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COMPLEXES OF ORGANOMETALLIC COMPOUNDS

XXXIX. SYNTHESIS, INFRARED AND MÖSSBAUER STUDIES ON MONO-ORGANOTIN(IV) COMPLEXES WITH TRIDENTATE LIGANDS

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Summary

Novel complexes RClSntrid, where R is Me, Ph, n-Oct, and $trid^{2-}$ are dianions of tridentate "planar" ligands with ONO and SNO donor atoms, were synthesized and investigated in the solid state by infrared and Mössbauer spectroscopy. Possible configurations are discussed; polymeric trigonal bipyramidal structures seem to occur, although five-coordinated monomers as well as octahedral dimers (via oxygen or sulfur bridges) are not excluded.

Introduction

During our studies on the coordination of R_2Sn^{IV} and Sn^{IV} by the dianions of tridentate "planar" ligands having ONO and SNO donor atom systems, the complexes R_2Sn trid* (R = Me, Ph), $Sn(trid)_2$, $[HNEt_3][Cl_3Sn$ trid$]$ and hal_2Sn-trid (hal = Cl, Br) were prepared, and their configurations investigated in the solid state and in solution, mainly by spectroscopic techniques (including Mössbauer) as well as by the X-ray determination of crystal and molecular structures [1—7]. Spectroscopic results were interpreted in terms of trigonal bipyramidal configurations for R_2Sn trid and hal_2Sn trid [1, 2, 5] compounds, while

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* H_2trid are H_2BAH, 3-(*o*-hydroxyphenylamino)crotonophenone; H_2SAH, *N*-(2-hydroxyphenyl)-salicylaldimine; H_2AAT, 4-(2-benzothiazolinyl)2-pentanone; H_2SAT, 2-(*o*-hydroxyphenyl)benzothiazoline.

TABLE 1

ANALYTICAL DATA [% FOUND (CALCD)], AND MÖSSBAUER PARAMETERS (mm s^{-1}) AT 80 K.

Compound[a]	M.p (°C)	C	H	N	O	S	Cl	Sn	δ[b]	ΔE[c]	Γ_{av}[d]
MeClSnBAH	230 (dec.)	48,48	3,88	3,18	7,74		8,57	28,15	0,86	2,24	1,07
		(48,56)	(3,83)	(3,33)	(7,61)		(8,43)	(28,23)			
MeClSnSAH	235 (dec.)	44,33	3,32	3,59	8,48		9,30	31,01	0,87	2,18	1,23
		(44,20)	(3,18)	(3,68)	(8,41)		(9,38)	(31,20)			
MeClSnAAT	206—207	38,30	3,72	3,93	4,08	8,59	9,57	31,88	1,00	1,97	1,20
		(38,49)	(3,78)	(3,74)	(4,27)	(8,56)	(9,47)	(31,70)			
MeClSnSAT	189—191	43,06	3,29	3,36	4,16	7,81	8,85	29,51	1,03	2,12	1,39
		(42,41)	(3,05)	(3,53)	(4,03)	(8,09)	(8,94)	(29,94)			
n-OctClSnBAH	155—156	55,57	5,95	2,92	6,13		6,74	22,78	0,96	2,22	1,04
		(55,58)	(5,83)	(2,70)	(6,17)		(6,84)	(22,89)			
n-OctClSnSAT	83— 84	50,52	5.40	2,95	3,35	6.32	7,30	24,09	1,06	2,01	1,03
		(50,99)	(5,30)	(2,83)	(3,23)	(6,48)	(7,17)	(24,00)			
PhSlSnBAH	350	54,88	3,92	3,03	6,35		7,43	24,34	0.82	2,13	1.07
		(54,76)	(3,76)	(2,90)	(6,63)		(7,35)	(24,60)			
PhClSnSAT$_1$	223 (dec.)	49,70	3,03	3,04	3,68	6,85	7,99	25,71	0,99	2,00	1,27
		(49,77)	(3,08)	(3,05)	(3,49)	(6,99)	(7,73)	(25,89)			

[a] Symbols as in the Introduction. [b] Isomer shift with respect to the centroid of a room temperature $BaSnO_3$ spectrum. [c] Nuclear quadrupole splitting. [d] Full width at half height of the resonant peaks, average.

octahedral type configurations were assigned to Sn(trid)$_2$ and [HNEt$_3$]-[Cl$_3$Sn trid] [3, 4].

Ruddick and Sams studied the novel compound Ph$_3$SnSAH and re-investigated R$_2$SnSAH (surprisingly ignoring the existing literature), and attributed to these compounds octahedral and trigonal bipyramidal configurations, respectively, on the basis of infrared and Mössbauer data [8]. Our recent X-ray studies, on the other hand, reveal that the structural aspects of this class of compounds are not as straightforward as would appear at first sight. The solid state molecular structures of Ph$_2$SnSAT [6] and Me$_3$SbSAH [9] essentially correspond to trigonal bipyramidal and octahedral type (both distorted) monomers, respectively, while in Me$_2$SnSAH the specific distortion of the basically trigonal bipyramidal structure allows association of two molecules across a Sn$_2$O$_2$-ring (two short and two long bonds), so the tin could be considered to be six-coordinate [7].

We have now prepared a series of novel complexes RClSn trid (R = Me, Ph, n-Oct), and carried out a preliminary investigation of their solid configurations by infrared and Mössbauer spectroscopies. This was done mainly with the aim of providing information on additional compounds of this general type, in order to throw light on the relationship between structure, Lewis acidity of Sn^{IV} acceptor and Mössbauer parameters.

Experimental

The compounds MeSnCl$_3$, PhSnCl$_3$ and Me$_2$SnCl$_2$ were Fluka and Alfa Inorganics products, while n-OctSnCl$_3$ was a gift from Deutsche Advance Produktion GmbH, Marienberg (Germany). The ligands H$_2$ trid and the complexes Me$_2$Sn trid were prepared by published methods [1, 2]. The novel complexes RClSn trid were synthesized by ligand exchange between Me$_2$Sn trid and RSnCl$_3$, essentially following the procedure described for the preparation of hal$_2$Sn trid [5]. Thus, 2 mmol of RSnCl$_3$ in 25 ml of anhydrous n-hexane were added, under gentle reflux, to 2 mmol of Me$_2$Sn trid in 50 ml of the same solvent, under N$_2$ atmosphere, causing the precipitation of crystalline RClSn trid, which was filtered off and dried under nitrogen. Analytical data are reported in Table 1.

The IR spectra were registered with a Beckman IR 12 instrument in the 4000—200 cm^{-1} region, on Nujol mulls between CsI windows. The Mössbauer spectra were taken with the Laben—Elscint instrumentation described earlier [10], operating with a Ba^{119}SnO$_3$ (N.E.N., 5 mC) source at room temperature, constantly accelerated in a triangular waveform motion, and maintaining (when required) the absorbers at liquid N$_2$ temperature in a A.E.R.E. cryostat. Other experimental details, including the computer reduction of data, were as previously reported [10]. Figure 1 shows the quality of the spectra, while Mössbauer parameters are reported in Table 1.

Discussion

The analytical data of Table 1 clearly show that stoichiometries correspond to RClSn trid. The occurrence of chelation by trid^{2-} on Sn^{IV}, through the ONO or SNO donor atoms, is strongly suggested by the IR spectra in the 1600—1500

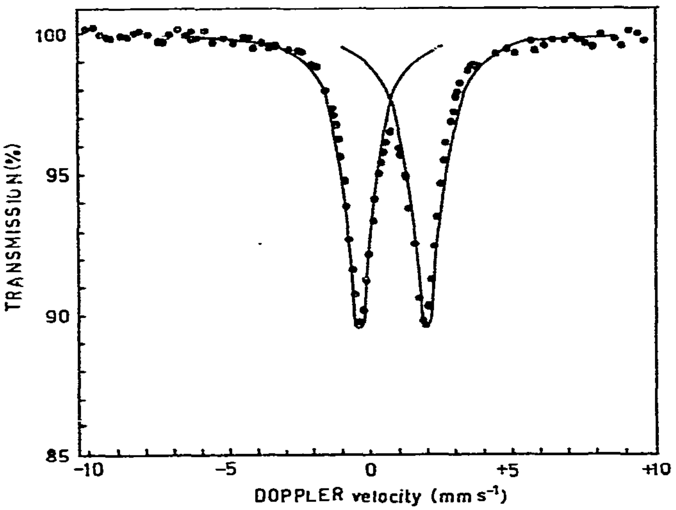
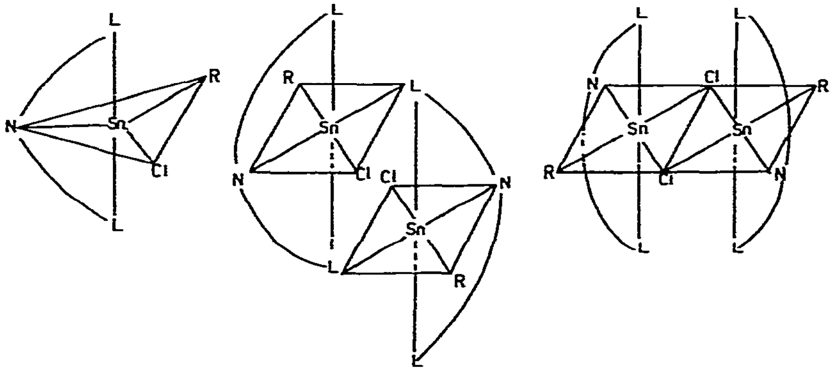


Fig. 1. Mössbauer spectrum of MeClSnBAH. Solid lines are computed Lorentzians.

cm^{-1} region, which essentially reflect those of corresponding R_2Sn trid compounds [1], and perhaps better those of hal_2Sn trid [5].

Possible configurations, which may be in principle advanced, also on the light of previous data on Sn^{IV}—$trid^{2-}$ complexes, are the trigonal bipyramidal monomer I, a related polymer with five-coordinated Sn^{IV}, and the dimers II and III with bridging oxygen and chlorine respectively, where Sn^{IV} would be six-coordinated (Fig. 2). The reliability of III may be discussed on the basis of energies of ν(SnCl) modes, which are expected to depend on the bonding situation sketched in III and I-II. In the IR spectra of MeClSnSAT and n-OctClSnSAT there appears a medium or strong broad band, centered at 300 and 285 cm^{-1} respectively, in place of ligand bands detected in R_2SnSAT [1]. These are instead observed in PhClSnSAT, with the difference that the 290 cm^{-1} band is much more intense than that of R_2SnSAT. The spectra of MeClSn-BAH, -SAH and -AAT, as well as of n-OctClSnBAH, show medium or strong bands at



(I) (II) (III)

Fig. 2. Possible structures of RClSn trid; L, L = O, O or O, S.

295—290 cm^{-1} while that of PhClSnBAH exhibits two medium absorptions at 295, 280 cm^{-1}, the latter being a Ph ring vibration [1]. It is very likely correct to attribute the 300—290 cm^{-1} bands discussed above to ν(SnCl) modes, and this energy range corresponds, inter alia, to that reported for $\nu(SnCl_3)$ frequencies in $RSnCl_3$ adducts, where chlorine atoms are certainly non-bridging [11]. This would exclude any bridging behaviour of Cl in RClSn trid, and rule out structure III.

It may be opportune to report here the more evident differences between RClSn trid and R_2Sn trid spectra in the 600—300 cm^{-1} region. Tin—phenyl vibrations are detected at 450 mw cm^{-1} and 455 mw cm^{-1} for PhClSn-SAT and -BAH respectively. The spectrum of MeClSnSAT shows a broad medium absorption around 550 cm^{-1}, where a ν(SnC) contribution may occur [11, 12]. The latter mode, expected [11, 12] to appear around 510—542 cm^{-1}, is difficult to assign in the case of MeClSn-BAH, -AAT and -SAH; the spectrum of the first reflects that of Me_2SnBAH [1], with four bands at 535 w, 555 mw, 570 mw and 590 vw cm^{-1}, while a band at 500 m, 540 s cm^{-1} of AAT and SAH derivatives could be assigned either to ν(SnC) or ligand vibrations [1]. No bands attributable to ν(SnC) in n-OctClSn-BAH and -SAT complexes could be identified in the expected region (~ 600 cm^{-1} [13, 10]) owing to the presence in that range of a band, common to all complexes except MeClSnAAT, probably due to a tin—oxygen vibration [10].

The Mössbauer isomer shift parameters, δ [14], reported in Table 1, fall in a Doppler velocity range typical of mono-organotin (IV) derivatives [15—17], and would suggest that the Sn^{IV} coordination numbers in RClSn trid are higher than four, although a choice between five- and six-coordination is not feasible (this according to the plot of δ vs. average ligand atoms electronegativity for RSn^{IV} derivatives so far investigated [15]). In particular, two sets of values may be identified: for $trid^{2-}$ with SNO donor atoms, δ ranges within 0.99 and 1.06 mm s^{-1}, while for ONO donor atoms the δ range is 0.82—0.96 mm s^{-1}, which reflects the increasing *s*-electron densities on the Sn^{IV} nucleus due to the greater electron-releasing tendency of S with respect to O [18]. No systematic effects appear to be associated with the inductive effects, of the alkyl and phenyl radicals bound to Sn^{IV} [17]. The nuclear quadrupole splitting parameters, ΔE [14], listed in Table 1 are again typical of RSn^{IV} compounds [15—17]. It has been observed that calculations (according to the point charge model [17, 18]) of partial quadrupole splittings due to trid/3 generate internally consistent values for the series hal_2Sn trid, RClSn trid and (in part) R_2Sn trid, using point charge equations related to trigonal bipyramidal structures of type I [5]. This would be consistent with the occurrence of five-coordination throughout all these compounds [5], but we do not intend to press this view too strongly at the present state of our researches. Anyhow, it is interesting to observe that ΔE values also show two sets of values: ΔE_{ONO} = 2.13—2.24 mm s^{-1}, and ΔE_{SNO} = 1.97—2.12 mm s^{-1}, which means that the electronic charge released by ligand atoms (lesser for ONO and larger for SNO, see δ values) concerns components of the electric field gradient tensor [14, 17, 18] other than the principal, V_{zz}, which lies along the Sn—C bond [17]. As a consequence, increase of donated charge (on the *x*, *y* e.f.g. directions) decreases the charge imbalance between the Sn—C axis and the perpendicular plane, thus reducing the ΔE value.

It is now interesting to mention that some preliminary measurements of the room temperature Mössbauer effect showed a small resonant absorption in the compounds so far investigated, i.e., MeClSnSAH·($\epsilon_{298} = 1.30$; $\epsilon_{298}/\epsilon_{77} = 0.09$; ϵ is per cent effect at room and liquid N_2 temperature respectively) and MeClSnSAT ($\epsilon_{298} = 1.95$; $\epsilon_{298}/\epsilon_{77} = 0.13$), which would suggest the occurrence of solid state polymers [19], perhaps having structures as I, any trid^{2-} acting as bi- and mono-dentate ligand on two Sn^{IV} atoms. It must be taken into account, on the other hand, that room temperature effects cannot be regarded as conclusive evidence for polymerization, although they are supported in this context by the absence of any effect in monomeric $Sn(trid)_2$ [4]; in fact, the recoil-free fraction is a function of many variables, and its magnitude at 298 K cannot be simply and generally attributed to polymeric structures independently from other factors [14, 20, 21].

It may be concluded that IR and Mössbauer data would suggest the formation of polymeric trigonal bipyramidal structures, although the occurrence of monomeric (I) and dimeric (II) species cannot be ruled out. We intend to investigate these structures by X-ray diffractometry, and discuss the spectroscopic data in the light of the true molecular structures.

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