A Convenient Synthesis and Structural Assessment of $[Sn(CH_3)_2(L_2)](ClO_4)_2$

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Synopsis. A general synthesis for a novel class of complexes of the type, $[Sn(CH_3)_2(L_2)](ClO_4)_2$ (L = 2-(substituted arylazo) pyridine) is reported. The structure of the complexes have been investigated by ^{119}tin Mössbauer spectroscopy and NMR coupling constant ^2J ($^{117/119}$Sn–CH). Further, the extent of distortion of tin–methyl groups in octahedral complexes have been calculated from the quadrupole shift (Q.S.) values using Parish's relationship.

Chelating abilities of heterocyclic ligands with R_2SnX_2 (R = alkyl or aryl and X = halides or pseudohalides) are long known and have potential as antitumour and antiviral agents.[1] These complexes are generally hexa-coordinated, $R_2SnX_2 \cdot L_2$ type where L = unidentate or 1/2 bidentate ligands and they can exist in three ideal stereoisomeric forms[2] which depend on the nature of R, X, and L. Mössbauer data[3] have been used extensively to distinguish the *cis-* and *trans-*configuration of the R groups. However, despite of the applications of $R_2SnX_2 \cdot L_2$ type complexes, the reaction of $R_2Sn(ClO_4)_2$ with such ligand systems have not been received much attention except for a recent report.[4] We now wish to report here a class of novel complexes of the type $[Sn(CH_3)_2(L_2)](ClO_4)_2$ where L represents 2-(substituted arylazo)pyridine because such complexes would constitute the first example of ionic *trans*-$[SnR_2]$-octahedral complex.

Experimental

Materials. All manipulations of air- and/or moisture-sensitive compounds were performed under inert environment. Solvents were dried by standard methods and distilled prior to use. The ligands viz., 2-(phenylazo)pyridine (L^1), 2-(*m*-tolylazo)pyridine (L^2), 2-(*p*-tolylazo)pyridine (L^3), 2-(*p*-chlorophenylazo)pyridine (L^4) were prepared by the method reported earlier[5] while 2-[*p*-(dimethylamino)phenylazo]pyridine (L^5) was an Aldrich reagent. $(CH_3)_2Sn(ClO_4)_2$ was prepared by reacting $(CH_3)_2SnCl_2$ (Fluka) and $AgClO_4$ in anhydrous methanol.[4]

Physical Measurement. The physical measurements were carried out as previously described.[4,5]

Synthesis of $[Sn(CH_3)_2(L_2)](ClO_4)_2$. The complexes were prepared by mixing the methanolic solution of the appropriate ligand (2 mol) and freshly prepared methanolic solution of $(CH_3)_2Sn(ClO_4)_2$ (1 mol), and the reaction mixture was refluxed for 4 h. The resulting colored solids were obtained after concentration. Recrystallization from methanol–petroleum ether (40—60 °C) mixture afforded colored crystalline products which were dried in vacuo.

The Characterization data for each complexes are given below.

$[Sn(CH_3)_2(L^1)_2](ClO_4)_2$ (1): Yield, 78%. Found: C, 40.20; H, 3.40; N, 11.80; Sn, 16.50%. Calcd for $C_{24}H_{24}N_6O_8Cl_2Sn$: C, 40.35; H, 3.36; N, 11.76; Sn, 16.63%. $\Lambda_{M(CH_3CN)}$: 251.9 Ω^{-1} cm^2 mol^{-1}.

$[Sn(CH_3)_2(L^2)_2](ClO_4)_2$ (2): Yield, 80%. Found: C, 42.12; H, 3.83; N, 11.30; Sn, 15.91%. Calcd for $C_{26}H_{28}N_6O_8Cl_2Sn$: C, 42.06; H, 3.77; N, 11.32; Sn, 16.00%. $\Lambda_{M(CH_3CN)}$: 241.7 Ω^{-1} cm^2 mol^{-1}.

$[Sn(CH_3)_2(L^3)_2](ClO_4)_2$ (3): Yield, 80%. Found: C, 41.89; H, 3.50; N, 11.30; Sn, 15.89%. Calcd for $C_{26}H_{28}N_6O_8Cl_2Sn$: C, 42.06 ; H, 3.77; N, 11.32; Sn, 16.00%. $\Lambda_{M(CH_3CN)}$: 259.2 Ω^{-1} cm^2 mol^{-1}.

$[Sn(CH_3)_2(L^4)_2](ClO_4)_2$ (4): Yield, 75%. Found: C, 36.50; H, 3.00; N, 10.80; Sn, 15.01%. Calcd for $C_{24}H_{22}N_6O_8Cl_4Sn$: C, 36.79; H, 2.81; N, 10.73; Sn, 15.16%. $\Lambda_{M(CH_3CN)}$: 220.3 Ω^{-1} cm^2 mol^{-1}.

$[Sn(CH_3)_2(L^5)_2](ClO_4)_2$ (5): Yield, 79%. The complex is highly hygroscopic therefore analysis and molar conductance measurements could not be performed, however the purity was established by PMR.

(Note: The melting points of the complexes were not determined owing to the unknown nature of the perchlorates).

Results and Discussion

The complexes (**1**)—(**5**) are readily isolated in high yields as brown crystalline solids by a convenient synthetic procedure. The complexes are stable in air and nonhygroscopic except complex (**5**). They are soluble in polar organic solvents. Elemental analysis supported the proposed stoichiometry of the products and the molar conductance data in acetonitrile lies between 220—259 Ω^{-1} cm^2 mol^{-1}, suggesting a 1 : 2 type of electrolytic nature.[4,6]

The ligand exists as stable *trans*-form and possesses azo and pyridine nitrogen atoms, both able to coordinate to tin.[5] In view of this, structural information on the new complexes is sought from their diagnostically important IR, ^{1}H NMR, and ^{119}Sn Mössbauer spectral data.

The significant IR absorption bands (Table 1) due to coordinated ligands are observed at ca. 1600 cm^{-1} $\nu_{(C=N)}$ and ca. 1400 cm^{-1} $\nu_{(N=N)}$ in the complexes, which are in agreement with the reported results.[5] Thus, confirm that the ligand behave in a bidentate manner. Furthermore, the complexes show a very intense broad band due to perchlorate anion at ca. 1080—1140 cm^{-1} and is assigned to asymmetric stretch (ν_3) while the band at ca. 625 cm^{-1} is assigned to asymmetric bend (ν_4). This concludes the lack of significant per-

Table 1. IR and ^{1}H NMR Data for the Complexes

	IR (cm^{-1})				NMR[b] (δ/ppm)		
Complex	$\nu_{(C=N)}$	$\nu_{(N=N)}$	$\nu_{(Sn-C)}$		Aromatic ligand protons	Aliphatic ligand protons	Sn–CH$_3$ protons[d]
			ν_{as}	ν_s			
(1)	1600	1400	566	550	9.13, d, 2H(H-6)[c] 7.73—8.73, m, 16H	—	1.07, s, 6H (91.5, 94.4)
(2)	1585	1391	564	546	9.08, d, 2H(H-6) 7.65—8.80, m, 14H	2.50, s, 6H	1.12, s, 6H (90.0—94.0)
(3)	1605	1391	566	542	9.10, d, 2H(H-6) 7.44—8.67, m(14H)	2.50, s, 6H	1.05, s, 6H (90.2, 94.2)
(4)	1579	1402	a)	552	9.00, d, 2H(H-6) 7.65—8.83, m, 14H	—	1.10, s, 6H (91.5, 95.1)
(5)	1600	1392	564	541	9.13, d, 2H(H-6) 6.80—8.20, m, 14H	2.53, s, 12H	1.03, s, 6H (90.6, 94.2)

a) Not identified with reasonable certainty. b) In CDCl$_3$+Acetone-d_6 solvents except (1) which is in CDCl$_3$. c) Unresolved doublet and refers to the proton adjacent to pyridine nitrogen. The ligand H-6 values were 8.83, 8.97, 8.83, 8.98, and 8.93 in CDCl$_3$ for L^1, L^2, L^3, L^4, and L^5, respectively. d) $^2J(^{117/119}\mathrm{Sn–CH})$ values in Hz are in parentheses.

chlorate coordination.[4,7] The bands due to $\nu_{(\mathrm{Sn-C_2})_{s,as}}$ have been detected (see Table 1). This suggests the non linearity of SnC$_2$ group in the complexes[4,5,8] (see further Mössbauer discussion).

The ^{1}H NMR spectra of the complexes show downfield shift of protons adjacent to pyridine nitrogen atom of the ligand (Table 1). This is in consistent with the pyridine nitrogen coordination.[5] The complexes display a sharp singlet ca. 1.1 ppm due to Sn–CH$_3$ protons alongwith the two doublet satellite resonance due to the coupling of methyl protons with ^{117}Sn and ^{119}Sn nuclei. An increase in the coordination number of the tin atom should give rise to an increase in the value of $^2J(^{117/119}\mathrm{Sn–CH})$.[9] The coupling constants determined for the complexes are ca. 90 and 94 Hz, respectively. The magnitude of ^2J is comparable to those observed for the comlexes in *trans*-R$_2$Sn octahedral geometry in solution.[10]

^{119}Sn Mössbauer spectral data of the complexes are collected in Table 2. The Quadrupole shift (Q.S.) values reported[4,5] for diorganotin complexes are 1.7—2.2 and 3.5—4.2 mm s^{-1} for *cis*- and *trans*-R$_2$Sn octahedral complexes, respectively. The observed Q.S. values for the complexes are in the range 3.12—3.65 mm s^{-1} and thus clearly belong to the latter type.[5,8] The lower values of Q.S. obtained for the complexes compared to the values reported for regular *trans*-R$_2$Sn octahedral geometry, suggests the possible distortion of C–Sn–C bond angle (133—150°) from the linearity (Table 2). The isomer shift (I.S.) values are typical of quadrivalent tin in organometallic compounds and confirm the presence of hexa-coordinated tin in each species.[5,8]

Table 2. ^{119}Sn Mössbauer Spectral Data[a] (mm s^{-1})

Complex	I.S.	Q.S.	$\Gamma\pm$	C–Sn–C angle[b]/°
(1)	1.09	3.12	0.83	133
(2)	1.38	3.65	1.04	150
(3)	1.40	3.59	1.00	148
(4)	1.30	3.59	0.89	148

a) Source: Ca^{119}SnO$_3$, at liquid nitrogen temperature. b) Calculated[4] using the Parish's relationship: $\mathrm{Q.S.}=4[R][1-3/4]\sin^2\theta]^{1/2}$.

Thus, the IR, ^{1}H NMR, ^{119}Sn Mössbauer spectral data are, therefore, consistent with distorted octahedral structure for all the complexes where tin–methyl groups are in *trans*-position while two bidentate ligands occupy the equatorial position. A perspective drawing of the octahedral complexes is represented in Fig. 1.

Conclusion. It is demonstrated that 2-(arylazo)pyridine ligands display high affinity towards Sn(CH$_3$)$_2$(ClO$_4$)$_2$. The second bidentate ligand occupy the *cis*-position of the halides in R$_2$SnX$_2$·L$_2$ system in *trans*-[R$_2$Sn] octahedral geometry and the perchlorates reside outside the coordination sphere. The complexes of the type [Sn(CH$_3$)$_2$(L$_2$)](ClO$_4$)$_2$ are stable and non explosives at least at ordinary temperature. Such types of complexes are rare since the reactivity of (CH$_3$)$_2$Sn(ClO$_4$)$_2$ have not been examined earlier presumably be due to its potential explosive and hygroscopic nature.

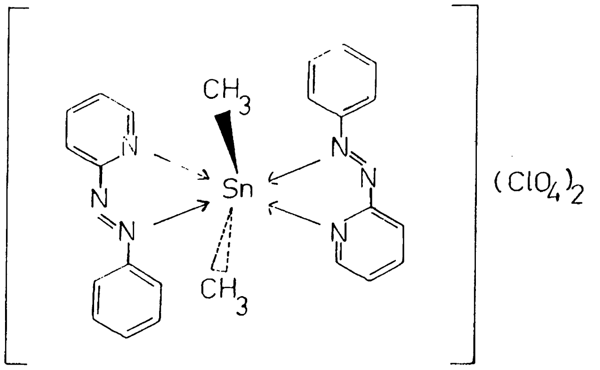

Fig. 1.

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