Structural Study of Tris(*N*,*N*-diethyldithiocarbamato-S,S')-3-methoxypropyltin(IV). Searching for Hypercoordinated Monoorganotin(IV) Species

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Dedicated to Professor Dr. Jaroslav Holoček on the occasion of his 70th birthday

ABSTRACT

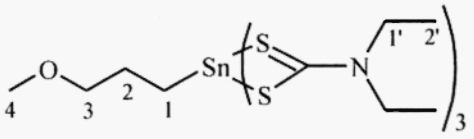
Tris(*N*,*N*-diethyldithiocarbamato-S,S')-3-methoxypropyltin(IV) has been prepared and its structure in various solvents and in the solid state was determined using NMR, IR, CP/MAS NMR, ESI MS and X-ray diffraction techniques, respectively. The tin central atom is seven-coordinated in the solid state and a similar structure is retained in solution; no intra- or inter-molecular attack of ligands oxygen donor atom to the tin centre was observed.

Keywords: Monoorganotin(IV) compound /)-ligand / NMR

INTRODUCTION

Through their interesting properties /1/ and potential use /2/, the monoorganotin(IV) compounds stand out among the main interests of organometallic chemistry. The first papers from the area of hypercoordinated organotin compounds can be found in the seventies of the last century /3/, but the hypercordinated monoorganotins are rather rare /4/. Some new examples of these compounds can be obtained from Jurkschat's /5/ and Holocek's /6/ papers, where the central metal atom is, in all examples, limited to a maximum of six-coordination.

In this paper we would like to communicate the first attempt to prepare a more than seven-coordinated monoorganotin(IV) compound, using 3-methoxypropyl as a chelating and three diethyldithiocarbamates as additional ligands (Scheme 1).



Scheme 1

EXPERIMENTAL

General Comments

All the solvents were obtained from commercial sources. Acetone, hexane, dichloromethane and pentane were used without further purification. Compound **1** (3-methoxypropyltin trichloride) was prepared according to literature procedure /7/. The IR measurements were performed on Perkin-Elmer equipment in nujol suspension and in $CHCl_3$ solution (cm^{-1}), respectively.

3-methoxypropyltin[tris(diethyldithiocarbamate)] (2). To a solution of 1 (0.3 g, 1.01 mmol) in 20 ml of acetone was added a solution of natrium diethyldithiocarbamate trihydrate (0.72 g, 3.20 mmol) in 30 ml of acetone. The reaction mixture was stirred overnight at room temperature, and then filtered off. The mother liquor was dried with sodium sulphate and the solvent evaporated *in vacuo*. Obtained yellowish crystals were washed with cold dry pentane. Yield: 0.51 g (79%), M.p. 92 – 93 °C. ^{1}H NMR ($CDCl_3$, 360.13 MHz, 300K): δ 1.26 (t, 6H, H2'), 2.14 (t, 2H, H1), 2.28 (m, 2H, H2), 3.31 (s, 3H, H4), 3.45 (t, 2H, H3), 3.76 (q, 4H, H1'). ^{13}C NMR ($CDCl_3$, 90.56 MHz, 300K): δ 10.72 (*C*2'), 25.43 (*C*1) – ^{1}J(^{119}Sn, ^{13}C) = 1006.4 Hz, 46.06 (*C*2) – ^{2}J(^{119}Sn, ^{13}C) = 63.1 Hz, 48.55 (*C*1'), 56.89 (*C*4), 72.94 (*C*3) – ^{3}J(^{119}Sn, ^{13}C) = 249.7 Hz, 199.06 (S–*C*–S), ^{119}Sn NMR ($CDCl_3$, 134.28 MHz, 300 K): δ – 774.2 ppm. ^{119}Sn CP/MAS NMR (74.63 MHz, 300K): δ – 828.3, –832.0. Anal. Calc. for $C_{19}H_{39}S_6N_3OSn$: M.W. = 636.23;C, 35.87; H, 6.18; N, 6.61; S, 30.18. Found: C, 35.92; H, 6.06; N, 6.51; S, 29.95. Positive-ion ESI mass spectrum (mass-to-charge (m/z), suggested structures of ions, relative abundance): m/z 564, $[M\text{-}CH_3OCH_2CH_2]^+$, 14%; m/z 489, $[M\text{-}(CH_3CH_2)_2NCS_2]^+$, 100%; m/z 266, $[M\text{-}CH_3OCH_2CH_2CH_2\text{-}2*((CH_3CH_2)_2NCS_2H)]^+$, 4%. Negative-ion ESI mass spectrum: m/z 405, $[M\text{-}(CH_3CHH_2)_2NCS_2\text{-}(CH_3CH_2)_2NC]^-$, 100%; m/z 148, $[(CH_3CH_2)_2NCS_2]^-$, 43%.

NMR measurements

The solution ^{119}Sn, ^{13}C and ^{1}H NMR spectra were acquired at 134.28, 90.56 and 360.13 MHz, respectively, on a Bruker AMX 360 NMR spectrometer, using a 5 mm tuneable broadband probe in the temperature range 170-300 K. The solutions were obtained by dissolving approximately 40 mg of **2** in 0.5 ml of $CDCl_3$ and toluene-d_8, respectively. Appropriate chemical shifts were calibrated on: ^{1}H – internal hexamethyldisiloxane (δ = 0.00 ppm), ^{13}C -peak of $CDCl_3$ (δ = 77.00 ppm), ^{119}Sn-external tetramethylstannane (δ = 0.00 ppm). The solid state ^{119}Sn spectra of the studied compound were recorded on a Bruker DSX 200 spectrometer equipped with a double-bearing CP-MAS probe at room temperature. The ^{119}Sn chemical shift was calibrated indirectly on external tetracylcohexyltin (δ = –97.35 ppm).

Mass spectrometry

Electrospray ionization (ESI) mass spectra were measured on the ion trap mass analyzer Esquire 3000 (Bruker Daltonics, Bremen, Germany) in the mass range m/z 50 – 1000. The mass spectrometer was tuned to give an optimum response for m/z 500. The samples were dissolved in acetonitrile and analysed by direct infusion at the flow rate of 2 μl/min both in the positive-ion and negative-ion modes. The ion source temperature was 300 °C, the flow rate and the pressure of nitrogen 4 l/min and 10 psi, respectively.

X-Ray

Crystal data for **2**: $C_{19}H_{39}N_3OS_6Sn$, M = 636.58, triclinic, *P –1* (No. 2), *a* = 10.6520(1) Å, *b* = 16.9580(2) Å, *c* = 17..6950(2) Å, α = 107.5700(5)°, β = 91.2470(6)°, γ = 104.8010(5)°, *V* = 2929.14(6) Å^3, Z = 4, D_x = 1.444 Mg m^{-3}. A yellow crystal of dimensions 0.35 × 0.25 × 0.18 mm was mounted on glass capillary and measured on a Nonius Kappa CCD diffractometer by monochromatized MoKα radiation (λ = 0.71073 Å) at 150(2)K. A total of 45653 measured reflections in the range *h* = –13 to 13, *k* = –22 to 22, *l* = –22 to 22 (θ_{max} = 27.5°), from which 13405 were unique (Rint = 0.030) and 12111 observed according to the $I > 2\ \sigma(I)$ criterion. Absorption corrections were carried out, using multiscan procedure (SORTAV, Blessin), (μ = 1.316 mm^{-1}, T_{min} = 0.660, T_{max} = 0.749). The structure was solved by direct methods (SIR92, Altomare, 1994), and refined by full-matrix least squares based on F^2 (SHELXL97).

In one of two symmetrically independent molecules the $-OCH_3$ group is disordered into two positions, which were refined with 0.5 occupancy.

The hydrogen atoms in the CH_2 moiety bonded to Sn were found on difference Fourier maps and refined isotropically; all others were fixed into idealised positions (riding model) and assigned temperature factors, either $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom), or $H_{iso}(H) = 1.5\ U_{eq}$ (pivot atom), for the methyl moiety. The refinement converged (Δ/σ_{max} = 0.002) to *R* = 0.024 for observed reflections and $wR(F^2)$ = 0.057, *GOF* = 1.048 for 585 parameters and all 13405 reflections. The final difference map displayed no peaks of chemical significance ($\Delta\rho_{max}$ = 1.171, $\Delta\rho_{min}$ = 1.059 e.Å^{-3} within 0.9 Å distances from Sn atoms). Crystals suitable for X-ray measurements were obtained by vapour diffusion of heptane into benzene solution of compound **2**.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 197196. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Compound **2** was prepared by the reaction of 3-methoxypropyltrichloride with diethyldithiocarbamate in acetone, providing a good yield. The purity of **2** was checked by elemental analysis, ESI-MS spectrometry and ^{1}H NMR spectra in chloroform, respectively.

The ^{1}H NMR spectral patterns (one set of signals) of **2** are similar at the higher temperatures in both (chloroform and toluene) solutions, but with a decrease in temperature of the toluene solution to 220K and

lower, a broadening of all signals is observed. Unfortunately only the moving and broadening (not decoalescence) of signals can be observed at the lowest temperature measured (170K). The ^{119}Sn NMR chemical shift value (which is taken as evaluating parameter of tin central atom coordination) is rather independent of temperature (–774.2 ppm at 300K and –778.2 ppm at 280K) in the chloroform solution. This value can be compared with the value found for the seven-coordinated *n*-butyl analogue (–660.3 ppm) /8/ in contrast to **1** (–138.5 ppm) /7/ which is only five-coordinated. However, the same parameter is much more dependent on temperature (–7.55.7 ppm at 340K, –794.8 ppm at 290K, –804.9 ppm at 260K, –837.6 ppm at 210K, and –839.4 ppm at 170K) in toluene solution. The value of δ (^{13}C) for CS_2 (199.06 ppm) indicates that the bidentate bonding fashion of the three diethyldithiocarbamate ligands is involved /9/. The coupling constant Sn-C readable from ^{13}C NMR spectra is another parameter which is, in the case of **2** (1006.4 Hz), comparable to values found for the *n*-butyl analogue (975.8 Hz) /8/ and **1** (845.3 Hz) /7/, respectively. All the above-mentioned parameters are concentration independent.

The IR spectra were measured in nujol suspension and $CHCl_3$, respectively; both spectra are very similar and reveal absorption band values (1430 cm^{-1} assigned to ν(C~N), 1008 cm^{-1} to ν(C-O-C) and 997 cm^{-1} to ν(C~S) in characteristic ranges /10/.

The ^{119}Sn CP/MAS NMR spectrum of **2** revealed the values of isotropic shifts –828.3 and –832.0 ppm. These two relatively narrow signals observed are probably caused by two types of independent molecules in the crystal lattice of **2** or by crystal packing. The values of δ(^{119}Sn) obtained in the solid state are similar to those in toluene solution at 200K. This fact supports the hypothesis of very close structures in solution and in the solid state.

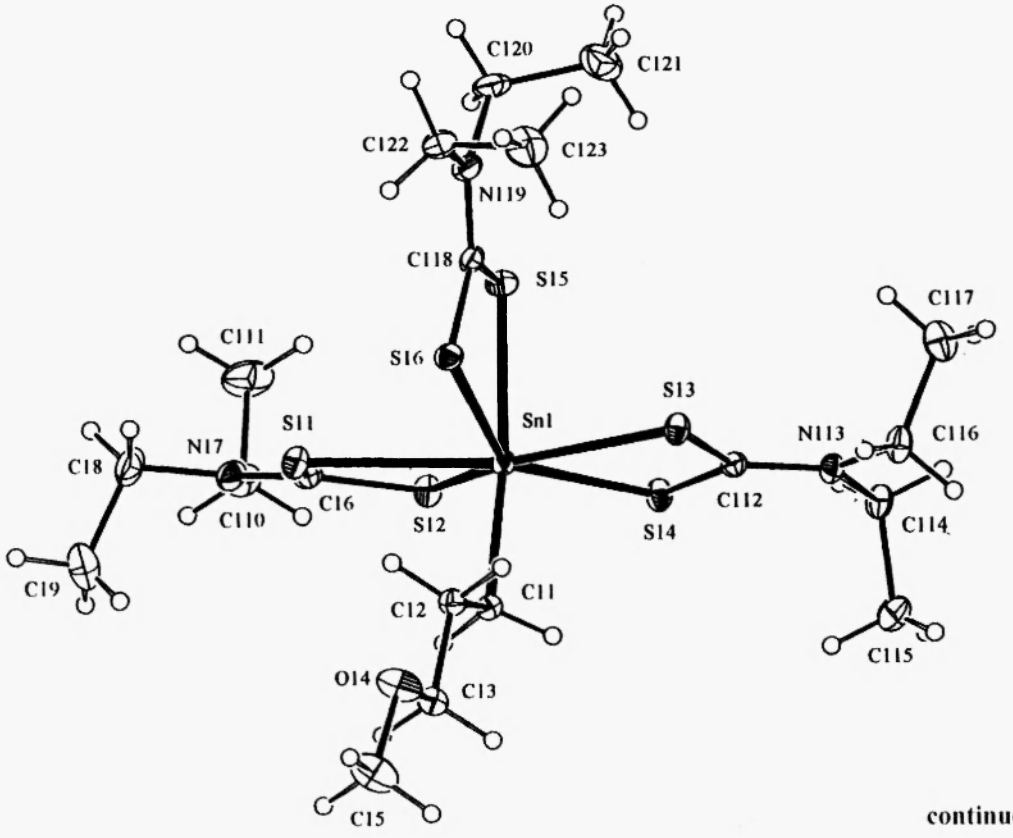


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Fig. 1: Molecular structure of compound **2** (ORTEP – 30% probability level), only one molecule is shown. Selected distances and bonding angles (Å, °): Sn1-C11 2.165(2), Sn1-S11 2.8115(5), Sn1-S12 2.6344(5), Sn1-S13 2.7460(5), Sn1-S14 2.6111(5), Sn1-S15 2.4815(5), Sn1-S16 2.7945(5), O14-Sn1 5.427(1), C11-Sn1-S15 163.49(5), C11-Sn1-S16 95.615(5), S11-Sn1-S12 65.19(2), C13-Sn1-S14 66.57(1), S15-Sn1-S16 67.92(2).

The crystal structure of **2** determined by X-ray diffraction on single crystal revealed two independent molecules in the crystal lattice. The distances, their differences, and angles determined, are very close to those found by Schlemper /11/ in the analogous *n*-butyltin compound. The non-existence of intramolecular contact Sn-O is evident from the determined Sn1-O14 (5.427(1) Å) and Sn2-O24 (4.909(3)-4.947(3) Å) distances.

From the abovementioned results, we can conclude that the structure of the title compound is similar in solution in different solvents, at various temperatures, and in the solid state. The dithiocarbamate ligands are bonded in bidentate bond fashion and the potential donor oxygen is out of the primary coordination sphere of the central tin atom.

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