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RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF COPPER (II) NICKEL (II), COBALT(II), ZINC(II), TIN(IV) AND CADMIUM(II) COMPLEXES WITH FERROCENYL PHENYL-N-THIOSEMICARBAZONES

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ABSTRACT

A few complexes of copper(II), nickel(II), cobalt(II), Zinc(II), tin(IV) and cadmium(II) with two newly synthesized organometallic compounds, 1-Formylferrocene phenyl-N-thiosemicarbazone (HFfptsc) and 1-acetyl ferrocene phenyl N-thiosemicarbazone (HAfptsc) have been isolated. The interaction of (HFfptsc) with Me_2SnCl_2 and MeSnCl_3 . Yield a series of organotin (IV) compounds. The reactivity of $\text{MeSn}(\text{Ffptsc})_2\text{Cl}$ towards MeSH , $\text{Me}_2\text{N SiMe}_3$, $\text{Me}_2\text{NsiMe}_3$, SiMe_3N_3 , and $\text{Me}_3\text{SiC}\equiv\text{C-Ph}$ are also described. These complexes have been characterized on the basis of elemental analysis, molecular weights, molar conductances, magnetic moments and spectroscopic (IR, ¹H-NMR, UV-vis) data.

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INTRODUCTION

Sulphur containing biomolecules available in the cells are considered as one of the reasons in the postulated mechanism of drug resistance and toxicity of cis-platin like drugs (Singh, 2012). Binding with such thio molecules in the cell decreases the intracellular accumulation of metallo drugs and consequently it cannot reach to bind the DNA found inside the cell and cause cell death. Therefore kinetic knowledge of the interaction of such metal complexes with DNA fragment vis-a-vissulphur containing biomolecule is of importance in rationalization of the antitumor activity as well as toxicity of such metallo drugs. Many chemotherapeutic drugs have been designed based on the ability of these synthetic drugs to target the DNA molecule. A new bidentate Schiff base derived from 2,4-dihydroxy benzophenone and aniline and its metal complexes were synthesized and evaluated for their DNA binding ability and the in vitro biological activity of these complexes were markedly better than that of the Schiff base. The results indicated that Cu(II) complexes bound to the DNA through noncovalent interactions (Subbaraj, 2014). The complexes of Zn(II) were observed good biological and exhibit enhanced activities as compared to their parental ligands (Singh, 2012).

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The complexes of Zn(II) showed good bacterial and fungicidal effects (Hanif, 2016). The oxidisableferrocenyl ligands have currently added much interest since the ferricinium ions have anti-tumour activity. Reports are also available on the activity of platinum and gold complexes (D.T.Hill, 1989) of 1,1'-bis(diphenylphosphino) ferrocene (Fdpp) against experimental tumours. However complexes of Fdpp do not readily undergo oxidation (Gorain, 1989 and Houlton, 1990). The synthesis of oxidisableferrocenyl ligands would allow the design of multifunctional drugs. Further a mention may be made that replacement of aromatic groups by ferrocenyl moiety in the penicillins and cephalosporins leads to high antibiotic activity (Edwards, 1975). Here we report ferrocenyl phenyl l-N-thiosemicarbazone ligands HFfptsc and HAfptsc (structure I) and their complexes with some metal (II) and organotin (IV) ions. The reactivity of $\text{MeSn}(\text{Ffptsc})_2\text{Cl}$ synthesized in the present investigation, towards MeSH , $\text{Me}_2\text{NsiMe}_3$, Me_3SiN_3 and $\text{Me}_3\text{SiC}\equiv\text{Cph}$ are also described.

MATERIALS AND METHODS

1-formylferrocene and 1-acetyl ferrocene (Fluka and Sigma Chemicals) were used as such. These ferrocene derivatives were also synthesized by the reported procedure (Graham, 1968). Other chemicals and solvents used were purified and dried before use by standard procedures.

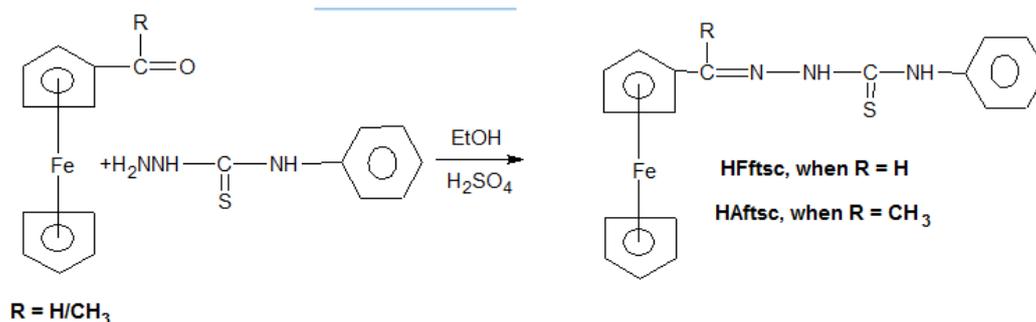


Table 1. Characterisation data of the complexes

Compounds	Mol. wt.	Colour	M.P.	Found (Calc.) %			
				C	H	N	M
C ₁₈ H ₁₇ N ₃ SFe (HFftsc)	360 (362)	Brown	180°C(d)	59.40 (59.52)	4.56 (4.68)	11.42(11.57)	–
C ₃₆ H ₃₂ N ₆ S ₂ Fe ₂ Ni(1) (Ffptsc) ₂ Ni	750 (782)	Reddish Brown	190°C(d)	55.10 (55.21)	3.90 (4.08)	10.60 (10.73)	–7.35 (7.56)
C ₃₈ H ₃₆ N ₆ S ₂ Fe ₂ Ni(2) (Afptsc) ₂ Ni	800 (810)	Redish Brown	200°C	56.13 (56.26)	4.25 (4.44)	10.20 (10.36)	7.10 (7.24)
C ₅₄ H ₄₈ N ₉ S ₃ Fe ₃ Co(3) (Ffptsc) ₂ Co	–	Deep brown	190°C(d)	56.50 (56.61)	4.03 (4.19)	10.88 (11.0)	5.0 (5.14)
C ₅₇ H ₅₄ N ₉ S ₃ Fe ₃ Co(4) (Afptsc) ₂ Co	–	Deep brown	195°C(d)	57.50 (57.64)	4.42 (4.55)	10.52 (10.61)	4.81 (4.96)
C ₃₆ H ₃₂ N ₆ S ₂ Fe ₂ Cu(5) (Ffptsc) ₂ Cu	–	Light Brown	180°C(d)	54.72 (54.87)	3.87 (4.06)	10.51 (10.67)	7.91 (8.07)
C ₃₈ H ₃₆ N ₆ S ₂ Fe ₂ Cu(6) (Afptsc) ₂ Cu	–	Reddish brown	200°C(d)	55.80 (55.93)	4.30 (4.41)	10.20 (10.30)	7.65 (7.79)
C ₃₆ H ₃₂ N ₆ S ₂ Fe ₂ Zn(7) (Ffptsc) ₂ Zn	770 (789)	Light yellow	400°C	54.60 (54.74)	3.92 (4.05)	10.51 (10.63)	8.10 (8.28)
C ₃₈ H ₃₆ N ₆ S ₂ Fe ₂ Zn(8) (Afptsc) ₂ Zn	808 (817)	Light Brown	>200°C	55.70 (55.80)	4.22 (4.40)	10.11 (10.20)	7.84 (8.0)
C ₃₆ H ₃₂ N ₆ S ₂ Fe ₂ Cd(9) (Ffptsc) ₂ Cd	815 (836)	Light Brown	>200°C	51.53 (51.66)	3.69 (3.82)	9.87 (10.04)	13.39 (13.44)
C ₃₈ H ₃₆ N ₆ S ₂ Fe ₂ Cd(10) (Afptsc) ₂ Cd	850 (864)	Brown	>200°C	52.12 (52.27)	4.20 (4.35)	9.51 (9.62)	13.51 (13.60)
C ₃₈ H ₃₈ N ₆ S ₂ Fe ₂ Sn(11) Me ₂ Sn(Ffptsc) ₂	855 (872)	Reddish brown	>200°C	52.12 (52.27)	4.20 (4.35)	9.51 (9.62)	13.51 (13.60)
C ₃₇ H ₃₅ N ₆ S ₂ Fe ₂ ClSn(12) MeSn(Ffptsc) ₂ Cl	872 (892)	Reddish Brown	>200°C	49.61 (49.72)	3.77 (3.91)	9.31 (9.40)	13.12 (13.29)
C ₃₈ H ₃₉ N ₆ S ₂ Fe ₂ Sn(13) MeSn(Ffptsc) ₂ (SMe)	890 (905)	Dark Brown	>200°C	50.20 (50.36)	4.10 (4.30)	9.11 (9.27)	12.93 (13.10)
C ₃₉ H ₃₁ N ₇ S ₂ Fe ₂ Sn(14) MeSn(Ffptsc) ₂ (NMe ₂)	890 (911)	Brown	200°C(d)	51.25 (51.35)	5.43 (5.59)	10.60 (10.75)	12.91 (13.02)
C ₃₇ H ₃₅ N ₆ S ₂ Fe ₂ Sn(15) MeSn(Ffptsc) ₂ (N ₃)	880 (899)	Brown	220°C(d)	49.20 (49.36)	3.72 (3.89)	13.90 (14.0)	13.8 (13.19)
C ₄₃ H ₄₀ N ₆ S ₂ Fe ₂ Sn(16) MeSn(Ffptsc) ₂ (C≡CPh)	920 (934)	Light brown	172°C(d)	55.10 (55.22)	4.15 (4.28)	8.80 (8.98)	12.60 (12.78)

The compounds Me₂SnCl₂ and MeSnCl₃ were prepared following the method of Luijten and Vander Kirk (Luijten, 1959) while Me₃Sic=Cph was prepared as described in literature (Petron, 1953; Birkofen, 1936). The reactions with organotin compounds were carried out under dry nitrogen atmosphere.

Preparation of ligands

Condensation of 1-Formylferrocene or 1-acetyl ferrocene (Baner, 1966) with phenyl thiosemicarbazide (1:1) molar ratio) in dry ethanol (under reflux) at pH~5(pH was adjusted by the addition of a few drops of alcoholic H₂SO₄) for 2 hr yielded a light brown solution, which on concentration and cooling gave a brown solid.

It was filtered off, washed with cold ethanol and recrystallised from chloroform, n-hexane (50:50) mixture to give a brown crystalline solid compound of HFftsc in 80% yield. As HAftsc could not be isolated in the pure state in situ preparative methods were employed for the synthesis of complexes.

Preparation of complexes

To a hot solution of HFftsc or HAftsc (0.5 mmol) ethanol (40 cm³) was added a solution of M(OAc)₂.2H₂O (0.25 mmol) (M=Co, Ni, Cu, Zn, Cd) in ethanol (15 cm³) with stirring when immediately a solid compound separated out. However, the reaction mixture was heated under reflux for 1 h and compound of the type ML₂ (where HL stands of HFftsc and HAftsc) was formed and collected on a filter, washed several times with warm ethanol and dried in vacuo; yield 70%. The compound (1) to (10) (Table 8.1) were prepared in a similar way. Other identical reactions of ligands with MCl₂.nH₂O (M=Co, Ni, Cu) or M(NO₃)₂.nH₂O yielded analogous complexes as obtained with M(OAc)₂.2H₂O but in poor yield. However, addition of aqueous ammonia to the reaction mixture (pH~9) improved the yield in good amount (about 75%). The HFftsc (0.025 mol) in methanol–nitromethane mixture (25 cm³) was added Me₂SnCl₂ or MeSnCl₃ (0.0125 mol) in dry toluene (30 cm³) with stirring. The reaction mixture was stirred for 10 h at 50–60°C and the solvent removed under reduced pressure. n-Hexane (15 cm³) was then added to this crude

product and cooled to -20°C to get red-brown crystals of $\text{Me}_2\text{Sn}(\text{Ffptsc})_2$ (11) and $\text{MeSn}(\text{Ffptsc})_2\text{Cl}$ (12) respectively. These were filtered, washed with *n*-hexane and dried in vacuo, yield 70%.

Reactions of $\text{MeSn}(\text{Ffptsc})_2\text{Cl}$ (12)

Reaction with MeSH

One equivalent of (12) was added to 1 equivalent of MeSH in a mixed solvent (50/50, v/v) of THF-toluene and stirred at room temperature in the presence of stoichiometric amount of Et_3N for 3 days. After removing $\text{Et}_3\text{N-HCl}$, the volume of the solution was reduced (in vacuo when dark brown crystals of $\text{MeSn}(\text{Ffptsc})_2$ (SMe) (13) were obtained on cooling to -20°C . It was filtered, washed with *n*-hexane and dried in vacuo, yield 70%.

Reaction with $\text{Me}_2\text{NSiMe}_3$

As in (13) above, (12) was treated with $\text{Me}_2\text{NSiMe}_3$ in equimolar quantities and $\text{MeSn}(\text{Ffptsc})_2(\text{NMe}_2)$ (14) was isolated in ~65% yield.

Reaction with $\text{Me}_3\text{Si}(\text{N}_3)$

The reaction of (12) with $\text{Me}_3\text{Si}(\text{N}_3)$ in THF similarly gave $\text{MeSn}(\text{Ffptsc})_2(\text{N}_3)$ (15) in ~60% yield.

Reaction with $\text{Me}_3\text{SiC}\equiv\text{CPh}$

The reaction of (12) with $\text{Me}_3\text{SiC}\equiv\text{CPh}$ (1:1 equivalent) in THF yielded a light brown complex, $\text{MeSn}(\text{Ffptsc})_2(\text{C}\equiv\text{CPh})$ (16) in 50% yield.

The physical measurements were carried out as described elsewhere (Dey, 1985; Dey, 1982 and Dey, 1987). The analytical data of the complexes are given in Table 1.

RESULTS AND DISCUSSION

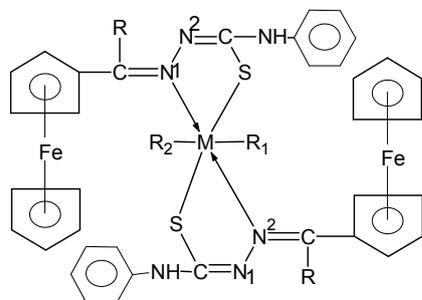
The reactions of phenyl thiosemicarbazide (Hfptsc) with 1-formylferrocene and 1-acetyl ferrocene (1:1 molar ratio) in ethanol with few drops of H_2SO_4 yielded the organometallic ligands, 1-formylferrocene phenyl thiosemicarbazone (HFfptsc) and 1-acetyl ferrocene phenyl thiosemicarbazone (HAfptsc) respectively. However, only Hfptsc could be isolated in a pure state and was used for complex formation of the type $[\text{M}(\text{Ffptsc})_2]$ (Table 8.1). As HAfptsc could not be isolated in the pure state, in situ preparative methods were employed for the isolation of complexes containing $[\text{Afptsc}]^-$ anion (Table 1). The reactions of metal (II) acetates with Hfptsc and HAfptsc in ethanol gave coloured complexes (1)–(10) of the type, $\text{M}(\text{L})_2$ (when $\text{HL}=\text{HFfptsc}$ and HAfptsc ; $\text{M}=\text{Cu}^{+2}$, Ni^{+2} , Zn^{+2} and Cd^{+2}) and $\text{M}(\text{L})_3$ (when $\text{M}=\text{Co}^{3+}$). The complexes (1)–(10) can also be obtained by the reactions of $\text{MCl}_2\cdot n\text{H}_2\text{O}/\text{M}(\text{NO}_3)_2\cdot n\text{H}_2\text{O}$ in ethanol at pH~9 (aqueous ammonia) with the above ligands. The reactions of organotin(IV) chlorides, such as Me_2SnCl_2 and MeSnCl_3 with HFfptsc in mixed solvents of MeOH-MeNO₂, yielded organotin(IV) derivatives $\text{Me}_2\text{Sn}(\text{Ffptsc})_2$ (11) and $\text{MeSn}(\text{Ffptsc})_2\text{Cl}$ (12) respectively. The complex $\text{MeSn}(\text{Ffptsc})_2\text{Cl}$ (12) reacted with MeSH, $\text{Me}_2\text{NSiMe}_3$, $\text{Me}_3\text{Si}(\text{N}_3)$ and $\text{MeSiC}\equiv\text{C-Ph}$ leading to the

formation of thiolato-, amino-, azido- and ethylbenzene (or phenylacetylide) complexes of tin(IV) of the type $\text{MeSn}(\text{Ffptsc})_2(\text{L}_1)$ [where, $\text{L}_1=\text{SMe}$, (13); $\text{L}_1=\text{NMe}_2$, (14) $\text{L}_1=\text{N}_3$, (15); $\text{L}_1=\text{C}\equiv\text{C-Ph}$, (16)]. It may be mentioned that not many reports are available on the reactions of $\text{Me}_3\text{Si}(\text{N}_3)$ with 'Sn-Cl' bond for the synthesis of azido complexes. The characterization data are given in Table 1. The new complexes are stable under ordinary conditions except the complex (16), which slowly decomposes in air and also at 172°C . The azidocomplex (15) decomposed with a mild explosion at $220-223^{\circ}\text{C}$. The elemental analysis of the compounds agree with the formulations shown in Table 8.1. The molecular weights (measured cryoscopically in chloroform and *p*-dichlorobenzene and also by Rast's method) also support these results. The complexes are soluble in chloroform, nitromethane, DMSO, DMF, partially soluble in alcohol, acetone and benzene and insoluble in ether. Their molar conductivity data in the range $5.5-15.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in DMF solution is characteristic of their non-electrolytic nature (Geary, 1971). All the complexes excepting (5) and (6) are diamagnetic in nature. The copper(II) complexes (5) and (6) exhibit magnetic moments 1.79 BM and 1.73 BM respectively at room temperature, a value close to the spin only value of 1.73 BM, expected for $S=1/2$ system. Based on these magnetic moment values, either a distorted octahedral or a square planar geometry may be proposed for the copper(II) complexes (Figgis, 1959; Figgis, 1964) in the solid state. The copper(II) complexes display two or three bands in the visible region, the bands at 785–755 nm being assigned to ${}^2\text{B}_{1g}\rightarrow{}^2\text{A}_{1g}$ and ${}^2\text{B}_{1g}\rightarrow{}^2\text{B}_{2g}$ transitions, while the second band at ~500 nm can be attributed to ${}^2\text{B}_{1g}\rightarrow{}^2\text{E}_g$ transitions, commensurate with a distorted octahedral Zstructure (Nishida, 1979 and Singh, 1982). The diamagnetic nickel(II) complexes (1) and (2) are probably square planar (Cotton, 1972). This observation is supported by the electronic spectral bands in the 700–650 and 470 nm regions assignable to ${}^1\text{A}_{1g}\rightarrow{}^1\text{A}_{2g}$ and ${}^1\text{A}_{1g}\rightarrow{}^1\text{B}_{1g}$ transitions in a square planar field around nicle(II) (Chandra, 1985 and Dey, 1972). The diamagnetic cobalt(III) complexes (3) and (4) show two broad bands ~650 nm and 468 nm regions, which may tentatively be assigned as the split components of the ${}^1\text{A}_{1g}\rightarrow{}^1\text{T}_{1g}$ transition and to ${}^1\text{A}_{1g}\rightarrow{}^1\text{T}_{1g}$ transition obscured by the ligand $\pi\rightarrow\pi^*$ transitions⁽²⁴⁾. This suggests a pseudo-octahedral structure for the complexes (3) and (4).

The UV-spectral bands of the ligand HFfptsc and the complexes were measured in chloroform. The absorption bands at ~260–270 nm may be due to the B band of the cyclopentadienyl ring (Dey, 1991). The d-d transition might influence these bands as reported earlier (Ajayi, 1967). A high energy band ~330 nm may be assigned to the M-L charge-transfer band. This band was found to shift by ~5–15 nm to a higher wavelength (Ajayi, 1969). The band ~462–470 nm is close to that in the free ligand (Rosenblum, 1963). The IR spectrum of the free ligand HFfptsc (KBr disc) displays no band in the 2570 cm^{-1} region for νSH group, instead an intense band located at 780 cm^{-1} for $\nu\text{C}=\text{S}$ is observed suggesting that in the solid state the ligand remains in thio-keto form. However, in solution, both the thioketo and thiolotautomeric forms may remain in equilibrium (Nakamoto, 1970). The free HFfptsc also shows bands at 3380 cm^{-1} (medium) and 1600 cm^{-1} (strong) assignable to $\nu\text{N-H}$ and $\nu\text{C}=\text{N}$ respectively. The characteristic bands of the ferrocene group appear at 3075,

1440, 880 and 510 cm^{-1} (ref.(29). In the complexes (1) to (16) the $\nu\text{N-H}$ band disappears and a new band due to azinechromophore ($>\text{C}=\text{N}-\text{N}=\text{C}<$) is observed at 1605 cm^{-1} (ref.30). Along with this, the lowering of $\nu\text{C}=\text{N}$ by $\sim 10\text{ cm}^{-1}$ indicates coordination of azomethine nitrogen atom.

The thioamide bands (I to IV) of the free ligand in the $1520\text{--}780\text{ cm}^{-1}$ region are affected appreciably in all the metal complexes. The thioamide band IV mainly due to $\nu\text{C}=\text{S}$ is located at 780 cm^{-1} . In the complexes (1) to (16), this band is shifted to $680\text{--}650\text{ cm}^{-1}$ as expected (Chandrasekar, 1981) and is confirmed by the appearance of a single band at $400\text{--}370\text{ cm}^{-1}$ assignable to $\nu\text{M-S}$ (Ransch, 1969). The bands in the $1225\text{--}880\text{ cm}^{-1}$ region due to $\nu\text{C-O}$ and $\nu\text{C-N}$ and out-of-plane and in-plane deformation modes of the phenyl ring moiety are not appreciably affected in the metal complexes, indicating that phenyl ring is not involved in bonding (Han, 2005). Thus in the complexes (1)–(16), the ligands HFfptsc and HAftsc function in a monobasic bidentate fashion bonding through S and N atoms. In addition to these infrared bands, the metal complexes display bands in the lower regions ($420\text{--}360\text{ cm}^{-1}$ and $350\text{--}300\text{ cm}^{-1}$) which are tentatively assigned to M-N and M-S stretching vibrations (Bermejo, 2008). A medium intense band observed at $\sim 330\text{ cm}^{-1}$ for the complex $\text{MeSn}(\text{Ffptsc})_2\text{Cl}$ (12) may be assigned to $\nu\text{Sn-Cl}$. The present findings indicate that only one type of complex ML_2 (where HL stands for HFfptsc or HAftsc) was isolated (where $\text{M}=\text{Ni}, \text{Cu}, \text{Zn}, \text{Cd}$). Efforts to prepare complexes with the keto form of the ligands were unsuccessful. The cobalt(III) ion, however, forms a tris complex of the type CoL_3 , the bonding mode being similar to the above complexes.



Proposed structure for the complexes (1), (2), (5)–(16)

Explanation of structure II

where $\text{R} \rightarrow \text{HCH}_3, \text{HCH}_3, \text{HCH}_3, \text{HCH}_3$

$\text{R}_1 \rightarrow$ _____

$\text{R}_2 \rightarrow$ _____

$\text{M} \rightarrow \text{Ni, Ni, Cu, Cu, Zn, Zn, Cd, Cd}$

Complex No. (1)(2)(5)(6)(7)(8)(9)(10)

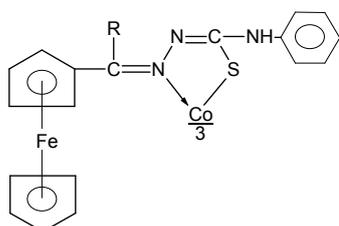
where $\text{R} \rightarrow \text{H, H, H, H, H, H, H, H}$

$\text{R}_1 \rightarrow \text{CH}_3, \text{CH}_3, \text{CH}_3, \text{CH}_3, \text{CH}_3, \text{CH}_3$

$\text{R}_2 \rightarrow \text{CH}_3, \text{Cl}, \text{CH}_3, \text{SN}(\text{CH}_3)_2, \text{N}_3-\text{C}=\text{C}-\text{C}_6\text{H}_5$

$\text{M} \rightarrow \text{Sn, Sn, Sn, Sn, Sn, Sn, Sn}$

Complex No. (11)(12)(13)(14)(15)(16)



III Proposed structure for the complexes (3), (4)

$\text{R} = \text{H}$ (3) and $\text{R} = \text{CH}_3$ (4)

The ^1H NMR spectra of HFfptsc in CDCl_3 and some of the complexes in CDCl_3 and DMSO-d_6 were measured. The NH proton signals at $\delta 11.25\text{ ppm}$ disappeared on deuteration. The integral ratio of these protons on cyclopentadienyl rings, phenyl ring, methyl group and proton on carbon and nitrogen is quite consistent with the formulations of the complexes. As expected, there is no remarkable change in the chemical shifts of ferrocenyl protons on chelation which appeared $\delta 4.0\text{--}4.2\text{ ppm}$ for unsubstituted and $\delta 4.9\text{--}5.1\text{ ppm}$ for substituted ferrocenyl protons. Phenyl ring proton signals $\delta 3.4\text{--}3.6\text{ ppm}$ also remain almost unchanged. However, the NH proton signals completely disappeared in all the complexes suggesting monobasic bidentate (NS donor) nature of the ligands.⁽³⁶⁾ This supports the results from the IR spectroscopic analyses. Besides, the sharp signals for CH_3S , $(\text{CH}_3)_2\text{N}$ and CH_3Sn protons at $\delta 3.3\text{ ppm}$, $\delta 3.4\text{ ppm}$ and $\delta 0.95\text{ ppm}$ respectively in the complexes (11)–(15) suggest the trans arrangement of these ligands. However, aromatic proton signals in the complex (16) appeared as multiplets $\sim \delta 6.8\text{--}8.0\text{ ppm}$. On the basis of the above discussions, the structures of the isolated complexes may tentatively (Drew, 2008; Maayan, 2009; Pallavicini, 2007 and Drew, 2008) be proposed as shown in structures II and III.

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