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SYNTHESIS AND SPECTRAL STUDIES OF METALLOPORPHYRINS OF IRON, COBALT, COPPER AND RHODIUM WITH CARBON, NITROGEN AND SULPHUR DONOR LIGANDS

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Abstract—[Rh(TPP)Cl] (TPP = *meso*-tetraphenylporphyrin) was prepared by reaction of [$RhCl_3 \cdot 3H_2O$] with HCHO in the presence of H_2TPP. Reaction of this complex with COS yielded [Rh(TPP)(CO)Cl]. $S_3N_3Cl_3$ reacted with [Fe(TPP)Cl] in THF in the presence of iron powder to give the air-sensitive complex [Fe(TPP)(NS)]. Reaction of $SOCl_2$ with [Fe(TPP)Cl] in the presence of zinc dust yielded [Fe(TPP)(SO_2)]. [Cu(TPP)(COS)] was prepared by interaction of COS with [Cu(TPP)]. Reaction of the blue solution of S_7NH with [M(TPP)] (M = Cu, Co) and [Co(TNPP)] (TNPP = *meso*-tetrakis(2-nitrophenyl)porphyrin) yielded [Cu(TPP)(S_3N)], [Co(TPP)(S_3N)] and [Co(TNPP)(S_3N)] complexes. Reaction of C_5H_6 with [Fe(TPP)Cl] in the presence of zinc dust yielded [Fe(TPP)(C_5H_5)], which reacted with NO to afford [Fe(TPP)(C_5H_5)(NO)]. These complexes have been characterized by elemental analysis, IR and electronic spectroscopy.

The reactions of the diatomic molecules O_2, NO and CO with metalloporphyrins and their relationship to the corresponding haemoprotein complexes have been intensively investigated.[1–8] Synthesis, structure and bonding of the transition metal complexes with ligands such as NS,[9–13] NSO,[14–16] NSO_2,[17] NS_2,[18] NS_3[19–25] and COS[26,27] have been a subject of much current interest. However, the complexes of metalloporphyrins with these ligands have not yet been described. We have recently reported for the first time the synthesis and characterization of a disulphidothionitrato(tetraphenylporphyrinato)iron(III) complex.[21] Herein we wish to report reactions of S_7NH, $S_3N_3Cl_3$, COS, $SOCl_2$, NO and C_5H_6, in the presence of zinc, with metalloporphyrins. A simple synthetic route for [Rh(TPP)Cl] by reaction of [$RhCl_3 \cdot 3H_2O$] with HCHO in the presence of H_2TPP has also been reported.

EXPERIMENTAL

All the reagents used were AnalaR or of chemically pure grade. The solvents were dried by standard procedures and were freshly distilled and degassed before use. Every reaction was carried out under dry nitrogen. H_2(TPP), H_2(TNPP), [Co(TPP)], [Cu(TPP)], S_7NH, $S_3N_3Cl_3$, COS and NO were prepared as previously described.[28–35]

The analyses for sulphur and chloride in the complexes were carried out by using standard methods.[36,37] Carbon and hydrogen in the complexes were analysed by the microanalytical section of the Central Drug Research Institute, Lucknow and the Indian Institute of Technology, Kanpur. The results are reported in Table 1. The IR spectra of samples were recorded with a Perkin–Elmer Model 580 spectrometer using KBr pellets. The electronic spectra of the samples were recorded with a Varian 634S and Simadzu-160 spectrophotometer. Important IR frequencies and the electronic data of the complexes are given in Table 2.

(a) *Chloro*(meso-*tetraphenylporphyrinato*)*rhodium* (III), [Rh(TPP)(Cl)]

To a solution of [$RhCl_3 \cdot 3H_2O$] (0.2 g, 0.76 mmol) in ethylene glycol (20 cm^3), formaldehyde (10 cm^3) was added and the resulting solution was refluxed until the colour of solution changed to pale yellow.

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Table 1. Analytical data of the metalloporphyrin complexes

Compound	Melting point (°C)	Elemental analysis (%) calculated (found)				
		C	N	H	Cl	S
[Rh(TPP)Cl]	> 300	70.4	7.5	3.6	4.9	—
		(70.3)	(7.4)	(3.7)	(4.7)	
[Rh(TPP)(CO)Cl]	> 300	69.3	7.3	3.7	4.7	—
		(69.4)	(7.2)	(3.6)	(4.5)	—
[Fe(TPP)(NS)]	> 300	73.8	9.7	3.8	—	4.7
		(74.0)	(9.8)	(3.9)	—	(4.5)
[Fe(TPP)(SO_2)]	> 300	72.0	7.8	3.6	—	4.5
		(72.1)	(7.7)	(3.8)	—	(4.4)
[Co(TPP)(S_3N)]	> 300	67.4	8.8	3.5	—	12.5
		(67.6)	(9.0)	(3.6)	—	(12.3)
[Cu(TPP)(S_3N)]	> 300	67.4	8.8	3.4	—	12.3
		(67.2)	(8.9)	(3.6)	—	(12.2)
[Co(TNPP)(S_3N)]	> 300	55.0	12.8	2.3	—	10.2
		(54.9)	(13.0)	(2.5)	—	(10.0)
[Cu(TPP)(COS)]	> 300	73.3	7.5	3.6	—	4.4
		(73.4)	(7.6)	(3.8)		(4.3)
[Fe(TPP)(CO)]	> 300	77.5	8.1	4.1	—	—
		(77.6)	(8.0)	(4.0)		
[Fe(TPP)(C_5H_5)]	> 300	80.4	7.7	4.5		—
		(80.2)	(7.6)	(4.6)	—	—
[Fe(TPP)(C_5H_5)(NO)]	> 300	77.1	9.3	4.2	—	—
		(77.0)	(9.2)	(4.3)		

This was then reduced to 10 cm^3 and was added dropwise over the course of 30 min to a hot, stirred solution of H_2(TPP) (0.204 g, 0.33 mmol) in ethylene glycol (40 cm^3). It was then refluxed for 25 h. On addition of distilled water (100 cm^3), the brown complex [Rh(TPP)Cl] separated out. This was centrifuged, washed several times with water and dried *in vacuo* (yield: 0.14 g, 56%).

(b) *Chloro-carbonyl*(meso-*tetraphenylporphyrinato*) *rhodium*(III), [Rh(TPP)(CO)(Cl)]

To a solution of [Rh(TPP)Cl] (0.1 g, 0.13 mmol) in toluene (30 cm^3), COS was bubbled for 8 h. The solution was kept overnight, then reduced to 5 cm^3 under reduced pressure. On addition of *n*-hexane (30 cm^3), the [Rh(TPP)(CO)Cl] complex separated out. This was centrifuged, washed with *n*-hexane and dried *in vacuo* (yield: 0.09 g, 87%).

(c) *Thionitrosyl*(meso-*tetraphenylporphyrinato*) *iron*(I), [Fe(TPP)(NS)]

A solution of $S_3N_3Cl_3$ (0.04 g, 0.16 mmol) in 25 cm^3 of tetrahydrofuran (THF) was added to a stirred solution of [Fe(TPP)Cl] (0.30 g, 0.43 mmol) in the presence of iron powder (1.0 g) and the reaction mixture was stirred for 3 h. It was then filtered, evaporated to dryness under reduced pressure and extracted with 20 cm^3 of dichloromethane. On the addition of methanol (60 cm^3), the dark blue complex [Fe(TPP)NS] separated out, which was filtered, washed with methanol and dried *in vacuo* (yield: 0.18 g, 58%).

(d) *Sulphur-dioxide*(meso-*tetraphenylporphyrinato*) *iron*(II), [Fe(TPP)(SO_2)]

$SOCl_2$ (2 cm^3) was added to a solution of [Fe(TPP)Cl] (0.2 g, 0.28 mmol) in benzene (40 cm^3) and zinc dust (4.0 g) added. The reaction mixture was stirred for 5 h. It was then filtered and reduced to 5 cm^3 under reduced pressure. On addition of methanol (30 cm^3), a greenish violet complex [Fe(TPP)(SO_2)] separated out, which was centrifuged, washed with methanol and dried *in vacuo* (yield: 0.098 g, 47%).

(e) *Disulphidothionitrato*(meso-*tetraphenylporphyrinato*)*cobalt*(III), [Co(TPP)(S_3N)]

A blue solution of S_7NH (0.12 g, 0.5 mmol) in 5 cm^3 of dimethylformamide (DMF) was added to a stirred solution of [Co(TPP)] (0.33 g, 0.5 mmol) in DMF (15 cm^3). The reaction mixture was further stirred for 8 h. It was then filtered and concentrated

Table 2. Electronic spectral data and important IR frequencies

Compound	Solvents	UV–vis		IR
		λ_{max} (nm)	(ε_{max}) (M^{-1} cm^{-1})	(cm^{-1})
[Rh(TPP)(CO)Cl]	CH_2Cl_2	415	(1.8×10^5)	
		527	(3.2×10^4)	ν(CO) = 2055
[Fe(TPP)(NS)]	Benzene	410	(2.1×10^5)	
		500	(3.1×10^4)	ν(NS) = 1270
		530	(2.7×10^4)	
		565	(1.6×10^4)	
[Fe(TPP)(SO_2)]	Benzene	408	(9.0×10^4)	
		510	(2.8×10^4)	ν(SO_2) = 1080, 1235
		580	(1.0×10^4)	
[Cu(TPP)(COS)]	CH_2Cl_2	410	(1.0×10^5)	
		420	(9.8×10^4)	ν(COS) = 1712
		540	(3.5×10^4)	
		575	(1.6×10^4)	
[Co(TPP)(S_3N)]	Benzene	410	(9.0×10^4)	ν(NS) = 749, 725
		532	(1.6×10^4)	ν(S—S) = 620
[Cu(TPP)(S_3N)]	Benzene	412	(1.37×10^5)	ν(NS) = 938, 734, 720
		468	(1.4×10^4)	
		538	(3.5×10^4)	ν(S—S) = 595
		560	(2.8×10^4)	
		608	(7.0×10^3)	
[Co(TNPP)(S_3N)]	Benzene	420	(1.5×10^5)	ν(NS) = 940, 735
		522	(2.5×10^4)	
		553	(2.0×10^4)	ν(S—S) = 605
		598	(9.0×10^3)	
[Fe(TPP)(C_5H_5)]	Benzene	410	(1.1×10^5)	ν(C_5H_5) = 852, 1405
		570	(9.0×10^3)	
[Fe(TPP)(C_5H_5)(NO)]	Benzene	410	(9.6×10^4)	
		502	(1.0×10^4)	ν(NO) = 1705
		531	(6.4×10^3)	
		572	(8.3×10^3)	

to 5 cm^3 under reduced pressure. On addition of methanol (50 cm^3), a brownish violet complex [Co(TPP)S_3N] separated out, which was filtered, washed with methanol and dried *in vacuo*. It was recrystallized from CH_2Cl_2–CH_3OH (yield : 0.23 g, 60%).

(f) *Disulphidothionitrato*(meso-*tetraphenylporphyrinato*)*copper*(III), [Cu(TPP)(S_3N)]

A blue solution of S_7NH (0.12 g, 0.5 mmol) in 5 cm^3 of dimethylformamide (DMF) was added to a stirred solution of [Cu(TPP)] (0.34 g, 0.5 mmol) in DMF (15 cm^3). The reaction mixture was stirred for 8 h. The reddish violet complex [Cu(TPP)(S_3N)] was isolated by a procedure similar to that given in (e) (yield : 0.2 g, 51%).

(g) *Disulphidothionitrato*[meso-*tetrakis*(2-*nitrophenyl*)*porphyrinato*)]*cobalt*(III), [Co(TNPP)(S_3N)]

To a stirred solution of [Co(TNPP)] (0.212 g, 0.25 mmol) in DMF (15 cm^3), was added a blue solution of S_7NH (0.06 g, 0.25 mmol) in DMF (5 cm^3). The reaction mixture was stirred for 8 h and the brownish violet complex [Co(TNPP)(S_3N)] was isolated by a procedure similar to that given in (e) (yield : 0.124 g, 52%).

(h) *Carbonylsulphide*(meso-*tetraphenylporphyrinato*)*copper*(II), [Cu(TPP)(COS)]

To a solution of [Cu(TPP)] (0.1 g, 0.148 mmol) in toluene (30 cm^3), COS was bubbled for 10 h. It was kept for 50 h, then reduced to 5 cm^3 under reduced pressure. On addition of *n*-hexane, the pinkish brown complex [Cu(TPP)COS] separated out. This was centrifuged, washed with *n*-hexane and dried *in vacuo* (yield: 0.085 g, 78%).

(i) *Carbonyl*(meso-*tetraphenylporphyrinato*)*iron*(II), [Fe(TPP)(CO)]

To a solution of [Fe(TPP)] (0.1 g, 0.15 mmol) in benzene (30 cm^3), COS was bubbled for 8 h. It was kept for 2 days, then reduced to 5 cm^3 under reduced pressure. On addition of *n*-hexane (30 cm^3), the blue complex [Fe(TPP)(CO)] separated out. This was centrifuged, washed with *n*-hexane and dried *in vacuo* (yield: 0.09 g, 86%).

(j) *Cyclopentadienyl*(meso-*tetraphenylporphyrinato*) *iron*(III), [Fe(TPP)(C_5H_5)]

Freshly distilled monocyclopentadiene (C_5H_6) (1 cm^3) and zinc dust (1.0 g) were added to a stirred solution of [Fe(TPP)Cl] (0.2 g, 0.284 mmol) in benzene (50 cm^3). The reaction mixture was stirred for 5 h. It was then filtered and reduced to 5 cm^3 under reduced pressure. On addition of methanol (25 cm^3), the brown complex [Fe(TPP)(C_5H_5)] separated out. This was centrifuged, washed with methanol and dried *in vacuo*, and the product was recrystallized from dichloromethane and methanol (yield: 0.108 g, 52%).

(k) *Nitrosyl-cyclopentadienyl*(meso-*tetraphenylporphyrinato*)*iron*(II), [Fe(TPP)(NO)(C_5H_5)]

To a solution of [Fe(TPP)(C_5H_5)] (0.1 g, 0.136 mmol) in chloroform (20 cm^3), nitric oxide was bubbled for 30 min. It was reduced to 5 cm^3 under reduced pressure. On addition of methanol (50 cm^3), the brown complex [Fe(TPP)(NO)(C_5H_5)] separated out. This was centrifuged, washed with methanol and dried *in vacuo* (yield: 0.056 g, 54%).

RESULTS AND DISCUSSION

[Rh(TPP)Cl] was prepared by the interaction of the carbonyl complex of rhodium (prepared by refluxing formaldehyde with [$RhCl_3 \cdot 3H_2O$] in ethylene glycol) with H_2TPP. The IR spectrum of [Rh(TPP)Cl] is similar to that reported previously and prepared by other methods.[38] The reaction of COS with [Rh(TPP)Cl] resulted in the formation of [Rh(TPP)(CO)Cl]. The IR spectrum of this complex showed an absorption band at 2055 cm^{-1} due to the carbonyl stretching frequency.

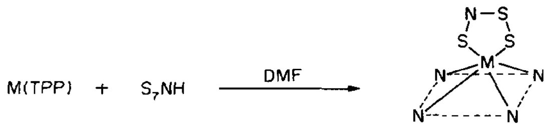
Reaction of a green solution of trithiazyl-trichloride in THF with Fe^{II}TPP, afforded [Fe^{III}(TPP)Cl]. When the same experiment was carried out in the presence of an excess of iron powder, the dark blue complex [Fe(TPP)(NS)], was isolated. The reaction system and the product [Fe(TPP)(NS)], are highly moisture-sensitive. From the six preparative experiments, only twice was the [Fe(TPP)(NS)] complex isolated.

$$\mathrm{Fe^{II}TPP} + (\mathrm{NSCl})_3 \xrightarrow{\mathrm{THF}} [\mathrm{Fe(TPP)(NS)}] + \cdots.$$

The IR spectrum of [Fe(TPP)(NS)] showed a peak at 1270 cm^{-1} due to the thionitrosyl stretching vibration, which is in the range of thionitrosyl stretching frequencies observed in linearly bonded thionitrosyl complexes.[13,39]

Reaction of $SOCl_2$ with [Fe(TPP)] in the presence of zinc dust in benzene resulted in the formation of a green complex, [Fe(TPP)(SO_2)]. A plausible mechanism involved the prior formation of sulphur monoxide which disproportionated to sulphur dioxide and sulphur, and the resulting sulphur dioxide coordinated to the metal centre,[40,41] The IR spectrum of [Fe(TPP)(SO_2)] showed absorption bands at 1235 and 1080 cm^{-1} due to the η'-planar (sp^2) coordinatd SO_2 group.[42]

Heptasulphurimide reacted with [M^{II}(P)] to afford the disulphidothionitrato complexes [M^{III}(P) (S_3N)].



M = Fe, Cu, CO P = TPP
M = Co P = TNPP.

The IR spectra of the complexes [Cu(TPP)(S_3N)], [Co(TPP)(S_3N)] and [Co(TNPP)(S_3N)] show absorption bands in the regions, 912–940 cm^{-1} and 720–749 cm^{-1} due to ν(NS) and 595–620 cm^{-1} due to ν(S—S), which are in close agreement with the values for the coordinated bidentate S_3N^- ligand.

Reaction of COS with [Cu(TPP)] at room temperature in toluene, yielded a pinkish brown complex [Cu(TPP)(COS)], in which COS was bonded to the metal through carbon and sulphur. This is supported by its IR spectrum which exhibited a band at 1712 cm^{-1}, the characteristic IR frequency of a bidentate COS group.[26] Reaction of COS with [Fe(TPP)] resulted in the formation of [Fe(TPP)(CO)], which in its IR spectrum showed an absorption band at 1972 cm^{-1} due to ν(CO) (cf. literature value, 1973 cm^{-1}).[43,44]

Monocyclopentadiene (C_5H_6) in the presence of zinc dust reacted with [Fe(TPP)] giving a brown complex [Fe(TPP)(C_5H_5)]. The IR spectrum of this complex exhibited absorption bands at 852, 875 and 1405 cm^{-1} due to the cyclopentadienyl ligand. NO reacted with [Fe(TPP)(C_5H_5)] to give the nitrosyl complex [Fe(TPP)(C_5H_5)(NO)]. The IR spectrum of this complex exhibited an absorption band at 1705 cm^{-1} due to the nitrosyl stretching frequency. The corrected stretching frequency (ν'(NO) 1655 cm^{-1}) of NO, calculated according to Ibers' rules,[45] falls above 1610 cm^{-1}. This is evidence for the presence of a linear nitrosyl group in this complex.

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