CHAPTER 6

Trimetallic Cu_2Fe complexes with a Ferrocenoyl ligand: Synthesis, Characterization and Electrochemical Studies.

6.1 Introduction

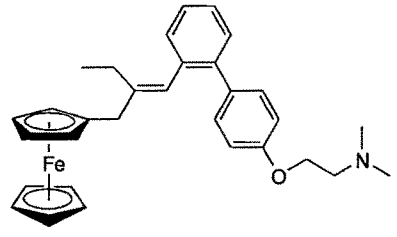
6.2 Experimental

6.3 Results and Discussion

6.4 References

6.1 Introduction

During the last decade ferrocene has proved to be a versatile molecular fragment attached to a molecule of interest in order to take the advantage of the special properties of ferrocene. The applications range from the development of ferrocifen (a), as a potent and selective anticancer agent based on the well known drug



(a)

Tamoxifen[1] to molecular sensors for the detection of toxic metal ions and anions for environmental applications.[2] The fully aromatic moiety undergoes highly reversible redox which is affected by the functional groups attached to cyclopentadienyl rings. Thus, ferrocenoyl group can be used as highly responsive redox couple. Functionalizing ferrocene with chelating arms can make it redox sensitive ion or molecular receptor. Initially, ferrocene-functionalized crown ethers and cryptands were synthesized, primarily, for the recognition of alkali and alkaline-earth metal cations.[3-7] More recently, however, research has begun to focus on the use of ferrocene-functionalized receptors for the recognition of more challenging guests such as anions[8-11] and transition metal cations.[12-18] A review of several significant ferrocene based receptors and electrochemical sensors for ions and neutral molecules are described below.

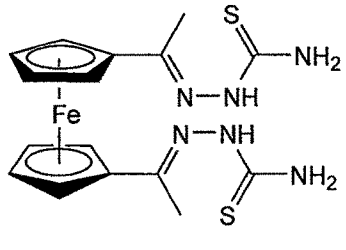
Ferrocene can be readily functionalized as mono or di-carboxaldehyde[19] and mono or di-acetyl derivatives followed by the condensation of carbonyl group with a variety of amines, hydrazines, semicarbazones or thiosemicarbazones leading to a range of chelating ferrocenyl ligands. Also, 1,1'-bis(amino)ferrocene,[20] substituted phenoxy analogues,[21] amino methyl derivatives[22] and 1,1'-bis(chlorocarbonyl)ferrocene have been reported.[23] These can be further condensed with a variety of aldehydes and amines to attach chelating arms. The chelating functional groups attached to ferrocene include oxime, variety of bidentate, tridentate amines, amino ethers, crown ethers,[24,25] aza crown ethers[26-28] and cryptands.[29,30] These

chelating arms can bind with specific cations or anions or neutral molecules. This results in a change in electrochemical response of the ferrocenoyl moiety due to the electronic perturbations. Thus functionalized ferrocene can behave as an electrochemical sensor for the specific ion or molecule. A number of such sensors have been developed with very significant contribution by P. D. Beer *et al.* [31-33]

1,1'-Ferrocenediyl analogues of N-aryl-salicylaldimine and its previous analogue, 1'-hydroxy ferrocenecarbaldehyde, were reported as initiators for titanium mediated lactide polymerization.[34] 1,1'-bisthiosemicarbazones were reported as self assembled dicopper double helicate and mononuclear silver complexes.[35] A ferrocenylated conjugate of adenine, shows hydrogen bonding interactions, which promote and stabilize nucleobase homotetrad formation.[36] An oligometallic complex with tris(1-pyrazolyl)borate derivative has been reported, in which electronic communication was proved by cyclic voltammetric studies.[37]

A series of (ferrocenylethylene)phosphanes with increasing number of ferrocenylethylene units, including $PdCl_2$, $PtCl_2$ and PdI_2 were synthesized, studied spectroscopically and structures of the complexes were determined. Attempts have been made to link phosphanes and acetylinic groups to ferrocene. Electrochemical investigations of the ligands and the corresponding palladium and platinum complexes revealed that the structural motif of the ligands do not support multistep redox processes within the materials. All compounds showed single, reversible redox processes whose potential is influenced by the substitution pattern of the ligands as well as the respective complex geometries.[38] The highly aromatic ferrocene can undergo self aggregation leading to ferrocene bound gold nanoparticles capped with mercaptoacetate.[39]

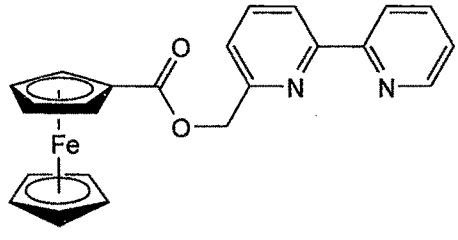
Ferrocene-containing double helical architecture generated from easy to prepare ferrocene containing bis-thiosemicarbazone ligand (b), was constructed via self assembly.[40]



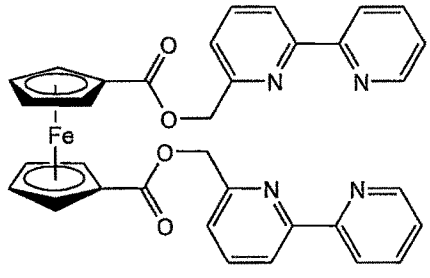
(b)

A bi-ferrocene trinuclear complex with Schiff base ligand, S-methyl-N-(ferrocenyl-1-methyl-methylidene) dithiocarbazate, with palladium was proved to have third-order nonlinear optical response. The geometry around the metal centre in this complex was found to be close to square planar and in novel *cis*-configuration with two ferrocene moieties on the same side.[41]

Bis[1,1'-N,N'-(2-picolyl)aminomethyl]ferrocene has been shown to coordinate with transition metal ions to form macrocyclic architectures with large well defined cavities suitable for host-guest interactions.[42] Ferrocene functionalized with bipy arms, were very well studied for their metal binding capacities and molecular recognition.[43,44] These ligands have shown their ability to coordinate in multimode fashion. Ferrocene, functionalized with ester bridged bipy arms[45-48] at 1 and 1,1'-disubstituted position, (c and d), were studied by Buda *et al.* [49]



(c)



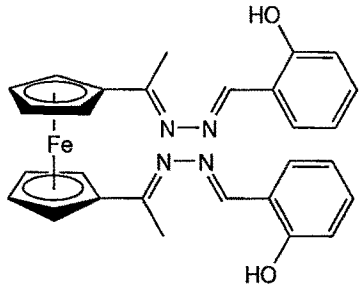
(d)

Although the chemistry of neutral molecule recognition is well developed,[50-53] there are only few reports of systems where binding of neutral molecules in solution has been followed electrochemically.[54-59] Mono- and bis-amido pyridine derivatives,[60] containing ferrocene units have been studied as receptors for neutral carboxylic acids.[61]

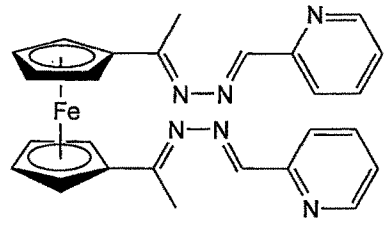
A number of polyethers bearing pyridyl or polypyridyl arms have also been reported. Functionalized ferrocene bearing oligoethylene glycol with pendant bipy subunits, was studied for the amino acid ester salt recognition.[62]

Flexible ligands either can coordinate to a single metal ion as a tetradentate chelate or can coordinate through each bidentate arm to a separate metal centre to give

bridged polynuclear species such as double helicates. Ferrocene based double helicates have been synthesized[63-65] as the metallocene units could accommodate a particular metal ion at its coordination site, with a concurrent stepwise redox change.[35] Further, to study this type of formation of double helicate and mononuclear complexes, new ligands, 1,1'-diacetylferrocene dihydrazone with salicyldehyde and pyridine-2-carbaldehyde, (e and f) and their complexes with copper(II) and silver(I) were synthesized.[66,67]



(e)



(f)

It has also been observed that the presence of ferrocenyl on the chelating groups can simultaneously affect the redox potential of a bound metal.[66] Thus it appears that there is electron delocalization between the ferrocenyl moiety and the bound metal. Electrochemical recognition of cations, anions and neutral molecules have been overviewed by Beer *et al.*[22] The mechanism of complexation redox coupling through hydrogen bonding, through space and direct co-ordination have been highlighted.[68] Diphenylphosphinoferrocene Gold(I) acetylides and their heterotri- and heterotetrametallic transition metal complexes using, titanium, molybdenum, iron, platinum, copper and silver were synthesized and extensively studied for their electrochemical behavior.[69]

An electrochemical study suggests that ferrocene moieties do not seem to communicate with each other, in either the free ligand or the respective complexes.[70] Thus, the incorporation of ferrocenyl in a bi- or trinuclear complex of a paramagnetic metal ion will be expected to affect the electrochemical properties of the metal ion.[71] In order to verify this, 1,1'-disuccinoyl ferrocene has been used as a trinucleating ligand along with bidentate capping ligands to synthesize new trinuclear Cu_2Fe complexes. The details of synthesis, characterization of the complexes and their electrochemical properties are presented here.

6.2. Experimental

Materials

AR quality Ferrocene (Aldrich), Succinic anhydride (Merck) and Aluminium Chloride (Merck), were used without further purification. phen, bipy, acac, 8hq, dpk and dbm were purchased from Merck and used as received, for the synthesis of binuclear complexes.

Ligand Synthesis

Synthesis of 1,1'-bis-(3-carboxypropanoyl)-cyclopentadienyl)-iron (dsf)

The basic binucleating ligand **dsf** was synthesized following the literature procedures.[72] The pure ligand gives single spot on TLC. Melting point of the ligand **dsf** is 163-164°C (165-166°C).

Elemental analysis is found to be C = 55.65%, H = 5.12%, (calculated for the formula $C_{18}H_{18}O_6Fe$, C = 55.98%, H = 4.66%).

Synthesis of binuclear Complexes

Synthesis of [dsf(Cuphen)$_2$](Ac)$_2$

0.200g (0.5183mmol) of the trinucleating ligand **dsf** in 10ml 50% aqueous ethanol in 100ml flat bottom flask was warmed to 60°C. (A dark red coloured solution resulted). Then 50% aqueous ethanolic solution of $[Cuphen]^{2+}$ complex prepared by mixing 0.2069g (1.0366mmol) of copper acetate monohydrate and 0.2054g (1.0366mmol) of phen (blue in color) was added slowly and drop wise. As the addition of $[Cuphen]^{+}$ to the solution of **dsf** began, the dark red coloured solution started becoming brown in colour. Addition was completed in half an hour. After complete addition, the mixture was allowed to stir for 5hrs to ensure completion of the reaction. The brown coloured product, complex **[dsf(Cuphen)$_2$](Ac)$_2$,** was filtered, washed with ethanol and dried in air. (Yield = 65%)

The reaction was repeated by taking equivalent amounts of all reactants and by replacing phen with equivalent quantities of bipy, dpk, 8hq, dbm and acac.

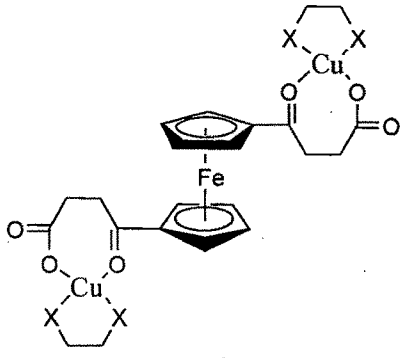


Fig.6.1

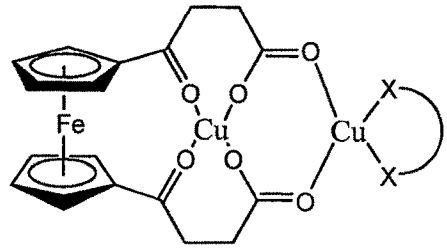


Fig.6.2

General structure of complexes of **Type – A** and **Type – B**

Physical Measurements

All the physical measurements, cyclic voltammetric studies, FAB-Mass analysis and ESR spectra were recorded using the instruments as mentioned earlier in chapter two (page no. 79).

6.3 Results and Discussion

The ligand **dsf** was synthesized by a known literature method. The melting point and elemental analyses of **dsf** are agreeable with the reported and calculated values, respectively. In order to further confirm its formation, FTIR spectrum was recorded.

The $\nu_{>C=O}$ corresponding to the carboxylic acid group in **dsf** has been observed at 1706cm^{-1}. The carbonyl stretching $\nu_{>C=O}$ has been observed at 1669cm^{-1}. The –C-H stretching and bending in $-CH_2-$ appears at 2924cm^{-1} and 1457cm^{-1}, respectively, while the ν_{C-C} and the stretching and bending of –C-H in the ferrocinoyl part of the molecule have been observed, respectively, at 1630, 2578 and 891cm^{-1}. The presence of these features in the FTIR spectrum of **dsf**, support its formation.

Characterization of the Cu_2Fe trinuclear complexes

The reactions of **dsf** with copper(II) in presence of bidentate π-acidic ligands resulted in the formation of Cu_2Fe trinuclear complexes. In presence of π-acidic phen, bipy and 8hq, the complexes have open form of **dsf** binding with two copper(II) ions, which are bound to the capping ligands. However, in presence of **dpk** and **dbm**, the

closed form of **dsf**, chelates with one copper(II). This bimetallic CuFe species, then acts as a ligand and binds with a Cudpk or Cudbm forming carboxylate bridges. The reaction in presence of acetylacetone results in the formation of $Cudsf(Ac)_2$ complex only. The elemental analyses agree with the proposed formulae as can be seen from the values in Table 6.1. Poor solubility of complexes in suitable solvents did not allow the measurement of molar conductivity values. However, FAB-mass spectra of three complexes could be recorded in m-nitrobenzyl alcohol matrix.

Table 6.1 Yields and elemental analysis of complexes.

Complex	Yield (%)	Elemental Analysis (%) C	H	N
[dsf(CuAc)$_2$]	14.03	42.13	3.57	------
$C_{22}H_{22}O_{10}Cu_2Fe$		(41.97)	(3.49)	
[dsf(Cuphen)$_2$](Ac)$_2$	33.65	55.65	4.02	5.49
$C_{46}H_{38}O_{10}N_4Cu_2Fe$		(55.81)	(3.84)	(5.66)
[dsf(Cubipy)$_2$](Ac)$_2$	32.21	53.79	4.50	6.43
$C_{42}H_{38}O_{10}N_4Cu_2Fe$		(53.56)	(4.03)	(5.95)
[dsf(Cu8hq)$_2$](Ac)$_2$	12.36	53.88	3.86	3.97
$C_{36}H_{28}O_8N_2Cu_2Fe$		(54.07)	(3.50)	(3.50)
[dsfCu$_2$dpk](Ac)$_2$	24.58	49.00	3.76	3.09
$C_{33}H_{30}O_{11}N_2Cu_2Fe$		(48.71)	(3.69)	(3.44)
[dsfCu$_2$dbm](Ac)$_2$	41.18	52.48	4.12	------
$C_{37}H_{34}O_{12}Cu_2Fe$		(51.05)	(3.98)	

In the FAB-mass spectrum of $[dsf(Cuphen)_2](Ac)_2$, the molecular ion peak corresponding to $[dsf(Cuphen)_2]^+$ appears at m/Z = 871. The complex species with bound acetate ions $[dsf(Cuphen)_2](Ac)$ and $[dsf(Cuphen)_2](Ac)_2+H^+$ appear with low abundance at m/Z 930 and 989, respectively. An important stable fragment $[dsfCuphen]-H^+$ has been observed with relatively high abundance at m/Z = 628. Some of the important fragments are shown in **Fig.6.3.**

Presence of a peak corresponding to the ligand dsf, at m/Z 386 was observed and supports the presence of ligand. The fragments, $[Cu(phen)]^+$ and $[Cu(phen)_2]^+$ were observed at m/Z 243 (calcd.243.54) and 423 (cacld.423.54) which confirm the copper-phen coordination. Corresponding important fragments with molecular formula are drawn below.

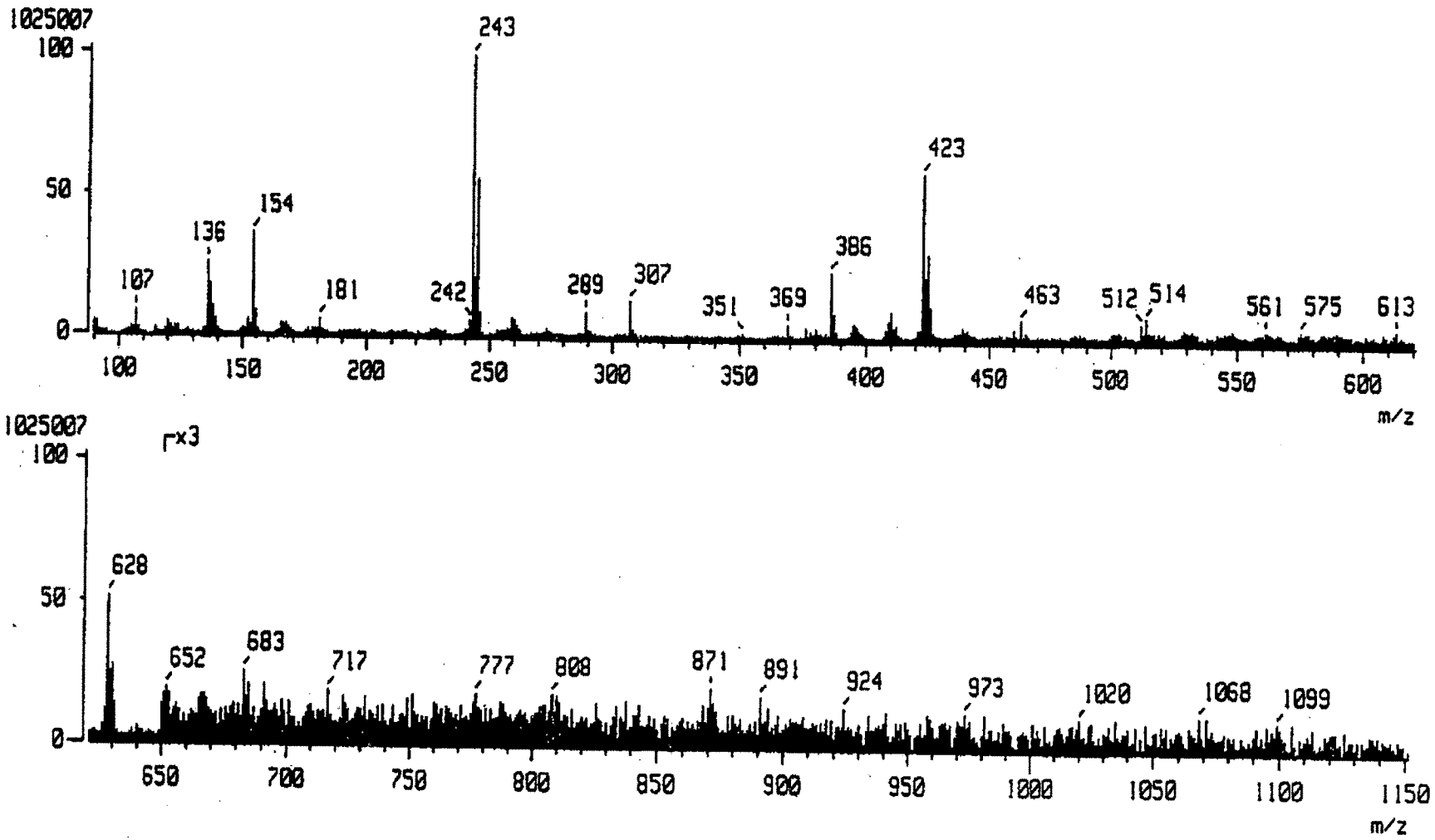
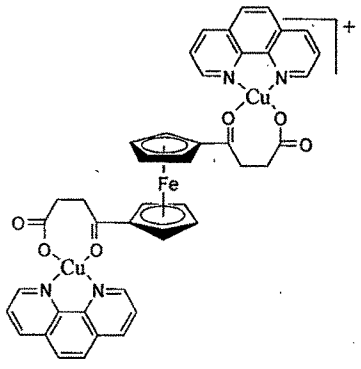
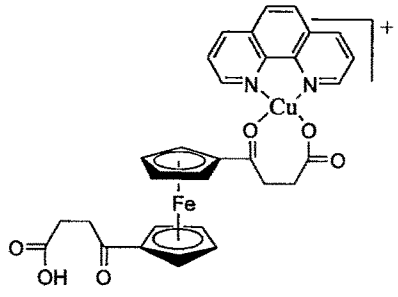


Fig.6.3 FAB-Mass spectrum of complex **[dsf(Cuphen)$_2$](Ac)$_2$**



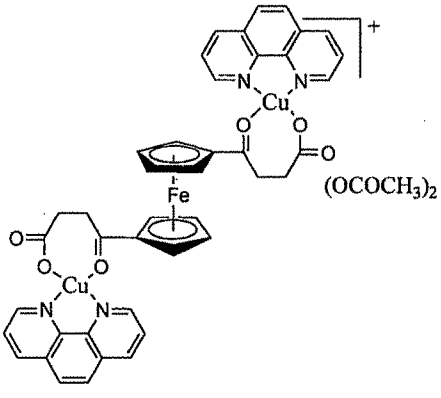
$[C_{42}H_{32}O_6N_4Cu_2Fe]^+$ m/Z = 870.92

Fig.6.4.1



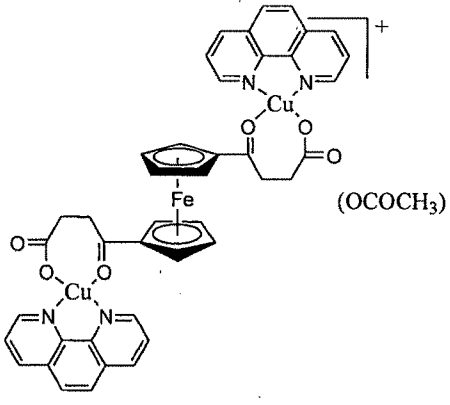
$[C_{30}H_{25}O_6N_2CuFe]^+$ m/Z = 629.38

Fig.6.4.2



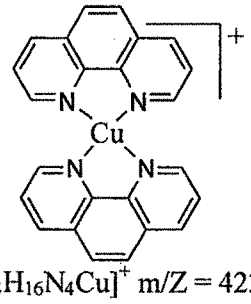
$[C_{46}H_{38}O_{10}N_4Cu_2Fe]^+$ m/Z = 988.92

Fig.6.4.3



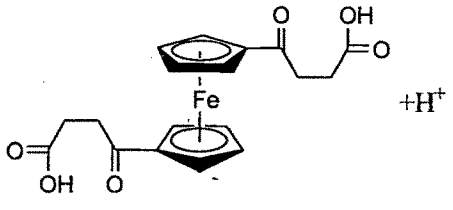
$[C_{44}H_{35}O_8N_4Cu_2Fe]^+$ m/Z = 929.92

Fig.6.4.4



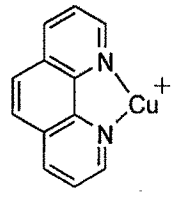
$[C_{24}H_{16}N_4Cu]^+$ m/Z = 423.54

Fig.6.4.5

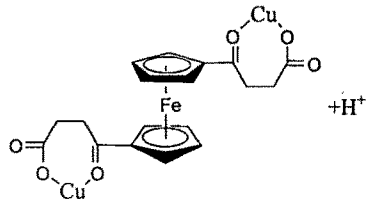


$[C_{18}H_{18}O_6Fe]+H^+$ m/Z = 386

Fig.6.4.6



$[C_{12}H_8N_2Cu]^+$ m/Z = 243.54



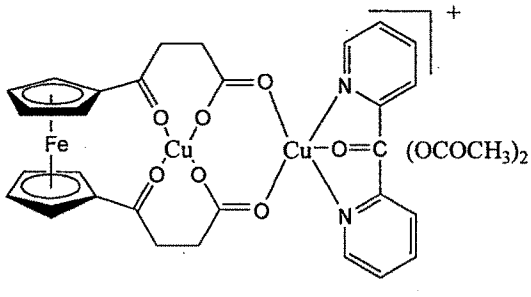
$[C_{18}H_{16}O_6Fe]+H^+$ m/Z = 512/514

Fig.6.4.7

Fig.6.4

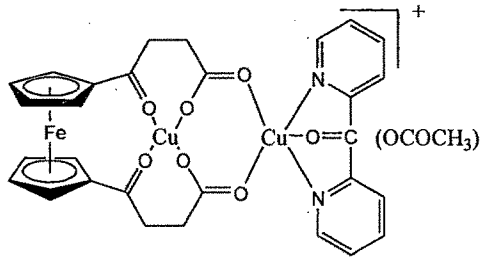
The presence of these fragments supports the formation of trinuclear complexes with suggested formula.

Peaks corresponding to the following fragments have been observed in the complex (**Fig.6.5**), **$[dsfCu_2dpk](Ac)_2$**. The parent ion $[dsfCu_2dpk](Ac)_2^+$ has been observed at m/Z 812 (calcd.812.92). $[dsfCu_2dpk]Ac$ and $[dsfCu_2dpk]^+$ have been observed at m/Z 753 (calcd.753.92) and at 693 (calcd.692.92) respectively. A fragment $[Cudsf].3H_2O$ has been observed at m/Z 502 (calcd.500.54). At m/Z 386, the ligand itself has been observed with the calculated m/Z 385.84. $[Cu(dpk)]^+$ has been observed at 247 (calcd.247.54), and $[Cu(dpk)_2]^+$ was observed at 431 (calcd.431.54). The appearance of peaks corresponding to these species confirms the formation of trinuclear complex as suggested in the formula.



$[C_{33}H_{30}O_{11}N_2Cu_2Fe]^+$ m/Z = 812.92

Fig.6.6.1



$[C_{31}H_{27}O_9N_2Cu_2Fe]^+$ m/Z = 753.92

Fig.6.6.2

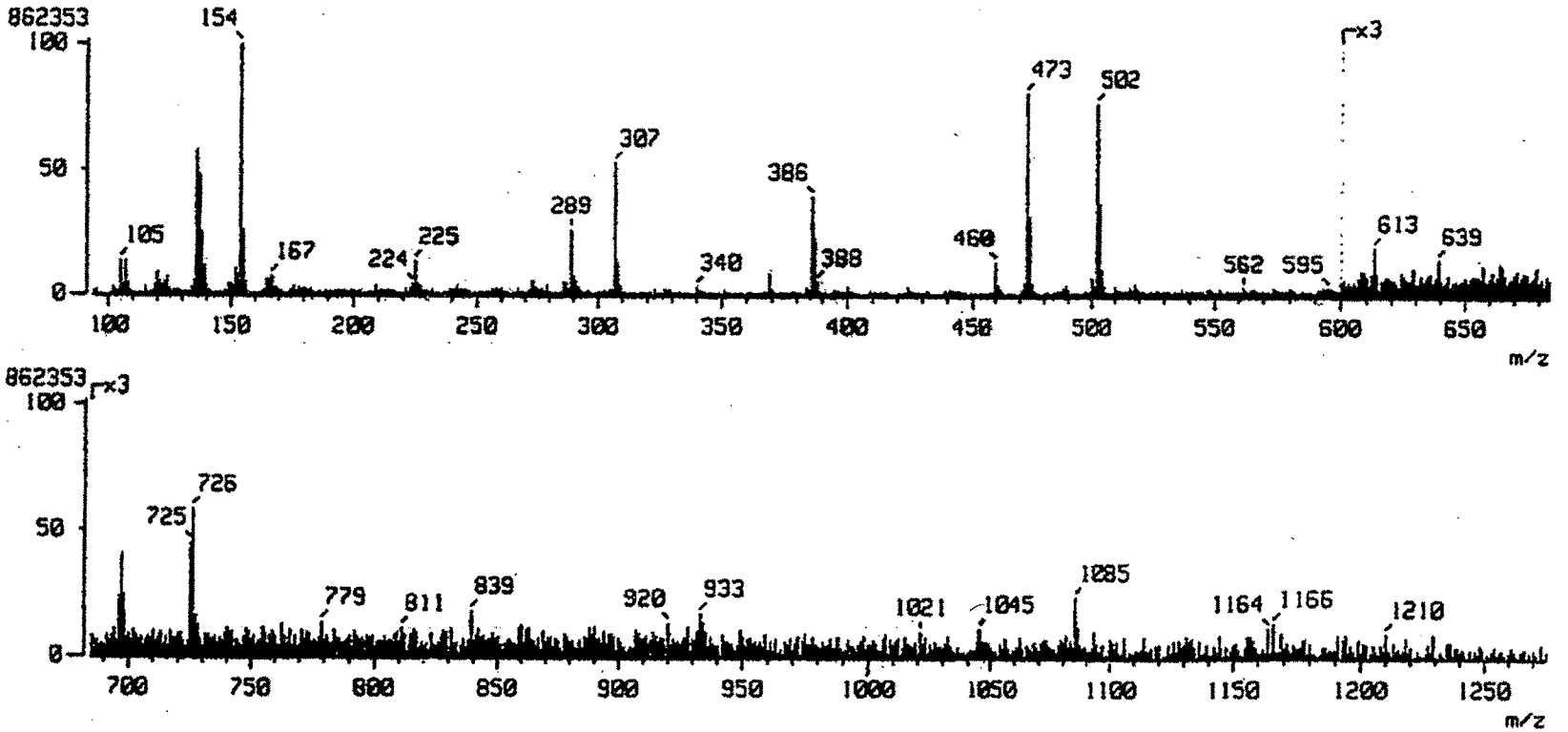
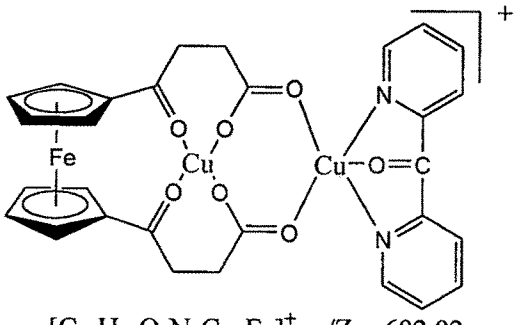
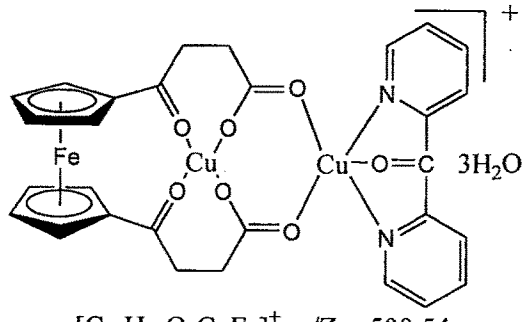


Fig.6.5 FAB-Mass spectrum of complex **[dsfCu$_2$dpk](Ac)$_2$.**

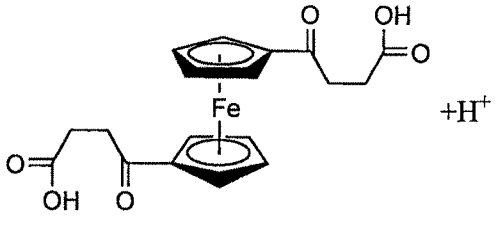
Some important fragments are drawn below (**Fig.6.6**).



$[C_{29}H_{24}O_7N_2Cu_2Fe]^+$ m/Z = 692.92
Fig.6.6.3



$[C_{18}H_{22}O_9CuFe]^+$ m/Z = 500.54
Fig.6.6.4



$[C_{18}H_{18}O_6Fe]+H^+$ m/Z = 386

Fig.6.6.5

Fig.6.6

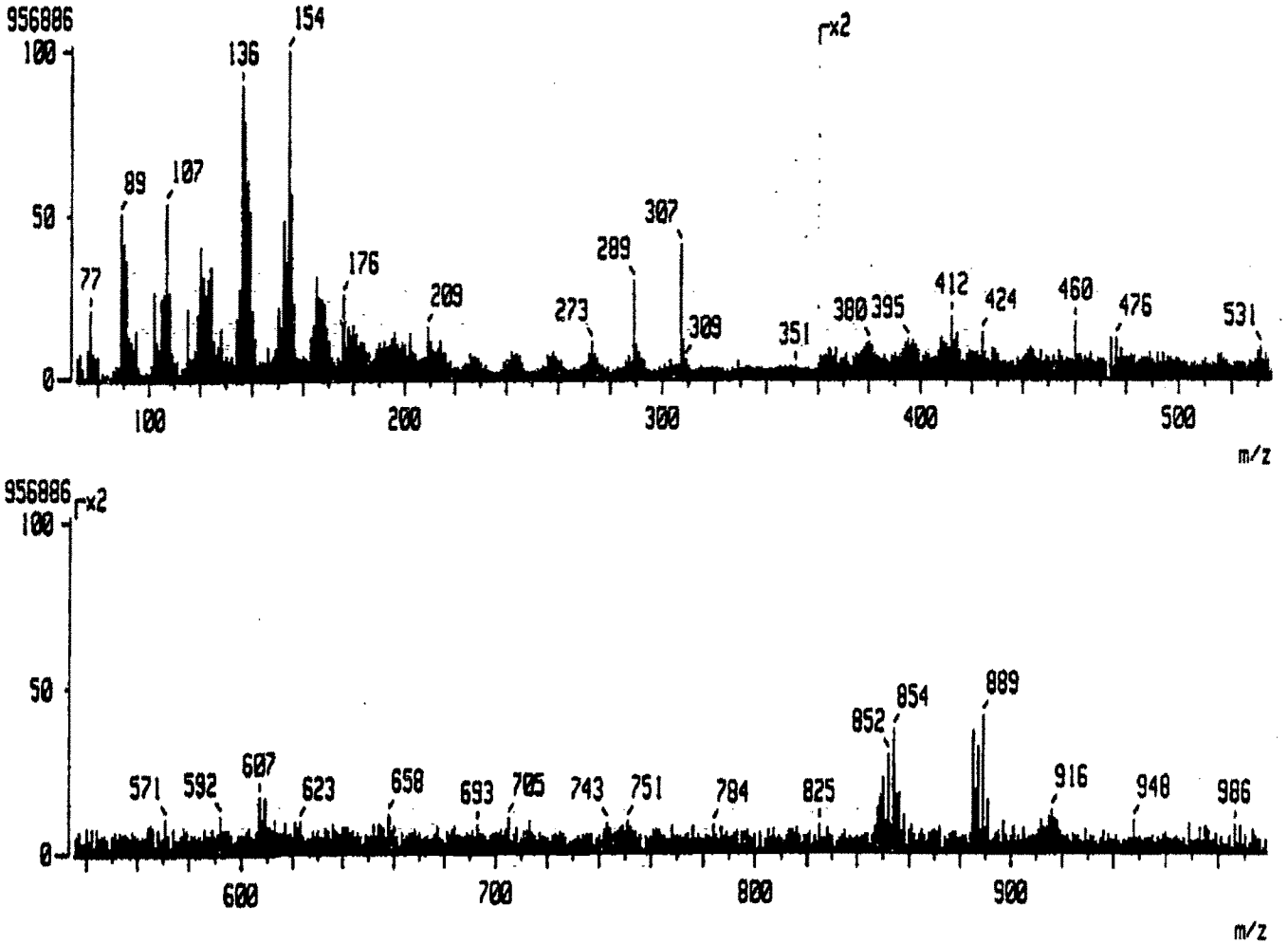
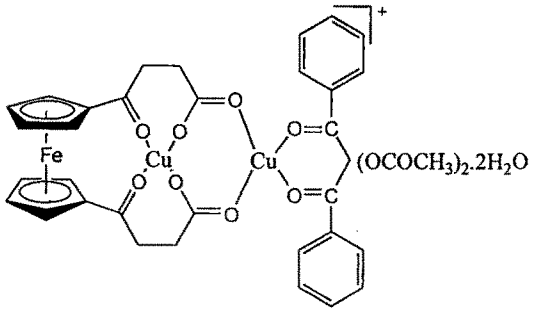
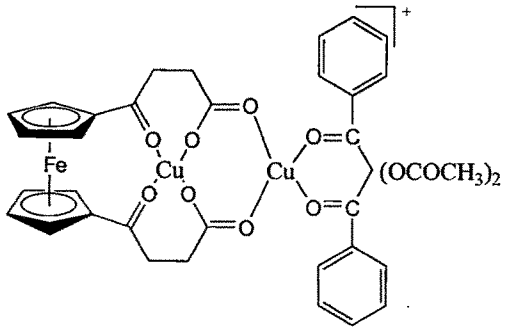


Fig.6.7 FAB-Mass spectrum of complex **[dsfCu$_2$dbm](Ac)$_2$.**



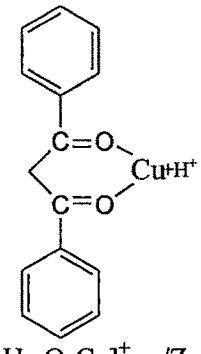
$[C_{37}H_{38}O_{14}Cu_2Fe]^+$ m/Z = 888.92

Fig.6.8.1



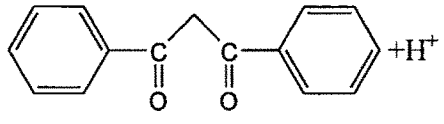
$[C_{37}H_{34}O_{12}Cu_2Fe]^+$ m/Z = 852.92

Fig.6.8.2



$[C_{15}H_{14}O_2Cu]^+$ m/Z = 289

Fig.6.8.5



$[C_{15}H_{13}O_2]^+$ m/Z = 225

Fig.6.8.6

Fig.6.8

Molecular ion peak corresponding to the fragment $[dsfCu_2dbm](Ac)_2.2H_2O$, (**Fig.6.7**) with two water molecules was observed at m/Z 889. The complex species associated with two acetate ions, $[dsfCu_2dbm](Ac)_2$ was observed at m/Z 854. The species corresponding to the **dsf** ligand $[dsf]^+$ was observed at m/Z 386, the species with $[Cu(dbm)]+2H^+$ formula, was observed at m/Z 289. The presence of the observed fragments supports the formation of trinuclear complex as suggested in the formula.

Electronic and vibrational Spectra

The electronic spectra of the six newly synthesized complexes were recorded in saturated methanolic solutions.

Table 6.2 Electronic Spectral data of the complexes.

Complex	Intra-ligand Transitions (nm)	Ligand Field Transitions (nm)
[dsf(CuAc)$_2$]	204.55, 272.67, 293.75	589.50,830.55,889.95.
[dsf(Cuphen)$_2$](Ac)$_2$	205.38,272.47,293.75	Not Observed.
[dsf(Cubipy)$_2$](Ac)$_2$	204.95, 272.54, 293.75	Not Observed.
[dsf(Cu8hq)$_2$](Ac)$_2$	204.40,272.66,293.75	587.02,789.01,814.07,836.42
[dsfCu$_2$dpk](Ac)$_2$	204.52, 272.72, 293.75	Not Observed.
[dsfCu$_2$dbm](Ac)$_2$	204.35,272.73,293.75	695.96

In all the complexes the intraligand transitions have been observed at 204, 272 and 294nm. The ligand field transitions were found to be present at 587, 789, 814 and 836nm in complex **[dsf(CuAc)$_2$]**, and at 589, 830 and at 889nm in the complex **[dsf(Cu8hq)$_2$](Ac)$_2$** and at 696nm in the complex **[dsfCu$_2$dbm](Ac)$_2$**.

The >C=O stretching of the **dsf** observed at 1706cm^{-1}, has been found to be shifted to 1654, 1662, 1655, 1667 and at 1653cm^{-1} in the complexes, respectively. This is due to the coordination of the >C=O group of the ligand with metal ion. The shift towards lower frequencies confirms the involvement of the carbonyl oxygen and also the presence of O→Cu π-interaction. The C-H stretching of $-CH_2$ has been observed to be approximately as in the free **dsf** without much change at 2924cm^{-1}. –C-H bending in $-CH_2$ has, however, prominently shifted to 1419cm^{-1} in the complex from the free ligand value of 1457cm^{-1}. The ν_{C-C} of the cyclopentadienyl ring has been observed in various complexes at 1466, 1560cm^{-1} in **[dsf(Cu8hq)$_2$](Ac)$_2$**, at 1456cm^{-1} in **[dsfCu$_2$dpk](Ac)$_2$** and at 1455cm^{-1} in **[dsfCu$_2$dbm](Ac)$_2$**. –C-H bending of methylene (-CH_2-) has been observed to be shifted from the free ligand value of 891cm^{-1} in ligand to 873cm^{-1} in **[dsf(Cuphen)$_2$](Ac)$_2$** complex, at 861cm^{-1} in **[dsf(Cubipy)$_2$](Ac)$_2$** complex, at 782cm^{-1} in **[dsf(CuAc)$_2$]** complex and at 820cm^{-1} in case of **[dsf(Cu8hq)$_2$](Ac)$_2$** complex, at 807 cm^{-1} in **[dsfCu$_2$dpk](Ac)$_2$** complex and at 755 in **[dsfCu$_2$dbm](Ac)$_2$** complex. The characteristic frequencies of phen have been observed at 722, 776, 848 and 1108cm^{-1}

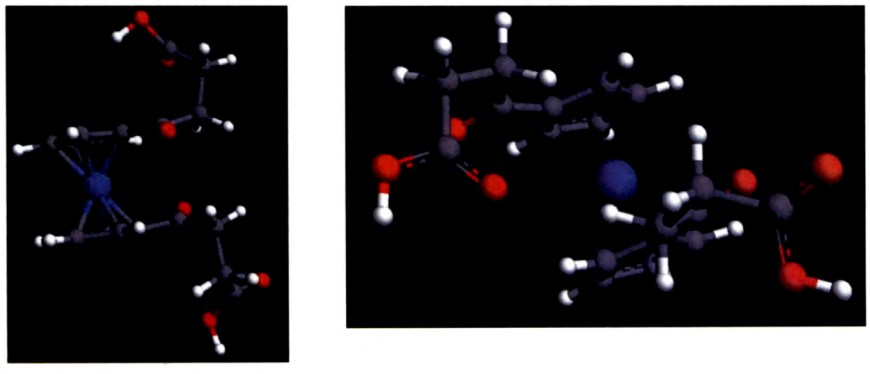
which confirm the presence and coordination of phen to the metal centre. In the complex **[dsf(Cu8hq)$_2$](Ac)$_2$** the ν_{CO} corresponding to the phenolic -OH was found to be present at 1378cm^{-1}. Carboxylate anion stretching frequencies have been observed between 1550-1604 and 1305-1400cm^{-1} in their respective complexes. Appearance of these frequencies confirms the presence and coordination of the carboxylate anion in complexes.
The important frequencies are summarized in Table 6.3.

Table 6.3 Important frequencies observed in the FTIR spectra of the complexes.

Major Freq.	Ligand **dsf**	Complexes **6.1**	**6.2**	**6.3**	**6.4**	**6.5**	**6.6**
>C=O (strech)	1706	1654	1662	1655	1654	1667	1653
C-C multi. Bond. (strech) arm.	1457	1529, 1553.	1498, 1534, 1588.	1548, 1579.	1466, 1500.	1570.	1526, 1545, 1611
C-H (strech. in alkane)	2924.	2923.	2854, 2923.	2925.	2925.	2924.	2925.
C-O (strech) in phenol	-------	------	-------	-------	1378.	------	------
C-N (vib) Arm. ter.		------	1344	1356.	1326.	1325	------
Arm Sub.	------	------	776 (3 adj. H atoms)	758. (4 adj. H atoms)	786. (3 adj. H atoms)	766. (4 adj. H atoms)	684, 720, 744 (5 adj. H atoms)
phen	------	------	722,776 848, 1108	------	------	------	------
bipy	-------	------	-------	728,777.	------	------	------
Ketone (strech) Unsat.	------	------	------	------	------	------	1680
Carboxylate Anion streching	------	1355	1387, 1399, 1588	1334, 1372. 1565	1573, 1599	1305, 1400, 1604	1316

6.4 Molecular modelling of dsf

Geometry of the trinucleating ligand **dsf** was optimized by *ab initio* quantum mechanical calculations[73] using 6-31G basis set[74-76]. For complexes, geometry was optimized by the semi-empirical quantum mechanical calculations using Universal Force Field (UFF).[77-85]



Optimized by UFF methods. Optimized by Ab-initio Calculations (using 6-31G basis set.)

(a) **(b)**

Fig.6.9 Geometries of the trinucleating ligand **dsf**

The Cu-Cu bond distances and Cu-Fe-Cu bond angles were calculated and correlated with their electrochemical properties.

In complex **[dsf(Cuphen)$_2$](Ac)$_2$** ,(**Fig.6.10**), the distance between Cu-Cu centre is 8.512745Å, where as the Cu-Fe-Cu angle is 107.77°. The Cu-Cu distance in the complex **[dsf(Cubipy)$_2$](Ac)$_2$** (**Fig.6.11**), was found to be 8.634870 Å and the Cu-Fe-Cu angle was 72.96°.

In case of secondary ligand **acac**, complex **[dsf(CuAc)$_2$]**, was isolated and elemental analysis matched with two acetates, coordinated with **dsf**. There are two possibilities to have coordination of two copper acetates with the ligand **dsf** as shown in following two figures (**Fig.6.12** and **6.13**).

In the trinuclear copper complex (**Fig.6.12**), the Cu-Cu distance was observed to be about 3.485Å, and the Cu-Fe-Cu angle was found 27.18°. In double helicate type complex (**Fig.6.13**), the Cu-Cu distance was found to be 8.564Å and the Cu-Fe-Cu angle

was 101.69° and the energies are 1261.202 and 1376.385Kcal/mole, respectively, in Type-A and Type-B complex. It can be concluded that, the formation of Type-A complex is energetically more favoured and hence forms the double helicate complex rather than the linear binuclear one.

In the trinuclear complex, **[dsf(Cu8hq)$_2$](Ac)$_2$** (**Fig.6.14**), the Cu-Cu distance was observed to be 6.682Å and the Cu-Fe-Cu angle was observed to be 122.98°. The Cu-Cu distance was found to be 3.636Å and the Cu-Fe-Cu angle was observed to be 26.71° in the trinuclear complex, **[dsfCu$_2$dpk](Ac)$_2$** (**Fig.6.15**).

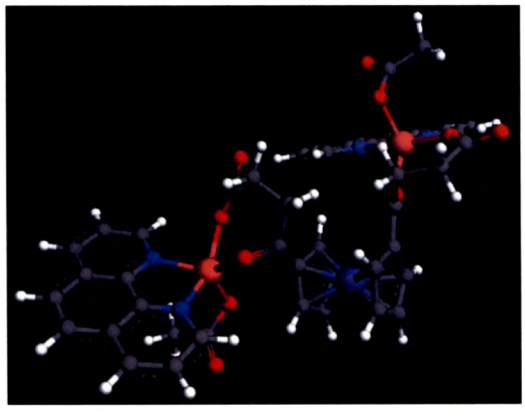


Fig.6.10 Geometry of the complex **[dsf(Cuphen)$_2$](Ac)$_2$**, optimized using UFF.

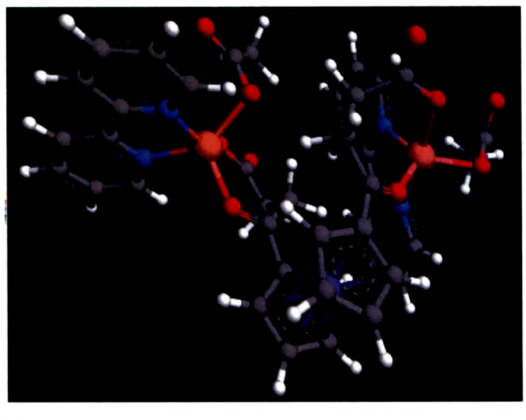


Fig.6.11 Geometry of the complex **[dsf(Cubipy)$_2$](Ac)$_2$**, optimized using UFF.

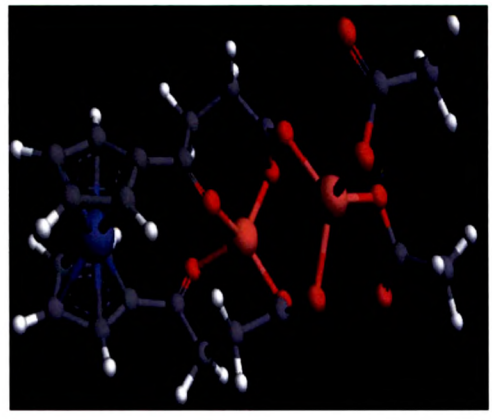


Fig.6.12 Geometry of the complex **[dsf(CuAc)$_2$]** (by **Type-A**), optimized by UFF.

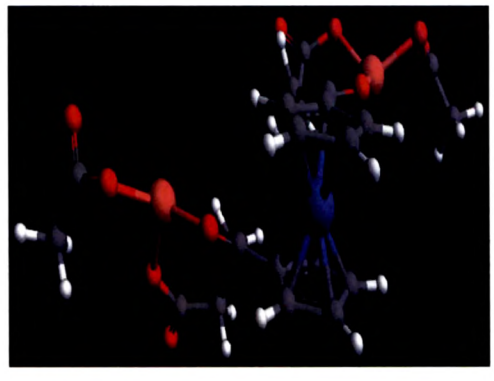


Fig.6.13 Geometry of the complex **[dsf(CuAc)$_2$]** (by **Type-B**), optimized by UFF.

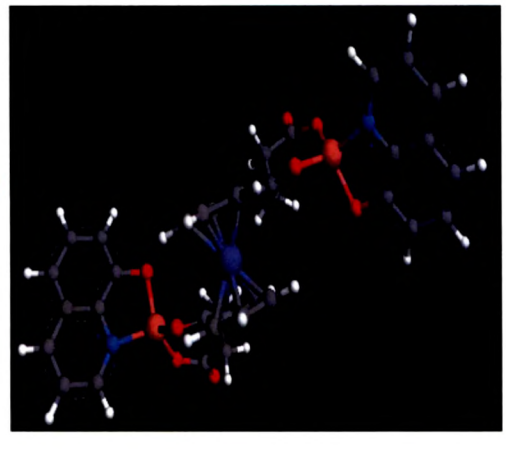


Fig.6.14 Geometry of the complex **[dsf(Cu8hq)$_2$](Ac)$_2$**, optimized by UFF.

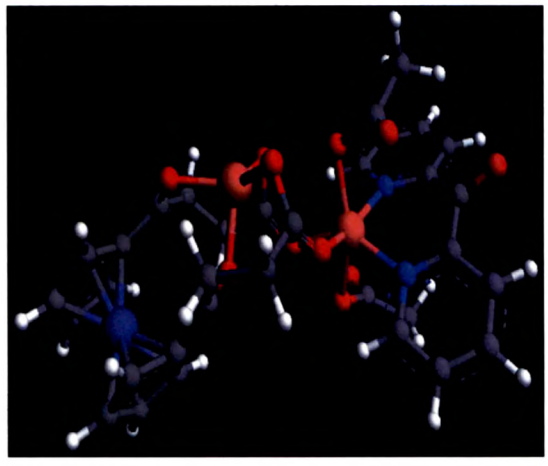


Fig.6.15 Geometry of the complex **[dsfCu$_2$dpk](Ac)$_2$**, optimized by UFF.

In the trinuclear complex, **[dsfCu$_2$dbm](Ac)$_2$** (**Fig.6.16**), the Cu-Cu distance was found to be 3.534Å and the Cu-Fe-Cu angle was observed as 24.73°.

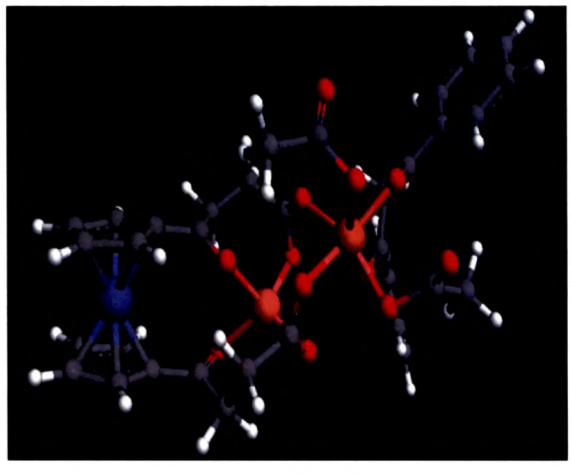
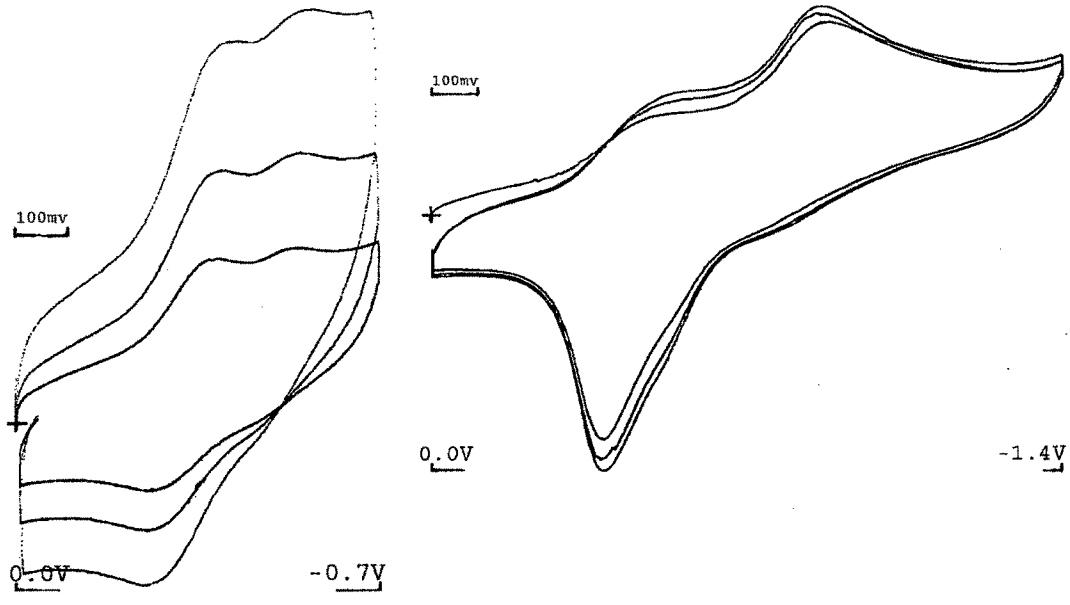


Fig. 6.16 Geometry of the complex **[dsfCu$_2$dbm](Ac)$_2$**, optimized by UFF.

6.5 Electrochemical studies

Functionalized metallocene could accommodate a particular metal ion at its coordination site and undergo concurrent redox change.[73] The aim of the electrochemical recognition field, is the development of new receptors, capable to modify selectively their electrochemical properties upon coordination with the target species. These systems should contain two components: i) one electro-active group (antenna) and ii) binding sites

specially designed for the specific guests. Ferrocene is particularly attractive functional antenna due to its electrochemical properties, which can be disturbed by guests coordinated in close proximity. In this context, Ferrocene functionalized polyamines are studied recently by X. Cui *et al.* [42] The electrochemical behavior of all the six Cu_2Fe hetero trinuclear complexes has been studied by cyclic voltammetry. The corresponding redox potentials are summarized in Table 6.4. Interestingly, all the complexes show very different potentials from each other.



(a) **(b)**

[Pt disk working electrode, Pt wire counter electrodes and Ag/AgNO$_3$ (0.1M in CH$_3$CN) as reference electrodes were used]

Fig.6.17 Cyclic *voltammograms* of **[dsf(Cubipy)$_2$](Ac)$_2$** (a) at different scan rates, and complex **[dsfCu$_2$dbm](Ac)$_2$** (b).

The complexes undergo reversible redox to Cu^I-Cu^I state between -0.280 to -0.840V, when the lower potential is restricted to -1.0V. There is second reduction at about -1.2V, when the lower limiting potential is restricted to -1.5V or beyond. This reduction process can be assigned to the reduction Cu^I-Cu^I species to Cu^0. When the second reduction is allowed, the process becomes irreversible in most of the cases, with the oxidation of Cu^I-Cu^I species to Cu^{II}-Cu^{II} species still occurring at the same potential.

In the complex [dsf(CuAc)$_2$], the reduction to Cu^I-Cu^I state occurs with one E_{pc} value at -0.8V, with two corresponding oxidation processes at –0.244 and -0.696V at 50mV scan rate. However, reduction to Cu^0 is electrochemically irreversible, the Cu^{II} complex is slowly generated and peaks corresponding to Cu^I-Cu^I to Cu^{II}-Cu^I and Cu^{II}-Cu^I to Cu^{II}-Cu^{II} processes are observed at approximately same potentials, as seen in the voltammograms with restricted limiting potentials. An additional oxidation and corresponding reduction is observed at lower negative potentials corresponding to free copper ions.

Table 6.4 Redox potentials of the complexes.

Complex	Cu^{II}-Cu^{II} to Cu^{II}-Cu^I		Cu^{II}-Cu^I to Cu^I-Cu^I	
	$E_{Pc}(1)$	$E_{Pc}(2)$	$E_{Pa}(1)$	$E_{Pa}(2)$
[dsf(CuAc)$_2$]	-0.804	-2.152	-0.244	-0.696
[dsf(Cuphen)$_2$](Ac)$_2$	-0.752	-1.352	-0.240	-0.588
[dsf(Cubipy)$_2$](Ac)$_2$	-0.280	-0.440	-0.160	----
[dsf(Cu8hq)$_2$](Ac)$_2$	-0.376	-0.784	----	----
[dsfCu$_2$dpk](Ac)$_2$	-0.312	-1.064	-0.184	----
[dsfCu$_2$dbm](Ac)$_2$	-0.416	-0.784	-0.264	----

*All the redox potentials of complexes with reference to Cp_2Fe/Cp_2Fe^+ couple.

In the complexes of [dsf(Cuphen)$_2$](Ac)$_2$ and [dsf(Cubipy)$_2$](Ac)$_2$ containing *phen* and *bipy* as capping ligands, reduction to Cu^I-Cu^I is stepwise and reversible with single E_{pc} at -0.752 (phen) and -0.280V (bipy), respectively. Again in both of these complexes, when reduction to Cu^0 is allowed, an electrochemically irreversible but chemically reversible process, with the peak corresponding to Cu^I-Cu^I to Cu^{II}-Cu^{II} oxidation appears at the same position as in the restricted potential scan. Similar observations are made in the complex [dsf(Cu8hq)$_2$](Ac)$_2$, except that, the reduction to Cu^I-Cu^I state is simultaneous process instead of being stepwise. In the Type-B complexes, a simultaneous reversible two electron redox corresponding to Cu^{II}-Cu^{II} to Cu^I-Cu^I and Cu^I-Cu^I to Cu^{II}-Cu^{II} has been observed with ΔEp values equal to 120mV corresponding to a two electron transfer process. In both of these complexes reduction to Cu^0 state is irreversible as is always expected in a copper complex.

The stepwise redox in the complexes of phen and bipy can be attributed to strong π-interaction between metal ion and these two ligands. This also indicates the electronic communication and delocalization of the added electron density over both copper centres through the ferrocenoyl bridge. In fact the reversibility of Cu^{II}-Cu^{II} to Cu^{I}-Cu^{I} in all of these complexes indicates the presence of significant π-interaction between the metal and either ferrocenoyl or capping ligands or both. It also indicates the possibility of significantly distorted coordination geometry which can readily accommodate either Cu^{I} or Cu^{II} with equivalent ease.

In Type-B complexes the first reduction to Cu^{I} state is observed at less negative potential in $[dsfCu_2dpk](Ac)_2$ than in the $[dsfCu_2dbm](Ac)_2$ complex. In the Type-B complexes also the first redox process corresponding to Cu^{II}-Cu^{II} to Cu^{I}-Cu^{I} is a two electron reduction process with ΔEp between 120 to 150mV. The process is easier with less negative E_{pc} value in the complex of $[dsfCu_2dpk](Ac)_2$ due to the presence of π-accepting pyridyl groups as compared to the complex of $[dsfCu_2dbm](Ac)_2$, where E_{pc} corresponding to the reduction to Cu^{I} is observed at lower potential of -0.41V.

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