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Studies of stannylated-1,2-dithiolato compounds: Synthesis and crystal structure of co-crystalline 4,5-bis[(triphenylstannyl)methylthiolato]-1,2-dithiole-3-thione $(Ph_3SnCH_2)_2$(dmt) and 5-[(triphenylstannyl)methylthiolato]-4-[(triphenylstannyl)thiolato]-1,2-dithiole-3-thione $(Ph_3SnCH_2)(Ph_3Sn)$(dmt) [72:28]

Jairo Bordinhão [a], Nadia M. Comerlato [a], Laila de Castro Cortás [a], Glaucio Braga Ferreira [a], R. Alan Howie [b], James L. Wardell [a,*]

[a] Departamento de Química Inorgânica, Instituto de Química, Universidade Federal do Rio de Janeiro, CP 68563, 21945-970 Rio de Janeiro, RJ, Brazil
[b] Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, AB24 3UE Scotland, United Kingdom

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Abstract

The synthesis of 4,5-bis[(triphenylstannyl)methylthiolato]-1,2-dithiole-3-thione in admixture with 4-[(triphenylstannyl)thiolato]-5-[(triphenylstannyl)methylthiolato]-1,2-dithiole-3-thione is reported from the reaction between Ph_3SnCH_2I and caesium 4,5-dithiolato-1,2-dithiole-3-thione. X-ray structure determinations at 120 and 298 K reveal that the compounds co-crystallise to form solid solution species, displaying 4-coordinate, distorted tetrahedral tin centres in both components. Crystallisation results in the spontaneous resolution of enantiomeric forms of both components.

Keywords: Dithiolato complexes; Organotin; 4,5-Dithiolato-1,2-dithiole-3-thione; X-ray crystallography; Solid solution; Spontaneous resolution

1. Introduction

We have reported the synthesis and characterisation of various tin complexes of 4,5-dithiolato-1,3-dithiole-2-thione, $[C_3S_5]^{2-}$, dmit^{2-}, (**1**), and 4,5-dithiolato-1,3-dithiole-2-one, $[C_3S_4O]^{2-}$, dmio^{2-}, also known as dmid^{2-}, (**2**) [1–6], including $[(Ph_3SnCH_2)_2$(dmit)] (**3**) [6], $[(Ph_3SnCH_2)_2$(dmio)] (**4**) [6], $[(Ph_3Sn)_2$(dmit)] (**5**) [1] and $[(Ph_3Sn)_2$(dmio)] (**6**) [1], see Fig. 1. A large number of studies of dmit compounds have been reported, a smaller number for dmio compounds [7] and fewer still for the compounds of the unsymmetrical isomer of dmit^{2-}, 4,5-dithiolato-1,2-dithiole-3-thione, dmt^{2-} (**7**), the latter being available on rearrangement of suitable dmit species (e.g., [8,9]).

We have carried out the reaction of Ph_3SnCH_2I with caesium 4,5-dithiolato-1,2-dithiole-3-thione, Cs_2dmt. As we now report, the compound, obtained after work-up and recrystallisation, was a co-crystalline mixture of 4,5-bis[(triphenylstannyl)methylthiolato]-1,2-dithiole-3-thione $(Ph_3SnCH_2)_2$(dmt) (**8**) and 4-(triphenylstannylmethyl)-thiolato-5-(triphenylstannyl)thiolato-1,2-dithiole-3-thione, $(Ph_3SnCH_2)(Ph_3Sn)$(dmt) (**9**). This was particularly

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[*] Corresponding author. Present address: Departamento de Química, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Avenida Antônio Carlos 6627, Pampulha 31270-901, Belo Horizonte, MG, Brazil.

E-mail address: j.wardell@abdn.ac.uk (J.L. Wardell).

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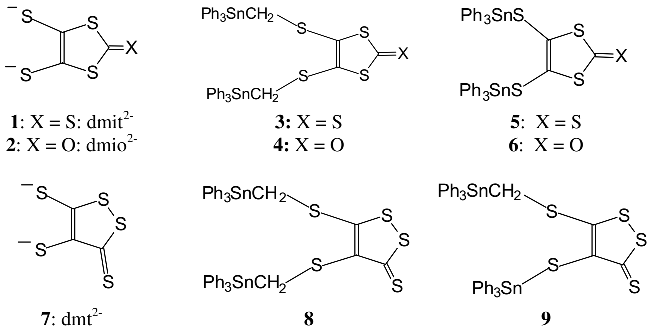

Fig. 1. Species mentioned in this article.

intriguing since the same batch of Ph_3SnCH_2I had been used in the preparations of **3** and **4** and no formation of a Ph_3Sn–S compound had been indicated in those syntheses.

2. Experimental

2.1. Synthesis

All the synthetic procedures were carried out under argon atmospheres using standard Schlenck techniques with solvents pre-dried prior use. Compounds, $PhSnCH_2I$ [10] and $(PhCO)_2dmt$ [8], were obtained by published procedures: Cs_2dmt was obtained from $(PhCO)_2dmt$, by a similar procedure used to obtain Cs_2dmit from $(PhCO)_2dmit$ [8]. The labile salt, Cs_2dmt, was stored under argon to avoid oxidation. Infrared spectra were obtained in CsI discs using a Nicolet Magna 760 FT-IR instrument. NMR spectra were run on Varian 300 MHz or Bruker 400 MHz Instruments. Melting points were measured on a Melt-TempII. Elemental analyses were obtained using a Perkin–Elmer 2400 apparatus.

2.2. Reaction between Ph_3SnCH_2I and Csdmt

(Iodomethyl)triphenylstannane (0.758 g, 1.55 mmol), was added under argon to a solution of Cs_2dmt (0.356 g, 0.77 mmol), prepared from $(PhCO)_2dmt$ and CsOH. The red reaction mixture was stirred for 12 h, in which time the solution colour changed from red to yellow. The reaction mixture was filtered and the precipitate collected and recrystallized from chloroform/methanol. M.p. 158–159 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ: 2.82 (s, 2H, $J^{119,117}Sn–^{1}H = 47.0, 45.0$ Hz), 2.89 (s, 1.5H, $J^{119,117}Sn–^{1}H = 43.2, 41.2$ Hz), 7.50–7.70 (m, 30H, Ph).

^{13}C (75 MHz, $CDCl_3$): δ: 10.5 (CH_2), 10.7 (CH_2), 128.9 ($^{119,117}Sn–^{13}C = 54$ Hz, *m*-Ph), 129.8 (*p*-Ph), 135.5 ($J^{119,117}Sn–^{13}C = 557, 530$ Hz, *i*-Ph), 136.7 ($^{119,117}Sn–^{13}C = 39$ Hz, *o*-Ph), 137.3 (C=C), 185.2 (C=C), 208.9 (C=S).

^{119}Sn NMR (113 MHz, $CDCl_3$): δ: −115.6, −115.9, −120.2.

2.3. X-ray crystallography

2.3.1. Data collection

Intensity data were obtained with Mo Kα radiation on two different sample crystals, one at 298 K and the other at 120 K. At 298 K, the data were obtained on a Bruker P4/Bruker-Nonius Kappa-CCD diffractometer under the control of XSCANS [11] and, for data reduction, SAINT [12] software. In this case no correction for absorption was carried out. At 120 K the data were obtained by means of the Enraf Nonius KappaCCD area detector diffractometer of the EPSRC National crystallographic service at the University of Southampton, UK. Now data collection was carried out under the control of the program COLLECT [13] and data reduction and unit cell refinement were achieved with the COLLECT and DENZO [14] programs. Correction for absorption, by comparison of the intensities of equivalent reflections, was applied using the program SADABS [15]. The program ORTEP-3 for Windows [16] was used in the preparation of the figures and SHELXL-97 [17] and PLATON [18] in the calculation of molecular geometry.

2.3.2. Structure solution and refinement

Initially the structures at the different temperatures were treated independently. In both cases the initial partial solution, obtained by the heavy atom method as implemented in the program SHELXS-97 [17], was expanded and refined by means of the program SHELXL-97 [17]. It became apparent that the molecules in the two samples were enantiomers. Thus, in order to ensure complete consistency in the atom labelling scheme used in the two refinements, the refinement against the 298 K data was repeated with suitably transformed (x, y, z replaced by $x, 1 - y, z$) coordinates from the 120 K refinement as the starting model. In the later stages of both refinements, hydrogen atoms were placed in calculated positions with aryl and methylene hydrogen atoms at C–H distances of 0.93 and 0.97 Å, respectively, at 298 K and 0.95 and 0.99 Å, respectively, at 120 K and in all cases refined with a riding model with $U_{iso}(H)$ set to $1.2U_{eq}(C)$. Finally, in both cases, complete refinenent was achieved with the introduction into the structural models of a partially occupied site for a sulphur atom [S(6)] associated with partial omission of both the methylene group [C(6)] and sulphur atom S(4) (see Fig. 2). Thus S(6) indicates relocation of the sulphur atom S(4) when the methylene group [C(6)] is absent. In other words, the structural model now represents a solid solution between 4,5-bis[(triphenylstannyl)-methylthiolato]-1,2-dithiole-3-thione, the major component (**8**), and 4-[(triphenylstannyl)thiolato]-5-[(triphenylstannyl)methylthiolato]-1,2-dithiole-3-thione, the minor component (**9**). The ratio of major to minor components was refined to values of 0.712(15):0.288(15) at 298 K and 0.718(9):0.282(9) at 120 K and are, within error, the same for both sample crystals, i.e., 0.72: 0.28. It was the presence of a residual electron density peak of ~3 e/Å^3 in the refinement, without S(6), against the 120 K data (and ~1 e/Å^3 for the 298 K