An Interesting Temperature Dependence of the Thermal Decomposition of Dithiocarbamate Tin(IV) Complexes - Molecular Precursors for Tin Sulphides

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ABSTRACT

Preparation of tin sulphides was investigated through thermal decomposition in different temperatures of two precursors: dichlorobis(diethyldithiocarbamato)tin(IV), $[Sn\{S_2CN(C_2H_5)_2\}_2Cl_2]$, (**a**) and dichlorobis(pyrrolidinedithiocarbamato)tin(IV), $[Sn\{S_2CN(CH_2)_4\}_2Cl_2]$, (**b**), in N_2. Pyrolysis experiments were performed in the range of 250-900°C and revealed an interesting dependence of the tin sulphide phase formed with the temperature employed in the experiment. All residues were characterised by X-ray powder diffraction, scanning electron microscopy (SEM), ^{119}Sn Mössbauer, ultraviolet-visible and Raman spectroscopies, and X-ray electron probe microanalysis (EPMA). Precursor (**a**) yielded residue (**1**), (**2**), (**3**) and (**4**) at 250°C, 450°C, 750° and 900°C, respectively. Complex (**b**) afforded product (**5**), (**6**), (**7**) and (**8**) at the same temperatures. Residue (**1**) and (**5**) could not be identified because of the presence of organic fragments. Product (**2**), (**3**) and (**4**) have been assigned, accordingly, to $\gamma-Sn_2S_3$, Sn_3S_4 and SnS_2 phases. The remaining residues (**6**), (**7**) and (**8**) obtained from (**b**) are not pure phase compounds but mixtures of different Sn(IV) sulphides.

Keywords: Organotin, tin sulphides, pyrolysis

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INTRODUCTION

Tin sulphides show interesting semiconducting properties and comprise a variety of materials presenting four main phases: SnS, SnS_2, Sn_2S_3 and Sn_3S_4 /1/. The more important tin sulphides are SnS and SnS_2. These sulphides present low bandgap values, similarly to the materials currently used in electronic devices, such as CdS, GaAs and silicon /2,3/.

Metallic sulphides are normally prepared by pyrolysis /4/ and this technique involves a molecular precursor that by thermal decomposition generates the metallic sulphide. Precursors such as $(Ph_3Sn)_2S$ and $Sn_4S_4R_6$ (in which, R = methyl, n-butyl or phenyl) have recently been used for the preparation of SnS and Sn_2S_3 /5, 6/. Thiolates, $[M(SR)_4]$ (M = metal of group IV), are potential single-source precursors for pyrolysis; however, they require the use of H_2S as co-reagent, which is very toxic /7/. In a previous study we have prepared Sn_2S_3 as single product of the thermal decomposition of dithiocarbamate organotin precursors /8/. Chemical vapour deposition (CVD), a pyrolysis type process, involves one or more appropriate molecular precursors in order to generate tin sulphide. Even so, in some cases, this methodology has been ignored for tin sulphides, due to the generation of contaminants and use of H_2S and H_2 mixtures as co-reagents /9, 10/. Recent work with deposition of tin sulphides employing Sn metal and S in different stoichiometry rendered different sulphide phases, SnS, SnS_2, Sn_2S_3, etc. /10/.

Dithiocarbamate organometallic compounds are normally synthesised by reaction of sodium or ammonium N,N-dialkyldithiocarbamate on metal halide substrates /11/. The reaction mechanism of dichlorobis(N,N-diethyldithiocarbamato)tin(IV) from tin(II) chloride and sodium diethyldithiocarbamate involves oxidation of Sn(II) to Sn(IV) by formation of secondary products, tin oxides and tetraethylthiuram disulphide /12,13/. The literature registers the synthesis, characterisation and the formation mechanism of complex **(a)** /12/.

In the search for new single-source precursors for tin sulphides we report in this work the syntheses, spectroscopic characterisation (IR, NMR and ^{119}Sn Mössbauer) and thermal decomposition of dichlorobis(diethyldithiocarbamato)tin(IV), $[Sn\{S_2CN(C_2H_5)_2\}_2Cl_2]$, **(a)** and dichlorobis(pyrrolidine-dithiocarbamato)tin(IV), $[Sn\{S_2CN(CH_2)_4\}_2Cl_2]$, **(b)** at different temperatures. We found an interesting dependence of the formed phase on the temperature used in the process. The residues were studied by X-ray diffraction (XRD), X-ray electron probe microanalysis (EPMA), scanning electron microscopy (SEM), ^{119}Sn Mössbauer, electronic and Raman spectroscopies.

EXPERIMENTAL

Reagents

Sodium diethyldithiocarbamate, carbon disulphide, pyrrolidine, ammonium hydroxide, tin(II) chloride, tetrahydrofuran (THF) and hexane were purchased from Merck, Aldrich, Synth and Quimex. The solvents THF and hexane used were previously dried by standard methods.

Characterisation and thermal decomposition of organotin precursors

IR spectra were obtained as KBr plates on a Mattson Galaxy model ST 3000 spectrometer in the 4000-200 cm^{-1} range. NMR spectra were record in $CDCl_3$ at 25°C on a Brucker Avance DRX 400. The values were referenced to internal $SiMe_4$ and $SnMe_4$. Elemental analysis was performed using a Perkin Elmer model PE 2400 CHN. Thermogravimetric curves were recorded on a Mettler TG-50 model STARe equipment with heating rate of 10 °C/min and N_2 flux of 200 mL/min until 750 °C.

Thermal decomposition of dithiocarbamate derivatives was carried out in a tube furnace in N_2 atmosphere, at 250, 450, 750 and 900°C, using a heating rate of 5 °C/min and gas flux of 100 mL/min. XRD patterns were collected with a Rigaku Geigerflex equipment using a Ni-filtered Cu Kα radiation (λ = 1.5418 Å) and a graphite monochromator in the diffracted beam. A scan rate of 4°C/min was applied to record a pattern in the range of 4 – 80°. ^{119}Sn Mössbauer measurements were performed on a conventional apparatus with the samples at liquid N_2 temperature and a $CaSnO_3$ source kept at room temperature. Raman spectra were recorded with a triple-monochromator XY-DILOR spectrometer, equipped with a CCD detector coupled to a microscope (OLYMPUS BH-2), with resolution of about 1 mμ (microRaman technique). Krypton laser operating at the red line(λ = 645.6 nm) was used and with 1.5 mW power. UV-visible spectra were performed on Shimadzu UV-2401 equipment. The scanning electron microscopies (SEM) were taken in JEOL JSM-840A equipment and the samples were previously covered with a thin gold layer. The X-ray electron probe microanalyses (EPMA) were carried out in a JXA 89000 RL wavelength/energy dispersive combined microanalyser, with samples covered with a thin film of carbon deposited by sputtering.

Synthesis of $[NH_4\{S_2CN(CH_2)_4\}]$

To a solution of pyrrolidine (0.64g, 9mmol) in 20 mL of diethyl ether, kept cold, was added dropwise carbon disulphide (0.68g, 9mmol). This mixture was stirred for one hour and ammonium hydroxide was added. The white solid formed, $[NH_4\{S_2CN(CH_2)_4\}]$, was filtered and re-crystallised from a mixture of water and ethanol. Yield 85%. Analysis for: $NH_4S_2C_5H_8N$. Found: C, 36.51%; H, 7.28%; N, 8.41%. Calc: C, 36.59%; H, 7.32%; N, 8.54%. M.p. 142-143 °C. IR (cm^{-1}, KBr): 998 (s, $\nu_{C\text{-}S}$); 1240 and 1325 (m, $\nu_{C\text{-}N}$); 1450 (s, $\nu_{C\text{-}N} + \nu_{C=N}$) . ^{1}H NMR (δ, D_2O): 1.85 (m, $2CH_2$); 3.58 (t, $2NCH_2$). $^{13}C\{^1H\}$ NMR (δ, D_2O): 25.01 ($2CH_2$); 55.27 ($2NCH_2$); 202.80 (SCN).

Synthesis of $[Sn\{S_2CN(C_2H_5)_2\}_2Cl_2]$, (a)

In a Schlenk flask charged with $[Na\{S_2CN(C_2H_5)_2\}]$ (1.03g, 6mmol), dissolved in 50 mL of THF, was added a solution of $SnCl_2$ (0.57g, 3mmol) in the same solvent. The orange solution formed was kept stirring for one hour in nitrogen, at room temperature. The white solids formed, SnO, and NaCl were separated from an orange solution by filtration. The solvent was removed and an orange solid, $[Sn\{S_2CN(C_2H_5)_2\}_2Cl_2]$ **(a)**, was obtained. This solid was re-crystallised with hexane/THF mixture and dried *in vacuo*. Yield 70%. Analysis results for: $[SnC_{10}N_2H_{20}S_4Cl_2]$. Found: C, 19.22 %; H, 4.05 %; N, 5.22 %. Calculated: C, 19.77 %;

H, 4.12 %; N, 5.72 %. M.p. (decomposition) = 200°C. IR (cm^{-1}, KBr): 310 (w, $\nu_{Sn\text{-}Cl}$); 385 (w, $\nu_{Sn\text{-}S}$); 989 (m, $\nu_{C\text{-}S}$); 1341 (vs, $\nu_{C\text{-}N}$); 1496 (vs, $\nu_{C\text{-}N} + \nu_{C=N}$). ^{1}H NMR (δ, $CDCl_3$): 1.19 ($2CH_2CH_3$); 3.93 ($2CH_2CH_3$). $^{13}C\{^{1}H\}$ NMR (δ, $CDCl_3$): 12.03 ($2CH_2CH_3$); 49.30 ($2CH_2CH_3$); 206.05 (SCN).$^{119}Sn\{^{1}H\}$ NMR (δ, $CHCl_3$): - 556.

Synthesis of $[Sn\{S_2CN(CH_2)_4\}_2Cl_2]$, (b)

Prepared similarly employing $[NH_4\{S_2CN(CH_2)_4\}]$ (0.98g, 6mmol) and $SnCl_2$ (0.57g, 3mmol). Yield 80%. Analysis results for: $C_{10}H_{16}SnN_2S_4$. Found: C, 24.72%; H, 3.30%; N, 5.65%. Calc: C, 24.91%; H, 3.32%; N, 5.81%. M.p. (decomposition) = 200°C. IR (cm^{-1}, KBr): 303 (m, $\nu_{Sn\text{-}Cl}$); 315 (w, $\nu_{Sn\text{-}S}$); 949 (s, $\nu_{C\text{-}S}$); 1327 (m, $\nu_{C\text{-}N}$); 1459 (s, $\nu_{C\text{-}N} + \nu_{C=N}$). ^{1}H NMR (δ, $CDCl_3$): 1.86 (m, $2CH_2$); 3.63 (t, $2NCH_2$).$^{13}C\{^{1}H\}$ NMR (δ, $CDCl_3$): 26.01 ($2CH_2$); 55.32 ($2NCH_2$); 202.85 (SCN). $^{119}Sn\{^{1}H\}$ NMR (δ, $CHCl_3$): -521.

RESULTS AND DISCUSSION

Characterisation of $[Sn\{S_2CN(C_2H_5)_2\}_2Cl_2]$ (a) and $[Sn\{S_2CN(CH_2)_4\}_2Cl_2]$ (b):

The ligand $[NH_4\{S_2CN(CH_2)_4\}]$ was satisfactorily characterised and the precursors were isolated as mixture-free derivatives showing acceptable elemental analysis. Compounds **(a)** and **(b)** were obtained as orange solids and soluble in polar organic solvents. The identity of compound (a) was confirmed. The ^{1}H and ^{13}C NMR spectra of compound (b) in $CDCl_3$ revealed signals for the organic groups attributed to the ligand. In the ^{119}Sn NMR experiments, performed in $CHCl_3$, only one signal was observed: $[Sn\{S_2CN(CH_2)_4\}_2Cl_2]$ **(b)**, δ -521 very close to resonance observed for **(a)**, δ -556. The ^{119}Sn chemical shifts are normally affected by the coordination number (NC) of tin centre [14] and by electronegativity of the ligands, temperature and concentration of the solutions. In complexes **(a)** and **(b)**, the Sn(IV) centre is de-shielded by the electronegative chlorine, which can shift the resonance to lower frequency.

Little change was detected in the C-S and C-N vibration modes in the IR spectra in going from the free ligand to complex **(b)**. The $\nu_{C\text{-}S}$, $\nu_{C=S}$ and $\nu_{C\text{-}N} + \nu_{C=N}$ stretching frequencies can indicate whether the dithiocarbamate acts as a mono or bidentate ligand /15-17/. A single band was detected, centred in the range of 1000-960cm^{-1}, suggesting that the carbon-sulphur bond is in fact something between a double and a single bond. The same happened to the CN connection, due to the strong band near 1500 cm^{-1}. Thus, the IR results indicate the presence of bidentate coordination mode of the ligand in complex **(b)**, in the solid state. Finally, the Sn-S and Sn-Cl bands were displayed at 315 cm^{-1} and 303 cm^{-1}, respectively /18/.

The ^{119}Sn Mössbauer spectra of the compounds were fitted supposing the existence of one tin site. The hyperfine parameters obtained for both complexes were quite different from $SnCl_2$ (*IS* = 3.71 and *QS* = 0.95 mms^{-1}) /19a/.

Decreases were observed in the isomer shifts (*IS*) and increases in the quadrupole splitting (*QS*) values for the complexes **(a)** (*IS* = 0.07 and *QS* = 0.75 mms^{-1}) and **(b)** (*IS* = 0.78 and *QS* = 1.72 mms^{-1}), compared to $SnCl_2$, and the parameters are characteristic of tin(IV). Variations in contribution of *s* character in tin molecular orbital change the values of isomer shift. The low value of δ for **(a)** and **(b)** might be explained on account of (i) the increasing of the coordination number and (ii) the change of oxidation state of tin atom. The quadrupole splitting is related to the symmetry of electronic density distribution around the Mössbauer atom. In **(a)** and **(b)**, the increase of this parameter comparing with $SnCl_2$ is due to the coordination process, which causes a considerable deformation in the electronic density at the metal centre. Fig. 1 shows the structure of **(a)** and **(b)**.

The structures of both compounds are very similar in solution, since there is no difference in the ^{119}Sn chemical shift of compounds **(a)**, δ -556 and **(b)**, δ -521. On the other hand, the Mössbauer parameters reveal that, in the solid state, the structures are slightly different, although both are in the range expected for Sn(IV) species /19b/. It is possible that compound **(b)** exists in the solid state with the chlorines in the axial position of the octahedral (trans isomer), unlike complex **(a)**, which displays a cis conformation, where the halide atoms occupy the equatorial position. Once in solution a fast exchange between cis and trans forms averages the tin resonance. It might be also related to differences in the packing forces in the crystals of **(a)** and **(b)**.

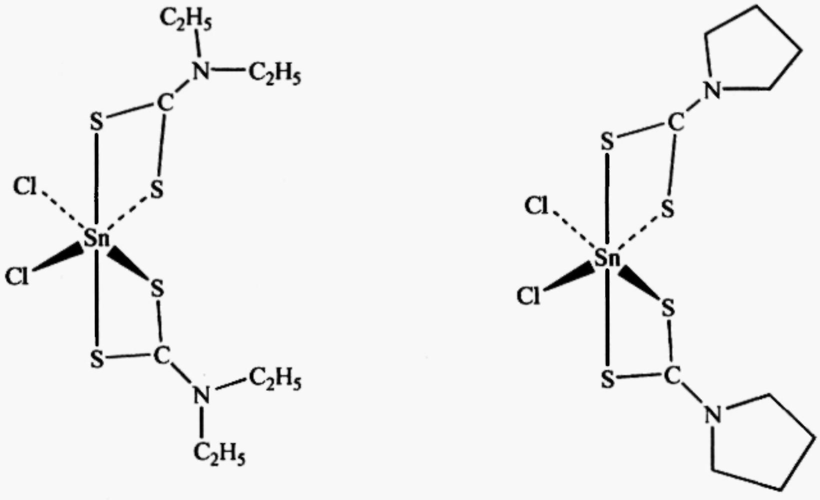


Fig. 1: Structure of compounds **(a)** and **(b)**.

Thermal decomposition of $[Sn\{S_2CN(C_2H_5)_2\}_2Cl_2]$ (a) and $[Sn\{S_2CN(CH_2)_4\}Cl_2]$ (b):

The thermogravimetric (TG) curve of **(a)**, Fig. 2, shows a mass loss from 50 to 200°C. A thermally stable residue was formed in the range of 385 – 450 °C. From 450 to 720°C there is a slow weight loss. Beyond 720°C the TG curve remains unchanged. For precursor **(b)** the TG curve shows a mass loss from ambient temperature and decomposition sets in abruptly around 150°C. Beyond this temperature the TG curve descends linearly up to 275°C. This decomposition is not complete even up to 725°C.

The pyrolysis experiments were performed until the temperature of 900°C in order to verify the thermal stability of the phases formed at 750°C, for both precursors.

Both precursors present an incomplete decomposition at 250°C, since EPMA indicates the presence of chlorine and nitrogen, apart from Sn and S. Above these temperature only Sn and S remain.

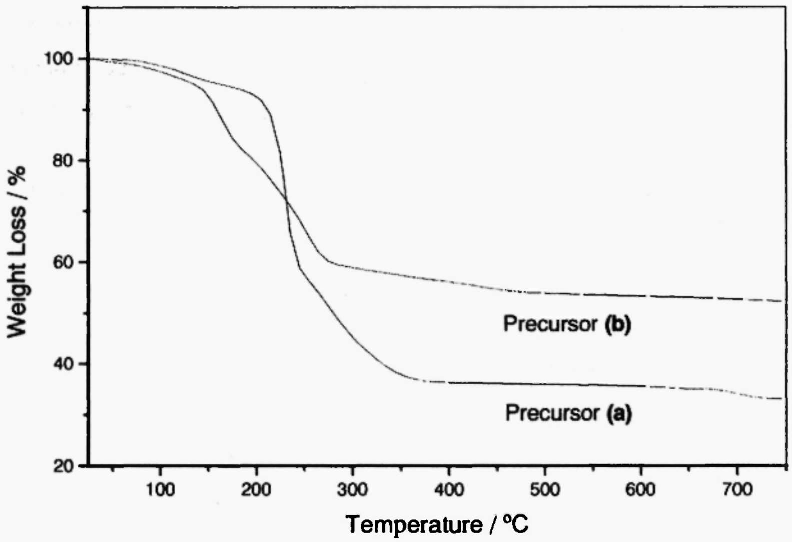


Fig. 2: Thermogravimetric curves for the decomposition of $[Sn\{S_2CN(C_2H_5)_2\}_2Cl_2]$ **(a)** and $[Sn\{S_2CN(CH_2)_4\}Cl_2]$ **(b)** in nitrogen.

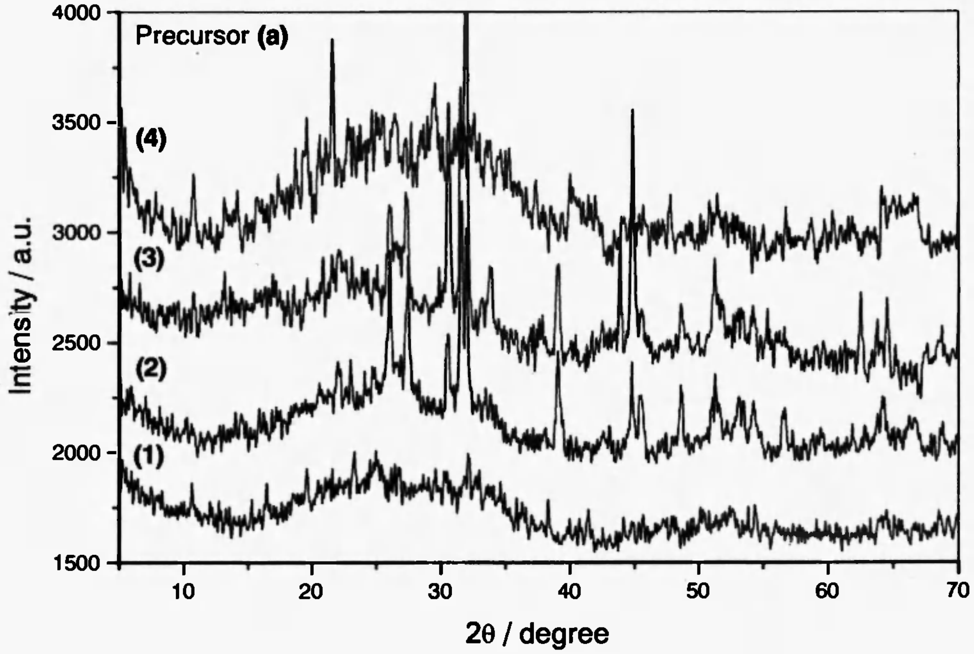
X-Ray powder diffraction study

Diffraction patterns of all residues are shown in Fig. 3. Both powders obtained at 250°C **(1)** and **(5)**, could not be entirely characterised, since they still possess organic fragments. However in view of the Mössbauer parameters there is only one type of Sn(IV).

Compound $[Sn\{S_2CN(C_2H_5)_2\}_2Cl_2]$ **(a)** has generated single-phase residues, which were less complicated to analyse than those from complex $[Sn\{S_2CN(CH_2)_4\}Cl_2]$ **(b)**.

At 450°C all organic part have been decomposed generating, in the case of **(a)**, γ- Sn_2S_3 **(2)** in orthorhombic phase (JCPDS-ICCD 1996), in view of the lines at 2θ/° 31.44 and 31.86. Up to 750°C, the residue obtained, **(3)**, revealed lines at 2θ/° 31.48 and 31.95 which we suppose can either be a mixture of SnS and γ- Sn_2S_3 or a new form of Sn_3S_4, which is more likely. Unfortunately, we have not been able to connect these lines with those available for known Sn_3S_4 phases in the JCPDS database. The product **(4)** displayed lines at 2θ/° 22.15, suggesting the formation of hexagonal SnS_2 at 900°C.

The X-ray diffraction patterns for those residues obtained from compound **(b)** were more complicated to analyse, since it generates mixtures of sulphides. The X-ray diffractogram of **(6)** revealed lines at 2θ/° 31.44 and 31.85, possibly related to a mixture of SnS and γ-Sn_2S_3 in orthorhombic phases, obtained at 450°C. The product produced at 750°C, **(7)**, possibly consists of a mixture of SnS_2 hexagonal Berndtite, with lines at 2θ/° 26.46, 33.82, 51.42°, and SnS orthorhombic Herzenbergite with diffraction patterns at 2θ/° 38.32 and 65.43 (JCPDS-ICCD). The material obtained up to 900°C, **(8)**, is much less crystalline in view of the diffraction lines.



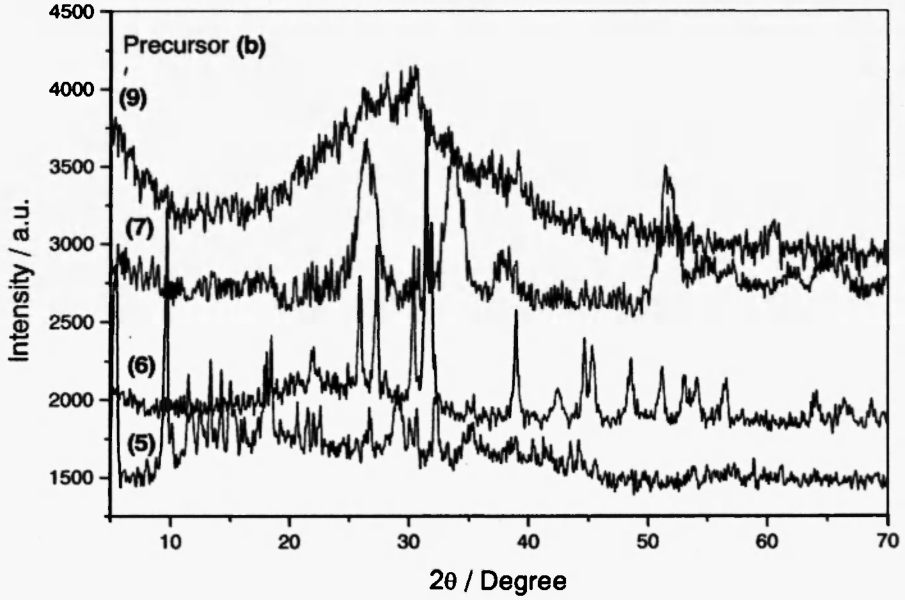


Fig. 3: X-ray diffractograms of the residues from [Sn{$S_2CN(C_2H_5)_2$}$_2Cl_2$] **(a)** and [Sn{$S_2CN(CH_2)_4$}Cl_2] **(b)**

^{119}Sn Mössbauer Spectroscopic results

The ^{119}Sn Mössbauer spectra were important to confirm the results of XRD. Table 1 displays the ^{119}Sn

Mössbauer parameters obtained for all residues from **(a)** and **(b)**.

As mentioned before, the residues obtained at 250°C for both compounds possess only one site of Sn(IV) in view of the ^{119}Sn Mössbauer spectra.

The residue of **(a)** treated at a temperature of 450°C displayed two sets of signals, IS 0.07 mms^{-1}, QS 0.60 mms^{-1} for Sn (IV) and IS 3.27 mms^{-1}, QS 1.03 mms^{-1} for Sn(II). Each signal occupies an area of 50%, which agrees quite well with the X-ray results, pointing out the formation of γ-Sn_2S_3 **(2)**, that is in fact a mixture of SnS_2 and SnS. Two sets of signals are observed in the ^{119}Sn Mössbauer spectra for the residue obtained at 750°C, IS 0.07 mms^{-1}, QS 0.60 mms^{-1} for Sn (IV) and IS 3.10 mms^{-1}, QS 1.04 mms^{-1} for Sn(II). The Sn(IV) nuclei occupy an area of 33% and the Sn(II) 67%. It can be a good indication of Sn_3S_4 **(3)** formation, that is composed of 1/3 of Sn(IV) and 2/3 of Sn(II), however X-ray powder diffraction results were not conclusive. The residue at 900°C displayed only one set of signals, IS 0.11 mms^{-1} and QS 0.50 mms^{-1}, which corresponds to 100% of Sn(IV). It reinforces the results obtained by XRD that suggest the formation of a pure phase of SnS_2 **(4)**.

Table 1

^{119}Sn Mössbauer parameters {isomer shift **(IS)**, quadrupole spliting **(QS)**, area and width} obtained at liquid nitrogen temperature for the residues of **(a)** and **(b)**.

Residues	IS/mm s^{-1}	QS/mm s^{-1}	Area/%	Width/ mm s^{-1}
Residues of **(a)**				
at 250 °C **(1)**	0.14	0.50	100/Sn(IV)	0.98
at 450 °C **(2)**	0.07	0.60	49/Sn(IV)	0.98
	3.27	1.03	51/Sn(II)	0.96
at 750 °C **(3)**	0.07	0.60	33/Sn(IV)	0.98
	3.10	1.04	67/Sn(II)	0.97
at 900 °C **(4)**	0.11	0.50	100/Sn(IV)	0.96
Residues of **(b)**	0.01	0.40	26/Sn(IV)	0.89
at 250 °C **(5)**	0.99	0.58	74/Sn(II)	0.92
at 450 °C **(6)**	0.58	0.95	25/Sn(IV)	0.90
	3.31	0.91	75/Sn(V)	0.94
at 750 °C **(7)**	0.06	0.57	95/Sn(IV)	0.98
	3.27	1.07	5/Sn(II)	0.98
at 900 °C **(8)**	0.03	1.40	87/Sn(IV)	0.90
	0.69	0.70	13/Sn(II)	0.96

The ^{119}Sn Mössbauer spectrum for each residue obtained from complex **(b)** displayed two sets of signals; **(5)** IS 0.58 mms^{-1}, QS 0.95 mms^{-1} for Sn(IV) and IS 3.31 mm^{-1}, QS 0.91 mms^{-1} for Sn(II); **(6)** IS 0.58 mms^{-1}, QS 0.95 mms^{-1} for Sn(IV) and IS 3.31 mm^{-1}, QS 0.91 mms^{-1} for Sn(II); **(7)** IS 0.06 mms^{-1}, QS 0.57 mms^{-1}

for Sn(IV) and IS 3.27 mm^{-1}, QS 1.07 mms^{-1} for Sn(II); **(8)** IS 0.03 mms^{-1}, QS 1.40 mms^{-1} for Sn(IV) and IS 0.69 mm^{-1}, QS 0.70 mms^{-1} for Sn(II), respectively. The area occupied by each centre indicates the formation of more than one phase at each studied temperature.

As observed in the TG curves, the thermal decomposition process of **(a)** is less complicated that of **(b)**. It is possible that the ethyl group, attached to the nitrogen atom of the dithiocarbamate ligand, leaves the molecule much faster and more easily than the $(CH_2)_4$ group. The formation of a particular tin sulphide phase is strongly dependent upon the mechanism of pyrolysis. In spite of the similarity of **(a)** and **(b)** the decomposition process, according to the TG curves, occurs in different ways, affording different residues, as attested by the ^{119}Sn Mössbauer results.

Electronic Spectroscopic results

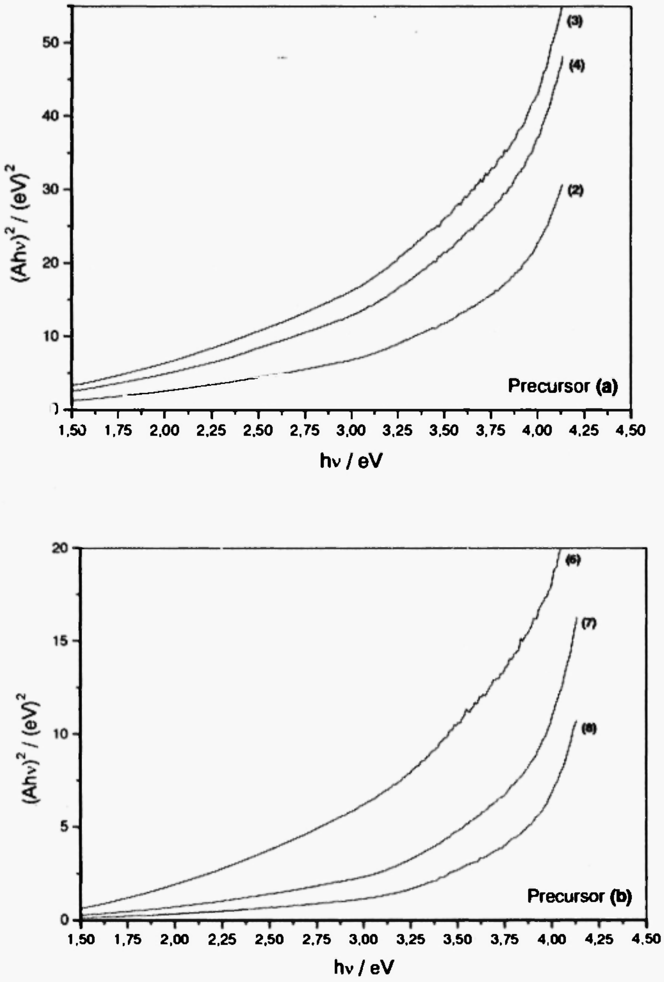


Fig. 4: Bandgap energies obtained for residues of **(a)** and **(b)**.

An electronic spectroscopic study has provided information about the bandgap energies of the residues. In the graphic of $(Ah\nu)^2$ *vs* hν, *A* represents absorbance, ***h*** is the Planck constant, and *ν* is the frequency, Fig. 4. The bandgap energies for the residues obtained at 450, 750 and 900°C for complex $[Sn\{S_2CN(C_2H_5)_2\}_2Cl_2]$ **(a)**, which correspond to the formation of Sn_2S_3 **(2)**, Sn_3S_4 **(3)** and SnS_2 **(4)** are 3.63, 3.83 and 3.80 eV. The values obtained for Sn_2S_3 and SnS_2 are higher than those found in the literature, 0.95 and 2.18 eV, respectively /20/.

It is possible that the decrease of the particle size has increased the bandgap due to the quantum confinement phenomena. However, it is still in the range of 0 – 5.0 eV, which is considered for semiconducting materials. The residues of $[Sn\{S_2CN(CH_2)_4\}Cl_2]$ **(b)** provided similar bandgaps despite not being pure phase materials 3.63, 3.88 and 3.92 eV.

Raman Spectroscopic result

Raman spectroscopy experiments were carried out in order to confirm the tin phase formed in the residue at 900 °C from precursor **(a)**, Fig. 5.

The band near 50 cm^{-1} is a function of laser orientation. An intense band in 317 cm^{-1} and a weaker near 209 cm^{-1} are characteristic of SnS_2. The intense band is attributed to symmetry mode *A* and the other refers to symmetry mode *E* /20/.

These results confirm the formation of SnS_2, in agreement with Mössbauer and XRD data. The formation of SnS_2 at high temperature, described here, agrees with results obtained by CVD of tin metal and sulphur /10/.

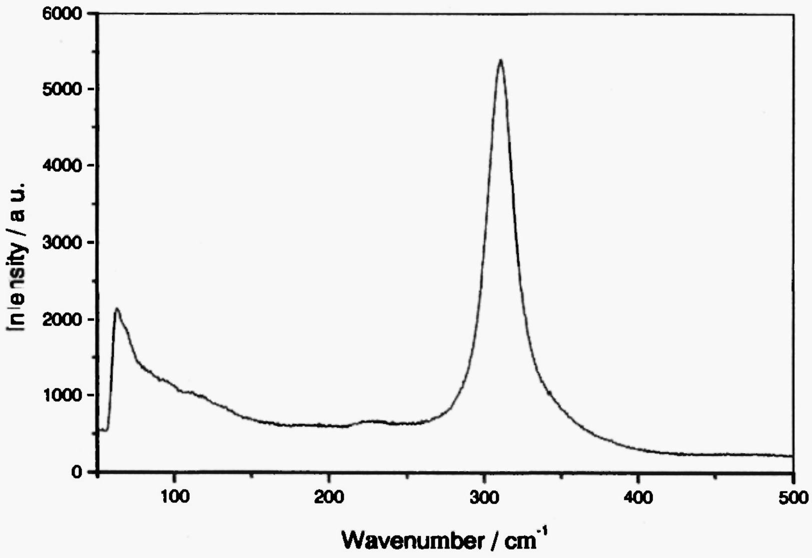
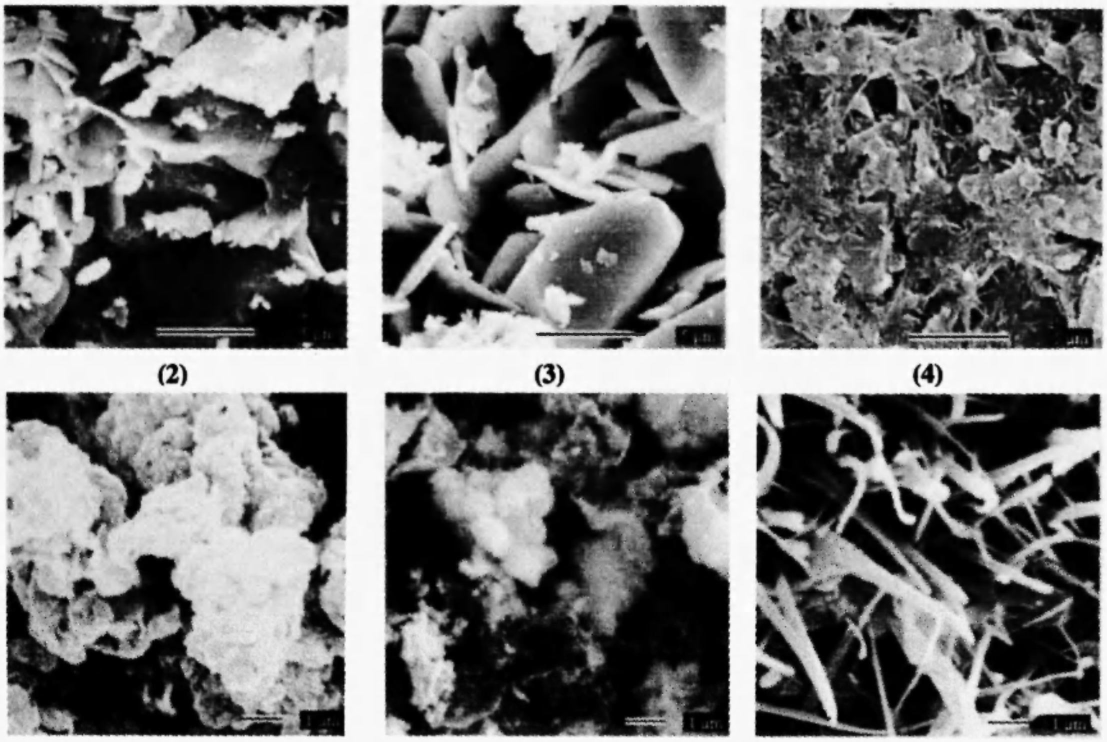


Fig. 5: Raman spectra of SnS_2 obtained at 900°C from compound (a).

The pure phase SnS_2 was obtained in a temperature range of 950-850°C for a molar ratio of 1:2 for Sn and S.

Scanning Electron Microscopy (SEM)

The SEM images have revealed the formation of residues with particle size of microns, Fig. 6. Those residues obtained from precursor **(a)**: **(2)** and **(3)** are more crystalline than the corresponding material prepared from **(b)** confirming the XRD results. The shape of the crystals is very similar to those obtained in previous work [8]. The high temperature, 900°C, employed in the preparation of residue **(4)** has effected an agglutination of the crystals in a sinterization process. Those residues obtained from precursor **(b)**, **(6)** and **(7)**, form agglomerates, and residue **(8)** starts to form filings at 900°C.



(2) **(3)** **(4)**

(6) **(7)** **(8)**

Fig. 6: MEV results for **(2)** 450°C, **(3)** 750°C and **(4)** 900°C and **(6)** 450°C, **(7)** 750°C and **(8)** 900°C.

CONCLUSIONS

The synthesis, characterisation and thermal decomposition study of two dithiocarbamate tin compounds is described. The results revealed that both compounds generate, at low temperature, residues which still retain organic fragments. As the temperature increases only Sn and S remain in the residues. Compound

$[Sn\{S_2CN(C_2H_5)_2\}_2Cl_2]$ (**a**) can generate three tin sulphide phases, depending on the temperature employed in the pyrolysis: γ–Sn_2S_3 (**2**), Sn_3S_4 (possibly) (**3**) and hexagonal SnS_2 (**3**). On the other hand, compound $[Sn\{S_2CN(CH_2)_4\}Cl_2]$ (**b**) generates a mixture of sulphides. Therefore, we conclude that compound (**a**) is more appropriate for the production of tin(IV) sulphides.

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