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THE THERMAL PROPERTIES OF TIN(IV) DIETHYLDITHIOCARBAMATE

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ABSTRACT

The TG, DTA, HTRS, and DRS curves of $Sn(Et_2dtc)_2Cl_2$ are presented. The compound dissociates to give $Sn(NCS)_2Cl_2$ as an intermediate species followed by dissociation to yield tin sulfide. Chromatographic examination of the compound showed that it was neither cationic or anionic in nature. The compound is essentially non-volatile, in contrast to other transition-metal chelates of diethyldithiocarbamic acid.

INTRODUCTION

The compound, tin(IV) diethyldithiocarbamate, in contrast to other metal diethyldithiocarbamates previously studied[1,2], is a non-volatile chelate. Since the non-volatility of this compound is contrary to other chelates of this type, an attempt is made here to explain this abnormal behavior by an examination of its thermal and chromatographic behavior. The compound, $Sn(Et_2dtc)_2Cl_2$, was studied by thermogravimetry (TG), differential thermal analysis (DTA), high-temperature reflectance spectroscopy (HTRS), dynamic reflectance spectroscopy (DRS), and ion-exchange chromatography.

EXPERIMENTAL

Preparation of $Sn(Et_2dtc)_2Cl_2$

The compound was prepared by adding a 0.1 M solution of tin(IV) chloride to a 0.1 M solution of sodium diethyldithiocarbamate in the presence of sufficient HCl to prevent the hydrolysis of the tin(IV) ion. An initial metal-to-ligand ratio of 1:4 was used to carry out the precipitation. A precipitate formed immediately and after stirring the mixture for about 1 h, it was filtered off, washed with hot water until free of the acid salt and dried for 48 h in a vacuum desiccator at room temperature. The analysis of the compound gave the following results. Sn: calc., 24.41%; found, 24.6%. Cl: calc., 14.58%; found, 14.7%.

The complex is insoluble in water, slightly soluble in acetone and ethanol, and very soluble in benzene and in chloroform.

Instrumentation

The TG curves of the compound were obtained on a DuPont Model 950 thermobalance using dynamic nitrogen, air, or oxygen atmosphere. Sample sizes ranged in mass from 6–12 mg; a furnace heating rate of 10°C was employed.

A DuPont Model 920 thermograph and/or a Deltatherm III DTA instrument was used to obtain the DTA curves in a dynamic nitrogen furnace atmosphere. Sample sizes ranged in mass from 5 to 10 mg; a furnace heating rate of 10°C/min was employed.

The reflectance studies were carried out using a heated sample holder previously described by Wendlandt[3–5] and a Beckman Model DK-2A spectroreflectometer. White glass fiber cloth covered with a thin cover glass was used as the reflectance standard. A heating rate of 5 to 10°C/min was employed for the DRS mode.

Ion-exchange chromatography

A cellulosic cation exchanger was employed (Chromedia CM II, weak, Whatman). The cation exchanger was treated with 0.5 M HCl until disappearance of Fe^{3+} ions, water until disappearance of the acidity, and then successively with 2 M NaCl and water. After the last washing with water, ethanol was passed through the exchanger and then a mixture of water–ethanol–benzene in the ratio of 10:65:25; the latter solvent mixture was the solvent of the compound under examination. The columns (diameter 1.5 cm, height 15 cm) were charged with 0.5 ml of saturated solution of the compound of the complex; the rate flow was 0.5 ml/min.

Preliminary tests were carried out to check that the functional groups of the exchanger under the chosen operative conditions allowed an efficient ion exchange. For this purpose, 0.5 ml of 0.01 M $Co(NO_3)_2$ in the solvent mixture, was charged on the column. The Co^{2+} ion was retained on the column after elution with the above solvent. However, it was removed from the column by elution with a mixture of 2 M $NaNO_3$, ethanol and benzene, in the ratio of 10:65:25.

RESULTS AND DISCUSSION

The TG curves of $Sn(Et_2dtc)_2Cl_2$ in N_2 and in air atmospheres are shown in Fig. 1.

In the N_2 atmosphere, the compound exhibited a gradual mass-loss, starting at ambient room temperature. However, the rate of decomposition increased above about 150°C, giving a break in the curve, but not a plateau, in the 200–225°C temperature range. The approximate composition of the compound in this region corresponded to $Sn(NCS)_2Cl_2$. This compound then dissociated to give the metal sulfide. This type of thermal degradation sequence agrees well with the data presented by Bernard and Borel[6] on the TG of similar type compounds.

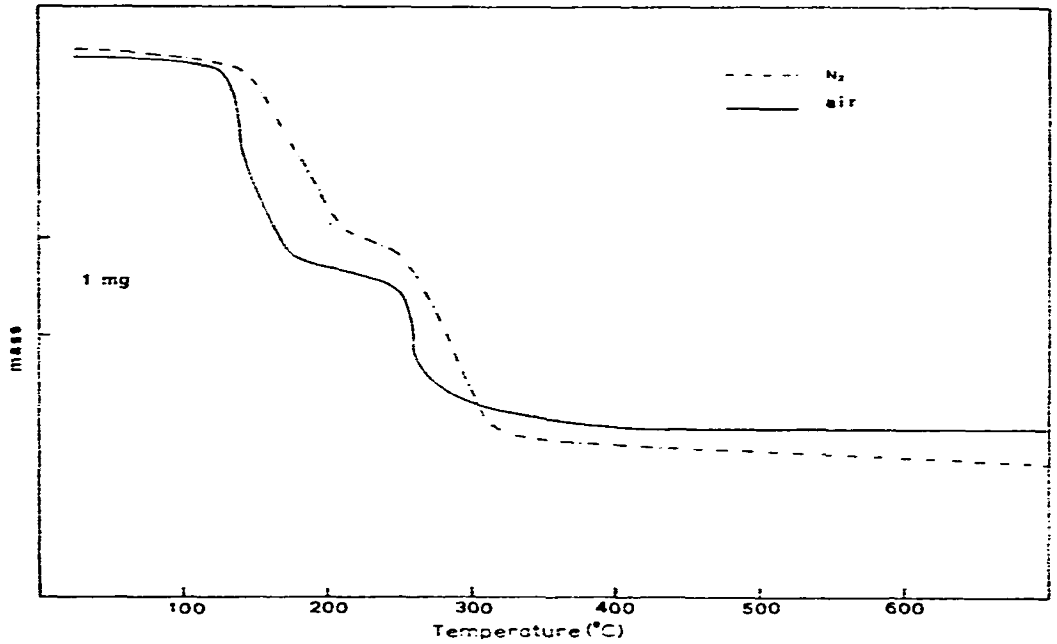


Fig. 1. Mass-loss curves of $Sn(Et_2dtc)_2Cl_2$ in N_2 and in air atmospheres.

In an air atmosphere, the compound exhibited a similar TG curve but the residue was tin oxide rather than the sulfide (calc., 30.99%; found, 30.9%). The compound does not appear to be volatile in an air atmosphere.

The DTA curve of $Sn(Et_2dtc)_2Cl_2$ in a dynamic N_2 furnace atmosphere is given in Fig. 2.

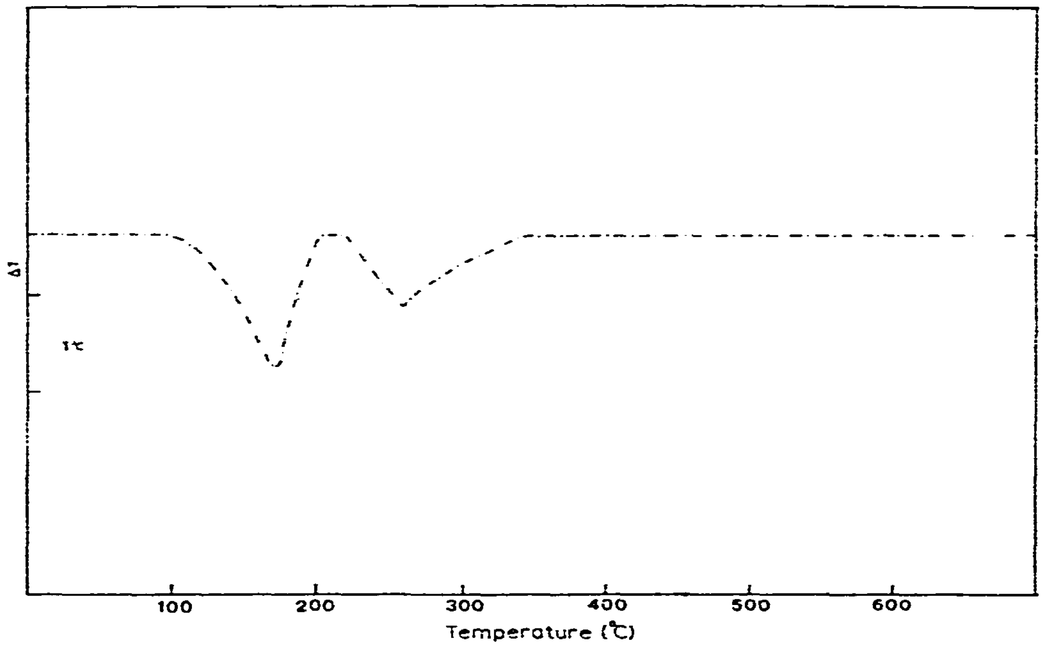


Fig. 2. DTA curve of $Sn(Et_2dtc)_2Cl_2$ in a N_2 atmosphere.

Two endothermic peaks are exhibited in the DTA curve. The first peak is probably due to the formation of Sn(NCS)$_2$Cl$_2$ while the second is caused by the decomposition of the latter to the sulfide. Both peaks are in agreement with the results obtained from the TG curve.

The HTRS and DRS curves of Sn(Et$_2$dtc)$_2$Cl$_2$ are given in Figs. 3 and 4, respectively.

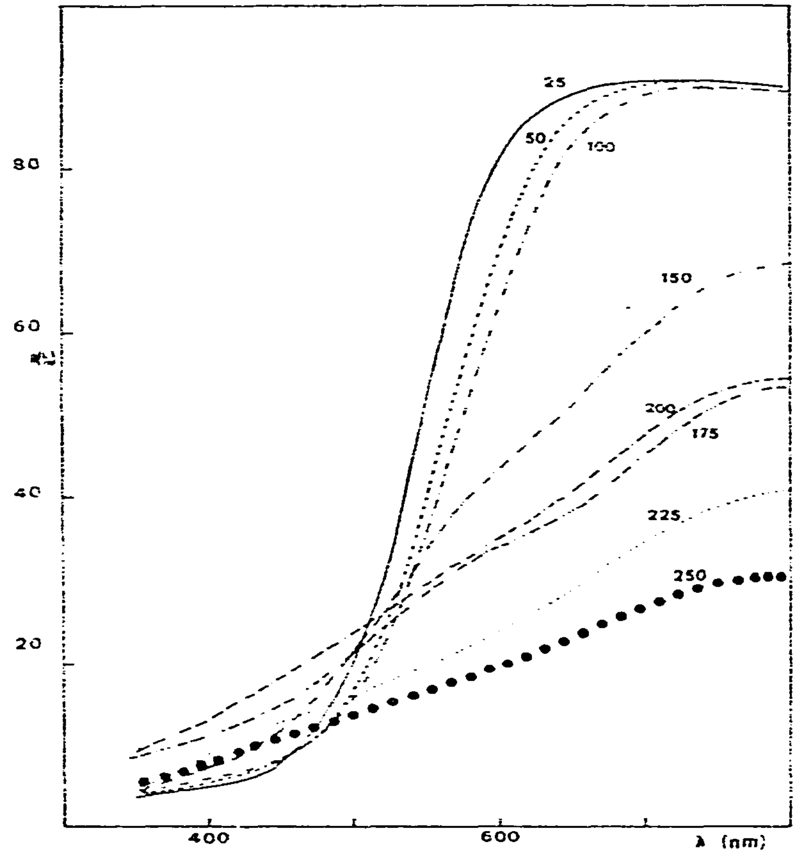


Fig. 3. HTRS curves of Sn(Et$_2$dtc)$_2$Cl$_2$.

The HTRS curve at 25 °C contained a maximum in reflectance at wavelengths above about 600 nm. Above 100 °C, the reflectance of the compound decreased rapidly until the maximum temperature of 250 °C was attained. The DRS curve indicated that the major change in the reflectance of the compound occurred above 125 °C.

From the ion-exchange chromatography of the compound it was shown that the compound is not cationic in nature. Also considering that the stoichiometry of the compound is of the ratio, 1:2:2 of tin–ligand–chlorine, the presence of anionic species can also be excluded. Hence, the two chlorine atoms must be coordinated to the tin forming a hexacoordinated compound. The presence of the two chlorine atoms in the inner coordination sphere is justifiable through the formation mechanism of the

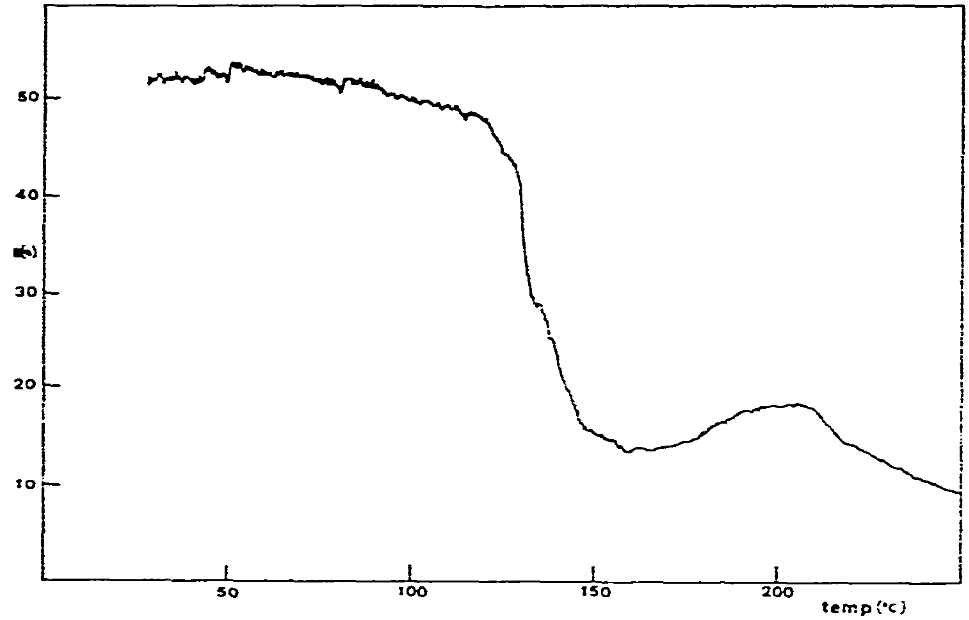
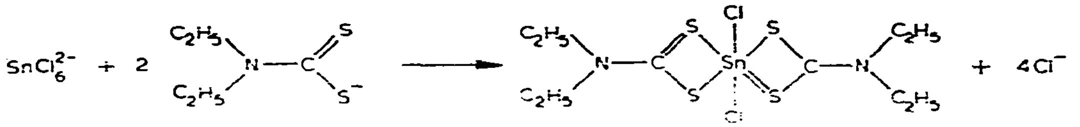


Fig. 4. DRS curve of $Sn(Et_2dtc)_2Cl_2$.

chelate. In fact, the tin in chloride solution gives the complex, $SnCl_6^{2-}$. In the presence of diethyldithiocarbamate ions a substitution reaction occurs, or:



This type of configuration justifies the thermal behavior of the complex and the fact that the chlorine is eliminated only during the second step of the thermal dissociation reaction.

The volatility of the metal diethyldithiocarbamates appears to go through a maximum in the transition metal ions. The stability of the metal–ligand bond and the thermal stability of the compounds are a function of the metal ionization potential and its ionic radius. The metal ions that give compounds with the higher thermal stability are those with the smaller ionic radius and higher ionic charge. Charles[7] noted that in the chelates of 8-quinolinol, the cobalt(II), nickel(II), copper(II), and zinc(II) complexes melted without decomposition while the other complexes studied all decomposed before fusion. With the metal diethyldithiocarbamates, the volatility is a maximum for cobalt(II), nickel(II), copper(II) and zinc(II), and is very low for the tin(IV) complex.

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