

STUDY OF STRUCTURE OF BIS(TRIPHENYLSTANNYL) CHROMATE(VI) BY INFRARED, MÖSSBAUER, AND ^1H , ^{13}C AND ^{119}Sn NMR SPECTRA

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The infrared, Mössbauer, and ^1H , ^{13}C and ^{119}Sn NMR spectra have been used to study the structure of bis(triphenylstannyl) chromate(VI) in solid state and in solvents of both noncoordinating and coordinating types. In solid state the compound forms a three-dimensional polymer: the tetrahedral CrO_4 group and *trans*-trigonally bipyramidal $(\text{C}_6\text{H}_5)_3\text{SnO}_2$ grouping are connected mutually symmetrically by bridges represented by the common oxygen atoms. The three phenyl groups in the $(\text{C}_6\text{H}_5)_3\text{SnO}_2$ grouping are located in the equatorial plane of the trigonal bipyramide which is completed by two bridge oxygen atoms in axial positions. Solutions in noncoordinating solvents contain monomeric bis(triphenylstannyl) chromate(VI). The ester molecule contains two tetrahedral, $(\text{C}_6\text{H}_5)_3\text{SnO}$ groups bound by oxygen bridges to a CrO_4 group which shows the C_{2v} symmetry. In coordinating solvents the title compound forms a molecular complex having the coordination number 5 at the central tin atom.

In literature there exist plenty of information about the exceptional activity of the catalytic systems based on organometallic esters of chromic acid as precursors in the process of polymerization of 1-alkenes, especially ethylene. In contrast to these numerous patents, little has been done in the field of the corresponding basic research. Bis(triphenylstannyl) chromate $((\text{C}_6\text{H}_5)_3\text{SnO})_2\text{CrO}_2$ belongs to the most important compounds of this class¹, however, there exists only basic information about it². The present communication deals with a study of structure of the compound in solid state and in solutions in nonpolar (noncoordinating) and polar solvents by means of infrared, Mössbauer, and ^1H , ^{13}C and ^{119}Sn NMR spectra.

EXPERIMENTAL

Bis(triphenylstannyl) chromate was prepared by a known procedure². The infrared spectra of the compound were measured in the region of $4000\text{--}200\text{ cm}^{-1}$ using a Perkin-Elmer apparatus model 684. The spectrum of the compound in solid state was measured by the KBr-disc

technique and in Nujol suspension. The spectra of the solutions (chloroform, carbon disulphide, dimethyl sulphoxide) and that of the Nujol suspension were measured in KBr cells or in polyethylene cell. The Mössbauer spectra were measured with a KFKI apparatus (Budapest, Hungary) at room temperature using $\text{Ba}^{119\text{m}}\text{SnO}_3$ as the source. The spectral parameters were obtained by computer treatment of the experimental data using the least squares method for fitting of the measured values with a simple symmetrical doublet of the Lorentzian lines. The ^1H , ^{13}C , and ^{119}Sn NMR spectra were measured in deuteriochloroform and hexadeuteriodimethyl sulphoxide using a JNM-FX 100 apparatus (JEOL, Japan) at 99.602 MHz (^1H , internal tetramethylsilane), 25.047 MHz (^{13}C , int. tetramethylsilane), and 37.14 MHz (^{119}Sn , external tetramethyltin). The ^{13}C and ^{119}Sn NMR spectra were identified and interpreted as in refs.^{3,4}.

RESULTS

Infrared Spectra

The infrared spectra of the studied compound in solid state (KBr disc, Nujol suspension) and in solutions in noncoordinating solvents (chloroform, carbon disulphide) do not much differ in the region of $4\,000 - 1\,000\text{ cm}^{-1}$. This spectral region contains all the bands due to vibrations of phenyl group at the usual wave numbers⁵; these bands only have identification value. The wave numbers of the bands of $1\,000$ to 200 cm^{-1} region, which are important for estimation of structure of the compound both in solid state and in solutions, are given in Table I. From the Table it can be seen that also in this region the wave numbers of all bands belonging to phenyl group have practically constant values. On the contrary, the wave numbers of the bands of CrO_4 group depend distinctly on the state of the compound.

The infrared spectrum of the solid substance resembles very much that of ionic chromates^{6,7} which contain the tetrahedral CrO_4^{2-} ion possessing the T_d symmetry. Therefore, in accordance with the selection rules of vibrational spectroscopy their infrared spectra only contain a distinct ν_3 band (F_2 symmetry) in the region $\sim 885\text{ cm}^{-1}$ and a less intensive ν_4 band (F_2) at about 390 cm^{-1} , which are both infrared-active, and, furthermore, two very weak (forbidden) bands ν_1 (A_1) and ν_2 (E) at ~ 855 and $\sim 350\text{ cm}^{-1}$, respectively. The spectral bands found by us in bis(triphenylstannyl) chromate at 861 vs, 806 sh, 390 m, and 310 vw (KBr disc) and 860 vs, 806 sh, 390 m, and 320 vw (Nujol suspension) cm^{-1} have similar values of wave numbers and intensities and, therefore, the CrO_4 group is assigned the T_d symmetry in this case, too.

The infrared spectra of bis(triphenylstannyl) chromate dissolved in nonpolar solvents (chloroform, carbon disulphide) lack both the characteristic, distinct, relatively broad band at $\sim 860\text{ cm}^{-1}$ and the weak, forbidden band at $\sim 806\text{ cm}^{-1}$. In their place there appear (in carbon disulphide solution) four new sharp bands of almost the same intensity at 970, 952, 792, and 677 cm^{-1} . In chloroform solution two of these bands (975 and 945 cm^{-1}) only can be observed, the region of ~ 800 to 650 cm^{-1} being overlapped by the absorption of the solvent itself. The presence

of four bands in the region $975-677\text{ cm}^{-1}$ corresponds to the idea of decreased symmetry of the CrO_4 group (C_{2v} or C_s) which causes splitting of the original, three times degenerated vibrational level $\nu_3 (F_2)$ in the sense ($A_1 + B_1 + B_2$ or $3A$), and the ν_1 vibration (totally symmetrical), which is forbidden in the T_d symmetry, becomes allowed. Similar changes occur also in the ν_4 and ν_2 vibrations. The medium intensive band at 390 cm^{-1} (ν_4, F_2) is replaced by three bands 420 sh, 360 w, and 345 sh (in carbon disulphide) and 420 sh, 360 sh, and 340 vw (in chloroform); the $\nu_2 (E)$ vibration could be represented by the very weak band at about 310 cm^{-1} with slight indication of splitting into a doublet.

A band of medium intensity at about 370 cm^{-1} which appears in spectra of both the solid and dissolved compound is assigned to the Sn-O bond in accordance with refs^{8,9}. Very important information for structure determination of the com-

TABLE I
Infrared spectra of bis(triphenylstannyl) chromate in the region $1\ 000-200\text{ cm}^{-1}$

KBr	Nujol	CHCl_3	CS_2	Denotation
—	—	970 s	975 s	$\nu_3, \text{CrO}_4 (C_{2v} \text{ or } C_s)$
—	—	945 s	952 s	$\nu_3, \text{CrO}_4 (C_{2v} \text{ or } C_s)$
900 sh	905 vw	905 vw	908 w	$\gamma(\text{CH})$
—	—	882 vw	887 vw	$\gamma(\text{CH})$
861 vs	860 vs	—	—	$\nu_3, \text{CrO}_4 (T_d)$
806 sh	806 w	—	—	$\nu_1, \text{CrO}_4 (T_d)$
—	—	—	792 s	$\nu_3, \text{CrO}_4 (C_{2v} \text{ or } C_s)$
726 s	725 s	—	728 s	$\gamma(\text{CH})$
694 s	693 s	—	696 s	ring puckering
—	—	—	677 m	$\nu_1, \text{CrO}_4 (C_{2v} \text{ or } C_s)$
661 w	665 vw	—	665 vw	X-sensitive
—	—	630 vw	—	—
615 vw	614 vw	610 vw	—	$\alpha(\text{CCC})$
446 s	449 s	446 s	446 m	X-sensitive
—	—	420 sh	420 sh	$\nu_4, \text{CrO}_4 (C_{2v} \text{ or } C_s)$
390 m	390 m	—	—	$\nu_4, \text{CrO}_4 (T_d)$
370 m	365 m	370 m	—	$\nu(\text{SnO})$
—	—	360 sh	360 w	$\nu_4, \text{CrO}_4 (C_{2v} \text{ or } C_s)$
—	—	340 w	345 sh	$\nu_4, \text{CrO}_4 (C_{2v} \text{ or } C_s)$
310 vw	320 vw	310 vw	315 vw	ν_2, CrO_4
273 s	272 s	271 vs	270 s	$\nu_a(\text{Sn}-\text{C}_5\text{H}_6)$
—	—	236 m	—	$\nu_s(\text{Sn}-\text{C}_6\text{H}_5)$
—	216 w	219 w	—	$\delta(\text{Sn}-\text{C}_6\text{H}_5)$

pound is obtained from the spectral region of $300-200\text{ cm}^{-1}$. It contains the bands corresponding to symmetrical and antisymmetrical vibration of the Sn-C(phenyl) bond. According to the selection rules of vibrational spectroscopy, the two components are active in both infrared and the Raman spectra, unless the $(\text{C}_6\text{H}_5)_3\text{Sn}$ is strictly planar. The planar arrangement of this group excludes the presence of the symmetrical component ν_s ($\sim 230\text{ cm}^{-1}$) in the infrared spectrum, the antisymmetrical component ν_a ($\sim 270\text{ cm}^{-1}$) only being active. Quite the opposite is true, of course, of the Raman spectra. As it is seen from Table I the chloroform solution of the compound exhibits the both bands: ν_s (271 cm^{-1}), ν_a (236 cm^{-1}), whereas in carbon disulphide the ν_s component cannot be detected due to absorption of the solvent itself. In Nujol suspension, however, the band ν_a only is found at 272 cm^{-1} (the region below 250 cm^{-1} is insensitive in KBr). Hence the arrangement of the $(\text{C}_6\text{H}_5)_3\text{Sn}$ group is planar (D_{3h} symmetry) in the solid compound, whereas in solution the particles of the compound contain the mentioned group in non-planar arrangement (C_{3v} symmetry is presumed). All our attempts at verification of these results by means of the Raman spectra failed: the compound decomposes during irradiation with the laser beam (low thermal and photolytic stability).

For completion and comparison, we also measured the spectra of bis(triphenylstannyl) chromate in chloroform solution with addition of 5% (v/v) dimethyl sulphoxide. The addition of this coordination solvent caused the symmetrical ν_s component (236 cm^{-1}) to disappear. Moreover, the spectrum did not contain the band at 860 cm^{-1} (ν_3 , CrO_4), but it contained an intensive band at 800 cm^{-1} . The other bands of CrO_4 group are overlapped by the absorption bands of dimethyl sulphoxide. Even in this case, however, it can be presumed that the CrO_4 group possesses a lower symmetry (C_{2v} or C_s) in solution in the presence of a coordinating solvent, the $(\text{C}_6\text{H}_5)_3\text{Sn}$ being planar.

The Mössbauer Spectrum

The Mössbauer spectrum of bis(triphenylstannyl) chromate(VI) represents a well-resolved symmetrical doublet with the following parameters: Isomeric shift (I.S.) $1.28 \pm 0.03\text{ mm s}^{-1}$, quadrupole splitting (Q.S.) $3.36 \pm 0.03\text{ mm s}^{-1}$, the line width (Γ) $1.03 \pm 0.03\text{ mm s}^{-1}$, relative absorption (ϵ) 0.0086 ± 0.0005 . The I.S. value specifies the presence of formally four-valent tin in the molecule, the ratio Q (Q.S./I.S.) equal to 2.56 exceeds distinctly the lower limit (2.1) of the values characteristic for stannic compounds having the coordination number above 4 at the central atom¹⁰. The given Q.S. value is typical of all the triorganyltin(IV) compounds with the tin coordination number equal to five in which the planar R_3Sn group is completed by further two donor oxygen atoms arranged in the shape of trigonal bipyramide with the oxygen atoms at the axial positions (*trans*- R_3SnO_2)¹¹. The fact that the Mössbauer spectrum was measured at room temperature represents

an indirect evidence for relatively firm intermolecular associates in the compound lattice¹².

The NMR Spectra

The parameters of ¹H, ¹³C, and ¹¹⁹Sn NMR spectra of bis(triphenylstannyl) chromate(VI) in deuteriochloroform and hexadeuteriodimethyl sulphoxide are given in Table II. The ¹H NMR spectrum of the compound in deuteriochloroform exhibits only a single signal at 7.39 ppm (centre of the multiplet). The spectrum of the same compound in a mixture (15 : 1, v/v) of deuteriochloroform and hexadeuteriodimethyl sulphoxide shows two multiplet signals at 7.33 and 7.69 ppm. According to ref.¹³ the signal at 7.39 ppm (in pure deuteriochloroform) represents the irresolvable system of *o*-, *m*-, and *p*-hydrogen atoms of the phenyl ring in the non-planar arrangement of the (C₆H₅)₃Sn group, the signal at 7.33 ppm (in the above-mentioned solvent mixture) belongs to *m*- and *p*-hydrogen atoms, and the signal at 7.69 ppm is due to *o*-hydrogen atoms in the (C₆H₅)₃Sn group with planar geometry. In pure hexadeuteriodimethyl sulphoxide the spectrum was similar (Table II). By means of selective decoupling it could be proved that the protons with the chemical shift of 7.78 ppm are bound to carbon atoms at *ortho* positions (C₍₂₎).

TABLE II
The ¹H, ¹³C, and ¹¹⁹Sn NMR spectral parameters of bis(triphenylstannyl) chromate in solutions

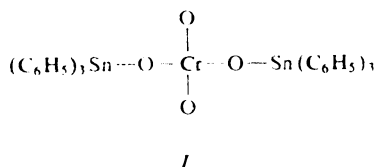
NMR parameter		C ² HCl ₃ ^a	(C ² H ₃) ₂ SO
δ(¹ H), ppm		7.39 (m)	7.41 (m, H ₍₃₎ + H _{(4)) 7.78 (m, H₍₂₎)}
δ(¹³ C), ppm	C ₍₁₎	139.2	143.41
	C ₍₂₎	136.5	136.54
	C ₍₃₎	128.7	128.35
	C ₍₄₎	129.8	129.13
δ(¹¹⁹ Sn), ppm		-81.5	-234.6
ⁿ J(¹¹⁹ Sn ¹³ C), Hz	n = 1	77.1	815.4
	n = 2	48.7	47.6
	n = 3	66.3	69.6
	n = 4	—	14.6

^a Taken from ref.³.

Marked differences can also be observed between the ^{13}C and ^{119}Sn NMR spectra measured in deuteriochloroform and hexadeuteriodimethyl sulphoxide. The parameters $\delta(^{119}\text{Sn})$, $\delta(^{13}\text{C})$ of the carbon atom at ipso-position ($\text{C}_{(1)}$) and $^1J(^{119}\text{Sn}^{13}\text{C})$ of the spectrum of the compound in deuteriochloroform solution exhibit the values characteristic of triphenylstannic compounds with tetrahedral coordination at the tin atom, whereas the same parameters in the spectrum of the compound in hexadeuteriodimethyl sulphoxide solution are characteristic of the complex triphenylstannic compounds with *trans*-trigonally bipyramidal arrangement of the three phenyl groups and further two donor atoms around the central tin atom (the coordination number 5)⁴.

DISCUSSION

Solutions of bis(triphenylstannyl) chromate in noncoordinating solvents contain – according to the results of our measurements – the simple molecules *I*, whose central Cr(VI) atom is coordinated with four oxygen atoms, out of which two form the



connecting bridges with the triphenylstannic groups. Two pairs of differently bound oxygen atoms cause lower symmetry of the CrO_4 group (C_{2v}). The four-valent tin atoms Sn(IV) with three phenyl groups in non-planar arrangement (C_{3v}) and the bridge oxygen atom form a $(\text{C}_6\text{H}_5)_3\text{SnO}$ grouping which is close to the tetrahedral arrangement. These ideas agree fully with the results obtained by analysis of the infrared and NMR spectra of the compound in chloroform and/or carbon disulphide solutions. Formally the same molecular structure is found in all purely organic esters of chromic acid and these of the type $(\text{R}_3\text{MO})_2\text{CrO}_2$ (R = an organic group, M = Si or Ge)¹⁴⁻¹⁷.

The presence of a coordinating solvent in the solutions (dimethyl sulphoxide) makes itself felt by formation of a complex with donor-acceptor bond between the solvent oxygen atom (donor) and the central tin atom of bis(triphenylstannyl) chromate. Consequently, substantial structural changes take place in the triphenylstannic grouping. The original quasi-tetrahedral arrangement of the $(\text{C}_6\text{H}_5)_3\text{SnO}$ is transformed into the *trans*-trigonally bipyramidal arrangement $\text{O} \cdots \text{Sn}(\text{C}_6\text{H}_5)_3\text{O}$ with planar $(\text{C}_6\text{H}_5)_3\text{Sn}$ group forming the equatorial plane; the two oxygen atoms assume the axial positions. The formation of this donor-acceptor molecular complex in solution, of course, will not affect perceptibly the structure of CrO_4 group

which retains the lower C_{2v} symmetry in this case, too. The triphenylstannyl group of bis(triphenylstannyl) chromate tends thus — under suitable conditions — to form complex compounds with electron pair donors. The oxygen atom of dimethyl sulphoxide is a substantially stronger donor than that of CrO_4 group. Therefore, it is not surprising that in solutions of non-polar solvents the addition of dimethyl sulphoxide causes formation of a complex but no distinct mutual association of bis(triphenylstannyl) chromate molecules.

In solid state, however, the conditions for this association are fulfilled obviously, too. The infrared spectra of bis(triphenylstannyl) chromate confirm high symmetry (T_d) of CrO_4 group and planar arrangement of $(C_6H_5)_3Sn$. The Mössbauer spectrum shows the parameters typical of *trans*-trigonally bipyramidal $(C_6H_5)_3SnO_2$ grouping and polymeric character of the compound. Thus it seems likely that in solid state the bis(triphenylstannyl) chromate(VI) molecules are mutually associated to form a three-dimensional polymer in which each oxygen atom of each tetrahedral CrO_4 group is bound to the tin atom of a $(C_6H_5)_3Sn$ group which, in turn, is bound by another oxygen bridge to a further tetrahedral CrO_4 group (Fig. 1). A similar arrangement of solid bis(methylstannyl) chromate is suggested by Clark & Goel¹⁸, too.

According to our results, bis(triphenylstannyl) chromate in non-polar solvents forms isolated molecules whose structure is similar to that of the homologous bis(triphenylsilyl) chromate(VI) determined by direct diffraction method¹⁷. The two compounds, however, differ markedly in their structures in solid state. Whereas bis(triphenylsilyl) chromate gives molecular crystals, bis(triphenylstannyl) chromate forms three-dimensional polymers.

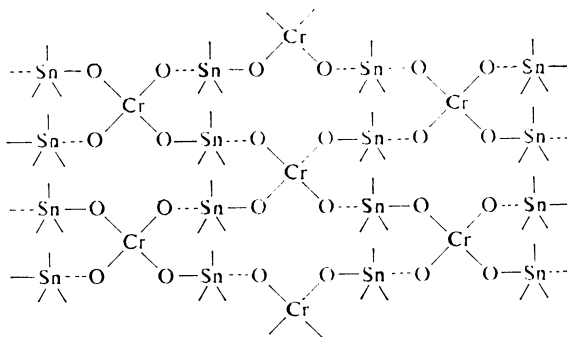


FIG. 1

Schematic representation of structure of solid bis(triphenylstannyl) chromate(VI). The phenyl rings are omitted for simplicity

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