Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt19

Transition and Non-Transition Metal Complexes with 1-Formylferrocene 4-Methoxybenzoylhydrazone and 1-Acetylferrocene 4-Methoxybenzoylhydrazone

Kamalendu Dey [a] & Kartik Kumar Nandi [a]
[a] Department of Chemistry , University of Kalyani , Kalyani, 741235, West Bengal, India

To cite this article: Kamalendu Dey & Kartik Kumar Nandi (1999) Transition and Non-Transition Metal Complexes with 1-Formylferrocene 4-Methoxybenzoylhydrazone and 1-Acetylferrocene 4-Methoxybenzoylhydrazone, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 29:3, 419-447, DOI: 10.1080/00945719909349461

To link to this article: http://dx.doi.org/10.1080/00945719909349461

SYNTH. REACT. INORG. MET.-ORG. CHEM., 29(3), 419–447 (1999)

TRANSITION AND NON-TRANSITION METAL COMPLEXES WITH 1-FORMYLFERROCENE 4-METHOXYBENZOYLHYDRAZONE AND 1-ACETYLFERROCENE 4-METHOXYBENZOYLHYDRAZONE

Kamalendu Dey* and Kartik Kumar Nandi

Department of Chemistry, University of Kalyani
Kalyani - 741235, West Bengal, India

ABSTRACT

Reactions of 1-formylferrocene 4-methoxybenzoylhydrazone (HFfmbh) and 1-acetylferrocene 4-methoxybenzoylhydrazone (HAfmbh) with hydrated metal salts yield complexes of the type $[Co(L)_2 2H_2O]$ and $[M(L)_2]$ (where, M = Ni(II), Cu(II), Zn(II) or Cd(II) and HL = HFfmbh or HAfmbh). HFfmbh and HAfmbh reacted with $(\pi\text{-}C_5H_5)_2TiCl_2$, Me_2SnCl_2 and $MeSnCl_3$ leading to the formation of the complexes $(\pi\text{-}C_5H_5)_2Ti(Ffmbh)_2Cl$, $(\pi\text{-}C_5H_5)_2Ti(Afmbh)_2Cl$, $Me_2Sn(Ffmbh)_2$, $Me_2Sn(Afmbh)_2$, $MeSn(Ffmbh)_2Cl$ and $MeSn(Afmbh)_2Cl$. Reactions of $MeSn(Ffmbh)_2Cl$, synthesized in this study, with MeSH, $Me_3Si(NMe_2)$, $Me_3Si(N_3)$ and $Me_3Si\text{-}C\equiv C\text{-}Ph$ afforded $MeSn(Ffmbh)_2L^1$ (where L^1 = SMe, NMe_2, N_3 and $C\equiv C\text{-}Ph$). The complexes have been characterized on the basis of elemental analyses, magnetic moment, molar conductance, molecular weight and spectroscopic (electronic, IR

www.dekker.com

and ^1H NMR) data. Both ligands function in a monobasic bidentate fashion in the complexes and the deprotonated enolic form of the ligand is involved in the coordination to the metal.

INTRODUCTION

Studies on metal complexes with organometallic ligands including ferrocenyl ligands are of current interest[1-8]. A search for readily oxidisable ferrocenyl ligands has added a further incentive to studies in the field, as the ferricinium ions possess antitumour activity, whereas the parent ferrocene does not[2]. The activity of platinum and gold complexes[9,10] of 1,1'-bis-(diphenylphosphino)ferrocene (Fdpp) against experimental tumours has been reported. However, Fdpp complexes are not readily oxidised[11,12]. The syntheses of oxidisable ferrocenyl ligands would allow the design of multifunctional drugs. Enhanced antibiotic activity of penicillin and cephalosporine has been noted by replacing aromatic groups with the ferrocenyl moiety[13].

The enzyme inhibiting properties of hydrazone ligands have been reported[14]. The tuberculostatic properties of hydrazides and their derivatives have been extensively studied[15] and the condensation products of hydrazides with different carbonyl compounds (aldehydes/ketones) are known to be less toxic than the parent hydrazides; and this is probably due to the blocking of the free amino group.

In earlier publications Dey *et al.*[16-20] and Iskander *et al.*[21,22] have reported the synthesis, characterization and reactivity of several new hydrazone ligands and their transition and non-transition metal complexes. By comparison, few reports are available on metal complexes of ferrocene-containing hydrazone ligands[1,6,7,23,24] and details of their preparation, properties and structure are lacking.

Because of this and as part of our systematic studies on hydrazide and hydrazone ligands, we describe here the synthesis and characterisation of two new ferrocene substituted aroylhydrazones, 1-formylferrocene 4-methoxybenzoylhydrazone (HFfmbh) and 1-acetylferrocene 4-methoxybenzoylhydrazone (HAfmbh) [eq. (1)], and their complexes with nickel(II), cobalt(II), copper(II), zinc(II), cadmium(II), organotin(IV) and organotitanium (IV) ions.

This paper also describes the reactions of MeSn-(Ffmbh)$_2$Cl, (15), synthesized in the present investigation, with MeSH, Me$_2$NSiMe$_3$, Me$_3$SiN$_3$ and Me$_3$SiC≡CPh.

$$\underset{(R = H\ \text{or}\ Me)}{\eta^5\text{-}C_5H_5.FeC_5H_4COR} + \underset{(Hmbh)}{H_2NNHC(O)C_6H_4.OMe\text{-}p} \xrightarrow[H_2SO_4]{EtOH} \underset{\text{Reflux}}{}$$

$$\eta^5\text{-}C_5H_5Fe.C_5H_4C(R){=}NNHC_6H_4.OMe\text{-}p \qquad (1)$$

R = H, HFfmbh

R = Me, HAfmbh

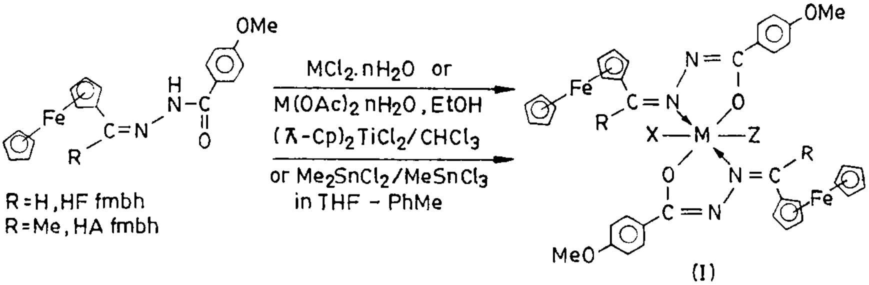
RESULTS AND DISCUSSION

Syntheses

The condensation of 4-methoxybenzoylhydrazide (Hmbh) with 1-formylferrocene or 1-acetylferrocene (1:1 molar ratio) in methanol in the presence of methanolic H_2SO_4 yielded the new aroyl hydrazones, 1-formylferrocene 4-methoxybenzoylhydrazone (HFfmbh) and 1-acetylferrocene 4-methoxybenzoylhhydrazone (HAfmbh), respectively [eqn. (1)].

Reactions of HFfmbh or HAfmbh with hydrated metal salts, cyclopentadienyltitanium(IV) dichloride and organotin(IV) chlorides yielded a large number of metal complexes which are shown in **Fig. 1** and **Table I.**

The reactivity of the 'Sn-Cl' bond in the complex MeSn-(Ffmbh)$_2$Cl (**15**) with different substrates was studied leading to the syntheses of many new organotin(IV) derivatives. Thus, (**15**) on reaction with MeSH in THF-toluene (Et_3N) gave [MeSn(Ffmbh)$_2$(SMe)] (**17**). Similarly, the complex [MeSn(Ffmbh)$_2$Cl] (**15**) reacted smoothly with $Me_3Si(NMe_2)$, $Me_2Si(N_3)$ and $Me_3SiC\equiv C\text{-}Ph$ in a mixed solvent system and afforded amino-, azido- and phenyl ethynyl complexes of organotin(IV) *via* desilylation of the reagents. Since the byproduct, Me_3SiCl, is a low-boiling liquid and miscible with common organic solvents, it is easily removed by low-pressure distillation. Hence, the new organometallic compounds of the



(I)

Explanation of Structures (I)

Complex No. (See Table I)	M	R	X	Z
(1)	Ni	H	-	-
(2)	Ni	CH_3	-	-
(3)	Cu	H	-	-
(4)	Cu	CH_3	-	-
(5)	Co	H	H_2O	H_2O
(6)	Co	CH_3	H_2O	H_2O
(7)	Zn	H	-	-
(8)	Zn	CH_3	-	-
(9)	Cd	H	-	-
(10)	Cd	CH_3	-	-
(11)	Ti	H	π-Cp	Cl
(12)	Ti	CH_3	π-Cp	Cl
(13)	Sn	H	CH_3	CH_3
(14)	Sn	CH_3	CH_3	CH_3
(15)	Sn	H	CH_3	Cl
(16)	Sn	CH_3	CH_3	Cl

Fig. 1. Structural formulations of the isolated complexes.

TABLE I

Elemental Analyses[a], Molecular Weights[b,c] and Molar Conductance Values of Compounds

Compound	Colour	Mol.Wt.	Yield (%)	M.P. (°C)	Analyses Found (Calc.) % C	H	N	M	Λ_M $\Omega^{-1}cm^2mol^{-1}$
[HFfmbh]	Orange	350^c	80	180 (d)	62.83	5.2	7.52	-	-
$C_{19}H_{18}O_2N_2Fe$		(361.84)			(63.10)	(4.97)	(7.73)		
[HAfmbh]	Orange	358^c	85	200 (d)	63.85	5.32	7.44	-	-
$C_{20}H_{20}O_2N_2Fe$		(375.84)			(63.70)	(5.27)	(7.53)		
[Ni(Ffmbh)$_2$] (**1**)	Orange-red	790^b	70	> 300	58.22	4.1	7.15	7.2	6.6
$C_{38}H_{34}O_4N_4Fe_2Ni$		(780.37)			(58.43)	(4.35)	(7.17)	(7.52)	
[Ni(Afmbh)$_2$ (**2**)	Red-brown	-	70	> 300	59.09	4.71	6.43	7.1	6.8
$C_{40}H_{38}O_4N_4Fe_2Ni$					(59.37)	(4.70)	(6.92)	(7.26)	
[Cu(Ffmbh)$_2$] (**3**)	Red	-	65	> 300	57.4	4.1	7.32	8.42	12.4
$C_{38}H_{34}O_4N_4Fe_2Cu$					(58.07)	(4.32)	(7.13)	(8.09)	
[Cu(Afmbh)$_2$] (**4**)	Red	822^b	65	> 300	58.8	4.4	6.9	8.1	12.2
$C_{40}H_{38}O_4N_4Fe_2Cu$		(813.22)			(59.02)	(4.67)	(6.88)	(7.81)	
[Co(Ffmbh)$_2$(H$_2$O)$_2$] (**5**)	Brown	820^b	70	195	55.62	4.71	6.78	7.42	4.62
$C_{38}H_{38}O_6N_4Fe_2Co$		(816.61)			(55.84)	(4.65)	(6.85)	(7.21)	
[Co(Afmbh)$_2$(H$_2$O)$_2$] (**6**)	Brown	852^b	70	215	57.21	5.20	6.42	6.82	4.91
$C_{40}H_{42}O_6N_4Fe_2Co$					(56.83)	(4.97)	(6.63)	(6.97)	

$[Zn(Ffmbh)_2]$ **(7)**	Yellow	-	60	195 (d)	58.2	4.4	6.8	8.2	12.42
$C_{38}H_{34}O_4N_4Fe_2Zn$					(57.93)	(4.31)	(7.11)	(8.30)	
$[Zn(Afmbh)_2]$ **(8)**	Yellow	-	60	290 (d)	59.4	4.8	6.6	8.2	12.6
$C_{40}H_{38}O_4N_4Fe_2Zn$					(58.89)	(4.66)	(6.87)	(8.02)	
$[Cd(Ffmbh)_2]$, **(9)**	Yellow	848[b]	60	> 300	54.48	3.82	6.91	13.38	12.1
$C_{38}H_{34}O_4N_4Fe_2Cd$		(834.09)			(54.67)	(4.07)	(6.71)	(13.47)	
$[Cd(Afmbh)_2]$, **(10)**	Yellow	-	60	> 300	55.70	4.6	6.21	13.10	12.61
$C_{40}H_{38}O_4N_4Fe_2Cd$					(55.67)	(4.4)	(6.49)	(13.03)	
$[(\pi\text{-}Cp)Ti(Ffmbh)_2Cl]$, **(11)**	Brown	858[b]	75	280 (d)	59.46	4.38	6.62	5.4	12.10
$C_{43}H_{39}O_4N_4ClFe_2Ti$		(870.01)			(59.30)	(4.48)	(6.43)	(5.50)	
$[(\pi\text{-}Cp)Ti(Afmbh)_2Cl]$ **(12)**	Brown	-	70	300 (d)	60.0	4.62	6.41	5.21	12.2
$C_{45}H_{43}O_4N_4ClFe_2Ti$					(60.13)	(4.78)	(6.23)	(5.33)	
$[Me_2Sn(Ffmbh)_2]$ **(13)**	Red	872[b]	70	290 (d)	55.3	4.42	6.6	13.42	9.6
$C_{40}H_{40}O_4N_4Fe_2Sn$		(870.49)			(55.14)	(4.49)	(6.43)	(13.63)	
$[Me_2Sn(Afmbh)_2]$ **(14)**	Red	-	70	298 (d)	55.81	4.82	6.02	13.12	8.2
$C_{42}H_{44}O_4N_4Fe_2Sn$					(56.10)	(4.89)	(6.23)	(13.21)	
$[MeSn(Ffmbh)_2Cl]$ **(15)**	Orange-red	888[b]	70	200 (d)	52.4	4.2	6.4	13.02	10.62
$C_{39}H_{37}O_4N_4ClFe_2Sn$		(890.84)			(52.53)	(4.15)	(6.28)	(13.32)	

(Continued)

TABLE I (Contd.)

Compound	Colour	Mol.Wt.	Yield (%)	M.P. (°C)	Analyses Found (Calc.) % C	H	N	M	Λ_M $\Omega^{-1}cm^2mol^{-1}$
[MeSn(Afmbh)$_2$Cl] (**16**)	Red	-	70	215 (d)	53.4	4.24	6.21	12.84	10.51
$C_{41}H_{41}O_4N_4ClFe_2Sn$					(53.54)	(4.46)	(6.09)	(12.91)	
[MeSn(Ffmbh)$_2$(SMe)] (**17**)	Brown	918^b	70	290 (d)	53.10	4.21	6.3	13.0	8.6
$C_{40}H_{40}O_4N_4SFe_2Sn$		(902.39)			(53.19)	(4.43)	(6.20)	(13.15)	
[MeSn(Ffmbh)$_2$(NMe$_2$)] (**18**)	Brown	-	65	200 (d)	54.8	4.8	7.2	13.3	8.4
$C_{41}H_{43}O_4N_5Fe_2Sn$					(54.70)	(4.78)	(7.78)	(13.19)	
[MeSn(Ffmbh)$_2$(N$_3$)] (**19**)	Brown	-	60	210 (d)	52.4	4.3	10.7	13.0	7.24
$C_{39}H_{37}O_4N_7Fe_2Sn$					(52.15)	(4.12)	(10.92)	(13.22)	
[MeSn(Ffmbh)$_2$(C≡C-Ph)] (**20**)	Light brown	947^b	50	190 (d)	59.2	4.2	5.6	12.5	7.10
$C_{47}H_{42}O_4N_4Fe_2Sn$		(956.39)			(58.97)	(4.39)	(5.85)	(12.41)	

(a) Calculated values are in parenthesis, (b) Rast's method and (c) Cryoscopy.

type $[MeSn(Ffmbh)_2(L^1)]$ were obtained in very pure form and good yield [where L^1 = NMe_2, (**18**); L^1 = N_3, (**19**); L^1 = -C≡C-Ph, (**20**)] as shown in **Fig.** 2.

Characterisation and Spectroscopic Data

Both ligands are orange coloured and stable at ordinary conditions and have a sharp melting point at 210°C for HFfmbh and 195°C for HAfmbh. The metal complexes are also coloured and stable under laboratory conditions.

The elemental analyses of the ligands as well as the complexes agree well with their formulations (**Table I**). The molecular weights (measured by cryoscopic or Rast's methods) are also in good agreement with the theoretical values. Both ligands are soluble in methanol, chloroform and dimethyl sulfoxide, while the complexes are soluble in coordinating solvents like dimethyl sulfoxide, dimethylformamide, pyridine and also in other solvents like chloroform and methanol. All the complexes are insoluble in *n*-hexane and ether. The molar conductance values of the complexes in DMSO solutions show very low values, in the range of 4.5-12.6 $\Omega^{-1}cm^2mol^{-1}$ (**Table I**), indicating their non-electrolytic[26] nature.

Magnetic Moments and Electronic Spectra

The UV-Vis. spectral bands of the ligands HFfmbh and HAfmbh in DMSO and some of the complexes in the same solvent are recorded in **Table II**.

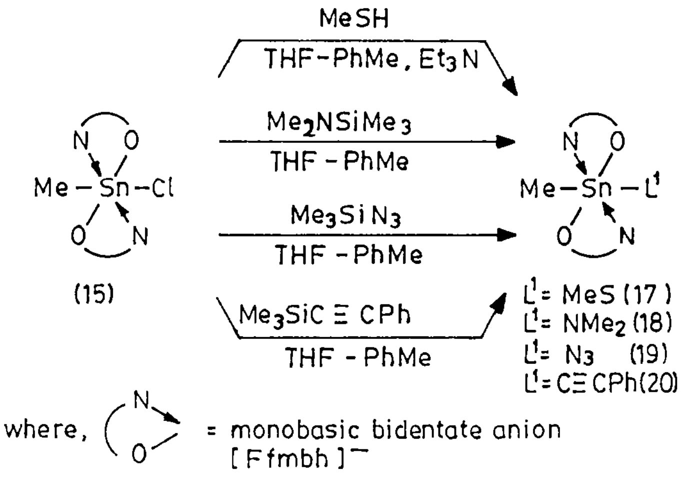


Fig. 2. Reactions of [MeSn(Ffmbh)$_2$Cl].

The band observed in the 260-270 nm region in both ligands and complexes is due to the B band of the cyclopentadienyl ring (the complexes show a small bathochromic shift)[23,24]. The broad band at 450 nm, due to a charge transfer transition between the cyclopentadienyl ring and the iron of the ferrocenyl moiety has been observed in very close position both for the ligand and the complexes[23,26]. The $\pi \rightarrow \pi^*$ transition bands for the ligands were observed at 295-298 nm, but in the case of the complexes this band was shifted to higher frequency by about 10-15 nm. This indicates an increase in conjugation in the complexes[23]. All complexes, other than Cu(Afmbh)$_2$ (**3**), Cu(Afmbh)$_2$ (**4**), Co(II)(Ffmbh)$_2$(H$_2$O)$_2$ (**5**), and Co(II)(Afmbh)$_2$(H$_2$O)$_2$ (**6**), are diamagnetic. The copper(II)

TABLE II

Electronic Spectral Bands of the Ligands and Some of the Complexes with Probable Assignments and Magnetic Moments of the Complexes

Compounds	Medium	λ_{max} in nm	Teentative assignments	μ_{eff} B.M. room temperature
HFfmbh	DMSO	265-298, 450	$\pi \rightarrow \pi^*$ transition charge transfer band	-
HAfmbh	DMSO	266-298, 450	$\pi \rightarrow \pi^*$ transition charge transfer band	-
[Ni(Ffmbh)$_2$] (1)	DMSO	700-650	$^1A_{1g} \longrightarrow {}^1A_{2g}$	Diamagneti
		465 (br)	$^1A_{1g} \longrightarrow {}^1B_{1g}$	
[Ni(Afmbh)$_2$] (2)	DMSO	700-660	$^1A_{1g} \longrightarrow {}^1A_{2g}$	Diamagnetic
		470 (br)	$^1A_{1g} \longrightarrow {}^1B_{1g}$	
[Cu(Ffmbh)$_2$ (3)	DMF	778-750 (two bands)	$^2B_{1g} \longrightarrow {}^2A_{1g}$; $^2B_{1g} \longrightarrow {}^2B_{2g}$	1.74
		500 (br)	$^2B_{1g} \longrightarrow {}^2E_g$	
[Cu(Afmbh)$_2$] (4)	DMF	780-752	$^2B_{1g} \longrightarrow {}^2A_{1g}$; $^2B_{1g} \longrightarrow {}^2B_{2g}$	1.71
		500 (br)	$^2B_{1g}$ ^2E_g	
[Co(Ffmbh)$_2$(H$_2$O)$_2$] (5)	Nujol mull	1000 (br)	$^4T_{1g} \longrightarrow {}^4T_{2g}$	4.85
		476	$^4T_{1g} \longrightarrow {}^4T_{1g}(P)$	
[Co(Afmbh)$_2$(H$_2$O)$_2$] (6)	Nujol mull	1000 (br)	$^4T_{1g} \longrightarrow {}^4T_{2g}$	4.90
		476	$^4T_{1g} \longrightarrow {}^4T_{1g}(P)$	

complexes (**3**) and (**4**) exhibit magnetic moments of 1.74 BM and 1.71 BM, respectively, at room temperature. The values are quite close to the spin-only value, *viz*, 1.73 BM, expected for a S=½ system. So the complexes Cu(Ffmbh)$_2$ (**3**) and Cu(Afmbh)$_2$ (**4**) may attain a distorted-octahedral or square-planar geometry around copper(II) ion[27,28]. These copper(II) complexes display two or three bands in the visible region. The tentative assignments of the bands (**Table II**) are commensurate with a distorted octahedral structure[29,30].

The cobalt(II) complexes [Co(II)(Ffmbh)$_2$(H$_2$O)$_2$] (**5**) and [Co(II)(Afmbh)$_2$(H$_2$O)$_2$] (**6**) show magnetic moment values of 4.85 BM and 4.90 BM, respectively, at room temperature. These high values of the magnetic moments and the stoichiometries suggest a coordination number of six for the central cobalt(II) ion attaining a pseudo-octahedral geometry. Molecular weights (Rast's method) also support this inference. The Nujol mull electronic spectra of the chelates (**Table II**) are consistant with a pseudo-octahedral environment around the cobalt(II) ion[31]. The spectra show a split band at *ca*. 476 nm and a broad band at around 1000 nm, besides very weak bands in the form of shoulders at 714-666 nm. The first and second band can, respectively, be attributed to $^4T_{1g} \longrightarrow {}^4T_{1g}(P)$ and $^4T_{1g} \longrightarrow {}^4T_{2g}$ transitions in an 'O_h' symmetry. The weak bands are most likely due to different forbidden transitions which are usually obscured in the spectra of octahedral cobalt(II) complexes[31,32].

The nickel(II) complexes (**1**) and (**2**) are diamagnetic and are probably square-planar. This contention is supported by the electronic spectral bands in the 700-650 nm and 465 nm regions assignable to $^1A_{1g} \longrightarrow {}^1A_{2g}$ and $^1A_{1g} \longrightarrow {}^1B_{1g}$ transitions in a square-planar field around nickel(II) ion[33,34].

The diamagnetic zinc(II) and cadmium(II) complexes (**7**) - (**10**) are possibly tetrahedral.

The organotitanium(IV) compounds $(\pi\text{-Cp})\text{Ti(Ffmbh)}_2\text{Cl}$ (**11**) and $(\pi\text{-Cp})\text{Ti(Afmbh)}_2\text{Cl}$, (**12**) show a new band around 460-400 nm in addition to the bands for the free ligands. This may be ascribed to charge transfer bands[35] in accordance with the titanium(IV) configuration.

Infrared Spectra

The infrared spectra of the ligands and the metal complexes were recorded in KBr and are depicted in **Table III** with some tentative assignments of important characteristic bands.

Both ligands, HFfmbh and HAfmbh, show bands due to ν(N-H) at 3310 cm^{-1} and 3220 cm^{-1}, respectively. The band due to ν(C=O) for the ligands appeared in the 1642-1636 cm^{-1} region. These bands are completely missing in the complexes, suggesting the enolisation of the ligands during complexation[7]. This is also supported by the fact that no band for OH in the spectra of the ligands and also in the complexes are observed.

TABLE III

Important IR Spectral Bands of Ligands and Complexes (in cm^{-1})

Compounds	ν(Fc)	ν(C=N^1)	ν(C=N^2)	ν(Amide)	ν(N-N)	ν(C-O)	ν(M-N)	ν(M-O)	ν(C-H)
HFfmbh^b	3080, 1428 1110, 1012, 840, 500	1600 (s)	-	-	1040– 1010	1280 (s)	-	-	3200– 3100
HAfmbh^b	3080, 1428 1110, 1012 840, 500	1605 (s)	-	-	1042– 1010	1285 (s)	-	-	3200– 3080
[Ni(Ffmbh)$_2$] **(1)**	3080, 1420 1110, 1012, 840, 505	1590 (s)	1618– 1600 (br)	1620 (s)	1050– 1015	1275– 1265 (br) 1230 (m)	440	310	3200– 3100
[Ni(Afmbh)$_2$] **(2)**	3080, 1428	1595 (m)	1616– 1605 (br)	1520 (s)	1045– 1020 1232 (m)	1275– 1265 (br)	440	300	3200– 3100
[Cu(Ffmbh)$_2$] **(3)**	3080, 1428, 1110, 1000, 840, 502	1595 (m)	1610 (s)	1525 (s)	1050– 1020	1260 (m) 1230 (m)	430	295	3200– 3080
[Cu(Afmbh)$_2$] **(4)**	3080, 1428, 1110, 1010, 840, 502	1580 (s)	1620 (s)	1510 (s)	1048– 1015	1265 (s) 1230 (m)	445	290	3200– 3100
[Co(Ffmbh)$_2$(H$_2$O)$_2$] **(5)**	3080, 1440, 1110, 1012, 845, 505	1592 (m)	1605 (s)	1535 (s)	1045– 1020	1275 (m) 1230 (m)	330	280	3200– 3100
[Co(Afmbh)$_2$(H$_2$O)$_2$] **(6)**	3080, 1440, 1110, 1012, 845, 502	1595 (sh)	1602 (s)	1540 (s)	1040– 1020	1278 (s) 1240 (m)	328	282	3200– 3100

$[Zn(Ffmbh)_2]$ (**7**)	3080, 1440, 1110, 1012, 840, 505	1590 (m)	1605 (s)	1525 (s)	1050– 1020	1280 (m) 1240 (s)	310	270	3200– 3100
$[Zn(Afmbh)_2]$ (**8**)	3080, 1428, 1110, 1012, 840, 505	1592 (m)	1610	1530 (s)	1052– 1020	1270 (m) 1240 (s)	315	266	3200– 3100
$[Cd(Ffmbh)_2]$ (**9**)	3080, 1428, 1110, 1002, 840, 505	1592 (m)	1602 (s)	1540 (s)	1045– 1010	1265 (s) 1242 (m)	302	260	3200– 3100
$[Cd(Afmbh)_2]$ (**10**)	3080, 1428, 1110, 1002, 845, 500	1590 (m)	1600 (s)	1540 (s)	1050– 1020	1262 (s) 1245 (m)	300	265	3200– 3100
$(\pi\text{-}Cp)Ti(Ffmbh)_2Cl$ (**11**)[c]	3080, 1428, 1110, 1012,	1592 (m)	1615– 1600 (s)	1580 (s) 1240 (m)	1042– 1015	1275– 1265 (br) 1230 (m)	520	605	3200– 3100
$(\pi\text{-}Cp)Ti(Afmbh)_2Cl$ (**12**)[c]	3080, 1428, 1110, 1012, 840, 500	1590 (m)	1615– 1605	1582 (s) 1240 (m)	1040– 1010	1275– 1265 (br) 1235	515	602	3200– 3100
$[Me_2Sn(Afmbh)_2]$ (**13**)	3080, 1428, 1100, 1012, 840, 505	1585 (m)	1605 (s)	1520 (s) 1265 (w)	1050– 1020	1260 1230	420	518	3200– 3100
$[Me_2Sn(Afmbh)_2]$ (**14**)	3080, 1428, 1100, 1012, 840, 505	1586 (m)	1610 (s)	1578 (m) 1230 (s)	1045– 1020	1285– 1260 (br) 1240 (m)	418	516	3200– 3100
$[MeSn(Ffmbh)_2Cl]$ (**15**)[d]	3080, 1428, 1100, 1012, 845, 505	1572 (m)	1610 (sn)	1525 (s) 1260	1045– 1020	1250 (s) 1280 (m)	415	520	3200–

(Continued)

TABLE III (Contd.)

Compounds	ν(Fc)	ν(C=N^1)	ν(C=N^2)	ν(Amide)	ν(N-N)	ν(C-O)	ν(M-N)	ν(M-O)	ν(C-H)
[MeSn(Afmbh)$_2$Cl] (**16**)^d	3080, 1428, 1100, 1012, 840, 502	1575 (m)	1610 (s)	1530 (s)	1050-1015	1245 (s) 1230 (m)	412	500	3200-3100
[MeSn(Ffmbh)$_2$(SMe)] (**17**)	3080, 1428, 1110, 1002, 845, 500	1570 (m)	1608 (s)	1530 (s) 1260 (m)	1050-1020	1250 (s) 1232 (m)	415	520	3200-3080
[MeSn(Ffmbh)$_2$(NMe$_2$)] (**18**)	3080, 1428, 1100, 1012, 840, 505	1570 (m)	1607 (s)	1532 (s) 1260 (m)	1048-1015	1250 (s) 1230 (m)	420	515	3200-3100
[MeSn(Ffmbh)$_2$(N$_3$)] (**19**)	30180, 1428, 1100, 1012, 840, 500	1570 (m)	1608 (s)	1530 (s) 1260 (m)	1048-1010	1248 (s) 1230 (m)	425	518	3200-3100
[MeSn(Ffmbh)$_2$(C≡C-Ph)] (**20**)^e	3080, 1428, 1110, 1012, 842, 505	1570 (m)	1608 (s)	1530 (s) 1260 (m)	1050-1015	1250 (s) 1230 (m)	410	520	3200-3080

(a) Fc = $C_5H_5FeC_5H_4$-;

(b) the ν(NH) band was observed at 3300-3220 cm^{-1} and the band for C=O was observed at 1642-1636 cm^{-1};

(c) the band for ν(Ti-Cl) was observd at ~365 cm^{-1};

(d) the band for ν(Sn-Cl) was observed at ~340 cm^{-1};

(e) the ν(C≡C) was observed at 2175-2065 cm^{-1}.

Instead, a band due to ν(C-O) at about 1280-1220 cm^{-1} was observed for the complexes, which also supports the above observation. The above facts suggest that the ligands remain in the keto form in the solid state but in solution, both the keto and enol form may remain in equilibrium[34], and during complexation deprotonation occurs from the enol form.

The free ligands also show a strong band at 1600 cm^{-1} assignable to the ν(C=N) vibration, which was shifted to a lower value by ~10 cm^{-1} in the complexes[3,23,24]. The lowering is due to coordination to the metal ion, although few examples for the increase of the ν(C=N) vibration due to coordination have been reported[21]. Also a sharp band in the range 1628-1600 cm^{-1} was observed in the complexes and this can be attributed to the stretching mode of the azine chromophore (>C=N-N=C<)[7,36].

The presence of coordinated water molecules in the cobalt(II) complexes (**5**) and (**6**) is evidenced by the appearance of broad bands[37] in the region 3540-3350 cm^{-1} along with bands at 880-845 cm^{-1} and at 415-410 cm^{-1}. TG data also support this tentative assignment.

The characteristic bands for the ferrocenyl group appearing in the ligands remained almost unchanged in the complexes[23,38] (**Table III**). In the far-infrared region the complexes (**1**) to (**10**) show medium or strong bands at 440 cm^{-1} and 300 cm^{-1}; these can be assigned as ν(M-N) and ν(M-O) vibrations.

In the organotin(IV) complexes new bands at 540 cm^{-1}, 420 cm^{-1} and 340 cm^{-1} may be attributed to ν(Sn-O), ν(Sn-N) and ν(Sn-Cl) respectively[39]. In addition to the bands for the ferrocenyl group, the organotitanium(IV) complexes show bands at 3105 cm^{-1} and 1032 cm^{-1}, which is attributed to the π-bonded cyclopentadienyl group[40]. Also, the bands for ν(Ti-N) and ν(Ti-O) appeared at 520 cm^{-1} and 605 cm^{-1}, respectively.

^1H NMR Spectra

^1H NMR spectra of the free ligands HFfmbh and HAfmbh and some of their metal complexes have been recorded in DMSO-d_6 with TMS as internal reference and are summarized in **Table IV** with some tentative assignments.

^1H NMR spectra support the conclusion derived from IR and electronic spectra. The ligands HFfmbh and HAfmbh exhibit two peaks in the ^1H NMR spectra at δ 4.2 ppm (s) and at δ 4.8 ppm (br). These are assigned to proton signals of unsubstituted and substituted cyclopentadienyl rings of the ferrocene moiety[41], respectively. Aromatic proton signals appeared at δ 7 to 7.8 ppm (multiplet). Signals for the NH protons appeared at δ 10.8-11.15 ppm (s, br), which disappeared in the complexes. This indicates that the ligands coordinate to the metal ions in the enolic form and by deprotonation[3]. In addition to the signal at δ 3.65 (s) for O-CH_3 protons, the ligand HAfmbh displays a signal at δ 2.21 (s) for =C-CH_3 protons[3,42].

TABLE IV

Proton NMR Spectral Data (in δ ppm) of Ligands and Some Complexes[a]

Compounds	C_5H_5 unsub-stituted	C_5H_4 sub-stituted	Ph	NH	$O-CH_3$	$N=C-CH_3$ $N=C-H$	$C-CH_3$/ $N-CH_3$	$Sn-CH_3$
HFfmbh	4.2 (s)	4.8 (br)	7-7.8 (m)	10.8-11.15 (s)	3.65 (s)	8.2 (s)	-	-
HAfmbh	4.1 (s)	4.8 (br)	7.2-7.8 (m)	10.8-11.5 (s)	3.65 (s)	2.21 (s)	-	-
[Ni(Ffmbh)$_2$] (1)	4.3 (s)	4.7 (br)	6.8-7.6 (m)	-	3.65 (s)	8.0 (s)	-	-
[Ni(Afmbh)$_2$] (2)	4.2 (s)	4.8 (br)	6.7-7.6 (m)	-	3.65 (s)	2.2 (s)	-	-
[Zn(Ffmbh)$_2$] (7)	4.1 (s)	4.75 (br)	6.8-7.58 (m)	-	3.66 (s)	8.1 (s)	-	-
[(π-Cp)Ti(Ffmbh)$_2$Cl] (11)	4.2 (s)	4.7 (br)	6.5-7.2 (m)	-	3.75 (s)	8.25 (s)	-	-
[MeSn(Ffmbh)$_2$Cl] (15)	4.0 (s)	4.8 (br)	6.7-7.2 (m)	-	3.71 (s)	7.34 (s)	-	0.85 (s)
[MeSn(Ffmbh)$_2$(SMe)] (17)	4.1 (s)	4.78 (br)	6.7-7.1 (m)	-	3.64 (s)	7.33 (s)	3.2 (s)	0.82 (s)
[MeSn(Ffmbh)$_2$(NMe$_2$)] (18)	4.1 (s)	4.8 (br)	6.7-7.2 (m)	-	3.66 (s)	7.36 (s)	3.6 (s)	0.91 (s)
[MeSn(Ffmbh)$_2$(C≡C-Ph)] (20)	4.1 (s)	4.76 (br)	6.6-7.8 (m)	-	3.65 (s)	7.35 (s)	-	0.9 (s)

a) Solvent: DMSO-d_6 with TMS as internal standard reference

s = singlet; m = multiplet; br = broad.

In the complexes (measured in DMSO-d_6) the aromatic proton signals appeared downfield, as expected, due to increased conjugation during coordination[42]. But there is no appreciable change in the chemical shifts of ferrocenyl protons on chelation[41].

As expected, the organotitanium(IV) complexes (π-Cp)Ti(Ffmbh)$_2$Cl (**11**) and (π-Cp)Ti(Afmbh)$_2$Cl (**12**) show correct integrations which are consistent with the formulae. The sharp signals for S-CH_3, $N(CH_3)_2$ and Sn-CH_3 protons in the organotin complexes Me_2Sn(Ffmbh)$_2$ (**13**) to MeSn(Ffmbh)$_2$(N_3) (**19**) suggest the *trans* arrangements.

The aromatic proton signals in the complex MeSn(Ffmbh)$_2$(C≡C-Ph) (**20**) appeared around δ 6.8-8.0 ppm (m) and its correct integration supports the formulation of the said complex.

Due to a solubility problem it was not possible to get ^1H NMR spectra for all complexes (**Table IV**).

The structures (**Figs. 1 and 2**) of the compounds have been suggested tentatively on the basis of the above discussions.

EXPERIMENTAL

Materials

1-Formylferrocene and 1-acetylferrocene were purchased from Fluka and Sigma Chemicals, respectively, and were used without further purification. $(\pi\text{-}C_5H_5)_2TiCl_2$ was purchased from Alfa Inorganics. Other chemicals and solvents were purified and dried by standard procedures before use. Me_2SnCl_2 and $MeSnCl_3$ were prepared by the method of Luijten and Vander Kirks[25]. The reactions with organotitanium and organotin compounds were carried out in an atmosphere of dry nitrogen. Physical measurements were carried out as described previously[16-20].

Preparation of the Ligands

To a methanol solution (50 mL) of Hmbh (0.166 g, 1 mmol), a methanol solution (50 mL) of formylferrocene (0.227 g, 1 mmol) was added with stirring and the mixture was heated under reflux at pH ~5 (the pH was adjusted by dropwise addition of methanolic H_2SO_4) for 3 h. The orange-red solution thus obtained gave orange crystals of HFfmbh or HAfmbh on volume reduction and cooling. The product was filtered, washed with cold ethanol and dried *in vacuo*. Yield : 0.18 g (~85%) for HFfmbh and 0.19 g (~85%) for HAfmbh, respectively.

Preparation of Complexes

Nickel(II) Complexes. To a hot solution of HFfmbh (0.723 g, 2 mmol) or HAfmbh (0.751 g, 2 mmol) in dry ethanol (100 mL) was added a solution of $NiCl_2.6H_2O$ (0.237 g, 1 mmol) in dry EtOH (40 mL) with stirring. The reaction mixture was heated under reflux at pH ~ 7 for 2 h, and orange-red $[Ni(Ffmbh)_2]$ (1) or red brown $[Ni(Afmbh)_2]$ (2) was separated. The product was removed by filtration, washed with EtOH and dried in a vacuum desiccator over anhydrous $CaCl_2$. Yield: 0.60 g for (1)and 0.63 g for (2), respectively.

A similar reaction of HFfmbh or HAfmbh with $Ni(NO_3)_2.6H_2O$ or $Ni(OAc)_2.4H_2O$ gave (**1**) or (**2**) also.

Copper(II) Complexes. To a hot solution of HFfmbh (0.723 g, 2 mmol) or HAfmbh (0.751 g, 2 mmol) in methanol (100 mL) was added a solution of $CuCl_2.2H_2O$ (0.17 g, 1 mmol) in methanol (40 mL) with stirring. The resulting red-brown solution was heated under reflux at neutral pH for 2 h. The volume of the clear red solution was reduced to half of its original volume and cooled to ± 5°C to yield red $[Cu(Ffmbh)_2]$ (**3**) or $[Cu(Afmbh)_2]$ (**4**). The products were collected by filtration, washed with cold EtOH and dried *in vacuo*. In the above reaction $Cu(OAc)_2H_2O$ may also be used in place of $CuCl_2.2H_2O$. Yield: 0.55 g for (3) and 0.53 g for (4), respectively.

Cobalt(II) Complexes. A similar reaction of HFfmbh or HAfmbh (2 mmol) with $Co(OAc)_2.4H_2O$ (0.249 g, 1 mmol) in dry ethanol (60 mL) under N_2 gave a brown solution, which on concentration and cooling to ~10°C and subsequent treatment with petroleum ether, gave the brown complex $[Co(Ffmbh)_2 2H_2O]$, (**5**) or $[Co(Afmbh)_2.2H_2O]$ (**6**). It was filtered off, washed with petroleum ether and *n*-hexane and dried *in vacuo*. Yield: 0.55 g for (5) and 0.50 g for (6), respectively.

The complexes $[Co(Ffmbh)_2.2H_2O]$ (**5**) or $[Co(Afmbh)_2\text{-}2H_2O]$ (**6**) were also obtained using $CoCl_2.6H_2O$ at pH ~8 (dilute NH_4OH solution).

Zinc(II) and Cadmium(II) Complexes. Similarly, the yellow to light-yellow compounds [Zn(Ffmbh)$_2$] (**7**); [Zn(Afmbh)$_2$] (**8**); [Cd(Ffmbh)$_2$] (**9**) and [Cd(Afmbh)$_2$] (**10**) were isolated in about 60% yield by the reactions of HFfmbh and Hafmbh with Zn(Ch$_3$COO)$_2$.2H$_2$O (0.22 g) and Cd(CH$_3$COO)$_2$.2H$_2$O (0.27 g) adopting the same reaction conditions. Yield: 0.47 g for (7), 0.49 g for (8), 0.50 g for (9) and 0.52 g for (10), respectively.

Organotitanium(IV) Complexes. The following two methods were used to study the reactions of (π-Cp)$_2$TiCl$_2$ with HFfmbh or HAfmbh.

(i) To a solution of HFfmbh (0.361 g, 0.001 mol) or HAfmbh (0.375 g, 0.001 mol) in dry chloroform (80 mL) was added a fresh, hot solution of (π-Cp)$_2$TiCl$_2$ (0.124 g, 0.0005 mol) in dry chloroform (80 mL) with constant stirring. The mixture was then heated under reflux at neutral pH for 8 h and filtered while hot. The reddish-brown filtrate was concentrated in a rotary evaporator and *n*-hexane was added with stirring and a reddish brown precipitate of [(π-Cp)Ti(Ffmbh)$_2$Cl] (**11**) or [(π-Cp)Ti(Afmbh)$_2$Cl] (**12**) appeared. The compounds were collected by filtration, washed with EtOH and *n*-hexane and dried *in vacuo*. Yield: 0.32 g for (11) and 0.30 g for (12), respectively.

(ii) The mixture of solutions of HFfmbh (0.361 g, 0.001 mol) or HAfmbh (0.375 g, 0.001 mol) with (π-Cp)$_2$TiCl$_2$ (0.124 g, 0.0005 mol) in dry chloroform (150 mL) was stirred at room temperature in the presence of a stoichiometric amount of Et_3N (0.05 g, 0.0005 mol) for 3 days and then filtered. From the resulting brown solution the solvent chloroform was removed under reduced pressure to obtain a solid mass. To the solid was then added EtOH (70 mL) and the mixture was stirred vigorously and filtered. The residue was washed thoroughly with ethanol and finally recrystallized from chloroform-*n*-hexane (40:60, v/v) and dried *in vacuo*. Yield: 0.34 g for (11) and 0.31 g for (12), respectively.

Organotin(IV) Complexes. The following two methods were employed for the syntheses of organotin(IV) compounds.

(i) To a solution of HFfmbh (0.361 g, 0.001 mol) or HAfmbh (0.375 g, 0.001 mol) in 50 mL of nitromethane/methanol (1:1) was added a solution of Me_2SnCl_2 (0.105 g, 0.0005 mol) in toluene (50 mL) with stirring and stirring was continued for 10 h at 60°C. The solvent was removed at reduced pressure. The crude product was then extracted with *n*-hexane and cooled to -20°C, whereby $[M_2Sn(Ffmbh)_2]$ (**13**) or $[Me_2Sn(Afmbh)_2]$ (**14**) separated as red solids. They were filtered, washed with *n*-hexane-toluene mixture (40:60, v/v) and dried *in vacuo*. Yield: 0.33 g for (13) and 0.32 g for (14), respectively.

(ii) Similarly, the reaction of HFfmbh (0.361 g, 0.001 mol) or HAfmbh (0.375 g, 0.001 mol) with $MeSnCl_3$ (0.099 g, 0.0005 mol) in the same solvent as above afforded orange red $[MeSn(Ffmbh)_2Cl]$ (**15**) or red $[MeSn(Afmbh)_2Cl]$ (**16**). Yield:

0.26 g for (15) and 0.27 g for (16), respectively. The compounds are soluble in DMSO and are diamagnetic.

Reactions of [MeSn(Ffmbh)$_2$Cl] (15)

Reaction with MeSH. One equivalent of [MeSn(Ffmbh)$_2$Cl] (**15**) (0.891 g, 1 mmol) was added to one equivalent of MeSH (0.04 g, 1 mmol) in THF-toluene (50:50, v/v) (50 mL) and stirred at room temperature in the presence of a stoichiometric amount of Et_3N (0.1 g, 1 mmol) for 4 days. Solid $Et_3N.HCl$ separated and was removed by filtration and then the volume of the solution was reduced under vacuum. Standing at -20°C gave deep brown crystals of [MeSn(Ffmbh)$_2$(SMe)] (**17**) were obtained. They were filtered, washed with *n*-hexane and dried *in vacuo*. Yield: 0.70 g.

Reaction with $Me_3Si(NMe_2)$. The complex [MeSn(Ffmbh)$_2$Cl] (**15**) (0.891 g, 1 mmol) was treated with an equimolar quantity of $Me_3Si(NMe_2)$ (0.117 g, 1 mmol) as before in the same solvent system (60 mL) and [MeSn(Ffmbh)$_2$(NMe$_2$)] (**18**) was isolated. Yield: 0.72 g.

Reaction with $Me_3Si(N_3)$. The compound [MeSn(Ffmbh)$_2$Cl] (**15**) when treated with $Me_3Si(N_3)$ (1:1 equivalent) in THF for 3 days, yielded the brown compound [MeSn(Ffmbh)$_2$(N$_3$)] (**19**). The byproduct (Me_3SiCl) and the solvent were removed by distillation at low pressure. The crude product (**19**) was extracted with *n*-hexane-THF mixture (50:50, v/v). The solution was cooled to -20°C and the brown crystals which appeared were filtered, washed with *n*-hexane and dried *in vacuo*. Yield: 0.63 g.

Reaction with $Me_3SiC{\equiv}C$-Ph. Similarly, compound (**15**) (1 mmol), when treated with $Me_3SiC{\equiv}C$-Ph (1 mmol) (1:1 equivalent) in THF, yielded light-brown compound [MeSn(Ffmbh)$_2$(C≡C-Ph)] (**20**) in about 50% yield (0.48 g).

ACKNOWLEDGEMENTS

We are thankful to the CSIR, New Delhi, India, for financial assistance and one of us (KKN) is grateful to the CSIR, New Delhi, India, for a Research Associateship. We also thank the Central Drug Research Institute, Lucknow, for elemental analyses and spectroscopic data.

REFERENCES

1. M. Yongxiang and B. Gang, *Inorg. Chim. Acta*, **144**, 1265 (1988).
2. A. Houlton, J. R. Dilworth, R. M. G. Roberts, J. Silver and M. B. Drew, *Polyhedron*, **9**, 2751 (1990).
3. Z. Gang, L. Feng, X. Jishan and M. Yongxiang, *Polyhedron*, **7**, 303 (1988).
4. Z. Xiaoxian, L. Youngmin, N. Fajun and M. Yongxiang, *Polyhedron*, **11**, 447 (1992).
5. S. P. Singh and N. B. Singh, *Polyhedron*, **9**, 557 (1990).
6. S. R. Patil, U. N. Kantak and D. N. Sen, *Inorg. Chim. Acta*, **68**, 1 (1983).
7. S. R. Patil, U. N. Kantak and D. N. Sen, *Inorg. Chim. Acta*, **63**, 261 (1982).

8. H. Iami and T. Ota, *Bull. Chem. Soc. Japan*, 47, 2497 (1974).

9. B. Longato, G. Pilloni, G. Valle, and B. Gorain, *Inorg. Chem.*, 27, 956 (1988).

10. D. T. Hill, G. R. Girard, E. L. McCabe, R. K. Johnson, P. D. Stupik, J. H. Zhang, W. M. Reiff and D. S. Eggleston, *Inorg. Chem.*, 28, 3529 (1989).

11. B. Gorain, B. Longato, G. Fanero, D. Ajo, G. Pilloni, U. Russo, and F. R. Kressi, *Inorg. Chim. Acta*, 157, 259 (1989).

12. A. Houlton, J. R. Millu, R. M. G. Roberts and J. Silver, *J. Chem. Soc. Dalton Trans.*, 2181 (1990).

13. E. I. Edwards, R. Epton and G. Marr, *J. Organometal. Chem.*, 85, C-23 (1975).

14. J. C. Craiz, J. C. Rubo, D. Willis and J. Edger, *Nature* (London), 176, 34 (1955).

15. N. P. Buu-Hoi, N. D. Xuong, N. H. Nam, F. Binon and R. Royer, *J. Chem. Soc.*, 1358 (1953).

16. K. Dey, S. B. Ray, P. K. Bhattacharya, A. Gangopadhyay, K. K. Basin and R. D. Verma, *J. Ind. Chem. Soc.*, 62, 809 (1985).

17. K. Dey and D. Bandyopadhyay, *Trans. Met. Chem.*, 16, 267 (1991).

18. K. Dey, A. K. Sinha Roy, K. K. Bhasin and R. D. Verma, *Indian J. Chem.*, 230 (1987).

19. K. Dey, D. Bandyopadhyay and K. S. Mondal, *Indian J. Chem.*, 30(A), 872 (1991).

20. K. Dey and D. Bandyopadhyay, *Indian J. Chem.*, 31(A), 34 (1992).

21. L. E. Sayed and M. F. Iskander, *J. Inorg. Nucl. Chem.*, 33, 435 (1971).

22. M. F. Iskander, L. E. Sayed and M. A. Lasheen, *Inorg. Chim. Acta*, 16, 147 (1976).

23. M. Yongxiang, Z. Zhengzhi, M. Yun and Z. Gang, *Inorg. Chim. Acta*, 165, 185 (1989).

24. S. I. Goldberg, D. W. Mayo and J. A. Alford, *J. Org. Chem.*, 28, 1708 (1963).

25. J. G. A. Luijten and and G. J. M. Vander Kirk, "Investigation in the Field of Organotin Chemistry", Tin Research Institute, 1959.

26. a) M. Rosenblum, J. O. Santer and W.' G. Jowells, *J. Am. Chem. Soc.*, **85**, 1450 (1963).

b) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).

27. B. N. Figgis and C. M. Harris, *J. Chem. Soc.*, 855 (1959).

28. B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, Ed. F. A. Cotton. Interscience, **6**, 37 (1964).

29. G. Nishida and S. Kida, *Coord. Chem. Rev.*, **27**, 294 (1979).

30. N. K. Singh, J. Agarwal and R. C. Agarwal, *Indian J. Chem.*, **21**(A), 975 (1982).

31. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, p. 333 (1968).

32. R. L. Carlin, "Transition Metal Chemistry", E. Arnold, London, **1**, 1 (1965).

33. S. Chandra, *Polyhedron*, **4**, 663 (1985).

34. K. Dey and D. Bandyopadhyay, *Trans. Metal Chem.*, **16**, 267 (1991).

35. S. Kumar and N. K. Kaushik, *J. Inorg. Nucl. Chem.*, **43**, 2679 (1981).

36. N. S. Biradar and V. H. Kulkarni, *J. Inorg. Nucl. Chem.*, **33**, 2451 (1971).

37. K. Nakamoto, "Infrared spectra of Inorganic and Coordination Compounds", 2nd Edn., Wiley Interscience, New York, p. 167 (1970).

38. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd Edn., Wiley-Interscience, New York, p. 268 (1970).

39. A. Saxena, J. P. Tandon and A. J. Crows, *Polyhedron*, **4**, 1085 (1985).

40. G. Doyle and R. S. Tobias, *Inorg. Chem.*, **6**, 1111 (1967).

41. M. D. Rausch and A. Siegel, *J. Organometal Chem.*, **17**, 117 (1969).

42. Z. Hong-Yun, C. Dong-Li, C, Pei-Kun, C, De-Ji, C, Guang-Xia and Z, Hong-Quan, *Polyhedron,* 11, 2313 (1992).

Received: 8 September 1996
Accepted: 23 October 1998

Referee I: K. K. M. Yousuf
Referee II: M. Athar