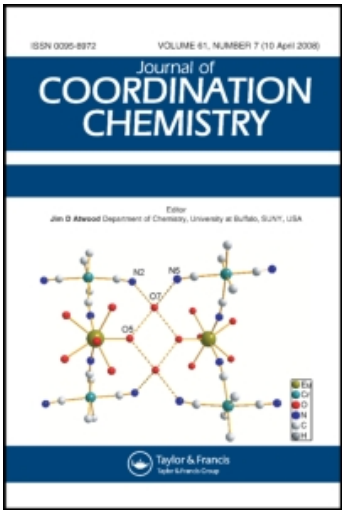

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Synthesis and Characterization of Organotin Substituted Heteropolytungstophosphates and Their Biological Activity

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SYNTHESIS AND CHARACTERIZATION OF ORGANOTIN SUBSTITUTED HETEROPOLYTUNGSTOPHOSPHATES AND THEIR BIOLOGICAL ACTIVITY

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Organotin-substituted Keggin or Dawson tungstophosphates $[(CH_3OOCCH_2CH_2Sn)_3(PW_9O_{34})_2]^{9-}$, $[(CH_3OOCCH_2CH_2Sn)PW_{11}O_{39}]^{4-}$, $[(CH_3OOCCH_2CH_2Sn)P_2W_{17}O_{61}]^{7-}$, $[(CH_3OOCCH(CH_3)CH_2Sn)_3(PW_9O_{34})_2]^{9-}$, $[(CH_3OOCCH(CH_3)CH_2Sn)PW_{11}O_{39}]^{4-}$ and $[(CH_3OOCCH(CH_3)CH_2Sn)P_2W_{17}O_{61}]^{7-}$ have been prepared by reactions of the β-methoxycarbonylethyltin, β-methoxycarbonyl-*i*-propyltin trichlorides with $PW_9O_{34}^{9-}$, $PW_{11}O_{39}^{7-}$ and $P_2W_{17}O_{61}^{10-}$, respectively. The products were isolated as K^+, and Bu_4N^+ salts, and were characterized by means of elemental analysis, IR ^1H NMR, ^{183}W NMR and ^{119}Sn NMR spectra, and polarography. The antitumour activity of the complexes as investigated and the effect of the polyanions and estertin on antitumour activity was examined.

Keywords: Antitumour activity; Organotin; Keggin structure; Dawson structure; synthesis

INTRODUCTION

Current interest in polyoxometallates (POMs) is driven by the potential application of these complexes in areas of catalysis, medicine and materials science.[1,2] It has been recognized for some time that the versatility of the polyoxometallates and their catalytic applications can be significantly increased by grafting organic and organometallic groups onto the polyoxometallate surface.

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The reactivity of mono- and polyvacant polytungstates with organotin was systematically investigated by Pope[3–6] and Knoth.[7–11] In order to develop the application of organometallo derivatives of polymetallates in medicine, our group has systematically investigated the synthesis of organotin, organotitanium and organozirconium complexes, and their antitumor activity.[12] Here we report the synthesis and characterization of estertin substituted heteropolytungstophosphates derived from the lacunar species $PW_9O_{34}^{9-}$, $PW_{11}O_{39}^{7-}$, and $P_2W_{17}O_{61}^{10-}$, and their antitumour activity.

EXPERIMENTAL

Preparation of Compounds

All the reagents were of analytical or guaranteed quality. The compounds β-$CH_3OOCCH_2CH_2SnCl_3$ and β-$CH_3OOCCH(CH_3)CH_2SnCl_3$ were prepared following Ref. [13] and identified by ^1H NMR. $Na_8H[A\text{-}PW_9O_{34}]\cdot 24H_2O$[14] (noted as PW_9), $Na_7PW_{11}O_{39}$[15] (noted as PW_{11}), $K_{10}P_2W_{17}O_{61}\cdot 15H_2O$[16] (noted as P_2W_{17}) were prepared following the published methods and were identified by polarography.

$K_4H_5[(CH_3OOCCH_2CH_2Sn)_3(PW_9O_{34})_2]\cdot 13H_2O$

To a solution of 0.94 g (3 mmol) of $CH_3OOCCH_2CH_2SnCl_3$ in 40 ml of H_2O was added sodium acetate to adjust the pH to 1.6. Then, 2.8 g (1 mmol) of $Na_8H[PW_9O_{34}]\cdot 24H_2O$ was quickly added with stirring. Within a few seconds, most of the tungstophosphate dissolved and the solution turned clear. The solution was stirred for 10 min and filtered. KCl was added to the filtrate until no more precipitate formed. The precipitate was filtered and recrystallized from hot water (yield 1.3 g). Analytical data are summarized in Table I.

$K_4[(CH_3OOCCH_2CH_2Sn)PW_{11}O_{39}]\cdot 12H_2O$

To a solution of 0.32 g (1 mmol) of $CH_3OOCCH_2CH_2SnCl_3$ in 40 cm^3 of H_2O was added sodium acetate to adjust the pH to 1.6, then 2.8 g, 1 mmol $Na_7PW_{11}O_{39}$ was added in small portions with stirring. The acidity of the mixture was adjusted to pH 6–6.5 with sodium acetate and stirred at 80°C for 30 min. After filtration, KCl was added until no more precipitation was observed. The white precipitate was filtered and recrystallized from hot water, yield 1.1 g.

TABLE I Analytical data for salts of HPA

Compounds	*Analysis (%) (calcd.)*							
	Sn	*W*	*P*	*K*	*H_2O*	*C*	*N*	*H*
$K_4H_5[(C_4H_7O_2Sn)_3{*}(PW_9)_2] \cdot 13H_2O$	6.53(6.54)	62.11(60.36)	1.30(1.13)	2.87(2.86)	4.26(4.29)	2.49(2.64)		0.45(0.48)
$K_4[(C_4H_7O_2Sn)PW_{11}] \cdot 12H_2O$	3.92(3.92)	65.23(66.41)	0.89(1.02)	5.41(5.15)	8.34(8.32)	1.33(1.40)		0.19(0.23)
$K_4H_3[(C_4H_7O_2Sn)P_2W_{17}] \cdot 11H_2O$	2.50(2.53)	65.10(66.02)	1.19(1.32)	3.29(3.31)	4.21(4.20)	1.01(1.02)		0.18(0.21)
$(Bu_4N)_4H_5[(C_4H_7O_2Sn)_3(PW_9)_2] \cdot 1H_2O$	3.94(3.94)	54.00(54.46)	1.00(1.03)			14.97(15.08)	0.91(0.91)	2.80(2.81)
$(Bu_4N)_4[(C_4H_7O_2Sn)PW_{11}] \cdot 2H_2O$	3.00(3.10)	50.11(52.39)	0.77(0.81)			21.35(21.24)	1.45(1.46)	3.86(3.85)
$(Bu_4N)_4H_3[(C_4H_7O_2Sn)P_2W_{17}] \cdot 1H_2O$	2.24(2.22)	58.00(58.19)	0.50(0.58)			15.21(15.26)	1.00(1.05)	2.87(2.88)
$K_4H_5[(C_5H_9O_2Sn)_3(PW_9)_2] \cdot 12H_2O$	6.50(6.51)	60.00(60.10)	1.24(1.13)	2.87(2.85)	3.92(3.94)	3.18(3.28)		0.34(0.36)
$K_4[(C_5H_9O_2Sn)PW_{11}] \cdot 13H_2O$	3.87(3.91)	64.27(66.13)	0.90(1.02)	5.00(5.12)	7.65(7.69)	1.80(1.83)		0.17(0.16)
$K_4H_3[(C_5H_9O_2Sn)P_2W_{17}] \cdot 11H_2O$	2.46(2.52)	66.11(65.83)	1.11(1.31)	3.28(3.30)	4.20(4.19)	1.29(1.27)		0.16(0.17)

*The $[RSn]^{3+}$ groups ($R = CH_3OOCCH_2CH_2$, $CH_3OOCCH(CH_3)CH_2$) are abbreviated as $C_4H_7O_2Sn$ and $C_5H_9O_2Sn$, respectively.

$K_4H_3[(CH_3OOCCH_2CH_2Sn)P_2W_{17}O_{61}]\cdot 11H_2O$

$K_4H_3[(CH_3OOCCH_2CH_2Sn)P_2W_{17}O_{61}]\cdot 11H_2O$ was prepared analogously. After adjustment of the pH of the solution, 0.32 g (1 mmol) of $CH_3OOCCH_2CH_2SnCl_3$ and 4.8 g (1 mmol) of $K_{10}[P_2W_{17}O_{61}]\cdot 15H_2O$ was added. The final pH was adjusted to 4.7 with potassium acetate. The solution was stirred at 80°C for 30 min. After filtration, the solution was evaporated to dryness. The white potassium salt was recrystallized from hot water.

Synthetic procedures for all the $CH_3OOCCH(CH_3)CH_2Sn$ substituted heteropolytungstophosphate potassium salts were analogous, except that $CH_3OOCCH(CH_3)CH_2SnCl_3$ was used in place of $CH_3OOCCH_2CH_2SnCl_3$.

The Bu_4N^+ salts of the title complexes were prepared similarly but powdered (Bu_4N) Br was added to the filtrate for crystallization of the product. Recrystallization from hot CH_3CN gave white powders.

Antitumor Activity of POMs

The antitumor activity of POMs on two human cancer cell lines was tested by the MTT experiment described below.

MTT is 3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyltetrazolium bromide, also named thiazolyl blue. It is a dye which can accept an H atom. Surviving tumor cells can reduce the yellow MTT to insoluble blue formazan, but dead tumor cells do not possess this capability. The formazan is dissolved by DMSO, then determined colorimetrically with a microplate reader (490 mm), that examined cell survival rate.

Subcultured Hela cells and SSMC-7721 cells were suspended in 0.25% trypsin. The cell suspension (1×10^5–10^6 cells cm^{-3}) was added to a 96-well plate at 100 µl per well, then incubated at 37°C in 5% CO_2 for 24 h. Then 100 µl samples containing POM was added. After 72 h, 20 µl of MTT (5 mg cm^{-3} in 0.01 M PBS) was added. The mixture was incubated for 4 h. The supernatant was removed, then DMSO (150 µl) was added. The mixture was shaken for 10 min at room temperature. Colorimeter analysis was determined with a microplate reader (490 nm), effective cell 50% lethal concentrations (IC_{50}) was calculated by statistical methods.

Analytical Methods

W, P and Sn were determined by ICP – AES. The H_2O content was determined by thermogravimetry. C, H and N were determined using a PE-2400 analyser. K was determined by atomic absorption spectroscopy (Table I).

^{119}Sn and ^{183}W NMR spectra were recorded at 16.6 MHz on a Unity-400 spectrometer. Chemical shifts are referenced to Na_2WO_4 for ^{183}W. For ^{119}Sn, the chemical shifts are referenced to $(CH_3)_4Sn$. ^1H NMR spectra were recorded on Brucker AC-80 spectrometer.

IR spectra were recorded on an Alpha Centauri FTIR spectrometer (4000–200 cm^{-1}) using KBr pellets. Polarograms were obtained using a 384B Polarographic Analyser, equipped with 303A type electrodes.

RESULTS AND DISCUSSION

Spectra

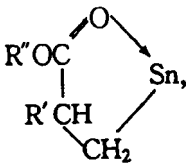
Observed frequencies and tentative assignments of the main IR and UV bands of the title complexes are given in Table II.

IR spectra of organotin-substituted heteropolyanions exhibit the following characteristics. The IR spectra of all the complexes exhibit the four characteristic $W-O_d$ (terminal oxygen), $W-O_b-W$ (bridging oxygen), $W-O_c-W$ (bridging oxygen) and $P-O_a$ (central oxygen) asymmetric stretching vibrational peaks for heteropolyanions with Keggin or Dawson structure, suggesting that the title complexes have the Keggin or Dawson structure. Replacement of RSn^{3+} in the polyanions causes a vibrational red shift in comparison with $PW_{12}O_{40}^{3-}$ or $P_2W_{18}O_{62}^{6-}$, due to an increase in negative charge on the polyanion. This result is consistent with other mixed-type polyanions.[16] The $P-O_a$ bond vibrations of $(RSn)_3(PW_9)_2$ split. This fact demonstrates that the $[RSn]^{3+}$ did not occupy the three vacant sites of the PW_9 anions to give $(RSn)_3PW_9$. The IR spectrum is similar to that of $Co_3(PW_9)_2$.[17] This is because of the fact that if $[RSn]^{3+}$ groups occupy the three vacant sites, it maintains the Keggin structure and the PO_4 asymmetric

TABLE II IR data (cm^{-1}) and UV maxima (nm)

Anions	$\nu_{as(W-O_d)}$	$\nu_{as(W-O_b-W)}$	$\nu_{as(W-O_c-W)}$	$\nu_{as(P-O_a)}$	$\nu_{C=O}$	λ_{max}
$(C_4H_7O_2Sn)_3(PW_9)_2$	949	881	805	1050, 1078, 1100	1742	200, 260
$(C_4H_7O_2Sn)PW_{11}$	950	881	806	1048, 1099	1742	199, 261
$(C_4H_7O_2Sn)P_2W_{17}$	950	909	784	1013, 1091	1735	254, 276
$(C_5H_9O_2Sn)_3(PW_9)_2$	948	881	805	1051, 1078, 1101	1740	201, 260
$(C_5H_9O_2Sn)PW_{11}$	951	881	802	1049, 1099	1735	199, 260
$(C_5H_9O_2Sn)P_2W_{17}$	952	909	783	1014, 1092	1735	255, 276
α-P_2W_{18}	966	916	792	1090, 1022		256, 277
α-PW_{12}	995	900	805	1081		265
$CH_3OOCCH_2CH_2SnCl_3$					1665	
$CH_3OOCCH(CH_3)$-CH_2SnCl_3					1660	

stretch is a single peak. In comparison with the $P-O_a$ bond vibration frequency of P_2W_{18}, that of $(RSn)P_2W_{17}$ changes little. This demonstrates that the RSn^{3+} group occupies the vacant site of P_2W_{17}. In comparison with estertin, the C=O frequencies increase. The structure of β-methoxycarbonylethyltin trichloride can be represented as



and the carbonyl stretching frequency is $1665\,cm^{-1}$. When β-methoxycarbonylethyltin reacts with HPA, the intramolecular carbonyl coordination to Sn is broken and Sn incorporates terminal O atoms of HPA. The C=O vibration increases to $1735-1742\,cm^{-1}$.

All the complexes are colourless, so the spectroscopic region of interest is in the near UV from 200 to 300 nm. In this range all Keggin complexes exhibited two strong charge transfer (ct) absorption at *ca.* 200 and 260 nm. The first results from the transfer O_d-W and the second (from $O_b/O_c \rightarrow W$) is the characteristic band of PW_{12} polyanions with the Keggin structure.[18] In comparison with α-P_2W_{18}, $P_2W_{17}(RSn)$ anions also exhibited two characteristic charge transfer bands at *ca.* 250 and 270 nm of the Dawson anion, indicating that $(RSn)P_2W_{17}$ anions have Dawson structure. The intense absorption band at *ca.* 270 nm has been attributed to a $O_b/O_c \rightarrow W$ ct band and the higher energy band to a $O_d \rightarrow W$ ct.

NMR Spectra

^1H NMR and ^{183}W NMR data are listed in Table III. Spectra of the title complexes are different from that of β-methoxycarbonylethyltin

TABLE III ^{183}W NMR[a] and ^1H NMR[b] data (ppm)

Anions	*δ*			
	^{183}W	Ome	*CH* (β)	*CH* (γ)
$(C_4O_2H_7Sn)_3(PW_9)_2$	−122.9(1)[c], −201.6(2)	3.72(s)	3.01(t)	1.66(t)
$(C_4O_2H_7Sn)PW_{11}$	−76.9(2), −91.5(2), −113.6(2) −130.7(1), −166.1(2), −174.7(2)	3.84(s)	3.01(t)	1.73(t)
$(C_4H_7O_2Sn)P_2W_{17}$	−92.7, −96.3, −103.6 −111.5, −120.6, −147.9 −115.8, −194.4, −209.9	3.81(s)	2.97(t)	1.78(t)
$C_4H_7O_2SnCl_3$		3.94(s)	2.94(t)	2.22(t)

[a] Bu_4N salts dissolved in CH_3CN. [b] Potassium salts dissolved in D_2O. [c] Relative intensity in parentheses.

trichlorides. In $CH_3OOCCH_2CH_2SnCl_3$, the Sn atom links with three chloride atoms and the hydrogen chemical shift of $SnCH_2$ is 2.22 ppm. In $(CH_3OOCCH_2CH_2Sn)_3(PW_9)_2$, the electron density on Sn increases, so $SnCH_2$ moves to higher field. This demonstrates that the $[RSn]^{3+}$ group is incorporated with the tungstophosphate and organic group did not separate from the Sn atom.

The ^{119}Sn NMR spectrum of $(CH_3OOCCH_2CH_2Sn)_3(PW_9)_2$ gives only a single line, implying that the tin environments are equivalent. The chemical shift of Sn is −578.6 ppm, while $(Ph)_4Sn$ is at *ca.* −128.1 ppm. Such a shift can be explained in terms of an increase in the electron density on the Sn atom when the $[RSn]^{3+}$ groups incorporate to form six-coordinate Sn compounds.[19]

The ^{183}W NMR spectrum of $(CH_3OOCCH_2CH_2Sn)_3(PW_9)_2$ consists of two lines with intensity ratio 1 : 2, indicating that there are two non-equivalent tungsten environments in the heteropolyanion. According to ^{183}W NMR patterns of trisubstituted heteropolyanions summarized by Pope,[5] the ^{183}W NMR of sandwiched structures show two lines with intensity ratio 1 : 2. This fact supports the stoichiometry of the new heteropolyanion, and demonstrates that $(CH_3OOCCH_2CH_2Sn)_3(PW_9)_2$ has nominal D_{3h} symmetry containing three $[(CH_3OOCCH_2CH_2)Sn]^{3+}$ groups sandwiched between two A-PW_9 anions.

The ^{183}W NMR of $(CH_3OOCCH_2CH_2Sn)PW_{11}$ confirms the incorporation of the $[RSn]^{3+}$ group in the polyoxoanion. Since the mono-substituted α-Keggin derivative displays the anticipated C_s structure, six resonances would be expected. The ^{183}W NMR spectrum of $(CH_3OOCCH_2CH_2Sn)PW_{11}$ gives six lines with intensity ratio 2:2:2:1:2:2, implying that $(CH_3OOCCH_2CH_2Sn)PW_{11}$ retains the α-Keggin structure.

The ^{183}W NMR spectrum of $(CH_3OOCCH_2CH_2Sn)P_2W_{17}$, in agreement with C_s symmetry, shows nine lines, similar to the case of α_2-P_2W_{17}. This $(CH_3OOCCH_2CH_2Sn)P_2W_{17}$ retains the Dawson structure.

^{31}P NMR of the $(CH_3OOCCH_2CH_2Sn)_3(PW_9)_2$ gives only one line with a chemical shift of −8.34 ppm, showing that the environments of the two phosphorus atoms are equivalent, and also demonstrating that the PW_9 unit in the $(RSn)_3(PW_9)_2$ is an A-type isomer in line with the results of Knoth.[20]

Polarography

$E_{1/2}$ values were determined at 298 K in 0.5 mol cm^{-3} acetate buffer solution with saturated calomel and dropping mercury electrodes. $E_{1/2}$ data of the title complexes are given in Table IV. Reduction processes involved the

TABLE IV Half-wave potentials (V) of the title anions at different pH values

Anions		pH		
		4.2	4.7	5.2
$(C_4H_7O_2Sn)_3(PW_9)_2$	W^{VI}–W^V	−0.868(4)	−0.900(4)	−0.934(4)
$(C_5H_9O_2Sn)_3(PW_9)_2$	W^{VI}–W^V	−0.840(4)	−0.872(4)	−0.909(4)
$(C_4H_7O_2Sn)PW_{11}$	W^{VI}–W^V	−0.466(2)	−0.528(2)	−0.699(2)
		−0.676(2)	−0.788(2)	−0.898(2)
$(C_5H_9O_2Sn)PW_{11}$	W^{VI}–W^V	−0.600(2)	−0.784(2)	−0.900(2)
		−0.712(2)	−0.940(2)	−1.112(2)
$(C_4H_7O_2Sn)P_2W_{17}$	W^{VI}–W^V	−0.601(2)	−0.724(2)	−0.693(2)
		−0.814(2)	−0.948(2)	−0.876(2)
				−1.111(2)
$(C_5H_9O_2Sn)P_2W_{17}$	W^{VI}–W^V	−0.401(2)	−0.524(2)	−0.654(2)
		−0.576(2)	−0.660(2)	−0.783(2)
		−0.811(2)	−0.900(2)	−1.098(2)

TABLE V Inhibitory effect of the title complex on some cells *in vitro*

Complexes	*Tumor cells*	*Dose* ($\mu g\,ml^{-1}$)	*Inhibitory rate* (%)	IC_{50}* ($\mu g\,ml^{-1}$)
$(C_4H_7O_2Sn)_3(PW_9)_2$	Hela	100	100	
				49.9
		10	10.2	
	SSMC-7721	100	100	
				47.6
		10	11.1	
$(C_5H_9O_2Sn)_3(PW_9)_2$	Hela	100	100	
				45.7
		10	11.6	
	SSMC-7721	100	100	
				40.3
		10	12.4	
$(C_4H_7O_2Sn)PW_{11}$	Hela	100	59.2	
				82.6
		10	5.9	
	SSMC-7721	100	71.2	
				70.1
		10	7.0	
$(C_5H_9O_2Sn)PW_{11}$	Hela	100	59.7	
				82.0
		10	6	
	SSMC-7721	100	73.4	
				68.3
		10	7.3	
$(C_4H_7O_2Sn)P_2W_{17}$	Hela	100	55.3	
				90.2
		10	5.2	
	SSMC-7721	100	56.9	
				86.3
		10	5.6	
$(C_5H_9O_2Sn)P_2W_{17}$	Hela	100	56.6	
				86.7
		10	5.4	
	SSMC-7721	100	61.9	
				79.1
		10	6.2	

*The 50% inhibitory concentration (IC_{50}) is defined as the concentration which suppresses growth of tumour cells by 50%.

reduction of tungsten and showed pH-dependent peaks, implying that reduction accompanied by protonation. The reduction of W^{VI} of $(RSn)_3(PW_9)_2$ shows an apparent one-step four electrons reduction peak. A straight line is obtained by logarithmic analysis of the polarographic wave. The number of electrons involved can be calculated from the slope of the line. This should allow one to discriminate between α- and β-isomers. For XW_9 (X = P, Si, As), the reduction of α-XW_9[18] is an apparent one-step four electron reduction and for β-XW_9 is a two-step two electron reduction process. Thus $(RSn)_3$ $(PW_9)_2$ anions are α-isomers. The polarographic waves for $(RSn)P_2W_{17}$ are expected three. $(CH_3OOCCH_2CH_2Sn)P_2W_{17}$ at pH = 4.2, 4.7 show only two reduction peaks because of overlap.

Antitumour Activity

The data summarized in Table V show that the title complexes display inhibitory action to Hela and SSMC-7721 tumour cells. The antitumor activity of tri-substituted compounds is higher than of mono-substituted compounds. We think that the centre of antitumor activity is the Sn atom. Because the Sn content of $(RSn)_3(PW_9)_2$ is more than in monosubstituted compounds, the same dosage gives a greater inhibitory rate. The influence of different organotin group on antitumor activity is small.

Acknowledgements

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