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A THERMAL SYNTHESIS OF A NEW TIN(IV) DITHIOCARBAMATE

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A new tin dithiocarbamate containing sulphur bridges, di-μ-sulphidobis [bis(*N,N*-diethyldithiocarbamato)tin(IV)], has been isolated from the thermal decomposition of tetrakis(*N,N*-diethyldithiocarbamato)tin(IV). A dimeric structure is proposed on the basis of results from mass spectrometry, infrared spectroscopy, thermal analysis and vapour pressure osmometry.

Previous papers [1—5] have dealt with the thermal decomposition of several tin dithiocarbamate complexes. In one of these papers [5], a recently developed thermal/mass spectrometric technique, termed Programmed Probe Analysis (PPA) [6], was used to distinguish tetrakis (*N,N*—diethyldithiocarbamato)tin(IV), $Sn(Et_2dtc)_4$, from bis (*N,N*—diethyldithiocarbamato)tin(II), $Sn(Et_2dtc)_2$. More recent mass spectral and PPA studies [7] have identified the major intermediates resulting from the vacuum decomposition of the tetrakis complex.

In this paper we report the synthesis and isolation of one of these intermediates, a new tin dithiocarbamate. The vacuum sublimation technique is used to prepare this new complex under conditions similar to those pertaining in PPA. This compound has been characterized by microanalysis, infrared spectroscopy, mass spectrometry, PPA and vapour pressure osmometry. A dimeric structure is proposed.

Experimental

All microanalyses were performed by the CSIRO Microanalytical Service, Melbourne University. Infrared spectra over the range 4000 cm^{-1} to 250 cm^{-1} were recorded on a Perkin Elmer 457 Grating infrared spectrophotometer using KBr pellets. Mass spectra were recorded on a JEOL JMS D—100 mass spectrometer Programmed Probe Analysis (PPA) [6] was carried out using the same instrument. The sample was heated at a rate of 10° per minute from ambient (25°) to 400°.

The thermal decomposition of the intermediate was investigated using a Rigaku-Denki thermal analysis system. Thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal analysis (DTA) records were obtained simultaneously for individual samples in both dynamic air and nitrogen atmospheres. Sample masses of approximately 10 mg were used and the rate of heating employed was 10° per minute up to 500°.

The determination of the molecular weight of the intermediate was carried out in chloroform using a Perkin Elmer 115 vapour pressure osmometer. The instrument was calibrated using benzil in chloroform as a standard.

Synthesis of tetrakis (*N*,*N* – diethyldithiocarbamato)tin(IV) has been described in detail previously [3, 8].

Results and discussion

The results are presented in the sequence in which the experiments were performed.

Mass spectrometric studies

A full interpretation of the PPA profile of $Sn(Et_2dtc)_4$ (Fig. 1) is beyond the scope of this paper. It is sufficient to point out that there are two peaks in the profile. If the complex is heated to 200° and maintained at that temperature, the

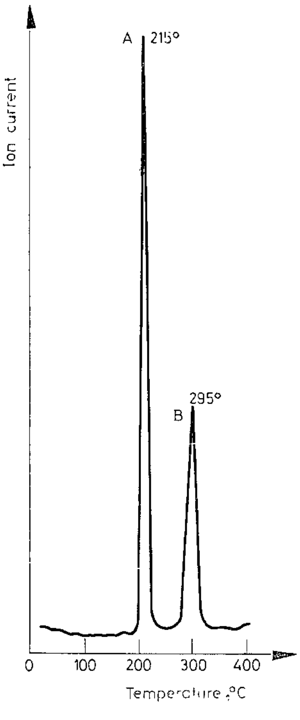

Fig. 1. PPA of $Sn(Et_2dtc)_4$

ion current initially rises, presumably corresponding to peak *A* in Figure 1, and then after a period of time falls to its background value. A white solid remains in the probe, which, if cooled and reheated gives a PPA profile containing a single

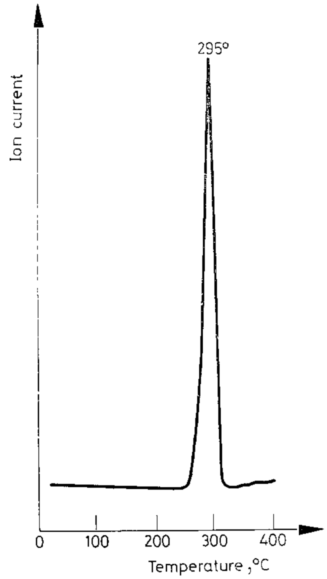

Fig. 2. PPA of intermediate

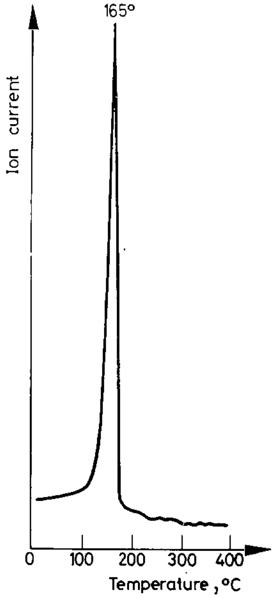

Fig. 3. PPA of $Sn(Et_2dtc)_2$

peak at 280–300° (Fig. 2). This peak corresponds to peak *B* in Fig. 1. There is a grayish residue in the probe after this reheating, indicating some thermal decomposition. The PPA profile of $Sn(Et_2dtc)_2$ is shown in Fig. 3.

The mass spectrum of the ions contributing to the PPA peak (Fig. 2) of the white solid is given in Fig. 4 and Table 1. There are strong similarities between this mass spectrum and that of the bis compound, $Sn(Et_2dtc)_2$ (Fig. 5). The latter compound is also white [5]. The PPA profiles of the white solid intermediate

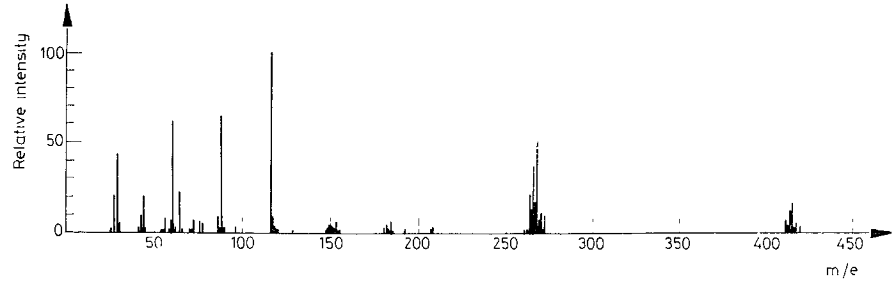

Fig. 4. 75 eV Mass spectrum of intermediate (temperature 280–300°)

Table 1

Mass spectrum of Di-μ-sulphidobis [bis(*N*,*N*– diethyldithiocarbamato)tin(IV)]

m/e	Intensity	Corresponding ion
416	15.0	$^*Sn(S_2CNEt_2)_2^+$
300	0.7	$SSn(S_2CNEt_2)^+$
268	52 0	$Sn(S_2CNEt_2)^+$
208	1.4	$Sn(S_2CNEt_2)_2^{2+}$
192	1.2	S_6^+
184	2 7	SnS_2^+
160	1.1	S_5^+
153	3.3	$SnSH^+$
149	4.2	$HS_2CNEt_2^+$
128	<0.5	S_4^+
120	2.2	Sn^+
116	100.0	$SCNEt_2^-$
96	[illegible]	S^+
88	65.0	$SCNHEt^+$
76	6.1	CS_2^+
72	6.7	Et_2N^+
64	22.0	S_2^+
60	62.0	$SCNH_2^+$
44	44.0	$EtNH^+$ and a weak SC^+
29	43.0	Et^+

* The m/e values are only reported for the principal isotope of tin, Sn^{120}.

(Fig. 2) and the bis compound (Fig. 3) are, however, significantly different. The latter vapourises completely in vacuo [5], whereas the former leaves a residue. The white solid intermediate is, therefore, not $Sn(Et_2dtc)_2$, but is probably a closely related structure.

The similarity in the mass spectra (Figs 4 and 5) would be explained if the white solid intermediate decomposed on heating to give the bis compound, $Sn(Et_2dtc)_2$. In this case, the group of peaks at m/e 416 in the mass spectrum of the intermediate (Fig. 4) would represent a molecular ion, as it does in the spectrum of the bis compound (Fig. 5). The mass spectra of the intermediate and the bis compound

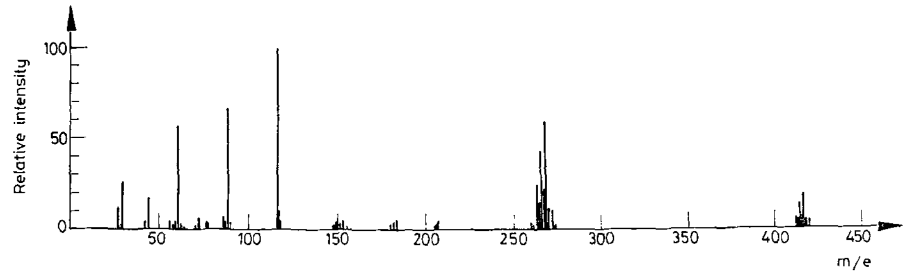

Fig. 5. 75 eV Mass spectrum of $Sn(Et_2dtc)_2$ (temperature 160°)

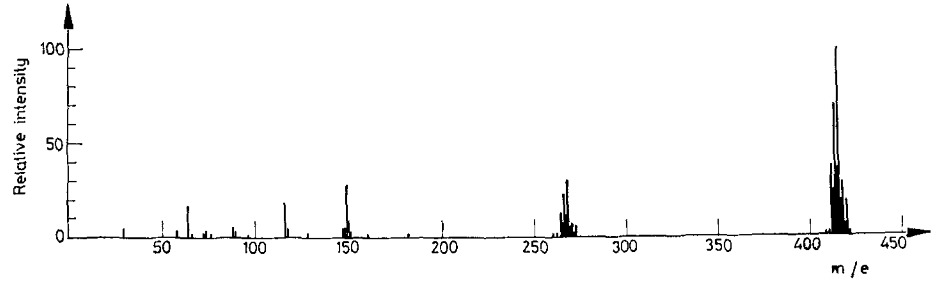

Fig. 6. 10 eV Mass spectrum of intermediate (temperature 280—300°)

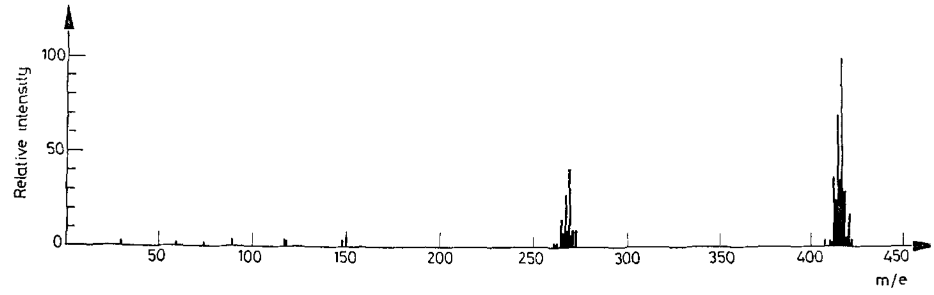

Fig. 7. 10 eV Mass spectrum of $Sn(Et_2dtc)_2$ (temperature 160°)

at low ionizing energies are shown in Figs 6 and 7. respectively. Evidently the groups of peaks at m/e 416 are relatively more intense in these spectra than they are at normal ionizing energies (Figs 4 and 5), which is consistent with these peaks being due to molecular ions [9].

A significant difference between the mass spectra of the intermediate (Figs 5 and 6) and those of the bis compound (Figs 5 and 7) is that only the former contain an m/e 64 peak. The intensities of the m/e 64, 65 and 66 peaks (Table 1a) conform to the isotope ratios expected for $(S_2)^+$ [10]. Weak peaks corresponding to a sequence of ions, $(S_3)^+$ to $(S_6)^+$, appear in the mass spectra of the intermediate (Figs 4 and 6), however, no $(S_8)^+$ is observed. Under low ionizing energy (10 eV), the relative enhancement of parent ions is favoured [9] and this phenemenon is observed for some allotropes of sulphur [11]. This is observed for the sulphur containing ions (S_2 to S_6) and therefore it is possible that they represent molecular ions of the particular sulphur allotropes.

Table 1a

Relative abundances for the S_2^+ ion and its isotopes

m/e Value	Intensity	Calculated intensity
64	100	100.0
65	2	1.5
66	10	8.9

These facts suggest that thermal decomposition of the intermediate under PPA conditions produces elemental sulphur, probably in the S_2 form. Small amounts of other allotropes are present, though not S_8, even though it is the most stable allotrope at these relatively low temperatures [12].

The presence of other peaks in the low energy spectrum of the intermediate may be the result of either low energy fragmentation processes or the formation of known decomposition products from the dithiocarbamate ligand [1, 3, 5] or a combination of both. It is likely that thermal decomposition of the ligands [3, 5] would leave a residue and, in fact, this is observed.

Synthesis of the intermediate (macroscale)

The amounts of the white intermediate that could be synthesized by the PPA technique, were of the order of μg, which was insufficient material for a complete characterization.

The intermediate was therefore synthesized using a vacuum sublimation technique. The tetrakis compound was maintained at 180–190° for several hours under vacuum. Yields of approximately 30% were obtained and 50–100 mg quantities of the intermediate were formed as residue.

Analysis of infrared data

To identify structural features of the intermediate on the basis of its infrared spectrum (Table 2) it is necessary to compare its spectrum with those obtained in previous infrared studies of metal dithiocarbamates and related compounds [13–17]. This comparative study reveals many similarities. However, in the tin-sulphur stretching region (300 to 400 cm^{-1}) [18], three bands are observed at 375, 342 and 310 cm^{-1} whereas tin dithiocarbamates normally have only one strong absorption band occurring at approximately 380 cm^{-1} [15]. We attribute the other two bands to sulphur bridges between tin atoms.

Table 2

Infrared data for Di-μ-sulphidobis[bis (*N,N*–diethyldithiocarbamato)tin(IV)]
(Principal bands — cm^{-1})

2980 (*w*)	2930 (*w*)	2870 (*w*)	1500(*vs*)
1460 (*m*)	1452 (*m*)	1435 (*s*)	1380 (*w*)
1372 (*w*)	1353 (*m*)	1340 (*w*)	1298 (*w*)
1273 (*vs*)	1205 (*s*)	1149 (*m*)	
1136 (*m*)	1094 (*w*)	1073 (*m*)	
988 (*m*)	911 (*m*)	841 (*m*)	781 (*w*)
570 (*m*)	375 (*m*)	342 (*m*)	310 (*s*)

vs = very strong
s = strong
m = medium
w = weak

The presence of only one strong absorption peak is the carbon-sulphur stretching region (950–1050 cm^{-1}) [16] suggests, according to Bonati et al. [14], that the diethyldithiocarbamate ligands are bound to tin in a bidentate mode.

Microanalysis

The microanalysis results are shown in Table 3, and agree with the empirical composition $C_{10}H_{20}N_2S_5Sn$.

Table 3

Microanalysis results for di-μ-sulphidobis[bis (*N,N*–diethyldithiocarbamato)tin(IV)]

Element	C, %	H, %	N, %	S, %
Found	28.69	4.20	6.27	35.7
Calculated	28.86	4.48	6.26	35.85

Molecular weight determination

The molecular weight, as determined by vapour pressure osmometry, is 890 ± 100. The high degree of uncertainty is primarily due to the low solubility of the intermediate in chloroform. Nevertheless, in conjunction with the results from the microanalysis the molecular formula $C_{20}H_{40}N_4S_{10}Sn_2$ ($MW = 894.6$) is indicated.

Thermal studies of the intermediate

The result of the thermal study undertaken in nitrogen (Fig. 8) indicates that the tin dithiocarbamate intermediate decomposes in a complex manner in the temperature range 240° to 400°. The complexity of this decomposition is shown by the number of peaks appearing in the DTA and DTG profiles (Fig. 8). An additional complication is that a DTA peak occurs at 300° without there being a corresponding simultaneous DTG peak. The nature of the process, giving rise to this DTA peak, is unknown.

The absence of a melting point suggests that initially decomposition occurs in the solid state.

Based on the total mass loss of 67.4%, (66.3% calculated) the residue, is proposed to be tin(II) sulphide, which is consistent with previous work [1, 3, 5].

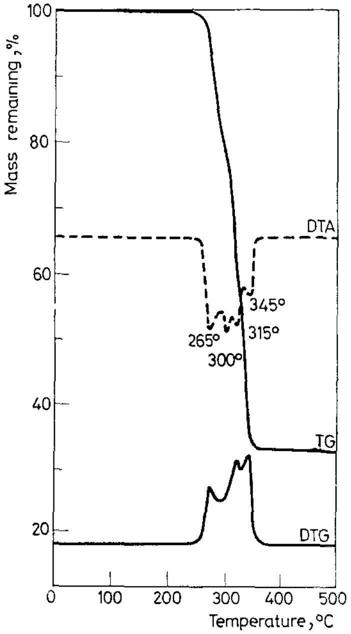

Fig. 8. Simultaneous TG/DTG/DTA of intermediate under nitrogen

The intermediate also decomposes in a very complex manner under air (Fig. 9). The major decomposition step, in the temperature range 225° – 325°, must involve two processes, one of which produces the endothermic DTA peak at 285°. The endothermicity suggests that the oxidation state of tin does not change. The mass loss suggests that decomposition of the dithiocarbamate ligands is involved, leaving a residue of mixed tin sulphides and oxides [4, 5].

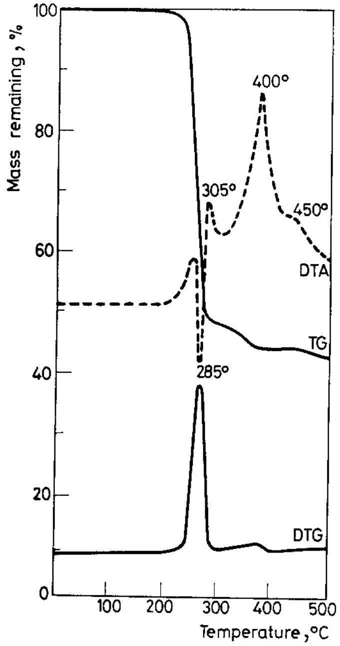

Fig. 9. Simultaneous TG/DTG/DTA of intermediate under air

The exothermic process probably involves the oxidation of the large molecular weight intermediates and associated tars which are either too involatile or too stable to escape from the furnace region. In recent studies [19] proposed intermediates, resulting from the decomposition of dithiocarbamate ligands, have left residual tars. The exothermic DTA peaks at 400 and 450° (Fig. 9) are either the result of further oxidation of the tars or the result of oxidation of the residue of mixed tin sulphides and oxides.

The overall thermal stability of the intermediate suggests that the suspected sulphur bridge between two tin atoms does not have a disulphide structure.

Conclusion

The general application of this type of synthesis is limited to tin(IV) dithiocarbamate complexes which are thermally unstable under vacuum. Only complexes possessing four dithiocarbamate ligands appear to be suitable.

Unpublished work [19] involving PPA on the methyl analogue of the tetrakis complex, $Sn(Me_2dtc)_4$, reveals that it forms the intermediate product $[SSn(Me_2dtc)_2]_2$ (where x is unknown but possibly two). Isolation in the pure form may, however, be difficult due to more extensive secondary decomposition. The same observations have been made for tetrak is (*N*,*N*-dibenzyldithiocarbamato)tin(IV), $Sn[(C_6H_5CH_2)_2dtc]_4$.

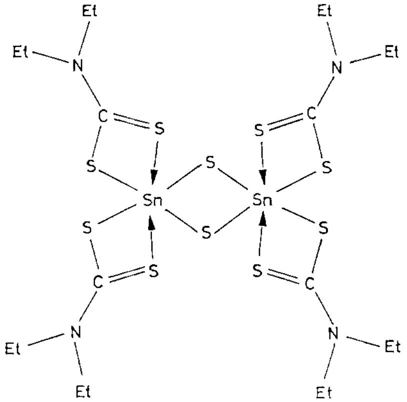

Fig 10. Structure of intermediate, di-μ-sulphidobis[bis(*N*,*N*-diethyldithiocarbamato)tin(IV)]

Complexes of the type, $Y_2Sn(Et_2dtc)_2$ (where Y = Cl, Br, I and phenyl), have been found to be volatile under vacuum [8] and hence do not form the intermediate.

Based on the results gained in this study and in the absence of X-ray crystallographic data, the following structure (Fig. 10) is proposed for the white solid intermediate formed in the thermal decomposition of tetrakis(*N*,*N*-diethyldithiocarbamato)tin(IV).

The results of the thermal studies indicate that the tin diethyldithiocarbamate intermediate is thermally more stable than other tin(IV) dithiocarbamates previously investigated [1–5].

We now propose that the intermediate, $S_2Sn_2(Et_2dtc)_4$, results form the reaction of sulphur, S_8, with $Sn(Et_2dtc)_2$ during the thermal decomposition of $Sn(Et_2dtc)_4$ [7]. This reaction and the tin-sulphur bridge structure of $S_2Sn_2(Et_2dtc)_4$ is strongly supported by the earlier work of Vieth *et al.* [20].

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Résumé — Un nouveau dithiocarbamate d'étain contenant des ponts de soufre, le di-μ-sulfidobis[bis(N,N-diéthyl-dithiocarbamato)étain(IV)], a été isolé lors de la décomposition thermique du tétrakis(N,N-diethyl-dithiocarbamato) étain(IV). Une structure dimère est proposée à partir des résultats obtenus par spectrométrie de masse, spectroscopie infrarouge, analyse thermique et osmométrie sous pression de vapeur.

Zusammenfassung — Ein neues, Schwefelbrücken enthaltendes Zinn-Dithiocarbamat, Di-μ-sulfidobis[bis(N,N-diäthyldithiocarbamato)Zinn(IV)], wurde bei der Zersetzung von Tetrakis(N,N-diäthyl-dithiocarbamato)Zinn(IV) isoliert. Aufgrund der Ergebnisse der Massenspektrometrie, der Infrarotspektroskopie, der Thermoanalyse und der Dampfdruck-Osmometrie wird eine Dimerstruktur vorgeschlagen.

Резюме — Новое соединение дитиокарбаматолова — ди-μ-сульфидобис [бис/N,N-диэтилдитиокарбамато(олово/IV)], содержащее мостиковую серу, было выделено при термическом разложении тетракис (N,N-диэтилдитиокарбамато) олово (IV). Для этого соединения предложена димерная структура на основе результатов масс-спектрометрического исследования, инфракрасной спектроскопии, термического анализа и осмометрического давления пара.