PREPARATION AND CHARACTERIZATION OF FE (II) COMPLEXES CONTAINING MIXED LIGANDS [+]

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Abstract

Iron (II) complexes with mixed ligands acetylacetone bis(semicarbazone)-LH_2 and some substituted phenols {2-aminophenol (P_1H) or 3-aminophenol (P_2H) or 4-aminophenol (P_3H) or 2-nitrophenol (P_4H)} have been prepared and characterized physico-chemically . They have been found to have general formulas $[Fe(LH_2)(P_mH)]X_n$ or $[Fe(LH_2)(P_zH)_2]X_n$ and $[Fe(LH)(P_m)]$ or $[Fe(LH)(P_zH)(P_z)]$ in neutral and basic medium , respectively (where $P_mH = P_1H$ or P_4H ; $X = SO_4^{2-}$ or Cl^- ; n = 1 or 2 ; P_m = deprotonated P_1H or P_4H ; $P_zH = P_2H$ or P_3H ; P_z = deprotonated P_2H or P_3H) .

المستخلص

تمّ تحضير معقدات للحديد (II) مع خليط من ليكاندي الاسيتيل أسيتون بس(سميكاربازون)- LH_2 وبعض الفينولات المعوّضة ٢ -أمينو فينول (P_1H) أو ٣- أمينو فينول (P_2H) أو ٤- أمينو فينول(P_3H) أو ٢- نيترو فينول (P_4H)}. شخصت المعقدات الناتجة بطرق فيزيائية-كيميائية ، ووجد أن لها الصيغ البنائية العامة $[Fe(LH_2)(P_mH)]X_n$ أو $[Fe(LH_2)(P_zH)_2]X_n$ و $[Fe(LH)(P_m)]$ أو $[Fe(LH)(P_z)(P_zH)]$ في كل من الوسطين المتعادل والقاعدي على التوالي (حيث $P_1H = P_mH$ أو P_4H، $X = SO_4^{-2}$ أو Cl^- ، n = ١أو ٢ ، $P_1H = P_m$ أوP_4H مزال منهما بروتون ، $P_2H = P_zH$ أو P_3H ، $P_2H = P_z$ أو P_3H مزال منهما بروتون)

Introduction

An extremely large number and wide range of iron (II) complexes are known . The d^6 configuration represents the most important oxidation state of iron having an octahedral geometry for most complexes [1].

Semicarbazone complexes of transition and non transition ions have been reported due to their biological importance [2-4]. Substituted phenols are ligands bonding through the oxygen atoms to the central metal ion forming compounds which are used in several purposes [5-7]

Recent years have witnessed a growing interest in the chemistry of mixed ligands complexes due to their importance in biological processes [8-11]

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To the best of the available knowledge, the synthesis and study of mixed ligand complexes with iron (II) of such ligands have not yet been reported . The aim of the present work, therefore, is to investigate the preparation and characterization of some new iron (II) complexes with mixed ligands {acetylacetone bis(semicarbazone) – LH_2 and substituted phenols (Figure 1)} .

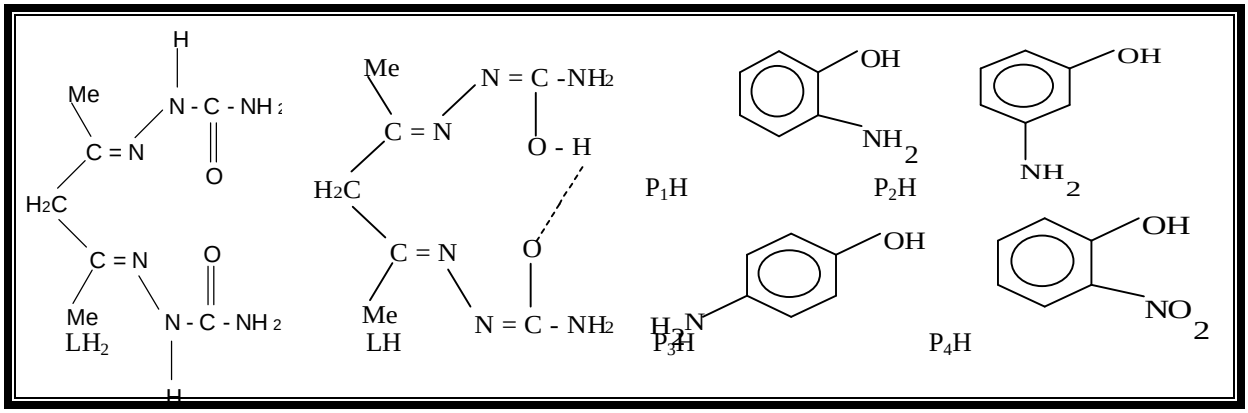


Figure 1 : **Structures of the ligands**

Experimental

1- Materials:

Chemicals : ferrous chloride, ferrous sulfate, semicarbazide hydrochloride, dimethyl-formamide, 2-aminophenol, 3-aminophenol, 4-aminophenol, 2-nitrophenol, acetylacetone from Fluka or BDH have been used as supplied .

2-Synthetic Methods:

Acetylacetone bis(semicarbazone) -LH_2 has been prepared according to the standard method[12]. 55.75 g (0.5 mole) semicarbazide hydrochloride and 41g (0.5 mole) sodium acetate are dissolved in 100 ml hot distilled water . The resulting solution is mixed with 25g (0.25 mole) acetylacetone dissolved in 50 ml ethanol gradually with constant stirring . The mixture has been refluxed for three hours to ensure the completion of the reaction and then cooled . The solid has been filtered, washed with cold water and then recrystallized from ethanol (white crystals, m.p. = 207 ^{o}C) .

A general procedure has been adopted for the preparation of the complexes in neutral and basic media . In neutral medium, a solution of 1g (0.0037 or 0.0050 mole) of ferrous sulfate or ferrous chloride in 5 ml water has been added to the solution of acetylacetone bis(semicarbazone) (0.0037 or 0.0050 mole) and one of the substituted phenol} 2-aminophenol, 2-nitrophenol (0.0037 or 0.0050 mole) or 3-aminophenol, 4-aminophenol (0.0074 or 0.0100 mole), respectively} in 15 ml hot ethanol . The mixtures have been refluxed for three hours followed by evaporation to half their volumes then cooled . The products are separated by filteration, washed with petroleum ether and dried . In basic medium, complexes have been prepared by applying same amounts used in neutral medium , and after mixing the metal salts with the ligands and heating on a waterbath, potassium hydroxide solution (1M) has been added until pH of the solutions has been about 8-9 . The mixtures have been heated on a waterbath for half an hour then allowed to stand then cooled . The products were filtered off, washed with petroleum ether and dried .

3- Analytical and Physical Measurements:

Iron contents have been determined by applying titration method after the decomposi-

tion of the complexes with concentrated nitric acid[13]. Conductivity measurements were carried out with an electrolytic conductivity measuring set LF-42 using 10^{-3} M dimethyl-formamide solution at room temperature . Magnetic susceptibility of the complexes have been measured by Bruker B.M6 .The infrared spectra have been recorded on a Pye-Unicam 1100 Infrared Spectrophotometer in the 400-4000 cm^{-1} range using KBr disk . Electronic spectra were recorded on Shimadzu UV-210A Spectrophotometer for 10^{-4} M solutions of the ligands and their complexes in dimethylformamide at 25 ^{o}C, using a 1cm cell .

Results and Discussion

The reaction of Fe (II) salts acetylacetone bis(semicarbazone) and substituted phenols in 1:1:1 molar ratio in both neutral and basic medium may be represented by the following reactions:

$FeX_n.YH_2O + P_mH + LH_2 \rightarrow [Fe(LH_2)(P_mH)]X_n + YH_2O$

$FeX_n.YH_2O + LH_2 + 2P_zH \rightarrow [Fe(LH_2)(P_zH)_2]X_n + YH_2O$

$FeX_n.YH_2O + P_mH + LH_2 + 2KOH \rightarrow [Fe(LH)(P_m)] + (Y+2)H_2O + K_nX_n$

$FeX_n.YH_2O + 2P_zH + LH_2 + 2KOH \rightarrow [Fe(LH)(P_zH)(P_z)] + (Y+2)H_2O + K_bX_n$

(where $X=SO_4^{-2}$, Cl^- ; n=1, 2 ; Y = 4, 7 ; b = 2 ; $P_mH = P_1H, P_4H$; $P_zH = P_2H$ or P_3H)

The solid complexes are colored, slightly soluble in water, moderately soluble in ethanol and dimethylformamide . The values of molar conductivities (Table 1) approach those expected for 1:2, 1:1 and non electrolytes for complexes prepared in neutral and basic medium [14], respectively .

The infrared spectra of LH_2 ligand (Table 2 , Figure 2) show a strong band at 1585 cm^{-1} which is attributed to C=N group shifts towards a lower frequency on coordination due to the decrease in the bond order as a result of metal nitrogen bond formation [3,15,16] . The next strong band at 1685 cm^{-1} which is assigned to the C=O group shifts towards a lower frequency on coordination establishing coordination of the ligand through the two carbonyl oxygen atoms [3,15,16] in neutral medium . In basic medium, this band disappears in the complexes and a new band is observed at 1225-1235 cm^{-1} due to C-O group, thereby establishing coordination of the ligand through the twoenolic oxygen atoms [3,15,16]. The absorption band of the ligand is in the range 3200-3300 cm^{-1} due to υ_{NH} , the broadening of this band is a consequence of hydrogen bonding phenomenon . On complexation, this phenome- non is more complicated due to different factors [3,4]such as the effect of hydrogen bonding (the breaking of hydrogen bonding on complexation causes high shift to υ_{NH}) and the effect of coordination (causes shift to a lower frequency) and also the presence of other groups (NH_2) absorption band appearing in the same position . This band, however remains unaltered in the complexes prepared in neutral medium indicating that there is no coordination through NH group [2,4] Meanwhile in basic medium, because of the presence of hydrogen bonding it is more difficult to notice the absence of NH group, but it is well known that this band has disappeared in basic medium [3,4] due to the enolic form . The other strong bands at 3410 cm^{-1} and 1450 cm^{-1} due to υ_{NH2} [3] remain unaltered on complexation indicaing that there is no coordination through the NH_2 group and the metal ion .

The infrared spectra of the substituted phenol ligands (Figure 2) show a band at about 1230 cm^{-1} which is attributed to C-O group [15,17] which shifts towards higher frequency region on complexation demonstrates that the phenolic oxygen is coordinated to the metal ion . The next band at 3300-3400 cm^{-1} which is attributed to OH group [15,17]shifts towards a lower frequency on coordination for complexes prepared in neutral medium . On the other

hand in basic medium , this band disappears due to the deprotonation .The spectra of P_1H , P_2H and P_3H show bands at 3200-3250 cm^{-1} due to NH_2 group which remains unaltered in the complexes of P_2H and P_3H indicating the absence of coordination through this group . While in P_1H complex , this band is shifted towards a lower frequency indicating the formation of chelation between the nitrogen of NH_2 group and the metal ion [16,17] . The ligand P_4H shows a band at 1525 and 1355 cm^{-1} due to the nitro group [16] shifted towards lower frequencies on coordination indicating the formation of chelation between the oxygen of nitro group and the metal ion .

Complexes 1-4 show a band at 570-590 cm^{-1} which is attributed to the presence of ionic chloride [15] . This is not observed in the spectra of the complexes prepared in basic medium (complexes numbers 5-8) indicating the absence of this ion. Complexes 9-12 show bands at 617-618 and 1130-1140 cm^{-1} which are attributed to the presence of ionic sulfate [15]Conversely these bands are not observed in the spectra of the complexes prepared in basic medium (complexes 13-16) indicating the absence of this group.

On the other hand, the spectra of the complexes show new bands around 450-500 cm^{-1} and 600-650 cm^{-1} due to υ_{Fe-N} and υ_{Fe-O} , respectively [1]. The presence of these bands support the formation of the complexes under investigation (Figure 2) .

Iron (II) complexes of high spin type require quite strong ligand fields to cause the formation of spin paired complexes . It has $3d^6$ configuration with a free ion ground term ^5D. For the weak field octahedral limit the ground state is $t_2g^4\ eg^2$ and ^5D term split into ^5Eg and ^5T_2g , therefore only one spin-allowed transition is expected in the electronic spectra of the weak field complexes . The octahedral iron (II) complexes usually exhibit a broad absorption band which frequently splits into two components . This splitting is probably due to the Jahn-Teller effect at least in solutions, since it is much larger than that which might arise through spin-orbit coupling . In the crystals, tetragonal distortion is sometimes present, this would cause a small splitting of ^5T_2g level into ^5Eg and ^5A_1g and would not account for the splitting of $^5T_2g \rightarrow {}^5Eg$ band . In the complexes which do not have six identical ligands around the iron atom the ^5Eg level undergoes a more splitting . The greater the dissimilarity of the ligand field strengths of the ligands the greater is the separation between the observed bands . The electronic spectra of the prepared complexes (Table 1) show a broad absorption band at about 10184-10406 cm^{-1} due to $^5T_2g \rightarrow {}^5Eg$ transition, as discussed above, demonstrates to the high spin distorted octahedral complexes [1,18]

The magnetic moment, for octahedral high spin complexes of iron (II) with ^5T_2g ground term, is about 5.5 B.M at room temperature; the spin-orbit coupling constant, λ = -100 cm^{-1}, and the moment is not expected to vary much with temperature . In complexes whose symmetry deviates from pure octahedral a reduction in the value of the moment towards the spin only value for four unpaired electrons is expected[17] . The room temperature magnetic moments calculated from the corrected magnetic susceptibilities of the prepared iron (II) complexes are in the range of 5.10-5.72 B.M. (Table 1) revealing the presence of four unpaired electrons and indicating high spin distorted octahedral iron (II) complexes [1,18].

Conclusion

This work in fact is a continuation of our studies including mixed ligand complexes . It has some observations achieved that lead to establish the following points :

1- Acetylacetone bis(semicarbazone) acts as tetradentate chelating ligand , jointed to iron (II) ion through the two oxygen atoms and the two nitrogen atoms .

2- Substituted phenols (P_2H , P_3H ,) act as monodentatae ligands ; whereas P_1H and P_4H act as bidentate chelating ligand .
3- In complex 1-4 , the chloride ionis joined to the metal ion in ionic manner
4- In complex 9-12 , the SO_4^{-2} group is joined to the metal ion in ionic manner .
5- Fe (II) ion is probably hexa-coordinated having high spin distorted octahedral geometry (Figure 3) .

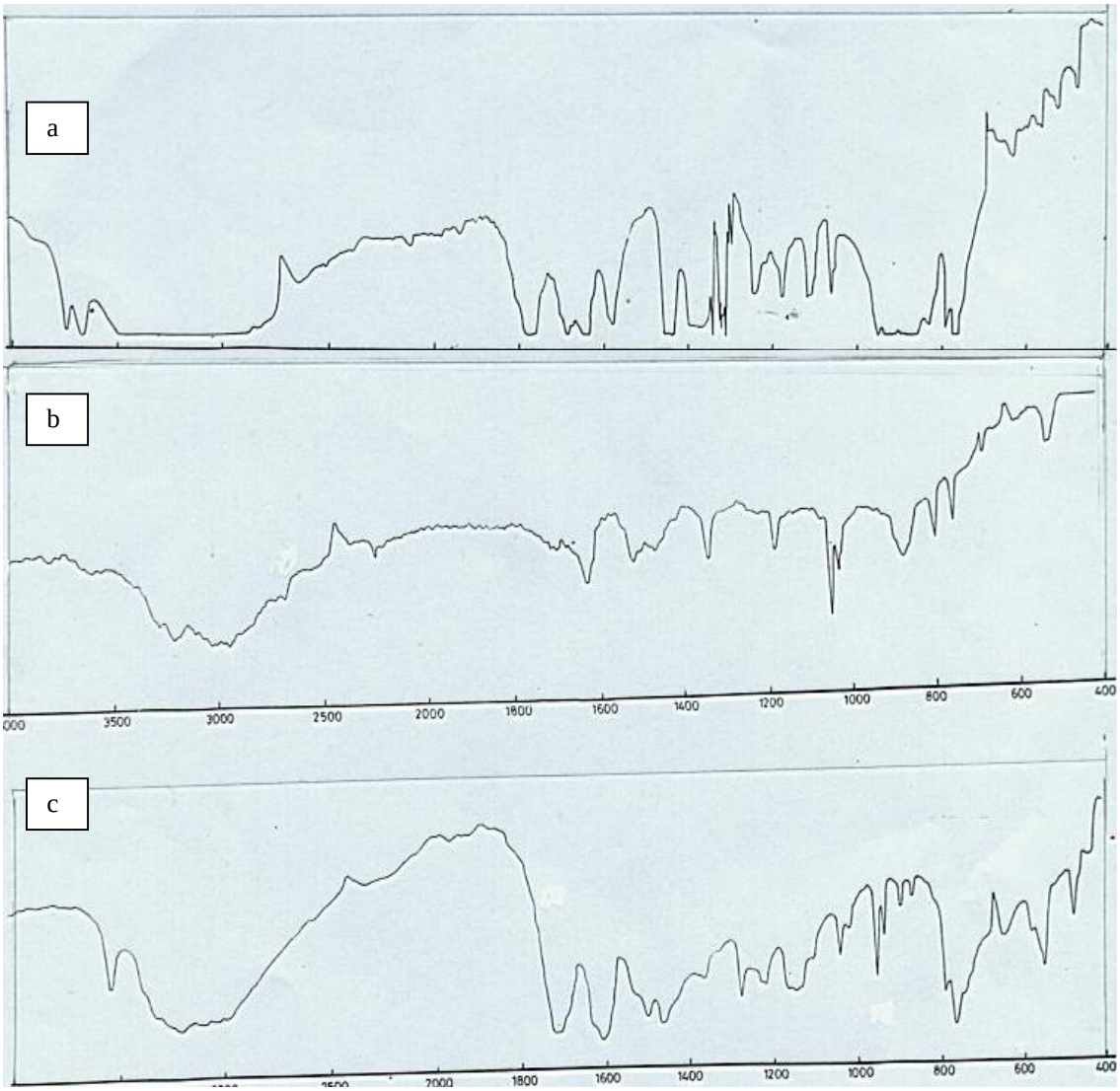
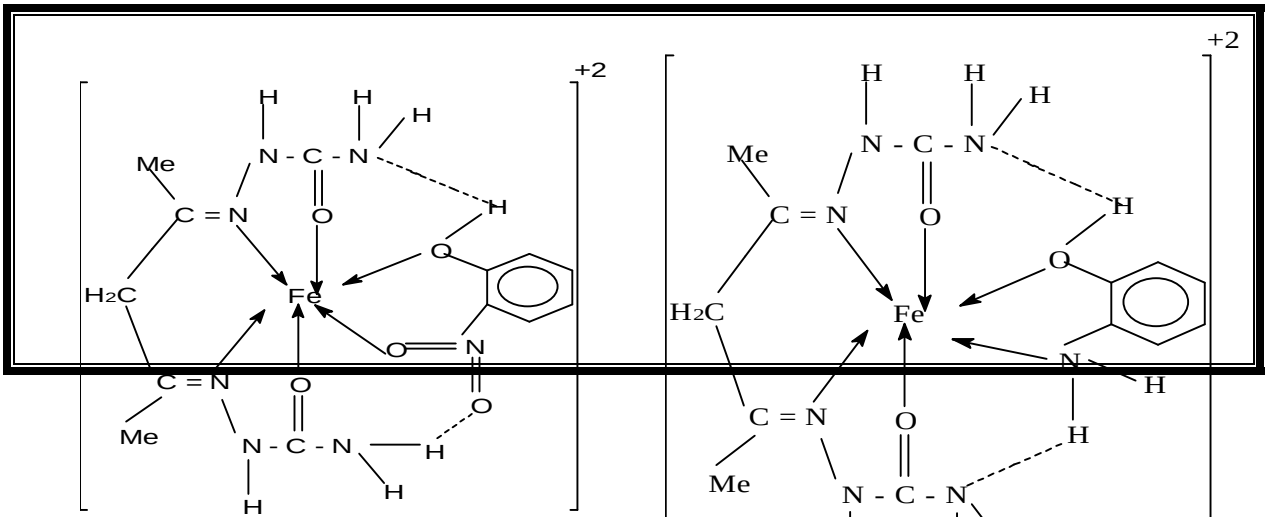
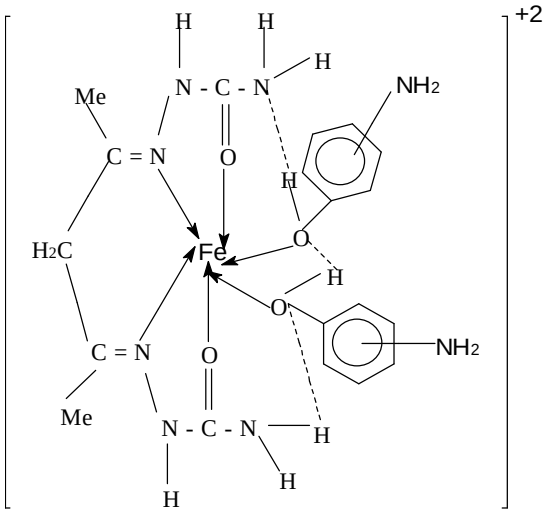


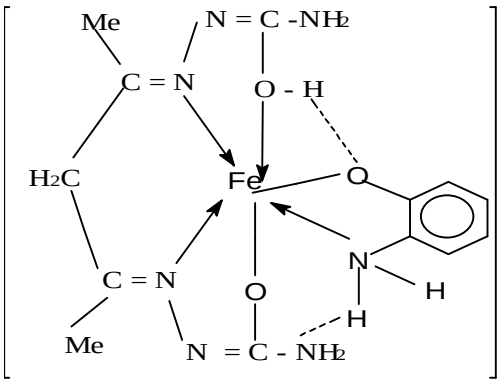
Figure 2: IR spectra of the ligand LH_2(a)and the ligand P_1H(b)and complex 1 (c)



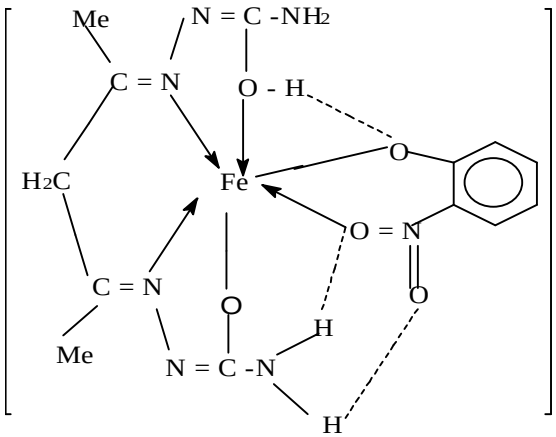
A_1 (complex 1 & 9)



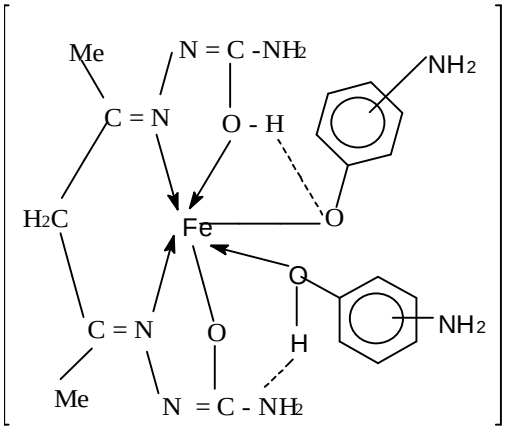
A_2 (complex 4 & 12)



A_3 (complex 2, 3,10 & 11)



B_1 (complex 5 & 13)



B_2 (complex 8 & 16)	B_3 (complex 6, 7, 14 & 15)

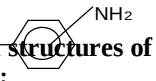


Figure 3 : **Model structures of the complexes** **A_1, A_2, A_3 = complexes in neutral medium ; B_1, B_2, B_3 = complexes in basic medium ; = 3-aminophenol or 4-aminophenol**

Table 1 : **Analytical Data and Some Physical Properties of The Complexes**

No.	Complexes	% yeild	Medium	Colour	Λ_M **	M.P (^{0}C)	μ_{eff} ***	%Fe Calc/ (Obs)	E.S (cm^{-1})
1	$[Fe(P_1H)(LH_2)]\ Cl_2$	78	Neutral	Brown	154	202d	5.10	12.40 (12.11)	10384
2	$[Fe(P_2H)_2(LH_2)]\ Cl_2$	55	Neutral	Brown	163	207d	5.72	12.40 (12.23)	10299
3	$[Fe(P_3H)_2(LH_2)]\ Cl_2$	60	Neutral	Dark brown	170	263d	5.45	12.40 (11.95)	10235
4	$[Fe(P_4H)(LH_2)]\ Cl_2$	73	Neutral	Brown	133	215d	5.61	11.63 (11.17)	10194
5	$[Fe(P_1)(LH)]$	82	Basic	Dark brown	11	220d	5.31	11.75 (11.35)	10183
6	$[Fe(P_2H)(P_2)(LH)]$	76	Basic	Brown	15	213d	5.67	11.75 (11.42)	10277
7	$[Fe(P_3H)(P_3)(LH)]$	78	Basic	Dark brown	23	264d	5.55	11.75 (11.81)	10352
8	$[Fe(P_4)(LH)]$	75	Basic	Dark brown	27	215d	5.61	11.05 (10.95)	10406
9	$[Fe(P_1H)(LH_2)]\ SO_4$	79	Neutral	Yellow	70	259	5.44	14.80 (13.99)	10406
10	$[Fe(P_2H)_2(LH_2)]\ SO_4$	61	Neutral	Yellow	72	232d	5.45	14.80 (14.18)	10320
11	$[Fe(P_3H)_2(LH_2)]\ SO_4$	66	Neutral	Brown	77	249	5.51	14.80 (14.72)	10288
12	$[Fe\ (P_4H)(LH_2)]\ SO_4$	70	Neutral	Yellow	74	224d	5.57	13.71 (13.51)	10395
13	$[Fe(P_1)(LH)]$	80	Basic	Dark brown	14	222d	5.41	14.80 (14.05)	10235
14	$[Fe(P_2H)(P_2)(LH)]$	77	Basic	Brown	16	217d	5.63	14.80 (14.15)	10299
15	$[Fe(P_3H)(P_3)(LH)]$	74	Basic	Dark brown	25	260d	5.51	14.80 (14.63)	10406
16	$[Fe(P_4)(LH)]$	70	Basic	Dark brown	23	211d	5.60	13.71 (13.42)	10384

** Λ_M = Molar conductivities in $\Omega^{-1}\,cm^2\,mol^{-1}$
***μ_{eff} = Magnetic moment in Bohr Magneton
d=decomposition point
E.S.= Electronic spectra

Table 2 : IR Spectra of The Complexes (Values in cm^{-1})

No.	υC=N semi	υNH_2 semi	υ_{NH} $\upsilon_{OH\ alc.}$ $\upsilon_{OH\ ph.}$	υ C=O semi	υC-O semi	υ_{C-O} phen	υ M-N	υM-O
$ASCH_2$	1585	1450 3395-3410	3200-3300 3320-3400	1685	-	1230	-	-
1	1550	1450 3395-3410	3200-3300 3320-3400	1630	-	1330	450 475	600 630
2	1560	1450 3395-3410	3200-3300 3320-3400	1640	-	1335	450	625 650
3	1540	1450 3395-3410	3200-3300 3320-3400	1625	-	1340	475	600 650
4	1540	1450 3395-3410	3200-3300 3320-3400	-	-	1330	475	620 640
5	1530	1450 3395-3410	3200-3300 3320-3400	-	1225	1340	475 500	610 650
6	1520	1450 3395-3410	3200-3300 3320-3400	-	1230	1340	500	610 640
7	1530	1450 3395-3410	3200-3300 3320-3400	-	1235	1350	450	620 650
8	1530	1450 3395-3410	3200-3300 3320-3400	1625	1235	1350	500	620 650
9	1550	1450 3395-3410	3200-3300 3320-3400	1640	-	1350	450 500	625 650
10	1500	1450 3395-3410	3200-3300 3320-3400	1630	-	1335	475	600 640
11	1500	1450 3395-3410	3200-3300 3320-3400	1630	-	1335	450	600 630
12	1520	1450 3395-3410	3200-3300 3320-3400	-	-	1340	450	600 635
13	1550	1450 3395-3410	3200-3300 3320-3400	-	1230	1340	450 500	600 645
14	1530	1450 3395-3410	3200-3300 3320-3400	-	1230	1340	500	610 645
15	1540	1450 3395-3410	3200-3300 3320-3400	-	1225	1350	450	610 645
16	1525	1450 3395-3410	3200-3300 3320-3400		1225	1350	450	600 635

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