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COMPLEXES OF ORGANOMETALLIC COMPOUNDS
XXVIII. THE SOLUTION CHEMISTRY OF BIS(ACETYLACETONE)-ETHYLENEDIIMINE ADDUCTS OF ORGANOTIN(IV) HALIDES

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SUMMARY

The nature of methanol solutions of a series of bis(acetylacetone)ethylenediimine adducts of organotin(IV) halides has been studied by electronic and PMR spectroscopy and by osmometry and conductivity. Effectively complete dissociation to the free ligand and solvated organotin(IV) halide moieties is inferred.

INTRODUCTION

The existence of a new class of organometal halide adducts, formed with the potentially tetradentate ONNO ligands bis(acetylacetone)ethylenediimine (Acen) and bis(acetylacetone)-1,2-propylenediimine (Acpn) was reported earlier[1]. Subsequent IR and Mössbauer studies on solid organotin(IV) halide–Acen adducts gave evidence for a polymeric structure of octahedral type, in which the organotin moieties are bridged by the neutral ligand, presumably through coordination on tin(IV) by NN basic atoms[2]. The work reported in this paper involved a study of the nature of solutions of the Acen adducts.

EXPERIMENTAL

The organotins were Fluka and Alfa Inorganics products. Reagents and solvents were analytical grade (C. Erba, Milano), which were purified and/or dried where necessary by standard procedures. The ligand Acen was prepared and recrystallized as elsewhere reported[3,4]. The 1/1 Acen adducts of Me_3SnCl, Me_2SnCl_2, Me_2SnBr_2, Bu_2SnCl_2, Ph_2SnCl_2 and $MeSnCl_3$ were prepared as previously described[1,2]. The new compound Ph_3SnClAcen was made by mixing n-hexane solutions of Acen and Ph_3SnCl. M.p. 86–87°. (Found: C, 59.34; H, 5.72; Cl, 6.11; N, 4.71; O, 5.50; Sn, 19.29. $C_{30}H_{35}ClN_2O_2Sn$ calcd: C, 59.08; H, 5.78; Cl, 5.81; N, 4.60; O, 5.25; Sn, 19.47%.)

The electronic spectra were measured at 25° in anhydrous methanol (the solute concentration ranging between 4×10^{-5} and 2×10^{-6} M), with Beckman DU and DK-2A spectrometers, 10 mm optical path cells. The results are reported in Fig. 1.

The PMR spectra were determined with a Jeol C60 spectrometer operating at

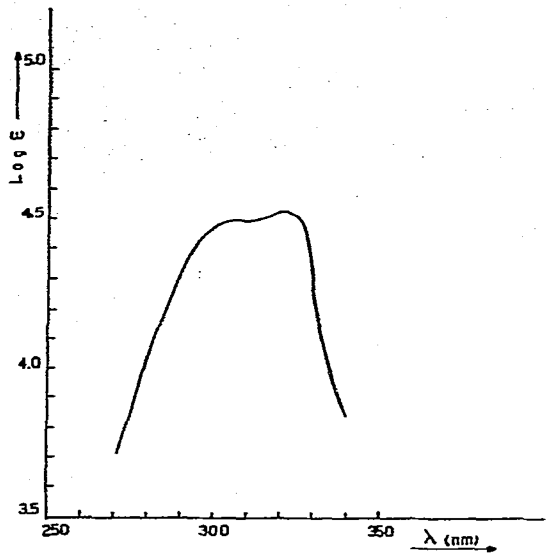

Fig. 1. The electronic absorption spectrum of Acen, $R_3SnClAcen$ (R = Me, Ph), R_2SnCl_2Acen (R = Me, Bu, Ph), Me_2SnBr_2Acen and $MeSnCl_3Acen$ in methanol solution. Absorptivities (ε, $M^{-1}\cdot cm^2$) at band maxima are as follows: λ=304 nm, log ε=4.529; λ=322 nm, log ε=4.548.

TABLE 1

PMR SPECTRA OF ORGANOTIN HALIDES AND THEIR Acen ADDUCTS

T=25°; δ(TMS) 0; solvent CD_3OD, unless otherwise stated.

Compound	Chemical shift (ppm)			$J(^{117}SnCH)$ (Hz)	$J(^{119}SnCH)$ (Hz)
	$SnCH_3$	CCH_3	$-CH_2-$		
Acen[a]		1.93	3.48		
$Me_3SnClAcen$	0.58	1.93	3.48	64	67
Me_3SnCl	0.58			64	67
$Ph_3SnClAcen$[b]		1.93	3.41		
$Ph_3SnClAcen$[c]		1.86	3.30		
		1.93	3.33		
			3.36		
Me_2SnCl_2Acen	1.12	1.96	3.51	90	94
Me_2SnCl_2	1.16			90	94
Me_2SnBr_2Acen	1.30	1.96	3.51	[e]	[e]
Me_2SnBr_2	1.36			86	90
Bu_2SnCl_2Acen[d]		1.95	3.49		
Ph_2SnCl_2Acen[b]		1.93	3.47		
$MeSnCl_3Acen$	1.14	2.00	3.55	[e]	[e]
$MeSnCl_3$	1.22			124	130

[a] δ(CH–) 5.00 ppm; this signal is obscured in the adducts by a solvent signal around δ 4.80 ppm. [b] Aromatics: δ 7.30–8.00 ppm, complex structure. [c] Solvent $CDCl_3$, at 100 MHz with Varian XL-100; δ(CH–) 4.97 ppm; aromatics at δ 7.20–7.80 ppm. [d] δ(SnC_4H_9) 0.8–1.8 ppm, complex structure. [e] Not measured owing to insufficient solubility (25° and 40°).

60 MHz, at 25° in nearly saturated CD_3OD solutions, with TMS as internal standard. The results are reported in Table 1. Integration was not effected for $MeSnCl_3Acen$ (owing to insufficient solubility) and for $Ph_3SnClAcen$ (for which the ethylene bridge proton signal was partly obscured by solvent signals).

TABLE 2

OSMOMETRIC (AT 37°) AND CONDUCTOMETRIC (AT 26°) DATA OF ORGANOMETAL HALIDES AND THEIR Acen ADDUCTS IN METHANOL SOLUTION.

Compound	Molar concn. ($\times 10^2$)	i[a]	Molar concn.	Λ molar ($ohm^{-1} \cdot cm^2 \cdot mole^{-1}$)
Me_3SnCl	5.71	0.90	7.05×10^{-3}	22.2
	3.73	0.92	7.05×10^{-4}	64.3
	2.53	0.90	7.05×10^{-5}	219.6
$Me_3SnClAcen$	2.12	1.90	8.40×10^{-3}	21.3
	1.74	1.93	8.40×10^{-4}	63.3
	1.01	1.92	8.40×10^{-5}	201.4
Ph_3SnCl	1.89	1.27	9.27×10^{-3}	9.6
	1.19	1.43	9.27×10^{-4}	33.0
	0.96	1.58	9.27×10^{-5}	106.5
$Ph_3SnClAcen$	2.98	2.25	9.20×10^{-3}	10.5
	1.86	2.28	9.20×10^{-4}	36.3
	0.97	2.55	9.20×10^{-5}	117.3
Me_2SnCl_2	4.36	1.25	1.04×10^{-2}	18.0
	2.16	1.64	1.04×10^{-3}	56.6
	1.13	1.93	1.04×10^{-4}	268.0
Me_2SnCl_2Acen	1.50	2.42	0.995×10^{-2}	18.4
	1.00	2.58	0.995×10^{-3}	57.5
	0.49	2.97	0.995×10^{-4}	261.0
Me_2SnBr_2	4.72	1.27	8.30×10^{-3}	33.1
	2.09	1.28	8.30×10^{-4}	84.1
	0.84	1.95	8.30×10^{-5}	290.2
Me_2SnBr_2Acen	2.08	2.29	8.20×10^{-3}	35.6
	1.65	2.46	8.20×10^{-4}	88.3
	1.15	2.56	8.20×10^{-5}	275.6
Bu_2SnCl_2	5.51	0.89	9.70×10^{-3}	8.9
	3.02	1.08	9.70×10^{-4}	30.9
	0.88	1.65	9.70×10^{-5}	213.4
Bu_2SnCl_2Acen	1.99	2.22	9.50×10^{-3}	9.2
	1.35	2.23	9.50×10^{-4}	33.4
	0.96	2.38	9.50×10^{-5}	217.0
Ph_2SnCl_2	2.70	1.63	8.60×10^{-3}	13.8
	1.08	2.20	8.60×10^{-4}	51.7
	0.84	2.65	8.60×10^{-5}	218.6
Ph_2SnCl_2Acen	2.49	2.30	8.50×10^{-3}	13.7
	1.01	2.46	8.50×10^{-4}	41.9
	0.51	2.98	8.50×10^{-5}	194.0
$MeSnCl_3$	3.99	1.31	7.30×10^{-3}	35.2
	3.12	1.38	7.30×10^{-4}	128.0
	1.11	1.68	7.30×10^{-5}	411.2
$MeSnCl_3Acen$	2.17	2.35	8.10×10^{-3}	48.2
	1.26	2.44	8.10×10^{-4}	116.2
	0.97	2.78	8.10×10^{-5}	370.5

[a] Van 't Hoff factor.

The osmometric data were obtained in methanol solution, at 37°, by a Mechrolab 301 A vapor pressure osmometer. The determined Van 't Hoff "i" factors are listed in Table 2.

The conductometric measurements were carried out with a LKB Conductolyzer Type 5300 B, at 26° in a dry methanolic solution, cell constant 4.9 cm^{-1}. The results are reported in Table 2.

Data for organotin halides, listed in Tables 1 and 2, were measured for comparison purposes.

DISCUSSION

The electronic spectra of all the adducts (Fig. 1) correspond with the spectrum of free Acen[5], which is consistent with previous reports on analogous derivatives of $ZnCl_2$ and lanthanide salts[6,7]. This strongly suggests that the Acen residues maintain in methanol the ketamino H-bonded configuration characteristic for the free ligand[5,8,9], which also occurs in the solid polymeric organotin(IV) halide–Acen adducts[2].

The PMR spectra of the Acen moieties in CD_3OD solution (Table 1) essentially correspond to that of free Acen[9]. The absence of NH signals around δ 11 ppm[9] is ascribable to deuteration due to exchange with D_2O. This would cause the observed coalescence into a singlet of the ethylene bridge proton signals[9]. In fact, the spectrum of Acen from $Ph_3SnClAcen$, measured for checking purposes ($CDCl_3$ solution, 100 MHz: see Table 1), shows the expected doublet for CCH_3[9], as well as the triplet for ethylene bridge protons observed for free Acen and ascribed to coupling between NH protons (of the H-bonded ketamino ring) and ethylene bridge protons[9].

Chelation of metal ion centers by neutral Acen through its ONNO basic atoms, is thus ruled out for the solutions[1,7]. It would be inconsistent, *inter alia*, with the electronic spectra of chelating tetradentate $Acen^{2-}$, which bear no similarity to that of the neutral H-bonded ligand[5,8], and with the existence of $R_3SnClAcen$, in which the tin atom would attain the highly uncommon coordination number seven.

In the PMR parameters for the adducts in CD_3OD the chemical shifts of $SnCH_3$ protons in CD_3OD solution, Table 1, are consistent with values in other solvents[10,11]. The data for Me_3SnCl and its Acen adduct coincide, which indicates that $Me_3SnClAcen$ is fully dissociated in CD_3OD. The chemical shifts for the other methyltin(IV) systems are slightly shifted downfield for the free organotin halide with respect to its adduct, the difference increasing from the dichlorides to the dibromides to the trichlorides. Changes of chemical shifts of methyltin(IV) protons were observed upon coordination[11,12]. The very limited effects mentioned above rule out the existence of extensive methyltin(IV)–Acen interaction, except possibly for $MeSnCl_3Acen$.

Complete dissociation is indicated for $Me_3SnClAcen$ and Me_2SnCl_2Acen by the coincidence of the $^{117}SnCH$ and $^{119}SnCH$ coupling constants measured for solutions of the organometal halide and its Acen adduct. According to the system by Holmes and Kaesz[13], 31% and 44% of *s*-character would be concentrated in Sn–C bonds for $(CH_3)_3Sn^{IV}$ and $(CH_3)_2Sn^{IV}$, respectively. This strongly suggests that CD_3OD molecules replaced Acen and (perhaps partly) chloride anions in coordinating Sn^{IV}, so that planar trigonal $(CH_3)_3Sn^{IV}$ and linear $(CH_3)_2Sn^{IV}$ are present in solution phase.

The comparison between Van 't Hoff "i" factors and conductances for the organometal halides and their Acen derivatives (Table 2) further confirms the nature of the adducts in methanol solution. Molar conductances of a given organotin(IV) halide and its Acen adduct, at about the same concentration, are of the same order, which suggests that essentially the same conducting species are present in both systems. On the other hand, the number of particles per mole released by organotin(IV) halide–Acen generally tends to be one unit larger than that released by the uncoordinated organotin halide (Table 2). It thus seems likely that the methanol solutions of our adducts consist of nearly independent Acen and organotin(IV) halide residues with some of the complex species perhaps being present in $MeSnCl_3$Acen and Ph_2SnCl_2Acen solutions.

We conclude that the polymeric octahedral solid state structures advanced[2] for the Acen adducts here investigated are not present in dilute methanolic solutions, in which practically independent organotin(IV) halide and Acen moieties appear to exist. The organotins interact with the basic solvent, and undergo partial dissociation, while the neutral ligand maintains its peculiar ketoamino H-bonded configuration.

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