Inorganica Chimica Acta, 68 (1983) 1–6

New Tin(IV) and Organotin(IV) Chelates of Ferrocenyl Hydrazones*

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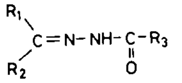
Received July 12, 1982

Several new tin(IV) and organotin(IV) complexes of the composition R_2SnL_2 (where R = chloro, butyl or octyl group and L = ferrocenyl hydrazone anion) have been synthesized by reacting tin(II) dichloride hydrate, dibutyltin(IV) oxide and dioctyltin(IV) oxide with ferrocenyl hydrazones of the type $FcCH{=}N{-}NH{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}Ar$ (where Fc = ferrocenyl moiety and Ar = phenyl, p*-chlorophenyl,* o*-nitrophenyl, salicyl or pyridyl group). These compounds have been characterized on the basis of elemental analysis and infrared and proton magnetic resonance spctral studies. A structure involving chelation by coordination through azomethine nitrogen atom and through amide oxygen atom by replacement of hydrogen atom via enolization is suggested.*

Introduction

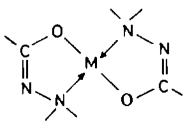
The reactions of aroyl hydrazones of the type (A)



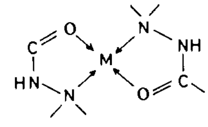
(A)

$$\begin{matrix} R_1 \\ & \diagdown \\ & & C{=}N{-}NH{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}R_3 \\ & \diagup \\ R_2 \end{matrix}$$

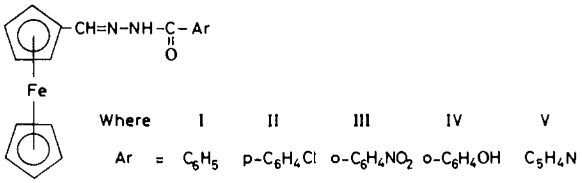
(where R_1 = H or CH_3; R_2 = CH_3 or C_6H_5 and R_3 = C_6H_5) with transition metal ions, especially Ni(II), Co(II) and Cu(II) were reported by Iskander *et al.* [1]. Recently Pardhy *et al.* [2] studied the organotin(IV) derivatives of some aroyl hydrazones. The hydrazones containing C=O and C=N coordinating sites can coordinate either in the enolic form (Ia) or in the keto form (Ib) to the metal ions. Group (IV) metal complexes of aroyl hydrazones have been the subject of detailed studies. Metal aroyl hydrazones are known to possess biological activity and they are potent inhibitors for many enzymatic reactions [3]. Recently Edwards *et al.* [4] have shown that replacement of aromatic groups by ferrocenyl moiety in the penicillins and cephalosporins leads to high antibiotic activity. In an earlier communication [5] we have reported the synthesis of a number of ferrocenyl hydrazones of the type (B) and have also shown that these ferrocenyl hydrazones act as ligands to coordinate with copper(II) ions. In this communication we wish to report the syntheses and spectral properties of tin(IV) and organotin(IV) complexes with such ferrocenyl hydrazones.



(I a)



(I b)



Where	I	II	III	IV	V
Ar =	C_6H_5	p-C_6H_4Cl	o-$C_6H_4NO_2$	o-C_6H_4OH	C_5H_4N

(B)

Experimental

Materials and Methods

Formylferrocene was purchased from Fluka A. G. (Switzerland) and used without further purification. N-aroyl hydrazines were prepared by reported

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*NCL Communication No. 2928.

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TABLE I. Elemental Analysis of Tin(IV) Complexes of Ferrocenylhydrazones.

S. No.	Complex[a]	Formula	M.p. (°C)	Elemental Analysis %		
				C	H	N
1.	I	$C_{36}H_{30}N_4O_2Cl_2Fe_2Sn$	>300	50.30 (50.70)	3.85 (3.52)	6.45 (6.57)
2.	II	$C_{36}H_{28}N_4O_2Cl_4Fe_2Sn$	>300	47.25 (47.18)	3.21 (3.46)	6.01 (6.09)
3.	III	$C_{36}H_{28}N_6O_6Cl_2Fe_2Sn$	>300	45.06 (45.85)	3.11 (2.97)	9.05 (8.92)
4.	IV	$C_{34}H_{28}N_6O_2Cl_2Fe_2Sn$	>300	47.45 (47.30)	3.52 (3.31)	9.49 (9.90)
5.	V	$C_{44}H_{48}N_4O_2Fe_2Sn$	125 (dec.)	59.49 (59.08)	5.67 (5.41)	6.06 (6.26)
6.	VI	$C_{44}H_{46}N_4O_2Cl_2Fe_2Sn$	193	55.06 (54.84)	4.64 (4.81)	5.73 (5.81)
7.	VII	$C_{44}H_{46}N_6O_6Fe_2Sn$	208	53.57 (53.67)	5.11 (4.78)	8.67 (8.53)
8.	VIII	$C_{42}H_{46}N_6O_2Fe_2Sn$	185 (dec.)	57.24 (56.26)	5.55 (5.17)	9.54 (9.37)
9.	IX	$C_{44}H_{48}N_4O_4Fe_2Sn$	176	56.04 (57.04)	5.85 (5.22)	5.51 (6.05)
10.	X	$C_{52}H_{64}N_4O_2Fe_2Sn$	semi-solid	61.41 (62.03)	6.50 (6.40)	5.28 (5.26)
11.	XI	$C_{52}H_{62}N_4O_2Cl_2Fe_2Sn$	145 (dec.)	57.00 (58.06)	6.41 (5.81)	4.73 (5.21)
12.	XII	$C_{52}H_{62}N_6O_6Fe_2Sn$	168 (dec.)	55.34 (56.95)	6.38 (5.70)	7.43 (7.66)
13.	XIII	$C_{50}H_{62}N_6O_2Fe_2Sn$	semi-solid	59.15 (59.50)	6.55 (6.20)	8.51 (8.33)
14.	XIV	$C_{52}H_{64}N_4O_4Fe_2Sn$	semi-solid	62.03 (60.12)	6.47 (6.21)	6.55 (5.39)

[a] See Fig. 1.

methods [6]. Ferrocenyl hydrazones were prepared by condensing formylferrocene with N-aroylhydrazines in ethanol as reported elsewhere [5]. Stannous chloride dihydrate ($SnCl_2 \cdot 2H_2O$), dibutyl- and dioctyltin oxides obtained commercially were of analytical grade.

Preparation

Dichlorotin(IV) Complexes

To an ethanolic solution of ligand (1.0 mmol), an ethanolic solution of stannous chloride dihydrate (0.50 mmol) was added with vigorous stirring and the mixture was heated under reflux till the separation of the compounds. The crystalline compounds were collected on a filter, washed with ethanol repeatedly, dried under vacuum and recrystallised from chloroform.

Dibutyl- and Dioctyltin(IV) Complexes

A benzene solution of organotin(IV) oxide and ferrocenyl hydrazone (in a molar ratio of 1:2) was heated under reflux for about 8 hours. The dark violet coloured solution was then concentrated, filtered and the filtrate was evaporated to dryness under vacuum. The crude products were recrystallised from benzene or chloroform.

The compounds prepared are listed with their melting points and elemental analyses in Table I.

Spectroscopic Methods

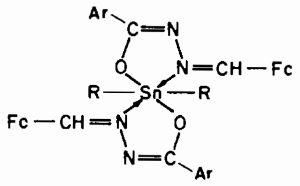
Infrared spectra were recorded on Perkin-Elmer model 283B spectrophotometer using cesium iodide optics. PMR spectra were recorded on a Varian Associates model T-60 using tetramethylsilane as an internal standard.

Results and Discussion

The ligands are mono-basic bidentate in nature having one carbonyl and one azomethine group. The reactions of $SnCl_2 \cdot 2H_2O$ with ferrocenyl hydrazones in ethanol yield stable, violet crystalline compounds,

TABLE II. Important IR Frequencies (cm^{-1}) of Tin(IV) Complexes of Ferrocenyl Hydrazones (Fig. 1).

S. No.	Compound	>C=N–N=C<	Amide-II	ν(C–O)	ν(Sn–C)	ν(Sn–Cl)
1.	I	1605(s)	1580(m)	1250(s)		325(m)
2.	II	1610(vs)	1575(s)	1250(s)		355(s)
3.	III	1605(vs)	1525(vs)	1245(s)		350(s)
4.	IV	1600(s)	1550(s)	1240(s)		310(m)
5.	V	1590(vs)	1500(vs)	1230(s)	595(m)	
6.	VI	1600(s)	1500(sh)	1235(s)	560(s)	
7.	VII	1610(s)	1530(s)	1240(m)	605(m)	
8.	VIII	1610(s)	1520(vs)	1240(s)	605(s)	
9.	IX	1610(s)	1515(s)	1250(m)	605(w)	
10.	X	1600(vs)	1500(vs)	1230(s)	590(w)	
11.	XI	1610(vs)	1505(s)	1240(s)	560(s)	
12.	XII	1610(s)	1505(sh)	1240(s)	610(w)	
13.	XIII	1610(s)	1510(s)	1240(m)	610(m)	
14.	XIV	1605(s)	1515(s)	1250(vs)	605(m)	



(Where Fc = C_5H_5–Fe–C_5H_4)

Compound	R	Ar
I	Cl	C_6H_5
II	Cl	p-C_6H_4Cl
III	Cl	o-$C_6H_4NO_2$
IV	Cl	C_5H_4N
V	C_4H_9	C_6H_5
VI	C_4H_9	p-C_6H_4Cl
VII	C_4H_9	o-$C_6H_4NO_2$
VIII	C_4H_9	C_5H_4N
IX	C_4H_9	o-C_6H_4OH
X	C_8H_{17}	C_6H_5
XI	C_8H_{17}	p-C_6H_4Cl
XII	C_8H_{17}	o-$C_6H_4NO_2$
XIII	C_8H_{17}	C_5H_4N
XIV	C_8H_{17}	o-C_6H_4OH

Fig. 1. Proposed structure for the compounds.

insoluble in alcohols but soluble in non-polar organic solvents such as carbon tetrachloride, chloroform and and benzene. The elemental analyses given in Table I show that $SnCl_2 \cdot 2H_2O$ forms tin(IV) complexes without loss of chloride ions. The reactions of dibutyl- and dioctyltin oxides with the ligands in benzene give red-violet compounds soluble in almost all known organic solvents. Elemental analyses of these complexes conform to the general formula R_2SnL_2 (where R = butyl or octyl group and L = ferrocenyl ligand anion). The infrared and proton magnetic resonance spectral studies suggest the structure shown in Fig. 1.

IR Spectra

The IR frequencies along with their relative assignments are given in Table II. It can be seen that the bands due to N–H and C=O (Amide I) stretching vibrations are not observed in the spectra of these complexes. Instead, new bands are observed around 1605 cm^{-1} and 1240 cm^{-1} which can be assigned to the stretching vibrational modes of conjugate –C=N–N=C– and C–O groups [7, 8]. These observations suggest that the ligands enolize in solution and then react with metal ions forming the metal complexes. It is also observed that (amide-II) band is shifted to a lower frequency by about 40 cm^{-1} while the ν(N–N) band is shifted to a higher frequency by about 15 cm^{-1}. The negative shift in amide-II and positive shift in ν(N–N) bands [9] support the coordination through azomethine nitrogen atom. The characteristic bands of ferrocenyl moiety [10] are also observed, suggesting the presence of ferrocenyl group in the complex.

In the case of compounds IX and XIV, identification of bands around 3100–2700 cm^{-1}, attributable to the intramolecular –OH bonding, is not possible due to the presence of alkyl and ferrocenyl group vibrations in the region. The compounds decomposed during deuteration.

The infrared absorption band observed at ~610 cm^{-1} in the spectra of compounds V to XIV may be assigned to ν(Sn–C), this band being absent in the spectra of compounds I to IV. It has been reported [11, 12] that Sn–C stretching vibration is responsible for two bands, one around 600 cm^{-1} and the other

TABLE III. PMR Chemical Shifts (δ, ppm) of Tin(IV) Complexes of Ferrocenyl Hydrazones.

Compound[a]	Ferrocenyl group		Azomethine proton	Aromatic group					R	OH	Solvent
	Unsubstituted (C_5H_5)	Substituted (C_5H_4)		2-H	3-H	4-H	5-H	6-H			
II	4.3(s)	4.76 5.2	7.23(s)	7.9	8.01		8.01	7.9			$CDCl_3$
III	4.33(s)	4.86 5.23	8.01(s)			8.33					$CDCl_3$
V	3.9(s)	4.26 4.83	7.01(s)	7.33	8.16	7.33	8.16	7.33	1.26(m)		$CDCl_3$
VI	3.93(s)	4.09 4.46	7.01(s)	7.23 (J = 8 Hz)	8.03 (J = 8 Hz)		8.03	7.23	1.16(m)		$CDCl_3$
VII	4.04(s)	4.26 4.60	7.23(s)			8.33			1.5(m)		$CDCl_3$
VIII	3.93(s)	4.37 4.86	7.23(s)	7.93 (J = 6 Hz)	8.66 (J = 6 Hz)		8.66	7.93	1.23(m)		$CDCl_3$
IX	3.93(s)	4.33 4.56	7.16(s)	6.76	7.26		7.26	6.76	1.2(m)	7.86	CCl_4
X	3.8(s)	4.16 4.76	7.00(s)	7.20	8.00	7.20	8.00	7.20	1.01(m)		CCl_4
XII	4.00(s)	4.43 4.90	7.33(s)			8.33			1.16(m)		CCl_4
XIII	4.00(s)	4.40 4.93	7.26(s)	8.40 (J = 5 Hz)	8.00 (J = 5 Hz)		8.40	8.00	1.2(m)		CCl_4
XIV	3.9(s)	4.16 4.50	7.01(s)			7.00			1.16(m)	12.30	CCl_4

[a] Spectra of compounds I, IV and XI could not be taken due to their limited solubility.

around 500 cm^{-1}, in the spectra of liquid alkyltin derivatives where the alkyl chains contain three or more carbon atoms. Whereas the band around 600 cm^{-1}, assigned to the trans isomer, is intensified, the one around 500 cm^{-1}, assigned to the gauche isomer, is weakened or does not appear at all in the case of solid derivatives.

The metal–nitrogen, metal–oxygen and metal–chlorine vibrational modes are generally found [13] to occur between 600–200 cm^{-1}. However, in the case of these complexes it is not easy to assign (M–N) and (M–O) vibrations, because the various skeletal vibrations of the ligands interfere with these vibrations. According to Nakamoto [14], no band in the spectra of the Schiff-base complexes can be assigned to ν(M–N) because of strong coupling between various modes. However, Ueno and Martell [15] have assigned the bands between 600–430 cm^{-1} to ν(M–N). Durig *et al.* [16], Adams [13] and other workers [17] have observed metal nitrogen stretching vibrations below 600 cm^{-1}. Tanaka *et al.* [18] and Kawakami *et al.* [19] have assigned bands at ~400 cm^{-1} and ~520 cm^{-1} to ν(Sn–N) and ν(Sn–O) respectively for the organotin oxinate complexes.

The overall range of the tin–chlorine stretching frequencies [20] is between 400 and 340 cm^{-1}. Poller and Toley [21] have assigned the bands in the range 360–340 cm^{-1} to ν(Sn–Cl) for the simple diorganotin(IV) dichloride compounds. In the present study only compounds I–IV exhibit strong bands in 360–310 cm^{-1} region attributable to ν(Sn–Cl).

PMR Spectra

The PMR spectrum of the ligand (I) in DMSO exhibits the unsubstituted cyclopentadienyl ring proton signals (chemical shift in δ, ppm) around 4.01 as singlet, substituted cyclopentadienyl ring proton signals around 4.4 and 4.6 as broad peaks, aromatic proton signals around 7.63 and azomethine protons at 8.16 The N–H proton appears at 11.36 as a broad peak and disappears on deuteration. The broadening of substituted proton signal peaks for ferrocenyl derivatives can be interpreted in terms of slowing down of the motions of cyclopentadienyl rings resulting from substitution [22].

In the spectra of the tin(IV) compounds either in chloroform-D or carbon tetrachloride (Table III) disappearance of N–H proton supports the enolization in solution. The OH proton signal does not appear as expected for enol form. The complete absence of N–H and O–H protons is suggestive of the mono-basic nature of the ligand. The azomethine proton suffers some deshielding and gives rise to a signal at 7.01–8.01, which indicates the coordination of the azomethine nitrogen to tin atom. The aromatic protons also apear in the low field as expected (~7.00).

In the spectra of compounds VI, VIII and XIII aromatic protons split into two groups. The 2,6 protons appear around 7.23–8.40 while 3,5 protons appear around 8.03–8.66. The protons at positions 2,6 are coupled with each other (coupling constants are given in Table III), while protons at positions 3,5 are coupled with each other with the same coupling constants. The same coupling constants for both kind of protons in the aromatic ring show that they are also coupled with each other. Aromatic protons also suffer some deshielding and shielding in compounds II and VI respectively. The deshielding and shielding are due to the electron donating and withdrawing nature of the substituents.

Unsubstituted cyclopentadienyl protons appear as singlet at 3.8–4.3 and protons from substituted cyclopentadienyl ring appear at 4.0–4.4 and 4.4–5.23 as broad peaks, as expected. This observation is in good agreement with the observations made by Rausch and Siegel [22] in the spectra of formyl- and acetyl-ferrocenes, suggesting that there is no remarkable influence on the chemical shift of ferrocenyl protons on chelation.

The spectra of dibutyl- and dioctyltin(IV) compounds exhibit complex resonance patterns for the alkyl groups which are similar to those observed in the spectra of uncomplexed dialkyltin dichlorides. In the spectra of the compounds IX and XIV hydroxyl protons appear at 7.86 and 12.30 respectively. The presence of hydroxyl protons in the compounds supports that the phenolic OH group is not involved in the chelate formation.

Acknowledgement

One of the authors (SRP) is thankful to Council of Scientific and Industrial Research, New Delhi, for awarding a research fellowship during the course of this work.

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