

Synthesis and Characterization of New O,O'-Bis(α -Naphthyl, β -Naphthyl and 2,3,5-Trimethylphenyl) Dithiophosphate of IRON (III and II)

Mukhtyar S. Saini^{1*}, Veer Singh¹, Aran Kumar¹ and Jaya Dwivedi²

¹Department of Chemistry, Govt. G. M. Science College, Jammu, Jammu & Kashmir, India

²Department of Chemistry, Banasthali University, Jaipur, Rajasthan, India

*Corresponding Author: mukhtyarsaini1969@gmail.com

Abstract: O,O'-Bis(α -naphthyl, β -naphthyl and 2,3,5-trimethylphenyl) Dithiophosphate complexes of Iron (III), (II) and Iron adducts corresponding to $[(RO)_2PS_2]_3M$, $[(RO)_2PS_2]_2M$, and $\{(RO)_2PS_2\}_2Fe(Et_3N)_2$ respectively, Where R = (α -naphthyl, β -naphthyl and 2,3,5-trimethylphenyl) and M = Iron (III), and Iron (II) have been synthesized by the reaction of sodium salts of O,O' α -naphthyl, β -naphthyl and 2,3,5-trimethylphenyl dithiophosphate with $FeCl_3$ and $FeCl_2$ in equimolar ratio 3:1 and 2:1 by refluxing into toluene results in the formation of the above complexes. The adducts were prepared by the reactions of $[(RO)_2PS_2]_2Fe$ and donor ligands (triethylamine) in 1:2 molar stoichiometry in THF under refluxing condition for 4-5 hours. These complexes have been characterized by elemental analysis, C, H, S, N, Fe and have been further characterized by some IR and NMR (^1H , ^{31}P and ^{13}C) spectroscopic studies which indicates bidentate linkages of dithiophosphate moieties leading to octahedral and square planar geometry around the Iron (Fe) atom.

Keywords: α -Naphthyl, β -Naphthyl, 2,3,5-Trimethylphenyl, Dithiophosphates, $FeCl_3$, $FeCl_2$, Triethylamine.

I. INTRODUCTION

Dithiophosphate ligands occupy an exceptional location as flexible chelating ligands [1-5]. These ligands are known to form a diversity of complexes with transition and non-transition elements [6-13]. In general, a bidentate nature of these ligands have been recognized [14-17]. Yet, they have also depicted other bonding modes e.g. monodentate [19], anisobidentate [20] and bridging [21].

Various dithiophosphate complexes finds wide-ranging applications in medicines [22], as catalyst in asymmetric synthesis [23], agriculture [24], sol-gel processing [25], anti-wear additive to gear and motor oils [26], as heat stabilizers for polymers [27], extraction [28] and analytical processes [29].

Keeping in sight the significance of iron to several biological [30-31] Iron-proteins are found in all living organisms, ranging from the evolutionarily primitive archaea to humans. The iron-sulfur clusters are pervasive and include nitrogenase, the enzymes responsible for biological nitrogen fixation.

Influential theories of evolution have invoked a role for iron sulfides in the iron-sulfur world theory. Iron-containing enzymes and proteins, often containing heme prosthetic groups, participate in many biological oxidations and in transport. Proteins found in higher organisms include hemoglobin, cytochrome and catalase and industrial processes.

Henry Bessemer invented a new steelmaking process, involving blowing air through molten pig iron, to produce mild steel. This made steel much more economical, thereby leading to wrought iron no longer being produced [32-36].

II. EXPERIMENTAL

A. General Procedures and Reagents

All the experimental work was carried out strictly under anhydrous conditions, nitrogen atmosphere and by means of modified Schlenk techniques. Triethylamine (Sd Fine Chem., b.p. 88.8 °C) was freshly distilled prior to use; chloroform and toluene were dried by refluxing over phosphorus pentoxide and sodium metal, respectively and kept under a nitrogen atmosphere. Naphth-1-ol, Naphth-2-ol (Sd Fine Chem.), 2,3,5-trimethylphenol (Aldrich), phosphorus pentasulfide (Merck), anhydrous $FeCl_3/FeCl_2$ (Sd Fine Chem. Ltd.) were procured commercially and were used as such. O,O'-Bis(α -naphthyl, β -naphthyl and 2,3,5-trimethylphenyl)dithiophosphate ligands $[(\alpha-C_{10}H_7O-, \beta-C_{10}H_7O-, \text{ and } (CH_3)_3C_6H_2O)_2PS_2H]$, $[(\alpha-C_{10}H_7O-, \beta-C_{10}H_7O-, \text{ and } (CH_3)_3C_6H_2O)_2PS_2HNEt_3]$, $[(\alpha-C_{10}H_7O-, \beta-C_{10}H_7O-, \text{ and } (CH_3)_3C_6H_2O)_2PS_2Na]$ and their complexes were prepared by literature methods [37-41] under anhydrous conditions.

Micro elemental analysis (C, H, N) was done on Vario EL III elemental analyzer while Sulfur was estimated as BaSO₄ (Messenger's method) and iron was estimated gravimetrically.

Molecular weights were determined cryscopically in freezing benzene. IR spectra were recorded in KBr mulls in the range 4000-200 cm⁻¹ on a Perkin Elmer = 377 spectrophotometer. The ¹H, ³¹P NMR and ¹³C spectra were recorded on a Bruker DRX 300 (120 MHz) spectrometer using TMS as the internal reference for ¹H NMR and 85% H₃PO₄ as an external reference for ³¹P NMR.

a) *Synthesis of compounds of types {(RO)₂PS₂}₃Fe (1-3), Where R = (α-naphthyl, β-naphthyl and 2,3,5-trimethylphenyl).*

• (I) *Synthesis of {(α-C₁₀H₇O)₂PS₂}₃Fe (1-3)*

For the synthesis of [(α-C₁₀H₇O)₂PS₂]₃Fe (1), (50 ml) methnolic solution of FeCl₃ (0.16 gm or 1.0 mmol) was taken in a 100 ml round bottom flask. To this solution, was added (~ 40 ml) methnolic solution of sodium salt of O,O'-Bis(α-naphthyl)dithiophosphate .[(α-C₁₀H₇O)₂PS₂Na] (1.2 g or 3.0 mmol) in a drop wise manner, through a dropping funnel.

After the complete addition of FeCl₃ solution, the reaction mixture was refluxed for 3 hours. Sodium chloride formed during the course of the reaction was filtered off through Sintered G4 glass disc and subsequently the excess of solvent was evaporated under reduced pressure.

Final drying of the product as black solids [((α-C₁₀H₇O)₂PS₂]₃Fe (1) and the product obtained in 85% yield. Similar methodology was applied for the synthesis of complexes (2-3).

b) *Synthesis of compounds of types {(RO)₂PS₂}₂Fe, Where R = (α-naphthyl, β-naphthyl and 2,3,5-trimethylphenyl).*

• (II) *Synthesis of {(α-C₁₀H₇O)₂PS₂}₂Fe (4-6)*

For the synthesis of [(α-C₁₀H₇O)₂PS₂]₂Fe (4), (~ 40 ml) methnolic solution of FeCl₂ (0.12g or 1.0 mmol) was taken in a 100 ml round bottom flask. To this solution, was added methnolic solution of sodium salt of O,O'-Bis(α-naphthyl)dithiophosphate .[(α-C₁₀H₇O)₂PS₂Na] (0.80 gm, 2.0 mmol) in a drop wise manner, through a dropping funnel and an immediate change in color was observed upon the addition of FeCl₂ solution. After the complete addition of FeCl₂ solution, the reaction mixture was refluxed for 3 hours. Sodium chloride formed during the course of the reaction was filtered off through Sintered G4 glass disc and subsequently the excess of solvent was evaporated under reduced pressure.

Final drying of the product as dark brown solids [((α-C₁₀H₇O)₂PS₂]₂Fe (4) and the product obtained in 85% yield. Similar methodology was applied for the synthesis of complexes (5-6).

c) *Synthesis of compounds of types {(RO)₂PS₂}₂Fe(Et₃N)₂ (7-9), Where R = (α-naphthyl, β-naphthyl and 2,3,5-trimethylphenyl).*

The new adducts of O,O'-Bis(α-naphthyl, β-naphthyl and 2,3,5-trimethylphenyl) dithiophosphates of iron(II), which have characteristic N-Fe-S linkages has been formed by occupying the vacant coordinating sites of the iron (II) in the O,O'-(α-naphthyl)dithiophosphate complexes by donor ligands triethylamine.

Adduct (7) was prepared by the reaction of {(RO)₂PS₂}₂Fe (0.81 gm, 1 mmol) and donor ligands triethylamine (0.20 gm, 2 mmol) in 1:2 molar stiochiometry in THF under refluxing conditions for 4-5 hours These adducts obtained as red brown solids 85% in yield. Similar methodology was applied for the synthesis of adducts (8-9).

TABLE I: SYNTHETIC AND ANALYTICAL DATA OF Fe (III) AND Fe (II) O,O'-(α-NAPHTHYL, β-NAPHTHYL AND 2,3,5-TRIMETHYLPHENYL) DITHIOPHOSPHATES

Sr. No.	Ligand (g) mmol	Metal Salt (g), mmol/ NEt ₃	M/R	Product/M.Wt/(Color/m.p/ Yield %)	Analyses/Calc./(Found)				
					C	H	Fe	S	N
1	[(α-C ₁₀ H ₇ O) ₂ PS ₂ Na] 1.2 g, 3.0 mmol	FeCl ₃ 0.16 g, 1.0 mmol	3:1	[(α-C ₁₀ H ₇ O) ₂ PS ₂] ₃ Fe, 1200. black /195/83.3	60.0 59.8	3.5 3.2	4.6 4.5	16.0 15.9	—
2	[(β-C ₁₀ H ₇ O) ₂ PS ₂ Na] 1.2 g, 3.0 mmol	FeCl ₃ 0.16 g, 1.0 mmol	3:1	[(β-C ₁₀ H ₇ O) ₂ PS ₂] ₃ Fe, 1200./ black, /210/83	60.0 59.8	3.5 3.2	4.6 4.4	16.0 15.8	—
3	[((CH ₃) ₃ C ₆ H ₂ O) ₂ PS ₂ Na] 1.16 g, 3.0 mmol	FeCl ₃ 0.16 g, 1.0 mmol	3:1	[((CH ₃) ₃ C ₆ H ₂ O) ₂ PS ₂] ₃ Fe, 1152, /black/225/86.9	56.2 56.0	5.7 5.1	4.8 4.7	16.7 16.5	—
4	[(α-C ₁₀ H ₇ O) ₂ PS ₂ Na] 0.80 g, 2.0 mmol	FeCl ₂ 0.12 g, 1.0 mmol	2:1	[(α-C ₁₀ H ₇ O) ₂ PS ₂] ₂ Fe, 818.7, /dark brown/92.5	58.6 58.2	3.4 3.1	6.8 6.7	15.6 15.4	—

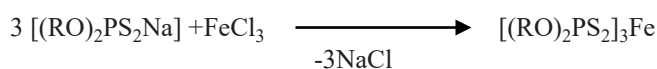
Sr. No.	Ligand (g) mmol	Metal Salt (g), mmol/ NEt ₃	M/R	Product/M.Wt/(Color/m.p/ Yield %)	Analyses/Calc./(Found)				
					C	H	Fe	S	N
5	[(β -C ₁₀ H ₇ O) ₂ PS ₂ Na] 0.80 g, 2.0 mmol	FeCl ₂ 0.12 g, 1.0 mmol	2:1	[(β -C ₁₀ H ₇ O) ₂ PS ₂] ₂ Fe, 818.7./dark brown/92.5	58.6 58.1	3.4 3.1	6.8 6.7	15.6 15.5	—
6	[((CH ₃) ₃ C ₆ H ₂ O) ₂ PS ₂ Na] 0.77 g, 2.0 mmol	FeCl ₂ 0.12 g, 1.0 mol	2:1	[((CH ₃) ₃ C ₆ H ₂ O) ₂ PS ₂] ₂ Fe, 786.8/ dark brown	54.9 54.2	5.6 5.2	7.0 6.9	16.3 16.1	—
7	[(α -C ₁₀ H ₇ O) ₂ PS ₂] ₂ Fe 0.81 g, 1 mmol	2Et ₃ N 0.20 g, 2 mol	1:2	[(α -C ₁₀ H ₇ O) ₂ PS ₂] ₂ Fe(Et ₃ N) ₂ , 989.19./red brown/8	61.1 60.8	5.7 5.2	5.4 5.3	12.5 12.3	2.7/ 2.4
8	[(β -C ₁₀ H ₇ O) ₂ PS ₂] ₂ Fe 0.81 g, 1 mmol	2Et ₃ N 0.20 g, 2 mmol	1:2	[(β -C ₁₀ H ₇ O) ₂ PS ₂] ₂ Fe(Et ₃ N) ₂ , 989.19./red brown/81.6	61.1 60.9	5.7 5.2	5.4 5.3	12.5 12.3	2.7/ 2.4
9	[((CH ₃) ₃ C ₆ H ₂ O) ₂ PS ₂] ₂ Fe 0.78 g, 1 mmol	2Et ₃ N 0.20 g, 2 mmol	1:2	[((CH ₃) ₃ C ₆ H ₂ O) ₂ PS ₂] ₂ Fe(Et ₃ N) ₂ , 986.8/red brown/86.7	58.2 58.0	7.5 7.2	5.6 5.4	12.9 12.7	2.8/ 2.5

III. RESULTS AND DISCUSSION

The reaction of sodium salts of O,O' α -naphthyl, β -naphthyl and 2,3,5-trimethylphenyl dithiophosphate with FeCl₃ and FeCl₂ in 3:1 and 2:1 stoichiometry by refluxing toluene results in the formation of the [(RO)₂PS₂]₃Fe and [(RO)₂PS₂]₂Fe respectively. The adducts were prepared by the reactions of [(RO)₂PS₂]₂Fe and donor ligands (triethylamine) in 1:2 molar stoichiometry in THF under refluxing conditions for 4-5 hours and these reactions are as below:

Scheme 1.1.1

Methanol

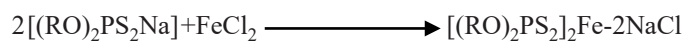


(1-3)

Where R = α -naphthyl, β -naphthyl and 2,3,5-trimethylphenyl.

Scheme 1.1.2

Methanol



(4-6)

Where R = α -naphthyl, β -naphthyl and 2,3,5-trimethylphenyl.

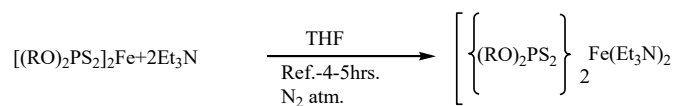
Synthesis of Triethylammonium Adducts (7-9)

The new adducts of O,O'-Bis(α -naphthyl, β -naphthyl and 2,3,5-trimethylphenyl) dithiophosphates of iron(II), which have characteristic N-Fe-S linkages has been formed by occupying the vacant coordinating sites of the iron (II) in the O,O'-(α -naphthyl, β -naphthyl and 2,3,5-trimethylphenyl) dithiophosphates complexes by donor ligands triethylamine.

Adduct (7) was prepared by the reaction of [(RO)₂PS₂]₂Fe and donor ligands (triethylamine) in 1:2 molar stoichiometry in THF

under refluxing condition for 4-5 hours. Similar methodology was applied for the synthesis of adducts (8-9). These adducts obtained as red brown solids 85% in yield.

Scheme 1.1.3



R = α -naphthyl, β -naphthyl and 2,3,5-trimethylphenyl. [7-9]

These adducts obtained as red brown solids 85% in yield. While the complexes (1-3) were obtained as black solids and complexes (4-6) were dark brown solid. Elemental analysis (C, H, S, N, Fe) of these complexes were found with their composition (Table IV) these complexes are soluble in common organic solvents.

IR spectra of these complexes have been interpreted on comparative basis with the literature [42-44] and were recorded in the range 4000-200 cm⁻¹. The IR spectra of these complexes shows formation of a new sharp peak for ν Fe-S bond in the region 385-360 cm⁻¹ for compound (1-9) and a sharp peak for ν P=S and ν P-S was observed in the region 672-670 cm⁻¹ and 615-605 cm⁻¹ respectively for compounds (1-9). Peak for ν Fe-N were also found in 736-734 cm⁻¹ other peaks observed for these complexes (7-9) are given in the Table II.

In the ¹H NMR spectra, spectra was recorded in CDCl₃ a triplet and quartet were observed for -CH₃ and -CH₂ protons of Et₃N moiety in the compounds (7-9) at δ 1.27-1.28 (J = 7.2 Hz) and δ 3.09-3.11 respectively. The chemical shifts of -CH₃ (attached to benzene ring) for compounds (3, 6 and 9) was recorded at δ 2.23-2.24. A multiplet characteristic for ring protons were observed at δ 7.34-7.45 for compounds (1-9). The detailed ¹H NMR spectral data are given in Table III.

TABLE II: IR SPECTRAL DATA Fe (III) AND Fe (II) *O,O'*-(α -NAPHTHYL, β -NAPHTHYL AND 2,3,5-TRIMETHYLPHENYL) DITHIOPHOSPHATES (IN cm^{-1})

Sr. No.	Compound No.	Aromatic $\nu\text{C-H}$	$\nu(\text{P})\text{-O-C}$	$\nu\text{P-O-C}$	$\nu\text{P=S}$	$\nu\text{P-S}$	$\nu\text{Fe-S}$	$\nu\text{Fe-N}$
1	$[(\alpha\text{-C}_{10}\text{H}_7\text{O})_2\text{PS}_2]_3\text{Fe}$	2950	1154s	937s	671 m	614,m	370m	---
2	$[(\beta\text{-C}_{10}\text{H}_7\text{O})_2\text{PS}_2]_3\text{Fe}$	2950	1154s	937s	672 m	615,m	365m	---
3	$[((\text{CH}_3)_3\text{C}_6\text{H}_2\text{O})_2\text{PS}_2]_3\text{Fe}$	2945	1154s	937s	672 m	610,m	360m	---
4	$[(\alpha\text{-C}_{10}\text{H}_7\text{O})_2\text{PS}_2]_2\text{Fe}$	2947	1154s	937s	671 m	612,m	375m	---
5	$[(\beta\text{-C}_{10}\text{H}_7\text{O})_2\text{PS}_2]_2\text{Fe}$	2948	1152s	940s	671 m	605,m	385m	---
6	$[((\text{CH}_3)_3\text{C}_6\text{H}_2\text{O})_2\text{PS}_2]_2\text{Fe}$	2950	1152s	942s	670 m	612,m	380m	---
7	$[(\alpha\text{-C}_{10}\text{H}_7\text{O})_2\text{PS}_2]_2\text{Fe}(\text{Et}_3\text{N})_2$	2947	1153s	938s	670 m	610,m	365m	736s
8	$[(\beta\text{-C}_{10}\text{H}_7\text{O})_2\text{PS}_2]_2\text{Fe}(\text{Et}_3\text{N})_2$	2949	1151s	941s	671 m	615,m	375m	734s
9	$[((\text{CH}_3)_3\text{C}_6\text{H}_2\text{O})_2\text{PS}_2]_2\text{Fe}(\text{Et}_3\text{N})_2$	2950	1152s	942s	672 m	610,m	385m	735s

Where, s = strong, b = broad, m = medium

TABLE III: ^1H AND ^{31}P NMR SPECTRAL DATA Fe (III) AND Fe (II) *O,O'*-(α -NAPHTHYL, β -NAPHTHYL AND 2,3,5-TRIMETHYLPHENYL) DITHIOPHOSPHATES IN CDCl_3 (δ ppm)

Sr. No.	Compound	^1H NMR	^{31}P NMR
1	$[(\alpha\text{-C}_{10}\text{H}_7\text{O})_2\text{PS}_2]_3\text{Fe}$	7.35-7.44, m, 42H ($-\text{C}_{10}\text{H}_7$);	84.5s
2	$[(\beta\text{-C}_{10}\text{H}_7\text{O})_2\text{PS}_2]_3\text{Fe}$	7.36-7.45, m, 42H ($-\text{C}_{10}\text{H}_7$);	82.4s
3	$[((\text{CH}_3)_3\text{C}_6\text{H}_2\text{O})_2\text{PS}_2]_3\text{Fe}$	2.23, s, 54H ($-\text{CH}_3$); 7.36-7.45, m, 12H ($-\text{C}_6\text{H}_2$);	81.5s
4	$[(\alpha\text{-C}_{10}\text{H}_7\text{O})_2\text{PS}_2]_2\text{Fe}$	7.36-7.46, m, 28H ($-\text{C}_{10}\text{H}_7$);	85.5s
5	$[(\beta\text{-C}_{10}\text{H}_7\text{O})_2\text{PS}_2]_2\text{Fe}$	7.37-7.45, m, 28H ($-\text{C}_{10}\text{H}_7$);	84.6s
6	$[((\text{CH}_3)_3\text{C}_6\text{H}_2\text{O})_2\text{PS}_2]_2\text{Fe}$	2.23, s, 36H ($-\text{CH}_3$); 7.36-7.45, m, 8H ($-\text{C}_6\text{H}_2$)	83.6s
7	$[(\alpha\text{-C}_{10}\text{H}_7\text{O})_2\text{PS}_2]_2\text{Fe}(\text{Et}_3\text{N})_2$	7.36-7.46, m, 28H ($-\text{C}_{10}\text{H}_7$), 1.27,t, 18H($-\text{CH}_3$), 3.09,q, 12H, ($-\text{CH}_2$)	84.6s
8	$[(\beta\text{-C}_{10}\text{H}_7\text{O})_2\text{PS}_2]_2\text{Fe}(\text{Et}_3\text{N})_2$	7.35-7.46, m, 28H ($-\text{C}_{10}\text{H}_7$), 1.28,t, 18H($-\text{CH}_3$), 3.10,q, 12H, ($-\text{CH}_2$)	84.5s
9	$[((\text{CH}_3)_3\text{C}_6\text{H}_2\text{O})_2\text{PS}_2]_2\text{Fe}(\text{Et}_3\text{N})_2$	2.24, s, 36H ($-\text{CH}_3$); 7.344-7.45, t, 8H ($-\text{C}_6\text{H}_2$), 1.28,m, 18H($-\text{CH}_3$), 3.11,q, 12H, ($-\text{CH}_2$)	85.5s

Where s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet

^{31}P NMR Spectra have provided quite useful information for the compounds (1-9) shows a singlet at 85.5-81.5 ppm which shows symmetrical nature of the phosphorus nuclei and bidentate mode of binding for the newly synthesized ligand. The ^{31}P NMR spectral data of all these complexes are given in Table III.

^{13}C NMR Spectral

^{13}C NMR spectral analysis of compounds, however, chemical shifts were observed for each carbon atom in these complexes has been shown in (Table IV).

Structural Aspect of the Compounds

It is interesting to note that in ^{31}P spectra of complexes (1-9), shows a singlet in the range 85.5-81.5 ppm respectively which shows that ligand has behaved as bidentate. Therefore in conjunction with literature reports, an octahedral geometry may be suggested around iron atom in complexes (1-3) and (7-9) while square planar for (4-6). The bidentate behaviour of the ligands and octahedral structure around iron atom is further supported by IR spectra. Octahedral geometry is present around iron atom in which axial positions are occupied by Et_3N atoms and iron atom is d^2sp^3 hybridized. On the basis of literature survey [42] [45] and above spectral studies, the below type of the structure can be proposed for these three types of the complexes.

TABLE IV: ^{13}C NMR SPECTRAL DATA OF Fe (III) AND Fe (II) O,O'-(α -NAPHTHYL, β -NAPHTHYL AND 2,3,5-TRIMETHYLPHENYL) DITHIOPHOSPHATES IN CDCl_3 (δ ppm)

Sr. No.	Compound	C-O	CH ₃ (at C ₂)	CH ₃ (at C ₃)	CH ₃ (at C ₅)	Aromatic Carbons										Et ₃ NH	
						C2	C3	C4	C5	C6	C7	C8	C-9	C-10	-CH ₃	-CH ₂	
1	[(α-C ₁₀ H ₇ O) ₂ PS ₂] ₃ Fe	151.4	---	---	----	127	123.2	116	126.1	120	125.9	121.7	128.5	133.6	---	----	
2	[(β-C ₁₀ H ₇ O) ₂ PS ₂] ₃ Fe	151.2	---	---	---	128	123.4	117	126.3	120.5	125.7	121.5	128.1	133.9	---	----	
3	[((CH ₃) ₃ C ₆ H ₂ O) ₂ PS ₂] ₃ Fe	151.5	15.7m	17.5m	21.5m	125	123.1	119	126.5	120.3	----	----	----	----	---	----	
4	[(α-C ₁₀ H ₇ O) ₂ PS ₂] ₂ Fe	151.6	---	---	---	134	123.7	118	126.4	120.7	125.6	121.3	128.8	133.4	---	----	
5	[(β-C ₁₀ H ₇ O) ₂ PS ₂] ₂ Fe	151.7	---	---	---	131	123.6	121	126.2	120.4	125.3	121.6	128.4	133.8	---	----	
6	[((CH ₃) ₃ C ₆ H ₂ O) ₂ PS ₂] ₂ Fe	151.9	19.6m	20.5m	23.8m	126	123.2	121.5	126.6	120.6	----	----	----	----	---	----	
7	[(α-C ₁₀ H ₇ O) ₂ PS ₂] ₂ Fe(Et ₃ N) ₂	151.1	---	---	---	132	123.5	115.5	126.8	120.9	125.1	121.2	128.3	133.7	8.51,s	46.1,s	
8	[(β-C ₁₀ H ₇ O) ₂ PS ₂] ₂ Fe(Et ₃ N) ₂	151.8	---	---	---	133	123.9	116	126.7	120.8	125.8	121.4	128.6	133.5	8.52,s	46.2,s	
9	[((CH ₃) ₃ C ₆ H ₂ O) ₂ PS ₂] ₂ Fe(Et ₃ N) ₂	151.3	17.4m	22.5m	24.2m	124	123.8	121	126.9	120.2	--	---	--	--	8.53,s	46.2,s	

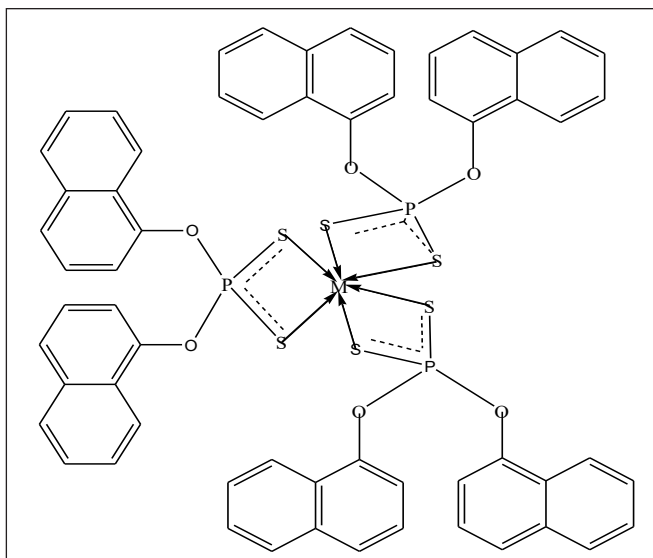


Fig. 1: Proposed Octahedral Geometry Around the Iron (III) in Complexes $[(\alpha\text{-C}_{10}\text{H}_7\text{O-})_2, (\beta\text{-C}_{10}\text{H}_7\text{O-})_2 \text{PS}_2]_3\text{Fe}$

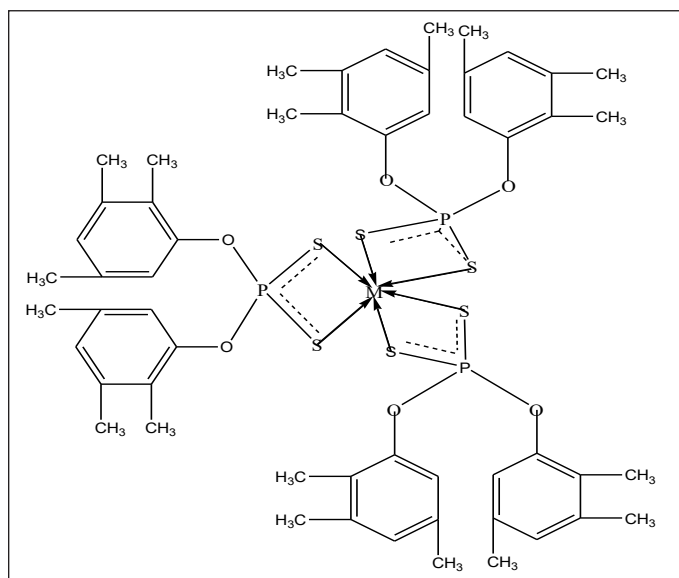


Fig. 2: Proposed Octahedral Geometry Around the Iron (III) in Complex $[((\text{CH}_3)_3\text{C}_6\text{H}_2\text{O-})_2 \text{PS}_2]_3\text{Fe}$

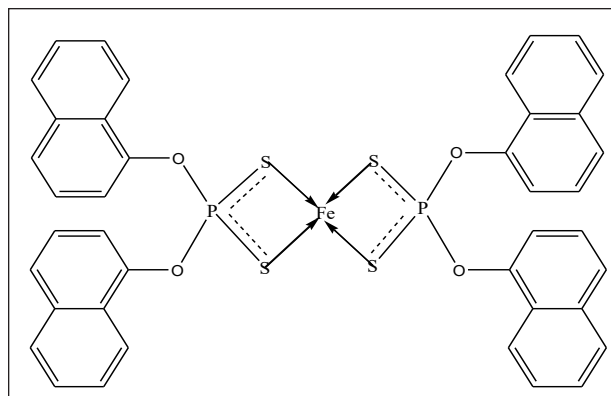


Fig. 3: Proposed Square Planar Structure of the Complexes of the Type $[(\alpha\text{-C}_{10}\text{H}_7\text{O-})_2, (\beta\text{-C}_{10}\text{H}_7\text{O-})_2 \text{PS}_2]_2\text{Fe}$

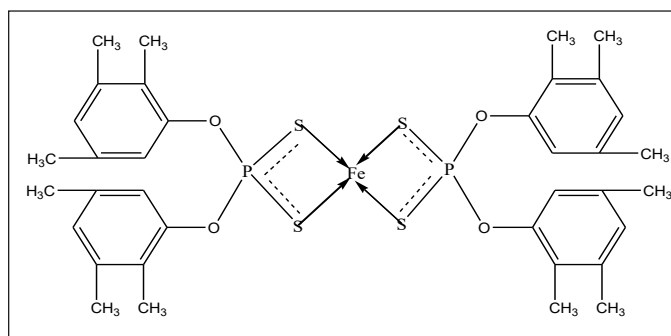


Fig. 4: Proposed Square Planar Structure of the Complex $[((\text{CH}_3)_3\text{C}_6\text{H}_2\text{O-})_2 \text{PS}_2]_2\text{Fe}$

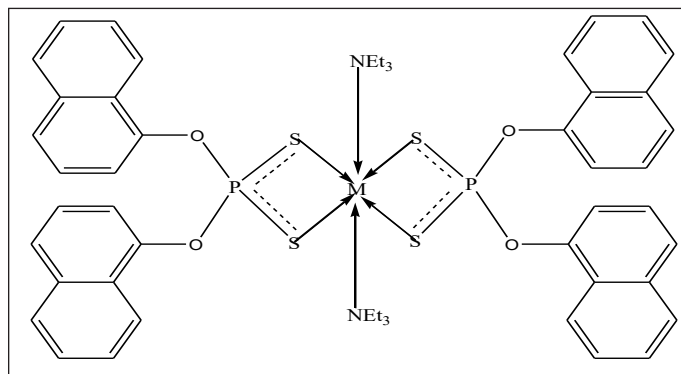
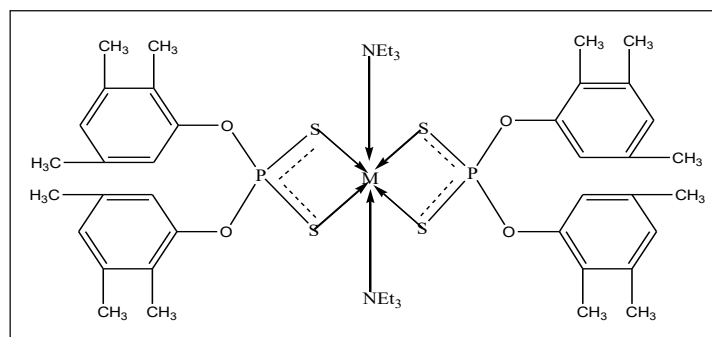
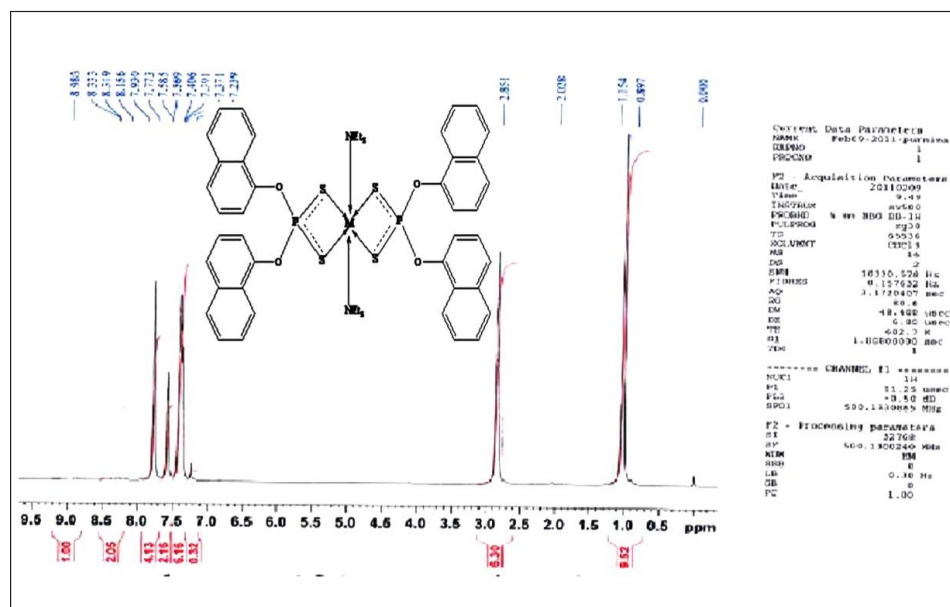
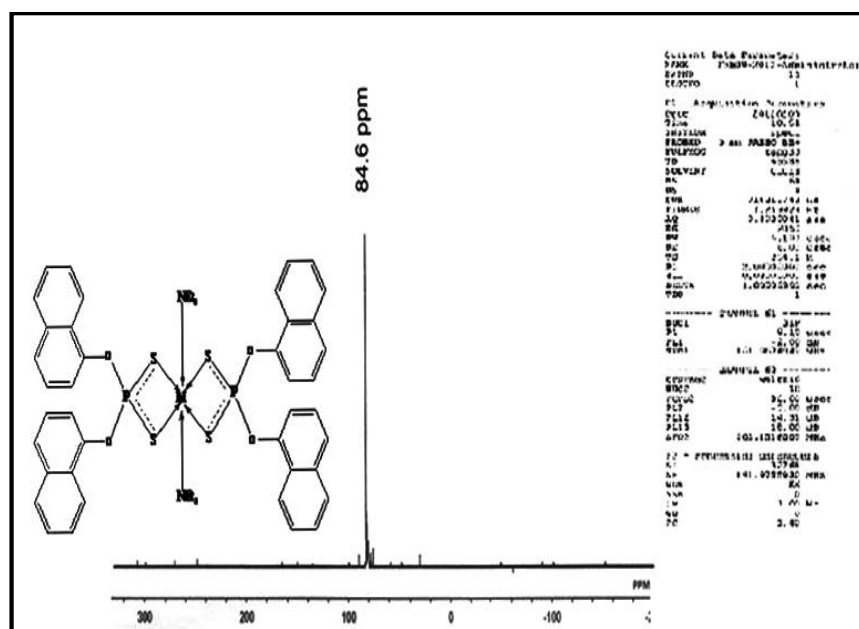


Fig. 5: Proposed Octahedral Geometry Around the Iron (II) in Complexes $[(\alpha\text{-C}_{10}\text{H}_7\text{O-})_2 \text{PS}_2]_2\text{Fe}(\text{Et}_3\text{N})_2$, $[(\beta\text{-C}_{10}\text{H}_7\text{O-})_2 \text{PS}_2]_2\text{Fe}(\text{Et}_3\text{N})_2$


 Fig. 6: Proposed Octahedral Geometry Around the Iron (II) in Complex $[((\text{CH}_3)_3\text{C}_6\text{H}_2\text{O})_2\text{PS}_2]_2\text{Fe}(\text{Et}_3\text{N})_2$

 Fig. 7: ^1H NMR Spectrum of $[((\alpha\text{-C}_{10}\text{H}_7\text{O})_2\text{PS}_2]_2\text{Fe}(\text{Et}_3\text{N})_2$

 Fig. 8: ^{31}P NMR Spectrum of $[((\alpha\text{-C}_{10}\text{H}_7\text{O})_2\text{PS}_2]_2\text{Fe}(\text{Et}_3\text{N})_2$

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