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TIN-119, PHOSPHORUS-31, CARBON-13 AND PROTON NUCLEAR MAGNETIC RESONANCE AND MÖSSBAUER STUDIES OF MONO-, DI- AND TRI-ORGANOTIN(IV) DIALKYLDITHIOPHOSPHATES

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Summary

^{119}Sn, ^{31}P, ^{13}C and ^{1}H NMR chemical shifts of organotin(IV) dialkyldithiophosphates have been measured in $CDCl_3$. The ^{119}Sn NMR chemical shifts and $|^{1}J(^{119}Sn-^{13}C)|$ and $|^{2}J(^{119}Sn-^{1}H)|$ of triorganotin(IV) dialkyldithiophosphates are consistent with tetrahedral, four-coordinated tin, although Mössbauer studies indicate five-coordinated tin in the solid state. The ^{119}Sn NMR chemical shifts, $|^{2}J(^{119}Sn-^{1}H)|$ and Mössbauer parameters of mono- and di-organotin(IV) dialkyldithiophosphates are indicative of weak coordination of the ligands to tin.

Introduction

Transition and non-transition metal dialkyldithiophosphate complexes are reasonably well known [1], but tin dialkyldithiophosphates, other than for their pesticidal activity [2], have not received much attention until recently [3–5]. Two significant general conclusions are obtained from structural data of metal dialkyldithiophosphates: (i) the $S_2P(OR)_2$ group can behave as either a mono- or a bi-dentate ligand, and (ii) substitution of one R group for another usually leads to a change in structure [1]. The configuration of organotin(IV) dialkyldithiophosphates in solution has been studied [3] on the basis of electronic, IR and ^{1}H NMR spectral data, but little information on the nature of the coordinate bond can be deduced on this basis.

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TABLE 1

TIN-119 NMR CHEMICAL SHIFTS OF SOME ORGANOTIN(IV) COMPOUNDS

Compound	Coordination number	Solvent	$\delta(^{119}Sn)$ [a]	Reference
$Me_3Sn[SSP(OEt)_2]$	–	$CDCl_3$	107.9	[b]
$Me_3Sn[SSP(OPr^i)_2]$	–	$CDCl_3$	103 9	[b]
$Et_3Sn(SSP(OEt)_2]$	–	$CDCl_3$	105.9	[b]
$Et_3Sn[SSP(OPr^i)_2]$	–	$CDCl_3$	100.3	[b]
$Pr_3Sn[SSP(OEt)_2]$	–	$CDCl_3$	97.1	[b]
$Pr_3Sn[SSP(OPr^i)_2]$	–	$CDCl_3$	91 3	[b]
$Bu_3Sn[SPP(OEt)_2]$	–	$CDCl_3$	99.3	[b]
$Me_2Sn[SSP(OEt)_2]_2$	–	$CDCl_3$	−159.6	[b]
$Me_2Sn[SSP(OPr^i)_2]_2$	–	$CDCl_3$	−162.2	[b]
$MeSn[SSP(OEt)_2]_3$	–	$CDCl_3$	−163.4	[b]
$MeSn[SSP(OPr^i)_2]_3$	–	$CDCl_3$	−185.7	[b]
Me_3SnCl	4	$CDCl_3$	~160.0[c]	10
	4	DMSO	179.3	10
	5	pyridine	55 to −9	10
Me_3SnOMe	4	benzene	120.9	17
Me_3SnOEt	4	benzene	110.5	17
$Me_3SnON{=}C_6H_{10}$	4	CH_2Cl_2	132	7
Me_3SnOAc	4	$CDCl_3$	129	10
Me_3SnSMe	4	$CHCl_3$	90	8
Me_3SnSEt	4	neat liquid	78	18
Me_3SnSPh	4	neat liquid	90.5	18
R_3SnOx (R = Me, Et, Pr, Bu)	4	$CDCl_3$	28 to 50	11
Me_2SnCl_2	4	benzene or $CHCl_3$	~140	10
$Me_2Sn(SMe)_2$	4	$CHCl_3$	144	8
$Me_2Sn(SEt)_2$	4	neat liquid	127	18
$Me_2Sn(SPr^i)_2$	4	neat liquid	110	18
$Bu_2Sn(OBu^t)_2$	4	neat liquid	−34	19
$Bu_2Sn(OR)_2$ (R = Me, Et, Pr^n, Bu^n, Bu^i)	5	neat liquid	−150 to −165	19
$Me_2SnCl_2 \cdot 2DMSO$	6	DMSO	−246	18
$Me_2Sn(Ox)_2$	6	$CDCl_3$	−235.8	11
$Me_2Sn(acac)_2$	6	$CHCl_3$	−365	16,20
$Me_2Sn(bzac)_2$	6	$CHCl_3$	−356	16
$Me_2Sn(SCSNEt_2)Cl$	5	CH_2Cl_2	−204	6
$Me_2Sn(SCSNMe_2)_2$	6	$CHCl_3$	−338	16
$Me_2Sn(SCSNEt_2)_2$	6	CH_2Cl_2	−336 (−333)	6 (16)
$Bu_2Sn[SCSN(CH_2Ph_2]_2$	6	CH_2Cl_2	−340	21
$Bu_2Sn[SCSN(CH_2)_4]_2$	6	CH_2Cl_2	−313	21
$Me_2Sn(tropolonate)_2$	6	$CDCl_3$	−197	16
$Me_2Sn(kojate)_2$	6	$CDCl_3$	−174	16
$Me_2Sn(OCOPh)_2$	6	$CDCl_3$	−125	21
$Bu_2Sn(OCOMe)_2$	–	neat liquid	−195	22
$MeSnCl_3$	4	neat liquid	6.03	23
	–	Me_2S	−167	18
$MeSn(OEt)_3$	6	50% in mesitylene	−434	24
	4	benzene	−130.6	17
$MeSn(OBu^t)_3$	4	neat liquid	−177	25
$MeSn(SMe)_3$	4	$CHCl_3$	167	8

TABLE 1 (continued)

Compound	Coordination number	Solvent	$\delta(^{119}Sn)$ [a]	Reference
$MeSn(SEt)_3$	4	neat liquid	144	18
$MeSn(SPr^i)_3$	4	neat liquid	119.5	18
$MeSn(SBu^t)_3$	4	neat liquid	65	18
$Me_2Sn(pan)(acac)$ [d]	7	$CHCl_3$	−463	20
$Me_2Sn(NCS)_2(Tpy)$ [e]	7	DMF	−409	20
$BuSn(Ox)_3$	7	$CHCl_3$	−561	20
$PhSn(SCSNEt_2)_3$	7	$CHCl_3$	−695	20

[a] In ppm downfield from external Me_4Sn (neat). [b] This work, 10–15% sample (v/v) in $CDCl_3$ was used and spectra were recorded at 22°C. [c] Chemical shift depends upon concentration. [d] pan = 1-(2-pyridylazo)-2-naphtholate. [e] TPy = 2,2′,2″-terpyridyl.

^{119}Sn NMR chemical shifts have been found to be influenced by changes in (i) the coordination number of tin, (ii) the bond angles at tin, (iii) the d_π–p_π bonding effect, or (iv) by the presence of electronegative substituents [6–11]. $|^1J(^{119}Sn–^{13}C)|$ and $|^2J(^{119}Sn–^1H)|$ have also been found to be sensitive to the coordination number of tin. We have, therefore, studied the ^{119}Sn, ^{31}P, ^{13}C and ^1H NMR spectra of mono-, di- and tri-organotin(IV) dialkyldithiophosphates and have supplemented such studies with an examination of their Mössbauer spectra, thus gaining some considerable insight into their structure and stereochemistry.

Results and discussion

Organotin(IV) dialkyldithiophosphates were prepared by the reactions of organotin(IV) chlorides with the sodium salts of dialkyldithiophosphates in stoichiometric ratio in refluxing benzene [3]. Triorganotin dialkyldithiophosphates were purified by distillation under reduced pressure ($\simeq$ 0.1 Torr) whereas mono- and di-methyltin dialkyldithiophosphates were purified by dissolving them in anhydrous hexane and filtering through Florisil columns (5 cm × 5 cm) under nitrogen atmosphere.

Tin-119 NMR spectral data for organotin dialkyldithiophosphates are given in Table 1, which also cites literature values for tin-119 NMR chemical shifts of other organotin(IV) compounds. It is apparent from Table 1 and other more extensive data [12] that for four-coordinated tin compounds, ^{119}Sn NMR chemical shifts are generally to higher field from tetramethyltin, while for compounds which have coordination number higher than four, the shifts are to lower field from tetramethyltin. In general as the coordination number of tin increases from four to five or six or seven the tin signal gradually moves to lower field e.g., δ 0 to −200 for five, −125 to −365 for six and −400 to −700 ppm for seven-coordinated compounds.

The tin-119 NMR chemical shifts for trialkyltin dialkyldithiophosphates occur in the range δ 91 to 108 ppm. Substitution of Et, Pr^n or Bu^n groups for methyl results in increased shielding of the tin nucleus as has been observed for other trialkyltin(IV) compounds [10,13,14]. The tin-119 NMR chemical shifts of trialkyltin(IV) dialkyldithiophosphates can thus be best interpreted in terms of four-coordinated tin (cf. Table 1). These compounds probably have an ester type of linkage similar to that observed in four-coordinated triorganotin(IV) thiolates, R_3SnSR' [8], for which the

TABLE 2

^1H, ^{13}C AND ^{31}P NMR SPECTRAL DATA OF ORGANOTIN(IV) DIALKYLDITHIOPHOSPHATES

Compound	^1H NMR			^{13}C NMR				$\delta(^{31}P)$
	δ(Me–Sn)	$^2J(^{119}Sn-^1H)$ (Hz)	$^2J(^{117}Sn-^1H)$ (Hz)	$\delta(\overset{CH_3}{\underset{R}{\,}}CH\text{–}OP)^a$ (R = H or Me)	δ(CH–OP)^b	δ(C–Sn)	$^1J(^{117/119}Sn-^{13}C)^c$ (Hz)	
$(EtO)_2PSSH$	–	–	–	15.5	62.9	–	–	85.7
$(Pr^iO)_2PSSH$	–	–	–	15.3	63.6	–	–	82.3
$MeSn[SSP(OEt)_2]_3$	2.17	97	93	–	–	–	–	89.2
$MeSn[SSP(OPr^i)_2]_3$	2.23	97	95	–	–	–	–	86.5
$Me_2Sn[SSP(OEt)_2]_2$	1.70	77	74.5	15.7	63.6	15.1	558.5	94.6
$Me_2Sn[SSP(OPr^i)_2]_2$	1.62	78	74	23.3	72.9	14.8	558.5	91.4
$Me_3Sn[SSP(OEt)_2]$	0.82	57	54	15.4	62.8	−2.2	359.2	95.1
$Me_3Sn[SSP(OPr^i)2]$	0.76	56	54	23.4	72.4	−2.1	366.0	92.1
$Et_3Sn[SSP(OEt)_2]$				15.9	63.4	8.3	332	97.1
$Et_3Sn[SSP(OPr^i)_2]$				23.5	72.6	8.1	340.5, 326.7	94.2
$Pr_3Sn[SSP(OEt)_2]$				15.5	63.0	19.2	331.2, 316.7	97.1
$Pr_3Sn[SSP(OPr^i)_2]$				23.2	72.0	19.1	331.2, 318.2	94.3
$Bu_3Sn[SSP(OEt)_2]$				15.5	62.9	16.4	329.8	97.1

[a] $^3J(^{13}C-C-O^{31}P)$ sometimes not distinguished if present then it is 3–8 Hz. [b] $2J(^{13}C-O-^{31}P)$ sometimes not distinguished if present then it is 5–8 Hz. [c] In some cases the individual coupling $^1J(^{13}C-^{119}Sn)$ and $^1J(^{13}C-^{119}Sn)$ could not be distinguished, when distinguished the lower values are due to $^1J(^{117}Sn-^{13}C)$.

^{119}Sn NMR chemical shifts occur in the range δ 80 to 110 ppm (Table 1).

The chemical shifts of dimethyltin bis(dialkyldithiophosphates) occur almost 300 ppm to lower field than that of dimethyltin dichloride in either CH_2Cl_2 or CCl_4 (ca. 140 ppm) [6,15] as well as from other four-coordinated diorganotin dithiolates, $R_2Sn(SR')_2$ (δ 122 to 144 ppm). This indicates that these bis(dialkyldithiophosphates) do not contain four-coordinated tin with an ester type linkage.

The dialkyldithiophosphates can be compared to the isoelectronic dithiocarbamates and other related dithio ligands. The tin-119 NMR chemical shifts of six-coordinated $Me_2Sn(dtcR)_2$ (R = Me or Et, dtcR = dithiocarbamate) and five-coordinated $Me_2SnCl(dtcEt)$ occur at ~ -335 and -204 ppm respectively, the range expected for these dialkyldithiophosphates if these are five- or six-coordinated. Recently, six-coordinated Me_2SnL_2 complexes (L = tropolonate, kojate and benzoate) [16] have been reported and the chemical shifts for these compounds occur in the region δ -125 to -197 ppm. The observed values of $\delta(^{119}Sn)$ for dimethyltin dialkyldithiophosphates can, therefore, be interpreted in terms of six-coordinated tin compounds in which the Sn–S=P interactions are weak, probably due to four-membered ring strain.

As for $Me_2Sn[SSP(OR)_2]$, the $\delta(^{119}Sn)$ values of monomethyltin(IV) tris(dialkyldithiophosphates) (δ -163.4 and -185.7 ppm) indicate that these compounds do not contain four-coordinated tin with an ester-type linkage as is observed in $RSn(SR')_3$ (δ + 65 to 167 ppm) [8,18]. The chemical shifts for six- and seven-coordinated compounds occur at much lower frequency than the observed δ values of monomethyltin tris(dialkyldithiophosphates) (Table 1). However, the chemical shifts for the latter compounds fit well with five-coordinated tin compounds. Such a geometry in which one of the ligands is chelated and the other two are non-chelated should lead to two ^{31}P signals in the ^{31}P NMR spectra. However, only one signal is observed, although this might well be the average of two signals arising from a fluxional five-coordinated geometry. Attempts to freeze out any such fluxional process, by observing the ^{31}P NMR spectrum of $MeSn[SSP(OPr^i)_2]_3$ in CD_2Cl_2 at -90°C were unsuccessful as the spectrum was unaffected (displayed single sharp line) by lowering the temperature. This indicates that all three ligands are equivalent either due to a fast ligand exchange process in lower-coordinated (penta- or hexa-) species or due to weak coordination of all ligands to the central tin atom in seven-coordinate species. In the absence of an X-ray analysis, an unambiguous differentiation between these two possibilities appears to be rather difficult.

The ^{1}H, ^{13}C and ^{31}P NMR spectra of these complexes have also been recorded and the resulting data are given in Table 2.

The ^{31}P NMR chemical shifts of these complexes and ligands occur in the range δ 85.7 to 97.1 and 82.3 to 94.3 ppm for $[(EtO)_2PSSM]$ and $[(Pr^iO)_2PSSM)]$ (M = H or Sn), respectively. The chemical shift difference between the ligand and the complexes ranges from 3.5 to 12.0 ppm. Such small changes can well be attributed to bond polarity, to the geometry of the molecule, and to the electron releasing nature of alkyl groups on tin which affects π-bonding with phosphorus [26]. It is, therefore, difficult to comment on the nature of the ligands in these organotin dialkyldithiophosphates on the basis of such small chemical shift differences.

$|^{2}J(^{119}Sn-^{1}H)|$ data for four- and five-coordinated trimethyltin compounds have been reported to lie in the ranges 54 to 59 and 59 to 71 Hz, respectively [27–29]. Similarly, $^{1}J(^{119}Sn-^{13}C)$ has been found in the ranges 313 to 376 and 402 to 502 Hz for four- and five-coordinated tributyltin compounds, respectively [30]. The observed values of $|^2J(^{119}\mathrm{Sn}-^1\mathrm{H})|$, 56–57 Hz for $\mathrm{Me_3Sn[SSP(OR')_2]}$, and of $|^1J(^{117/119}\mathrm{Sn}-^{13}\mathrm{C})|$ 330–366 Hz for $\mathrm{R_3Sn[SSP(OR')_2]}$ support the conclusions drawn from ^{119}Sn NMR data that these compounds are four-coordinated.

For four-coordinated dimethyltin compounds, $|^2J(^{119}\mathrm{Sn}-^1\mathrm{H})|$ values have been reported in the range of 60–71 Hz, and such values have been found to increase as the coordination number of tin increases from four to five to six or seven, and has been observed in the range 71–116 Hz depending upon stereochemistry [27,28,31]. $|^1J(^{119}\mathrm{Sn}-^{13}\mathrm{C})|$ values for four-coordinated dibutyltin compounds are of the order of 365–402 Hz, while for five- and six-coordinated compounds such values lie in the range of 500–910 Hz [30]. Recently, $|^1J(^{119}\mathrm{Sn}-^{13}\mathrm{C})|$ for six-coordinated dimethyltin compounds has been found in the range 618–977 Hz [11,16]. The observed values of $|^2J(^{119}\mathrm{Sn}-^1\mathrm{H})$ 77–78 Hz and $|^1J(^{117/119}\mathrm{Sn}-^{13}\mathrm{C})|$ 558.5 Hz for $\mathrm{Me_2Sn[SSP(OR')_2]_2}$ are slightly lower than those for six-coordinated compounds, indicating that the ligand moieties are weakly coordinated to the tin atom.

$|^2J(^{119}\mathrm{Sn}-^1\mathrm{H})|$ for $\mathrm{MeSn[SSP(OR')_2]_3}$ is 97.0 Hz which is higher than for four-coordinated tin compounds, (e.g. for $\mathrm{MeSn(SMe)_3}$ $|^2J|$ is 66.5 Hz) but lower than for six- or seven-coordinated mono-organotin compounds [26] indicating that the ligand moieties are weakly coordinated.

To explore further the type of coordination in these compounds, we have recorded the ^{119}Sn Mössbauer data at 77 K on representative compounds from each class i.e., $\mathrm{R_3Sn[SSP(OR')_2]}$, $\mathrm{R_2Sn[SSP(OR')_2]_2}$ and $\mathrm{RSn[SSP(OR')_2]_3}$. The resulting data are presented in Table 3 together with literature data that have been reported previously. All of our samples gave two-line spectra which we interpret as arising from a tin atom in an asymmetric environment.

Our data are significantly different from those reported earlier [32,33]. We find significantly higher isomer shifts than did the earlier workers and somewhat different quadrupole interactions. It is interesting to note that the largest differences between the earlier results and those presented here occur for those cases where the earlier workers report line widths which are as much as 50% greater than the normal ~ 1 mm $\mathrm{s^{-1}}$ values. A typical spectrum is shown in Fig. 1 and one notes a slight difference in line intensity of the two components of the doublet. Similar line

TABLE 3

^{119}Sn MOSSBAUER DATA FOR ALKYLTINDIALKYLTHIOPHOSPHATES AT 77 K

Compound	Isomer shift (±0.02) (mm $\mathrm{s^{-1}}$)	Quadrupole splitting (±0.02) (mm $\mathrm{s^{-1}}$)	Line width (±0.02) (mm $\mathrm{s^{-1}}$)	*QS/IS*	Ref.
$\mathrm{Me_3Sn[SSP(OEt)_2]}$	1.53	3.19	1.02, 1.08	2.08	
	1.38	3.09	1.38, 155	2.24	32
$\mathrm{Et_3Sn[SSP(OEt)_2]}$	1.53	2.91	1.28, 1.56	1.90	
$\mathrm{Me_3Sn[SSP(OPr^i)_2]}$	1.43	2.91	1.19, 1.11	2.03	
	1.35	2.92	1.21, 1.28	2.16	32
$\mathrm{Me_3Sn[SSP(OEt)_2]_2}$	1.57	3.07	0.96, 0.94	1.96	
	1.44	3.34	1.32, 1.62	2.32	33
$\mathrm{Me_2Sn[SSP(OPr^i)_2]_2}$	1.56	3.07	0.94, 0.96	1.97	
$\mathrm{MeSn[SSP(OPr^i)_2]_3}$	1.48	2.00	1.03 1.04	1.35	

intensity differences are observed in the other spectra but only in the case of $Me_3Sn[SSP(OPr^i)_2]$ was this very significant. In this particular case it was the low velocity component which was much more intense. This suggests the presence of impurities in this sample and indeed the ^{119}Sn NMR spectrum does confirm this (see Experimental). The origin of doublet line asymmetry has been well discussed [34], and in the absence of impurities, could arise either from preferential crystal orientation or from an anisotropy of the recoilless fraction [35]. Because some of the samples that we have examined are liquids and all have rather low absorption, even at liquid nitrogen temperature (Fig. 1), we were unable to carry out a temperature study which would confirm the Goldanskii–Karyagin effect [35]. We feel that the more likely origin of the asymmetry, particularly for the liquid samples, is from preferred crystal orientation.

There are no dramatic changes in Mössbauer parameters as the ligands about the tin are varied. Indeed, the isomer shift values change only from 1.43 to 1.57 mm s^{-1} but this is not unexpected as one can see by examining the shifts for series of organotin compounds tabulated by Greenwood and Gibb [36]. A greater variation in quadrupole splittings is found however and these are more informative. For a series of compounds of the type R_xSnL_y where R is a given alkyl group, and L is a particular ligand completing the coordination about tin, and which can be mono- or bi-dentate in character, it has been found that the quadrupole splittings vary in the

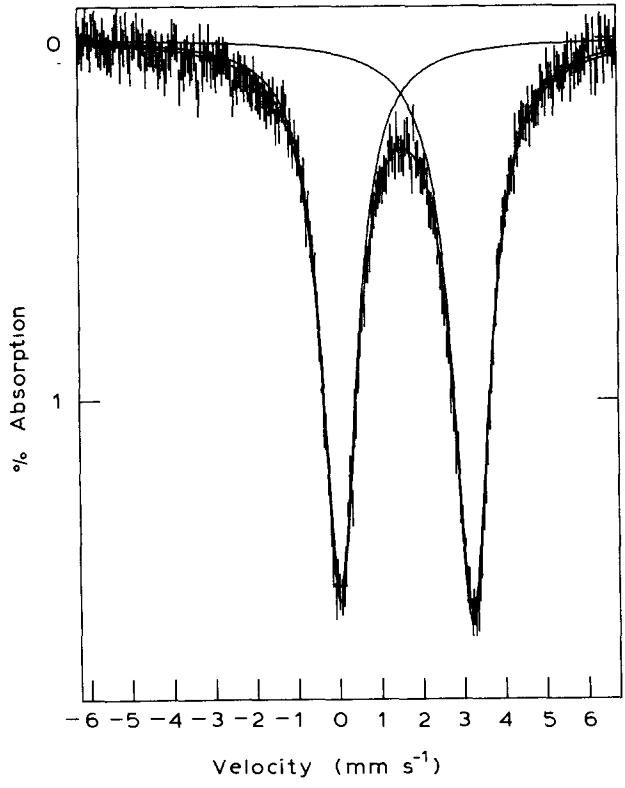

Fig. 1. ^{119}Sn Mössbauer spectrum of $(Me)_3Sn[SSP(OEt)_2]$ at 77 K.

Solvents were dried and distilled under nitrogen atmosphere prior to use. All compounds were prepared as reported earlier [3] by the reactions of organotin(IV) chlorides with stoichiometric amounts of the sodium salt of the dialkyldithiophosphoric acid in anhydrous, refluxing benzene. Triorganotin(IV) dialkyldithiophosphates were distilled immediately prior to obtaining the spectra; even so, Pr^i and Bu^n compounds contained traces of tin impurities as observed in the ^{119}Sn NMR spectra. Mono- and di-methyltin(IV) dialkyldithiophosphate were purified chromatographically. Crude products were dissolved in anhydrous hexane and were passed through Florisil columns (5 cm × 5 cm), eluting with hexane. Solvent was removed under reduced pressure, and the product was dried at 0.1 mm at 50°C for about 2 h.

Tin-119 Mössbauer spectra have been recorded on apparatus that has been described [43], and which was periodically calibrated by recording the spectrum of α-Fe using a ^{57}Co source Rh. The Mössbauer source was $Ca^{119}SnO_3$ purchased from Amersham-Searle and this was maintained at room temperature throughout while the samples were frozen in Kel-F holders and maintained at 77 K. All isomer shifts were measured with respect to $CaSnO_3$ at room temperature. Spectra were computer fitted using the program of A.J. Stone [44] which has been modified by Dr. D.G. Grundy of the Department of Geology, McMaster University.

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