacuum (yield 0.055 g, 65%).

(e) (meso-Tetraphenylporphyrinato)bis(triphenylphosphite)ruthenium(II), Ru(TPP)[P(OPh)$_3$]$_2$

Triphenylphosphite (0.5 ml) was added to a stirred solution of Ru(TPP)(CO)(EtOH) (0.05 g) in dichloromethane (30 ml). The reaction mixture was stirred for 5 h and the violet complex Ru(TPP)[P(OPh)$_3$]$_2$ was isolated by a procedure similar to that given in (d), yield 0.06 g, 71%.

(f) (meso-tetraphenylporphyrinato)bis(triethylphosphite)ruthenium(II), Ru(TPP)[P(OEt)$_3$]$_2$

Triethylphosphite (0.5 ml) was added to a stirred solution of Ru(TPP)(CO)(EtOH) (0.05 g) in dichloromethane (30 ml). The reaction mixture was stirred for 5 h. The brownish violet complex Ru(TPP)[P(OEt)$_3$]$_2$ was isolated by a procedure similar to that given in (d), yield 0.048 g, 72%.

(g) Thiocarbonyl-carbonyl(meso-tetraphenylporphyrinato)ruthenium(II), Ru(TPP)(CO)(CS)

Carbon disulphide (4 ml) was added to a solution of Ru(TPP)(CO)(EtOH) (0.1 g) in benzene (20 ml). The reaction mixture was refluxed for 2 h and reduced to 5 ml under reduced pressure. On addition of n-hexane (30 ml), the brown complex Ru(TPP)(CO)(CS) separated out, was centrifuged, washed with n-hexane and dried under vacuum (yield 0.09 g, 90%).

Results and Discussion

The insertion of ruthenium in the free-base porphyrin H$_2$(TPP) was carried out by slow addition of ruthenium carbonyl, which had been prepared by refluxing a solution of hydrated ruthenium trichloride in ethyl glycol in the presence of formaldehyde solution, to the solution of H$_2$(TPP) in the same solvent. The complex Ru(TPP)(CO)(EtOH) was isolated by recrystallization of the above crude product in CH$_2$Cl$_2$–EtOH (1:4). This complex exhibits a band in the visible spectrum at 530 nm and IR absorption band at 1953 cm^{-1} due to ν(CO) (lit. value: λ_{max} 532 nm, ν(CO) 1948 cm^{-1}) [12].

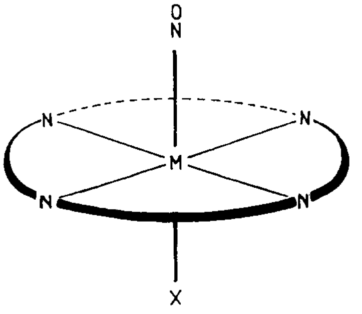

Fig. 1. Structure of Ru(TPP)(NO)X (X = Cl, Br).

Ru(TPP)(CO)(EtOH) reacts with nitrosyl halides NOX (X = Cl, Br) to give nitrosyl complexes of the type Ru(TPP)(NO)X (Fig. 1).

$$\mathrm{Ru(TPP)(CO)EtOH) + NOX} \xrightarrow{\text{benzene}} \mathrm{(Ru(TPP)(NO)X} + \ldots$$

These nitrosyl complexes are stable in air. Infrared spectra of Ru(TPP)(NO)X (X = Cl, Br) show absorption bands due to ν(NO) at 1880 and 1884 cm^{-1}, respectively besides the characteristic bands of tegraphenylphorphyrin ligand. The ^{1}H NMR (CDCl$_3$, 60 MH$_z$) spectrum of Ru(TPP)(NO)Br reveals δ, H 8.73(s); H$_o$ 8.10(m); H$_m$, H$_p$ 7.78(m). The corrected stretching frequencies of NO calculated according to Ibers' rules [20] fall above 1610 cm^{-1}. This is evidence for the presence of a linear nitrosyl (Ru–N–O) group in these complexes.

Ru(TPP)(CO)(EtOH) reacts with AsPh$_3$, P(OPh)$_3$ and P(OEt)$_3$ leading to complete substitution of the carbonyl in the axial position.

$$\mathrm{Ru(TPP)(CO)(EtOH)} + \mathrm{L} \longrightarrow \mathrm{Ru(TPP)L_2} + \ldots$$

The IR spectra of these complexes Ru(TPP)(AsPh$_3$)$_2$, Ru(TPP)[P(OPh)$_3$]$_2$ and Ru(TPP)[P(OEt)$_3$]$_2$ shows absorption bands due to L (L = AsPh$_3$, P(OPh)$_3$, P(OEt)$_3$) in addition to bands due to the coordinated tetraphenylporphyrin ligand.

The reaction of carbon disulphide (CS$_2$) with Ru(TPP)(CO)(EtOH) gives carbonylthiocarbonyl complex Ru(TPP)(CO)(CS). The IR spectrum of Ru(TPP)(CO)(CS) exhibits absorption bands at 1955 cm^{-1} due to ν(CO) and at 1385 cm^{-1} due to ν(CS).

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