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Complexes of Organometallic Compounds. XLVII. Synthesis of Dimethyltin(IV) Adenosinate and Its Characterization by Mössbauer and Infrared Spectroscopy

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The work reported here is part of a research project, under way in our laboratory, on compounds formed by tin(IV) with molecules participating in biological systems [1, 2]. We have been prompted to publish the present preliminary study on the title compound by the interest recently arisen about the interaction of organotin(IV) moieties with carbohydrates [3–6]. In particular, 2′,3′-O-(dibutylstannylene)nucleosides have been synthesized and characterized mainly by their 2′- and 3′-acyl derivatives through NMR spectroscopy, from which the occurrence of the 2-stanna-1,3-dioxolane ring has been inferred for these compounds [3]. Besides, the reaction of di-n-butyltin(IV) oxide with simple carbohydrates afforded 2,3-O-(dibutylstannylene)pyranosides, which too are characterized by a five-membered ring structure of the type cited above (as observed by NMR spectroscopy); in the case of α-(methoxy) anomers, intramolecular oxygen-to-tin coordination would occur [6].

After having investigated the interaction of adenine with organotin(IV) [2], we have planned to determine the spectral characteristics of tin adenosinates where the metal is bound to oxygen atoms of ribofuranose residues. We have selected first the dimethyltin(IV) moiety owing to its favourable spectral characteristics in the far IR, especially for bands attributable to $\nu(SnC_2)$ modes.

The compound has been prepared several times by following essentially the procedures employed for the O-(dibutylstannylene)-nucleosides and hexopyranosides referred to above: equimolar amounts, of the order of 2 mmol of Me_2SnO and adenosine (Fluka), suspended in 50–100 ml of CH_3OH, have been refluxed for 2 to 5 hours, then the white solid product was filtered off, washed and dried. This compound is nearly insoluble in CH_3OH, contrary to the $Bu_2^nSn^{IV}$ derivative [3]. Analytical data in Table I are fully consistent with 1:1 Me_2Sn^{IV}: adenosinate(2–) composition. In the present context, it would be reasonable to assume that our compound corresponds to 2′,3′-O-(dimethylstannylene) adenosine (Fig. 1); it may be recalled here that such a chelation of metal ions (other than tin) through O(2′), O(3′) of ribofuranose residues has been detected or proposed for several metal nucleosidates [7, 8].

TABLE I. Analytical Data [% found (calcd.)] and Mössbauer Parameters (mm s^{-1}, at liquid N_2 temperature) of Me_2SnAds.[a]

Decomp. point	C	H	N	O	Sn
268 °C	34.72	4.04	16.91	15.61	28.50
	(34.81)	(4.14)	(16.92)	(15.46)	(28.67)
δ[b]	ΔE[c]	Γ_+[d]	Γ_-[d]		
1.15	3.12	1.10	1.08		

[a] $(CH_3)_2Sn$(Adenosinate), $C_{12}H_{17}N_5O_4Sn$. [b] Isomer shift with respect to RT $BaSnO_3$. [c] Nuclear Quadrupole Splitting. [d] Full width at half height of the resonant peaks at larger (+) and lesser (–) velocity than the spectrum centroid.

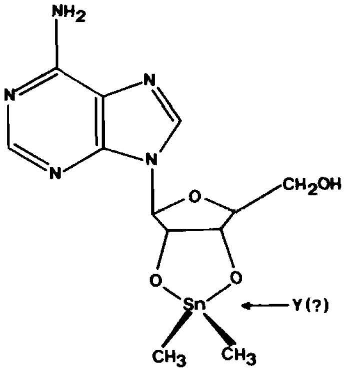

Fig. 1. Proposed molecular structure of Me_2Sn adenosinate, with possible intermolecular coordination to tin (Y could be a ribufuranosic oxygen, see text).

The Mössbauer parameters have been determined as usual [9] (the source, Ba $^{119m}SnO_3$, was moving in a sawtooth waveform, at constant acceleration). Contrary to our expectation, the magnitude of the experimental ΔE (Table I) strongly suggests a coordination number 5 for Sn in Me_2SnAds, being consistent with values typical of trigonal bipyramidal Alk_2SnX_3 species, where X are electronegative ligand atoms [10, 11]. A tetrahedral type configuration around Sn is ruled out, since in such cases ΔE is always less than 3.00 mm s^{-1} [12, 13]; in particular, the point charge model calculation [12] of the relative partial quadrupole splitting due to O Alk groups in Me_2SnAds, for an ideal tetrahedral structure, gives the values –0.02 mm s^{-1}, which is largely inconsistent with tabulated values [12]. Six coordination, in both *cis* and *trans*-octahedral configurations, is also excluded for Sn in Me_2SnAds, known ΔE's for these structural types being respectively lesser and larger than 3.12 mm s^{-1}, except for cases where bonds to tin occur through sulphur atoms [12]. In

TABLE II. Relevant Infrared Absorptions[a] (in the 4000–250 cm^{-1} region) of Ads[b] and Me_2SnAds.

Ads	Me_2SnAds	Assignments
3320 s	3320 s	$\nu(NH_2)$[c]
3130 s	3180 s	
2920 m	2930 ms	$\nu(CH)$[d]
2840 w	2890 ms	
1670 s	1670 s	$\delta(NH_2)$ (in plane)[c]
1605 s	1605 s	Vibr. of the purine nucleus[c]
1575 m	1575 m	
	1515 w	
1470 s	1470 ms	
1415 s	1430 ms	
1390 w		
1375 w	1375 w	
1335 m	1350 s	
1305 s	1305 ms	
1250 w	1255 w	
1225 w	1245 m	
1210 m	1210 m	Ads: the region ~1200–800 cm^{-1} contains ν(C–O) of the ribofuranose residue[e]
1180 w		
1145 w		
1130 w		
1110 mw		
	1110 vs	ν(C–O) in C–O–Sn?[f]
1095 w		
	1090 vs	ν(C–O) in C–O–Sn?[f]
1075 m		
1055 m	1050 s	
1040 ms		
1015 m	1030 w	
980 m	990 m	Purine ring?[g]
970 w	970 sh	
	935 w	
	925 w	
905 s	910 s	Purine ring?[g]
860 w	870 s	
845 m		
825 ms		
795 w	800 m	
770 m	780 m	
	755 m	
725 mw	725 s, bd	
705 w		
670 m, bd		
640 s	645 mw	
595 s	600 s	
	575 m	$\nu_{as}(SnC_2)$[f]
555 w	550 w	
540 m	540 w, bd	
530 m		
	515 w	$\nu_s(SnC_2)$?[f]
	450 mw	$\nu(SnO)$?[f]
	430 s	
415 w	405 m	
390 mw	375 m	
350 w		
320 m	315 m	
290 mw	290 m	
	280 m	

[a] Measured in nujol and hexachlorobutadiene mulls with a Perkin–Elmer mod. 457 spectrometer; s = strong, m = medium, w = weak, bd = broad, sh = shoulder, v = very. [b] Adenosine. Attributions are effected according to refs: [c] 15, 16; [d] 17; [e] 16, 18, 19; [f] see text; [g] 15, 17, 20.

conclusion, the bonding situation in our compound could correspond in some way to that advanced for cyclic di-n-butyltin(IV) 1,2-glycoxides, for which experimental data (including ΔE values, ranging between 2.72 and 2.85 mm s^{-1}) have been interpreted in terms of the presence of dimers originated by oxygen bridges, with 5-coordinated tin [14]. A similar type of intramolecular coordination could originate a solid state polymeric structure in Me_2SnAds.

In order to possibly gain a better knowledge of bonding in Me_2SnAds, we have moved to vibrational spectroscopy and measured the infrared spectra of Table II. The absorptions by adenosine (reported with the aim of comparing spectra obtained by the same instrument) correspond satisfactorily to literature data in the 4000–600 cm^{-1} region [16,21]. It is first observed that vibrations concerning the 6-amino group of adenine, as well as the purine ring, are fully coincident in adenosine and Me_2SnAds (Table II), which rules out any coordination of tin by N(1), N(3), N(7) and 6-NH_2 of the adenine residue. Such coordinations would in fact provoke evident spectral changes, as observed for example in a N(7) adenosinate of platinum where purine ring vibrations are consistently lowered [22], and in cobalt adeninates and adenosinates where drastic changes of $\delta(NH_2)$ bands are ascribed to the occurrence of coordination by the amino nitrogen [23].

Major differences between infrared spectra of adenosine and Me_2SnAds are found in the regions 1000–1200 and 400–600 cm^{-1} (Table II). In the first, δ(C–O) of two alcoholic functions of the ribofuranose residue [16, 18. 19] are expected to be substituted by ν(C–O) of C–O–Sm moieties. These are tentatively attributed to bands at 1090 and 1110 cm^{-1} in Me_2SnAds (Table II). Modes ν(C–O) in acyclic alkoxides $R_2Sn(OR')_2$ have been respectively assigned to a couple of bands occurring between 1055–1072 (ν_{as}) and 1027–1047 (ν_s) cm^{-1} [24], or to a single band between 1100–950 cm^{-1} [25]. In the 400–600 cm^{-1} region there are expected vibrations concerning SnC, SnO and eventual SnN bonds in Me_2SnAds. The band at 575 cm^{-1} is safely attributed to $\nu_{as}(SnC_2)$ [26], while it seems reasonable to assign the 515 cm^{-1} band to $\nu_s(SnC_2)$ [26] (Table II); this would imply that the CSnC skeleton is bent [26, 11] in Me_2SnAds. Vibrations occurring at 430 and 450 cm^{-1} are identified with $\nu(SnO)$ modes (Table II). These attributions are partially at variance with previous reports on $R_2Sn(OR')_2$, for which two bands at 679–602, 615–532 cm^{-1}, or at 616–581, 487–471 cm^{-1} have been assigned to ν_{as} and ν_s(Sn–O) respectively [24, 25]. In any event, it is known that tin–oxygen vibrations may take place in a wide energy range. No evidence is found of any ν(Sn–N) mode, which could occur around 600 cm^{-1}, by analogy with Bu^n_3Sn–pyrazole [27].

It is concluded that the expansion of the coordination number of tin in Me_2SnAds from 4 to perhaps 5, as suggested by the magnitude of the Mössbauer quadrupole splitting, cannot take place through intermolecular bonding by adenine nitrogens (which would be in principle possible, as demonstrated by some molecular structures, *e.g.*, that of a Ni adenosinate [28]). It follows that eventual solid state polymers would be formed by bridging Sn atoms through alkoxy oxygens, as assumed for cyclic alkoxides [14]. In the latter case, the two observed ν(C–O) vibrations (Table II) could be interpreted in terms of the presence of two different C–O groups, one of which would contain a three-coordinate oxygen atom. Our further work in this field will have the aim of testing the hypotheses above, and possibly of clarifying the nature of the tin environment in Me_2SnAds are related compounds.

Acknowledgments

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