SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
2 (1996)

N-BUTYLTIN(IV) PERCHLORATES AND METHANESULFONATES, THEIR COMPLEXES WITH PYRIDINE AND 2,2'-BIPYRIDINE

Martin HOLLEIN and Karel HANDLÍŘ
Department of General and Inorganic Chemistry

Received December 12, 1995

Tri-n-butyltin(IV) and di-n-butyltin(IV) methanesulfonates and perchlorates were prepared and reacted with pyridine (py) and 2,2'- bipyridine (bipy). The Complexes are formed by dibutyltin bis(methanesulfonate) with bipy (1:1), tributyltin perchlorate with py or bipy (both 1:1), and dibutyltin bis(perchlorate) with py or bipy (both 1:2). The compounds prepared were studied by multinuclear NMR spectroscopy and IR spectroscopy. The reaction of bis(tributyltin) oxide with aqueous solution of perchloric acid is mentioned as well.

Introduction

Many data about carcinostatic effects of organotin(IV) compounds have been published recently and certain hypotheses about conditions of their efficiency have been formulated. Firstly, the carcinostatic effects were proved mainly in the case of diorganotin(IV) compounds and also di-n-butyltin(IV) compounds. After the study of diorganotin(IV) complexes Crowe[1] expressed an assumption that a binding of organotin compound to complex facilitates the transport to the tumor cells where a reaction of organotin compound or its hydrolytic product

takes place. Therefore the complexes with carcinostatic effects should not be too strong. According to Barbieri[2], the effect of water on $R_2SnX_2.2L$ type complex consists in coordination of water molecules to the tin atom and consecutive hydrolysis and dissociation of the complex. Other studies have indicated that a higher solubility of organotin compound in water can increase the carcinostatic effect[3]. It can be summarized, that effective organotin compounds have an accessible place in the coordination sphere of the tin atom, they contain relatively stable bonds between the tin atom and the sulphur or nitrogen atoms as donor atoms of a ligand, and slow hydrolysis of these bonds is possible[4]. In addition these effective compounds should show certain solubility in water. These conditions are hard to meet in a controlled synthesis and are partly contradictory. N-butyltin(IV) compounds with strong polar anionic substituents as perchlorate or methanesulfonate in combination with nitrogen bases as a ligand seem to be promissing for the purpose.

Tributyltin methanesulfonate has been known since sixties as a biocid[5]. It is soluble in water (about 3% w/w) and probably forms ion $[Bu_3Sn(H_2O)_2]^+$ in solution (Ref.[6]). Its methyltin analogon has been synthesized and characterized by vibrational spectroscopy, too. Both compounds have a chain-like structure in the solid state with bridging SO_3Me groups and pentacoordinated tin atom with alkyl substituents in equatorial positions[7]. The SO_3Me groups are located in $Me_2Sn(SO_3Me)_2$ as a bridge too, but the tin atom has octahedral coordination sphere[8]. The di-n-butyltin bis(methanesulfonate), which is slightly soluble in water, has been synthesized too[9]. Butyltin(IV) methanesulfonates are not known to form complexes.

A different situation is encountered with organotin(IV) perchlorates. Triorganotin perchlorates, with chain-like structure with pentacoordinated tin atom and bridging ClO_4 groups (symmetry C_{2v})[10], form complexes of $[Me_3SnL_2]^+ClO_4^-$ (L = NH_3, *py*, MeOH, Me_2CO)[11] and $[Bu_3SnL_2]^+ClO_4^-$ (L = *py*, *bipy*)[12] types. In some cases the formation of Me_3SnL^+ adduct can take place and the fifth coordination site of the tin atom can be occupied by perchlorate[11]. On the other hand, dimethyl- and di-n-butyltin(IV) perchlorates were only prepared in water solutions[13,14]. $Bu_2Sn(ClO_4)_2$ is supposed to form $[Bu_2SnL](ClO_4)_2$ type of complexes with L = 2,2'-dipyridyldisulfide. It is a polymeric compound with octahedral coordination of tin atoms[15].

Experimental

Preparation of Compounds

Butyltin(IV) methanesulfonates were prepared using the reaction of corresponding oxides with methanesulfonic acid in boiling toluene[16]. Butyltin(IV) pechlorates had to be prepared from the corresponding chlorides using a reaction with dry silver perchlorate in dry benzene[17]. These compounds

are extremly hygroscopic and the di-n-butyltin bis(perchlorate) decomposes slowly already at room temperature.

The reaction of saturated water solution of bis(tributyltin) oxide with perchloric acid did not lead to the tributyltin perchlorate. The isolated products, mostly hydrates (Table I), decomposed durig attempts at dehydratation.

Prepared methanesulfonates and perchlorates were reacted with two- to fivefold excess of pyridine (*py*) or 2,2′-bipyridine (*bipy*) in boiling benzene or chloroform. The products were isolated either by crystallization after partial evaporation of the solvent or by precipitation with added petroleum ether, dried *in vacuo* and analysed. The results are summarized in Table II. All the substances prepared decompose during heating.

Spectral Measurements

The infrared spectra were measured using a Perkin-Elmer Infrared Spectrophotometer 684 with datastation DS 3600, mostly as Nujol suspensions. The infrared spectra were used both for confirming the presence or absence of certain functional groups and for assessing the bonding character of these functional groups in the compounds prepared.

The ^{1}H, ^{13}C and ^{119}Sn NMR spectra were measured on a Bruker AMX 360 apparatus. As the substances prepared have low solubilities, their saturated solutions in $CDCl_3$, *dmso*-d_6, CD_3NO_2 or D_2O were measured at room temperature, using a 5 mm zone tunable probe. Standard methods[18,19] were used to obtain the ^{1}H and ^{13}C NMR spectra. The ^{119}Sn NMR spectra were measured in the so-called "inverse gated" mode with proton noise decoupling during the acquisition period. The values of $\delta(^{119}Sn)$ were referred to external Me_4Sn standard.

Results and Discussion

Before we present the results of reacions of tributyl- and dibutyltin(IV) methanesulfonates and perchlorates with nitrogen bases, the reaction of bis(tributyltin) oxide with perchloric acid will briefly be discussed. This reaction has not yet been described in detail. Prismatic crystals of compound *I* are formed from the solution, if saturated water solution of bis(tributyltin) oxide and perchloric acid (molar ratio 1:2) is evaporated at room temperature. Further evaporation causes the crystal to melt into liquid phase *II*. On further evaporation the liquid phase crystallizes into the solid *III*. The results of analyses and the infrared spectra are summarized in Table I, the basic parameters of the NMR spectra in Table IV.

Table I Products of reaction of $(Bu_3Sn)_2O$ with $HClO_4$

Compound	t_{dec} °C	Composition	Structurally important IR bands
I	48 - 60	$(Bu_3Sn)_2O.HClO_4$	3421m, 1136vs, 1077vs, 624s
II	-	$Bu_3Sn(ClO_4).5H_2O$	3500b, 3250b, 1631w, 1083vs, 625s
III	32.5 - 37	$Bu_3Sn(ClO_4).3H_2O$	3403b, 3236b, 1650m, 1099b, 941m, 636s, 465m

Both IR and NMR spectra of the compound *I* indicate the structure of bis(tributylstannyl)oxonium perchlorate. The valence vibration $\nu(=OH^+)$ occurs at 3421 cm^{-1} as a relatively sharp band. The valence vibration ν_3 of the perchlorate is clearly split (hence its symmetry is reduced) probably as the consequence of ion - ion interaction in the solid state.

Compounds *II* and *III* differ considerably from compound *I*, mainly in the content of coordinated water. Significant upfield shift of $\delta(^{119}Sn)$ of compound *II* (neat) gives the evidence that the coordination number of the tin atom increases from 4 (in compound *I*) to 5[20]. Similar conclusions will apply with high probability to trihydrate *III*, too, as this compound has a comparable value of $^1J(^{119}Sn, ^{13}C)$, although the value of $\delta(^{119}Sn)$ is shifted downfield. It should be pointed out that a much more diluted solution was measured in comparison with compound *II*. From our previous studies significant upfield shift should be found with increasing concentration. Consequently it should be shifted into the range characteristic of the coordination number 5 of tin atom. The presence of only one absorbtion band ν_3 in IR spectra of products *II* and *III* indicates high symmetry of ClO_4^- approaching the T_d symmetry.

The products presented in Table II were prepared by reactions of starting methanesulfonates and perchlorates with pyridine (*py*) and 2,2´-bipyridine (*bipy*). The positions of the structurally important absorbtion bands in their IR spectra are given in Table III and the basic NMR parameters in Table IV.

Table II The products of the reactions of the starting compound with *py* and *bipy*

Compound	Designation, composition	
	py	*bipy*
Bu_3SnOSO_2Me	-[a]	-[a]
$Bu_3Sn(OSO_2Me)_2$	IV[b]	VII, 1 : 1
Bu_3SnClO_4	V, 1 : 1	VIII, 1 : 1
$Bu_2Sn(ClO_4)_2$	VI, 1 : 2	IX, 1 : 2

[a] - The substances do not react

[b] - *py* causes a solvolysis leading to the production of pyridinium methanesulfonate

Table III IR absorption bands of starting compounds and their adducts with *py* and *bipy*

Compound[a]	Structurally important IR absorption bands
Bu_3SnOSO_2Me	1264vs; 1128vs, 1042vs
$Bu_3Sn(OSO_2Me)_2$	1274vs; 1198vs, 1090vs[b], 1036vs[b]
V	1106m; 623m
VI	1107vs, 1053vs; 624m
VII	1253s; 1150vs, 1023s, 1017s
VIII	1067s; 925w, 623s, 459w
IX	1112vs, 1089vs, 927w, 623s, 461vw

[a] - because of extreme hygroscopicity of the butyltin perchlorates the IR spectra could not be measured

[b] - both bands are split: ±11 and ±6 cm^{-1}

The multinuclear NMR spectroscopy was the basic method for the analysis of the structural arrangement around the tin atom. We cannot give here the complete description of application of the NMR spectroscopy parameters for the explanation of the structure of organotin compounds in solutions. For this purpose we can recommend the comprehensive publications[21,22].

Table IV The parameters of NMR spectra of the compounds studied[1]

Compound	$\delta(^{119}Sn)$ ppm	$\delta(^{13}C_n)$, ppm / $^nJ(^{119}Sn, ^{13}C_n)$, Hz				some other signals	θ^f
		C_1	C_2	C_3	C_4		
I	138.2[a]	20.14	28.87	28.23	14.09	$\delta(^1H) = 3.05^g$	112.6°
		379.1	23.7	77.0	-		
II	58.4[e]	19.73	28.01	27.34	14.05	$\delta(^1H) = 4.70^g$	117.5°
		427.7	27.5	75.9	-		
III	92.6[a]	20.42	28.51	27.86	14.04	$\delta(^1H) = 5.50^g$	116.1°
		414.1	27.6	78.1	-		
Bu_3SnSO_3Me	61.5[b]	20.68	27.58	26.73	13.47	$\delta(^1H) = 2.70^g$	117.9°
		431.4	28.3	79.7	-	$\delta(^{13}C) = 39.71^h$	
	0.08[c]	19.63	27.54	26.01	-		122.0°
		473.2	28.7	78.0	-		

Table IV (continued)

Compound	$\delta(^{119}Sn)$ ppm	$\delta(^{13}C_n)$, ppm / $^nJ(^{119}Sn, ^{13}C_n)$, Hz				some other signals	θ^f
		C_1	C_2	C_3	C_4		
$Bu_3Sn(SO_3Me)_2$	-377.3[c]	33.59	27.12	25.69	13.70	$\delta(^1H) = 2.54$[g]	171.9°
		971.2	46.4	169.8	-	$\delta(^{13}C) = 39.73$[h]	
	-369.5[d]	-	-	-	-		-
Bu_3SnClO_4	196.8[a]	21.2	28.6	27.91	14.09		124.2°
		494.3	27.7	78.0	-		
V	61.5[a]	19.20	28.44	27.95	14.06		114.6°
		398.5	27.4	80.9	-		
	15.6[c]	19.46	27.63	26.46	13.65		121.3°
		466.2	28.3	76.0	-		
VI	-382.7[c]	33.33	27.19	25.56	13.57		-
		-	-	-	-		
VII	-355.3[b]	34.31	27.03	25.37	13.02	$\delta(^{13}C)$*bipy* [i]	164.1°
		893.3	49.9	168.1	-		
VIII	118.7[a]	20.45	28.86	28.16	14.11	$\delta(^{13}C)$*bipy* [j]	112.6°
		378.7	22.8	80.4	-		
	16.7[c]	19.50	27.62	26.45	13.64	$\delta(^{13}C)$*bipy* [k]	121.2°
		465.1	28.4	73.7	-		

Solvent: [a] - CD_3NO_2, [b] - $CDCl_3$, [c] - dmso-d_6, [d] - D_2O, [e] - neat

[f] - C-Sn-C angle calculated from equation $\theta = 0.1[^1J(^{119}Sn, ^{13}C) + 746]$[21]

[g] - except for the hydrogen atom signals of n-butyl substituents

[h] - except for the carbon atom signals of n-butyl substituents

[i] - 149.1, 123.6, 142.7, 127.6, 148.5 ppm

[j] - 151.4, 123.5+128.5, 142.0+142.3, 127.3+127.6, 148.9 ppm

[k] - 155.2, 120.8, 137.5, 124.4, 149.4 ppm

[l] - because of extreme hygroscopicity, the NMR spectra of dibutyltin bis(perchlorate) could not be measured

The value of $\delta(^{119}Sn)$ = 196.8 in tributyltin perchlorate is evidently unusual. It is extremely shifted downfield and it lies outside the interval of values typical of the coordination number 4 of tin atom. On the other hand the value of the coupling constant $^1J(^{119}Sn, ^{13}C_n)$ = 494.3 Hz is unusually high and it lies in the interval of values characteristic of the trigonal bypiramidal

coordination of tin atom. These results support the idea that planar Bu_3Sn^+ ions can be present in the solution[17]. The sp^2 hybridization can be assumed on the tin atom of the ion, and the same hybridization is on the tin atom in R_2SnX_3 type compounds according to the model of three-centre bond[23]. Taking into account the fact that the value of $^1J(^{119}Sn, ^{13}C_n)$ reflects the size of *s*-electron density around the tin atom, the high value of coupling constant is understandable.

The butyltin(IV) perchlorates form the adducts *V* and *VI* with pyridine of the following compositions $[Bu_3Sn.py]ClO_4$ and $[Bu_2Sn.py_2](ClO_4)_2$ Both analysis and ^1H NMR spectrum confirm that compound *V* is an adduct 1:1. This our result is in contradiction with the paper[12] giving the complex 1:2. Even if pyridine is used in an excess, the value of $\delta(^{119}Sn)$ are mains in the interval of values characteristic of the coordination number 4. Both these complexes are relatively weak, and strongly coordinating solvents decompose them. Thus pyridine is already displaced from the coordination sphere of the tin atom in dimethylsulfoxide and it is replaced by the solvent molecules, and products with the coordination number 5 for the tributyltin compound are formed. In the case of $[Bu_2Sn.py_2](ClO_4)_2$, products with the coordination number 6 are formed.

2,2′-Bipyridine reacts with the butyltin(*IV*) perchlorates like pyridine. However, compound *IX* is poorly soluble in common solvents. That is why the ^1H NMR spectrum, confirming the composition of the substance, was successfully measured only in *dmso*-d_6. The results of measements of NMR spectra of compound *VIII* are surprising. Although, it is an adduct of typical bidentate ligand, the value of $\delta(^{119}Sn)$ gives evidence that the coordination number of the tin atom is 4 (in CD_3NO_2). The assumption that the ligand is bonded only monodentately in the compound $[Bu_3Sn.bipy]ClO_4$ is confirmed by the ^{13}C NMR spectrum, in which one can identify two series of five signals of the carbon atom of the *bipy*. These two series combine into one if the solvent is dimethylsulfoxide. The process, which in fact is replacing of *bipy* from the coordination sphere of the tin atom, is accompanied also by typical increase in the coordination number of the tin atom to 5 as it is proved by significant upfield shift of $\delta(^{119}Sn)$.

In contrast to the perchlorates, the butyltin(IV) methanesulfonates react with *py* and *bipy* distinctly less willingly. Thus tributyltin methanesulfonate crystallizes from the solution in pyridine without any changes and no reaction is observed with *bipy* either. Dibutyltin bis(methanesulfonate) undergoes the solvolysis by action of pyridine and probably undergoes also partial decomposition, as the main product of the reaction is pyridinium methanesulfonate *IV*. Thus adduct *VII* is the only substance prepared from butyltin methanesulfonates. Its composition is $[Bu_2Sn.bipy](SO_3Me)_2$ as was confirmed by the analysis and ^1H NMR spectrum. The tin atom has the coordination number 6 in the compound and its coordination polyhedron is *trans*-octahedral, of course, with a considerable deformation as it follows from the angle θ = 164° calculated from $^1J(^{119}Sn, ^{13}C)$. Only five signals of the

carbon atoms of *bipy* were found in the ^{13}C NMR spectrum, which indicates its bidentate coordination.

In conclusion it is possible to state that the observed significant difference between the reactivity of the butyltin(IV) methanesulfonates and perchlorates results mainly from the basicity of their anionic parts. Very low Lewis basicity of the perchlorate causes coordination unsaturation of the tin atom and it makes the formation of adducts with nitrogen bases possible. However, these adducts are relatively weak, unfortunately, and stronger O-donors (bases) such as dimethyl sulfoxide and water cause their decomposition. On the other hand the methanesulfonate is a considerably stronger base and is able to form more stable coordination species. Then the tendency of the butyltin(IV) methanesulfonate to form complexes with the nitrogen bases used is significantly restricted.

Acknowledgements

The financial assistance of the Grant Agency of the Czech Republic (grant 203/94/0024) is gratefully acknowledged.

References

1. Crowe A.J., Smith P.J., Atassi G.: Chem.-Biol. Interact. **32**, 171 (1980).
2. Barbieri R., Pellerito L., Ruisi G., LoGiudice M.T., Huber F., Atassi G.: Inorg. Chim. Acta **66**, L39 (1982).
3. Willem R., Biesemans M., Kayser F., Bouâlam M., Gielen M.: Inorg. Chim. Acta. **197**, 25 (1992).
4. Huber F., Roge G., Carl L., Atassi G., Spreafico F., Filippeschi S., Barbieri R., Silvestri A., Rivarola E., Ruis G., Di Bianca F., Alonzo G.: J. Chem. Soc., Dalton Trans. **3**, 523 (1985).
5. Giesen M.: F.A.T.I.P.E.C. Congr. **8**, 185 (1966).
6. Blunden S.J., Hill R.: Inorg. Chim. Acta **87**, 83 (1984).
7. Yeats P.A., Sams J.R., Aubke F.: Inorg. Chem. **10**, 1877 (1971).
8. Yeats P.A., Ford B.F.E., Sams J.R., Aubke F.: J. Chem. Soc., Chem. Commun. **D**, 791 (1969).
9. Anderson H.H.: Inorg. Chem. **3**, 108 (1964).
10. Uson R., Fornies J., Uson M.A., Lalinde E.: J. Organomet. Chem. **185**, 359 (1980).
11. Clark H.C., O'Brien R.J., Pickard A.L.: J. Organomet. Chem. **4**, 43 (1965).
12. Basu Baul T.S,, Dey, D., Mishra D.D., Basaiawmoit W.L., Rivarola E.: J. Organomet. Chem. **447**, 9 (1993).
13. McGrady M.M., Tobias R.S.: Inorg. Chem. **3**, 1157 (1964).
14. Sato Y., Akamine H., Kawashima N.: Jpn. Kokai Tokkyo Koho JP

62,277,453, CA **108**: 187932.
15. Shukla P.R., Ahmad N., Sharma M.C., Narain G.: Asian J. Chem. **4**, 648 (1992).
16. Blunden S.J., Chapman A.H., Crowe A.J., Smith P.J.: Internat. Pest. Control **20**, 5 (1978).
17. Lambert J.B., Kuhlmann B.: J. Chem. Soc., Chem. Commun. **XX??**, 931 (1992).
18. Günter H., *NMR Spektroskopie*, THIEME, Studgart 1983.
19. Kalinowski H.O., Berger S., Braun S.: *Carbon-13 NMR Spectroscopy*, Whiley & Sons, Chichester 1988.
20. Holeček J., Nádvorník M., Handlíř K., Lyčka A.: J. *Organomet. Chem.* **315**, 299 (1986).
21. Holeček J., Lyčka A.: Inorg. Chim. Acta **118**, L15 (1986).
22. Holeček J.: *Study of Synthesis, Properties, Structure and Reactivity of Some Classes of Organometallic Compounds of IVb Group (in Czech)*, DrSc Thesis, VŠCHT Pardubice 1989.
23. McGrady M.M., Tobias R.S.: J. Am. Chem. Soc. **87**, 1909 (1965).