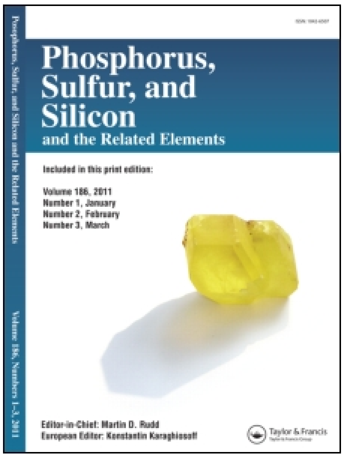

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Synthesis and Characterization of New Diorganotin(IV) Complexes with Dithiocarbamate Derivative of Glycine

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*The novel organotin(IV) complexes, $Ba[SnMe_2(dtc\text{-}gly)_2] \cdot 2\ CH_3OH$ (**1**) and $[Sn_3Bu_6Cl_2(dtc\text{-}gly)_2]$ (**2**), have been synthesized by reaction of SnR_2Cl_2 ($R = Me$ or Bu) with the dithiocarbamate derivative of glycine (dtc-gly). The new complexes have been characterized by elemental analysis, IR, ^1H NMR and ^{119}Sn NMR spectroscopy. Spectroscopic studies show that **1** contains a complex anion with dtc-gly acting as a unidentate ligand coordinated through the dithiocarbamate group. On the basis of ^{119}Sn NMR data, the coordination number of the tin atom in solution is four. Complex **2** has a trimeric structure in which two dtc-gly ligands are coordinated through both the carboxylate and the dithiocarbamate groups between three tin atoms.*

Keywords Aminoacid; dithiocarbamate; glycine; organotin

INTRODUCTION

Dithiocarbamates are organosulfur compounds with high donating properties. These compounds have attracted considerable attention in the last decades, because of their academic interest, industrial applications, and potential role in cancer disease treatment.[1–4] Dialkyldithiocarbamates ($R^1R^2N\text{-}CS_2^-$) are synthesized through the reaction of the corresponding amine with carbon disulfide in a basic medium. One of the variables which we can control is the effect of the organic chain linked to the dithiocarbamate unit. If an α-aminoacid is used instead of an amine, dithiocarbamate derivatives of α-aminoacids are obtained with the general formula:

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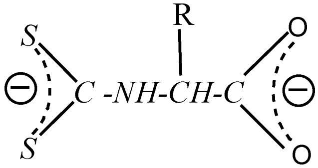


The simultaneous presence of the dithiocarbamate and the carboxylic group makes these ligands very interesting, as they can display variable coordination modes. On the other hand, the nature of the side chain (R) that is characteristic of the starting α-aminoacid may affect the donor properties of the dithiocarbamate moiety. α-Aminoacid dithiocarbamates (dtc-a.a) and their complexes with several metal cations have been synthesized and investigated mostly in the last two decades.[5] Recently we have reported the first organotin complexes of this type of ligands using proline as a cyclic α-aminoacid.[6]

Organotin(IV) compounds are amongst the most widely used organometallic compounds. Organotin dithiocarbamate complexes have been the subject of numerous spectroscopic and structural studies because of their industrial importance and their antifungal and insecticidal properties.[7] On the other hand the organotin(IV) complexes of amino acids have great diversity in structure and variable applications, as diorganotin complexes with derivatives of amino acids exhibit maximum antitumour activity.[8–10] In view of the interesting biological and industrial applications, and the structural variety of organotin(IV) complexes of both dithiocarbamate and amino acids, it has been considered worthwhile to synthesize organotin(IV) complexes with dithiocarbamate derivatives of α-aminoacids and to investigate the nature of their bonding to tin. In continuation of our research on this type of complexes, we have synthesized and characterized new complexes of diorganotin(IV) with the dithiocarbamate derived from glycine (a linear α-aminoacid). The results of this study are reported here.

RESULTS AND DISCUSSION

The dithiocarbamate derivative of glycine was prepared in the form of its barium salt Ba(dtc-gly) according to Eq. 1.[5a]

$$\mathrm{NH_2CH_2COOH + Ba(OH)_2 + CS_2 \rightarrow Ba(S_2CNHCH_2COO) + 2\ H_2O} \tag{1}$$

The new complexes were synthesized by reaction of an excess of $\mathrm{SnMe_2Cl_2}$ and $\mathrm{SnBu_2Cl_2}$ with a suspension of Ba(dtc-gly) in MeOH

(Eqs. 2, 3).

$$\mathrm{SnMe_2Cl_2 + 2\ Ba(S_2CNHCH_2COO)}$$

$$\rightarrow \mathrm{Ba[SnMe_2(S_2CNHCH_2COO)_2] + BaCl_2} \quad (2)$$

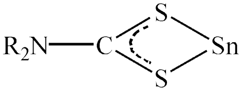
$$\mathrm{3\ SnBu_2Cl_2 + 2\ Ba(S_2CNHCH_2COO)}$$

$$\rightarrow \mathrm{[Sn_3Bu_6Cl_2(S_2CNHCH_2COO)_2] + 2\ BaCl_2} \quad (3)$$

The composition of the new complexes was confirmed by their analytical data. The nature of bonding in the complexes was recognized by spectroscopic studies.

IR Spectra

The appearance of a new band in the IR spectra of the two synthesized complexes at ~400 cm^{-1}, which may be assigned to ν(Sn-S),[11] indicates the bonding of the CSS group to the tin atom. It is well known that dithiocarbamates may coordinate to tin(IV) atom in three different ways acting as bidentate (**I**), anisobidentate (**II**), or monodentate (**III**) ligands.[7,12,13]



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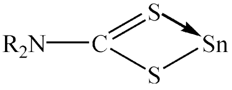
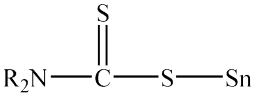


II



III

The band due to ν_{as}(CSS) is diagnostic in describing the mode of sulfur coordination to the tin atom. It is symmetrically split in the case of **1** indicating the unidentate mode of coordination. The appearance of only one band in the case of **2** indicates that both sulfur atoms are equally involved in the complexation (mode **I**). In the IR spectrum of complex **2** the appearance of a new band at 552 cm^{-1}, which can be assigned to a Sn—O bond, indicates the bonding of the carboxyl group to the tin atom. The absence of a strong band in the C=O stretching region (1700–1770 cm^{-1}) rules out, that the carboxylic group is bonded to the tin atom in a unidentate manner.[14] The magnitude of the $\Delta\nu$ value [where $\Delta\nu = \nu_{as}(\mathrm{COO}) - \nu_{s}(\mathrm{COO})$] has been shown to be useful in drawing structural conclusions.[10,14–17] The ν_{as}(COO) value in the complex **2** is higher than in the ligand, whereas the corresponding ν_s(COO) absorption moves to lower frequency compared to the ligand itself; thus $\Delta\nu$ is larger in the complex than in the ligand. On this basis, a strong interaction between the carboxylate group and the tin atom can be ruled out, and an asymmetric or weak bidentate bonding to Sn(IV) can be assumed.[10] The lack of Sn-O stretching band in the IR spectrum of **1** indicates no participation of the carboxyl group in bonding to the tin atom for this complex. Presence of both ν_s(Sn—C) and ν_{as}(Sn—C) in the IR spectra of the two complexes is consistent with a nonlinear C—Sn—C configuration.[18,19] The IR spectrum of**1** also shows vibrational frequencies of MeOH.

NMR Spectra

In the ^{1}H NMR spectra of the complexes, the integral ratio of the signals resulting from protons of the ligand to those resulting from protons of the organic groups on the tin provides a reliable measure of the metal to ligand ratio in the synthesized complexes. The ^{1}H NMR spectrum of **1** shows a singlet at 0.79 ppm for the $SnMe_2$ protons accompanied by satellites due to ^{1}H-^{119}Sn coupling. Substitution of $^2J(^{119}Sn\text{-}^1H)$ for this compound (77.7 Hz) in the Lockhart-Manders equation (Eq. 4),[20] gives a value of 128° for the Me-Sn-Me angle.

$$\begin{aligned}[\mathrm{Me-Sn-Me}] = 0.0161 \times [^2\mathrm{J}(^{119}\mathrm{Sn}-^1\mathrm{H})]^2 \\ - 1.32 \times ^2\mathrm{J}(^{119}\mathrm{Sn}-^1\mathrm{H})] + 133.4 \qquad (4)\end{aligned}$$

The appearance of only one peak for the two NH protons and also for the protons of the two CH_2 groups indicates equivalent sites for the two dtc-gly ligands. The ^{1}H NMR spectrum of compound **2** exhibits two merged triplets for the methylenic protons of the di-butyltin (IV) moiety due to the two non-equivalent surroundings of the butyl protons in the trimeric compound. For this complex, the $^2J(^{119}Sn\text{-}^1H)$ value cannot be extracted from the spectrum because of the complexity of the methylene multiplets. The appearance of two signals for two —CH_2 protons (totally 4H) and also for two —NH protons (totally 2H) suggests the existence of an equilibrium between monodentate and bidentate forms of the carboxylate group.[14]

The ^{119}Sn{H} NMR spectrum of complex **1** shows only one sharp singlet indicating the presence of a single species. This ^{119}Sn resonance appears significantly at lower frequencies than that of $SnMe_2Cl_2$ (+137 ppm),[21] which is in agreement with the removal of the electronegative groups. Although the shift ranges in organotin derivatives are dependent on the nature of the substituents at the tin atom, the following ranges have been proposed empirically for di- and tri-organotin complexes: +200 to −60, −90 to −190, −210 to −400, and −440 to −540 ppm for four, five, six, and seven-coordinate tin compounds, respectively.[22] On the basis of ^{119}Sn NMR data, it appears reasonable to assume that the coordination number of the tin atom in complex **1** is four in solution.

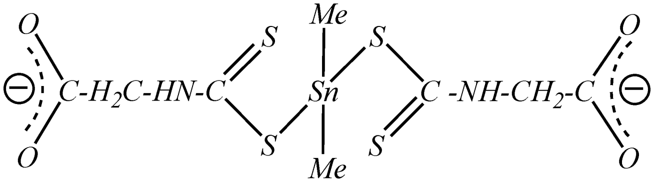


FIGURE 1 Suggested structure for $[SnMe_2(dtc\text{-}gly)_2]^{2-}$ (**1**).

^{119}Sn NMR was not reported for complex **2** because of its limited solubility in common organic solvents.

In view of the above discussion, compound **1** is an anionic complex with dtc-gly acting as a unidentate ligand, which is coordinated through the dithiocarbamate group; therefore the coordination number of the tin atom in **1** is four (Figure 1). Complex **2** has a trimeric structure, so that coordination of the glycine dithiocarbamate ligand takes place through both the dithiocarbamate and carboxylate group. In this complex the dithiocarbamate group acts as a bidentate ligand and for the carboxylate group an asymmetric or partially bidentate bonding to tin may be assumed (Figure 2). These conclusions are consistent with the HSAB principle and with a higher stabilization of sulfur-coordinated organotin complexes in comparison with those coordinated by hard donors (oxygen or nitrogen).[9]

EXPERIMENTAL

All chemicals and solvents were purchased from commercial sources. The dithiocarbamate derivative of glycine was prepared as the barium salt, Ba(dtc-gly) · 3 H_2O, through the reaction of glycine with CS_2 in a $Ba(OH)_2$ medium under N_2 atmosphere.[5a] IR spectra were obtained using a FT BOMEM MB102 spectrophotometer. The ^1H and ^{119}Sn NMR spectra were recorded with a Brucker Avance DPZ500 spectrometer at 500.130 MHz and 186.496 MHz using TMS and $SnMe_4$ as references, respectively. The C, H, and N analyses were performed by the microanalytical service of the N.I.O.C. Research Institute of Petroleum Industry.

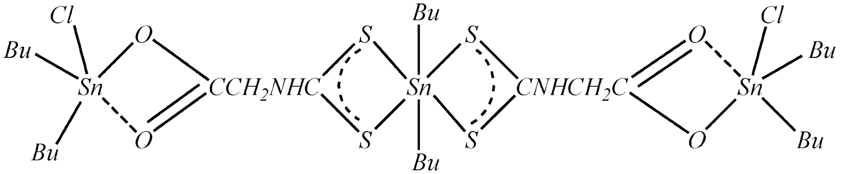


FIGURE 2 Suggested structure for $[Sn_3Bu_6Cl_2(dtc\text{-}gly)_2]$ (**2**).

Synthesis of $Ba[SnMe_2(dtc\text{-}gly)_2] \cdot 2\ CH_3OH$ (1)

A solution of Ba(dtc-gly).$3H_2O$ (1 mmol, 0.340 g) in 15 mL dry methanol was stirred at 35°C for 10 min. To this suspension a solution of $SnMe_2Cl_2$(2 mmol, 0.440 g) in dry methanol (10 mL) was added dropwise. A white precipitate was formed gradually. The mixture was stirred at room temperature for 3 h. Then the product was filtered, washed with MeOH, and dried in vacuum over $CaCl_2$. Yield: 0.25 g (90%); m.p. 139–141°C; *Anal.* Calcd. for $C_{10}H_{20}N_2O_6S_4BaSn$: C, 18.5; H, 3.1; N, 4.3; Ba, 21.2%. Found: C, 18.8; H, 3.1; N, 4.2; Ba, 20.7%. IR (KBr, cm^{-1}): ν (N—H), 3253; ν_{as}(COO), 1635; ν_s(COO), 1400; ν(C—N), 1513; ν_{as}(CSS), 923, 979; ν_s(CSS), 643; ν_{as}(Sn—C), 562; ν_s(Sn—C), 541; ν(Sn-S) 400; ^1H NMR (DMSO): $\delta = 0.79$ (s, $^2J(^{119}Sn\text{-}H) = 77.7$ Hz, 6H), 3.53 (s, 6H, CH_3 (methanol)), 3.98 (s, 4H, $-CH_2$), 10.48 (s, br, 2H, NH), ^{119}Sn NMR (DMSO): $\delta = 122.9$.

Synthesis of $[Sn_3Bu_6Cl_2(dtc\text{-}gly)_2]$ (2)

Complex **2** was synthesized as described for **1** from $SnBu_2Cl_2$ (2 mmol, 0.607 g) and Ba(dtc-gly). $3H_2O$ (1 mmol, 0.340 g). Yield: 0.37 g (70%); m.p. 137–139°C; *Anal.* Calcd. for $C_{30}H_{60}N_2O_4S_4Cl_2Sn_3$: C, 33.7; H, 5.6; N, 2.6%. Found: C, 33.3; H, 5.2; N, 3.0%. IR (KBr, cm^{-1}): ν(N—H), 3219; ν_{as}(COO), 1645; ν_s(COO), 1385; ν(C—N) 1509; ν_{as}(CSS), 1016; ν_s (CSS), 640; ν_{as}(Sn-C), 682; ν_s(Sn—C), 610; ν(Sn—O), 552; ν(Sn—S), 400; ^1H NMR ($CDCl_3$): $\delta = 0.95$ (two merged triplets, 18H), 1.40–1.45 (m, 12H), 1.79–1.89 (m, 24H), 4.27 (s), and 4.50 (s) (totally 4H), 7.6 (s, br), and 7.8 (s, br) (totally 2H, NH).

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