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The Preparation of Tin(II) Dithiocarbamates from Ammonium Dithiocarbamate Salts

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Ammonium dithiocarbamate salts, which can be formed directly from carbon disulfide and the appropriate dialkylamine, served as convenient precursors for tin(II)–DTC complexes. The compounds $Sn[S_2CNR_2]_2$, *(*$R = CH_3$ *and* C_2H_5*) were prepared in this manner and characterized by their ir, nmr, ESCA, and mass spectra as well as by thermogravimetric analysis.*

Introduction

Dithiocarbamates have properties which make them useful in applications including vulcanization accelerators, fungicides, and pesticides among others.[1] Many dithiocarbamate complexes of metal ions are known[1], but there is little published information on tin(II) dithiocarbamates. A patent[2] briefly describes $Sn[S_2CN(C_5H_{11})_2]_2$, while the x-ray crystal structure of $Sn[S_2CN(C_2H_5)_2]_2$ has appeared[3], although no further information on the latter compound has apparently been reported. In the present paper, we wish to report the synthesis and properties of bis(dimethyl- and bis(diethyl-dithiocarbamato)tin(II) ($SnDTCMe_2$ and $SnDTCEt_2$). Some advantages of the preparative method involving ammonium dithiocarbamate intermediates will be described.

Experimental

Materials and Instrumentation

All solvents used in this work were reagent grade and used without further purification. The diethylamine was distilled from potassium hydroxide and stored under nitrogen in the dark until used to prevent the formation of any degradation products. Commercially obtained (Matheson) dimethylamine (99.0%) was used without further purification. Anhydrous tin(II) chloride was prepared by the reaction of granulated tin with hydrochloric acid followed by crystallization of the hydrated species from the acid solution. It was subsequently dehydrated using acetic anhydride, filtered under a stream of anhydrous nitrogen, washed several times with cold petroleum ether, dried *in vacuo* for five hours at 200° C, and stored in the dark under nitrogen until used.

Infrared spectra were recorded on a Beckman Model 4250 spectrophotometer using polystyrene as the calibrant. Proton nmr spectra were obtained on Varian T-60 and HA-100 instruments. Conductivity studies were carried out using a Yellow Springs Model 31 conductivity bridge in conjunction with a set of standard conductivity electrodes. Photoelectron (ESCA) spectra were obtained on a DuPont Model 650 ESCA instrument. An Hitachi Perkin Elmer RMU-6H Mass Spectrometer was used to obtain mass spectra. Melting points were obtained in capillary tubes (unsealed) in a heated block and are uncorrected.

Analyses

Carbon, hydrogen, and nitrogen analyses were performed by PCR, Inc., Gainesville, Florida, and Het-Chem-Co., Harrisonville, Missouri. Tin composition (total tin) was determined gravimetrically by ignition of a sample with concentrated nitric acid followed by weighing as the tin(IV) oxide.

Synthesis of Bis(dimethyldithiocarbamato)tin(II)

Dimethylamine gas was bubbled through ice cold carbon disulfide under a stream of anhydrous nitrogen with stirring until a slurry of the white intermediate ammonium salt formed. With continued stirring, a solution of 0.338 g $SnCl_2$ in 20 ml absolute ethanol was added dropwise. The resulting orange precipitate was filtered under a stream of anhydrous nitrogen, washed with cold petroleum ether, and dried *in vacuo* for several hours (0.289 g, 45%). The product began to decompose at 185° C. Calculated for $SnC_6H_{12}N_2S_4$: C, 20.06; H, 3.36; N, 7.79; Sn, 33.05. Found: C, 20.09, H, 3.59; N, 8.07; Sn, 34.32.

The solubility of $Sn(DTCMe_2)_2$ in solvents suitable for cryoscopic freezing point measurements was too small for accurate molecular weight determination. The mass spectrum was consistent with the proposed formula with important peaks at m/e 361 ($^{120}Sn[S_2CN(CH_3)_2]_2^+$), 240 ($^{120}Sn[S_2CN(CH_3)_2]^+$), 121 ($(CH_3)_2$

NCS_2^+), 120 (Sn^+), 76 (CS_2^+), 32 (S^+), 26 (CN^+), 15 (CH_3^+), and 14 (N^+).

Synthesis of Bis(diethyldithiocarbamato)tin(II)

Two ml of purified diethylamine was slowly added dropwise with stirring to 10 ml ice cold carbon disulfide under a stream of anhydrous nitrogen. A solution of 0.279 g anhydrous $SnCl_2$ in 5 ml absolute ethanol was then added dropwise with stirring until a deep orange solid precipitated. (Note: It was necessary occasionally to reduce the volume of the reaction mixture to effect precipitation after addition of the ethanolic $SnCl_2$ solution).

This precipitate was then filtered under a stream of anhydrous nitrogen, washed with several portions of cold petroleum ether, and vacuum dried at room temperature for several hours (0.384 g, 63%). The compound had a decomposition point of 151° C. Calculated for $SnC_{10}H_{20}N_2S_4$: C, 28.90; H, 4.86; N, 6.75; Sn, 28.59. Found: C, 30.02; H, 5.00; N, 6.91; Sn, 29.64.

Molecular weight measurements in benzene solvent ($1.24 \times 10^{-2}M$) using an apparatus similar to that described by Shriver[4] gave an apparent molecular weight of 799±40 (theory for monomer 415, dimer 830). The mass spectrum of the product contained important peaks at m/e 417 ($^{120}Sn[S_2CN(C_2H_5)_2]_2^+$), 268 ($^{120}Sn[S_2CN(C_2H_5)_2]^+$), 149 ($(C_2H_5)_2NCS_2^+$), 120 ($Sn^+$), 76 ($CS_2^+$), 32 ($S^+$), 29 ($C_2H_5^+$), 26 ($CN^+$), 15 ($CH_3^+$) and 14 ($N^+$).

Results and Discussion

Synthesis

Metal DTC complexes have usually been prepared by two synthetic pathways: a) the metathetical reaction between an alkali–DTC salt and a metal compound[1,5], and b) the reaction of a metal hydroxide with carbon disulfide and the appropriate amine.

A literature survey reveals that method (a) is much the more common, but one patent[6] was found describing the preparation of a DTC complex starting from an alkylammonium dithiocarbamate:

$$n\,R_2NH_2^+S_2CNR_2^- + MCl_n \rightarrow M(S_2CNR_2)_n + n\,R_2NH_2^+Cl^-$$

We have investigated this approach and find that it offers some decided advantages over the other techniques just mentioned. First, the reaction of a dialkylamine and carbon disulfide yields the dialkylammonium–DTC salt directly:

$$2R_2NH + CS_2 \xrightarrow[0^\circ C]{CS_2} R_2NH_2^+S_2CNR_2(s)^-$$

$$R = CH_3(I),\ C_2H_5(II)$$

The ammonium salt may then be reacted *in situ* with a metal salt in alcohol or other solvent forming the metal–DTC complex.

The intermediates I and II were isolated and identified by their melting points, 125 and 82° C, respectively.[7] The pmr spectral parameters for I and II are given in Table I with tentative signal assignments. Spectra of the ammonium–DTC salts were unchanged after several weeks at room temperature in benzene and in carbon tetrachloride solution.

Test reactions involving metal ions which form known DTC complexes suggested that these complexes could be produced readily from ammonium–DTC starting materials. This method has the advantage that it is not necessary to isolate the intermediate ammonium–DTC salts but rather the metal–DTC complexes can be formed *in situ*. This is well illustrated by the preparation of tin(II) DTC complexes.

$Sn(DTCMe_2)_2$ (III) and $Sn(DTCEt_2)_2$ (IV) complexes were prepared by reacting the appropriate ammonium–DTC salt with stannous chloride in ethanolic solution. Both precipitated as bright orange crystalline solids which exhibited reasonable stability at room temperature. There was, however, some color change noted after several weeks, probably indicating decomposition.

The pmr spectra of III and IV are listed in Table I and the resonance positions are found to correspond acceptably with those of other metal–$DTCMe_2$ and –$DTCEt_2$ complexes.[8] The methyl resonance of III appeared as two closely spaced singlets perhaps as a result of restricted rotation about the C–N bond. The explanation must be considered very tentative, however, since the effect is absent in the ethyl derivative.

Thermogravimetry (TG) curves for III and IV appear in Figure 1. D'Ascenzo and Wendlandt[9] have studied several divalent metal–DTC compounds by TG and

TABLE I. PMR Spectra of $Sn(DTC)_2$ Complexes.

Complex	δCH_2(ppm)[a]	δCH_3(ppm)	δNH_2(ppm)	Solvent
$(CH_3)_2NH_2^+S_2CN(CH_3)_2^-$	–	2.25, 1.58	8.59	C_6H_6
$(C_2H_5)_2NH_2^+S_2CN(C_2H_5)_2^-$	4.05, 3.16[b]	1.33, 1.22[b]	8.90	CCl_4
$Sn[S_2CN(CH_3)_2]_2$	–	3.04, 2.90	–	C_6H_6
$Sn[S_2CN(C_2H_5)_2]_2$	3.62[c]	1.12[c]	–	C_6H_6

[a] δppm downfield from internal tetramethylsilane. [b] J≃ 7Hz. [c] J ≃ 7Hz.

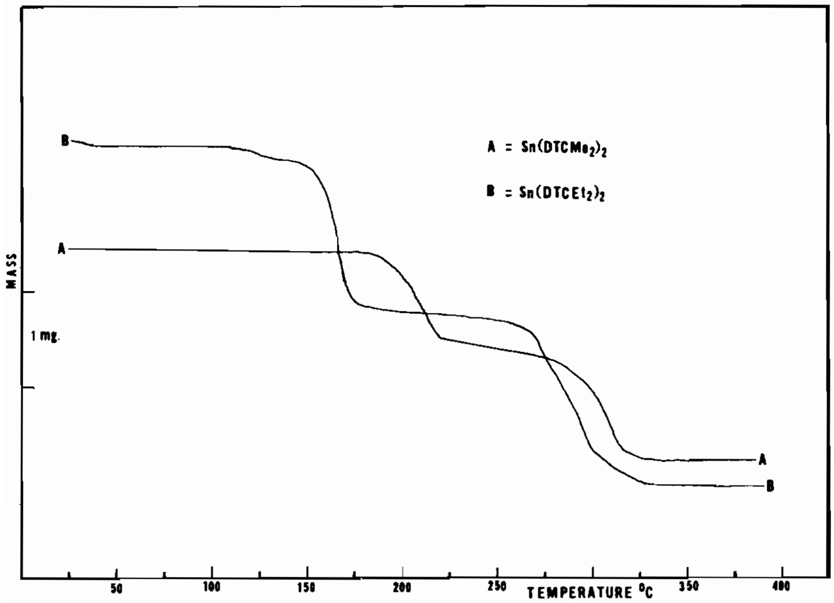

Figure 1. Thermogravimetry curves for $Sn(DTCMe_2)_2$ and $Sn(DTCEt_2)_2$.

found that diethyldithiocarbamato complexes of Co(II), Ni(II), Cu(II), Zn(II), and Hg(II) were volatile, usually at temperatures above 200° C. Although slight decomposition occurred during TG heating in most of the complexes, sublimation was the dominant effect. Figure 1 reveals the rather different thermal behavior of the tin–DTC complexes in which a two step weight loss is evident. In the case of III, weight loss steps of 30.4 and 34.1% occur, which indicates the loss of one, then a second DTC group (theoretical weight loss 33.5% each step). The weight loss curve of IV also shows two steps (in this case 36.3 and 38.5%) which may be compared to 35.7% weight loss steps expected for decomposition by consecutive DTC group loss. The nonvolatile residues of III and IV were 35.5 and 25.2%, respectively, which compare favorably with the values expected if tin alone were the residue (33.1% and 28.6%). Thus, the TG curves suggest the mechanism of thermal decomposition shown in equation [1]:

$$\begin{array}{l} Sn[S_2CNR_2]_2 \xrightarrow{\Delta} Sn(S_2CNR_2) + [S_2CNR_2] \\ \qquad\qquad\quad \downarrow \Delta \\ \qquad\qquad\quad Sn + [S_2CNR_2] \end{array} \qquad [1]$$

Support for this proposed mechanism comes from the mass spectra of III and IV (see Experimental) which both contain substantial peaks corresponding to $^{120}Sn[S_2CN(CH_3)_2]$ (m/e, 240) and $^{120}Sn[S_2CN(C_2H_5)_2]$ (m/e, 268). The other major peaks in the two spectra represent expected fragments of DTC group decomposition.

Freezing point depression measurements on IV in benzene solution gave an apparent molecular weight of 799. This corresponds approximately to a dimer species in this solvent. Conductivity measurements (Table II) on both DTC complexes in acetone and in dimethylsulfoxide solutions indicated that the compounds are essentially nonelectrolytes in these solvents. Titanium–DTC complexes have also been found[8] to be nonelectrolytes although essentially monomeric in benzene.

The infrared bands of III and IV are liested in Table III. Of particular interest are the C⩵N, C⩵S, and Sn⩵S stretching frequencies, which have been used to obtain information on the manner in which the DTC group bonds to the metal ion.[8, 10–13] Generally, the spectra of complexes with bidentate DTC groups contain only single bands for C⩵N and C⩵S absorp-

TABLE II. Conductivities of $Sn(DTC)_2$ Compounds.

Complex	Solvent	Molarity	Λ (cm²/ohm mol)
$Sn[S_2CN(CH_3)_2]_2$	acetone	$2.84 \times 10^{-4} M$	*3.69*
$Sn[S_2CN(C_2H_5)_2]_2$	acetone	$1.30 \times 10^{-4} M$	0.564
$Sn[S_2CN(CH_3)_2]_2$	dimethylsulfoxide	$3.89 \times 10^{-4} M$	11.0
$Sn[S_2CN(C_2H_5)_2]_2$	dimethylsulfoxide	$3.71 \times 10^{-4} M$	19.8, 17.8

TABLE III. Infrared Bands of Sn(DTC)$_2$ Complexes.

Complex	Bands (cm^{-1})
$Sn[S_2CN(CH_3)_2]_2$	2930 w, 1520 vs, br,[a] 1390 vs, br, 1255 vs, 1150 vs, br, 1052 s, 982 vs, 975 vs,[b] 890 w, 878 w, 580 vs, 450 vs, 390 w, 368 s,[c] 310 m
$Sn[S_2CN(C_2H_5)_2]_2$	2985 w, 2970 w, 2935 w, 2880 w, 1563 w, 1515 vs,[a] 1478 vs, 1472 vs, 1468 vs, 1442 vs, 1413 vs, 1385 vs, 1356 vs, 1302 vs, 1282 vs, 1268 vs, 1205 vs, 1152 vs, 1137 vs, 1103 m, 1098 s, 1083 s, 1078 s, 1069 s, 1010 s, 992 vs,[b] 919 vs, 914 vs, 895 m, 882 vs, 785 m, 780 m, 772 m, 605 w, 569 vs, 522 m, 492 w, 426 m, 381 vs,[c] 320 m, 313 m, 308 m

[a] $C\overset{\cdots}{-}N$ stretch. [b] $C\overset{\cdots}{-}S$ stretch. [c] Sn—S stretch.

tions, usually near 1500 and 1000 cm^{-1}, respectively. Spectra of complexes having both mono- and bidentate DTC ligands exhibit extra $C\overset{\cdots}{-}N$ and $C\overset{\cdots}{-}S$ absorptions near 1470 and 1000 cm^{-1}, such as is known for Sn (S$_2$CNEt$_2$)$_4$[13], which is actually six coordinate. According to our assignments, the $C\overset{\cdots}{-}N$ stretching bands of III and IV are those at 1520 and 1515 cm^{-1}, respectively, while those associated with $C\overset{\cdots}{-}S$ stretching appear at 975 and 992 cm^{-1}. Clearly in the case of the methyl derivative, only one $C\overset{\cdots}{-}N$ band is present indicating only bidentate DTC behavior. The $C\overset{\cdots}{-}S$ stretch region of III contains closely spaced doublet peaks (separation ~7 cm^{-1}) similar to those observed for Ti(S$_2$CNMe$_2$)$_5$ Cl.[8] The spectrum of IV is quite complex and the assignments should be regarded as tentative. The general conclusion that the DTC groups in III and IV are bidentate is entirely consistent with the published X-ray crystal structure of Sn(S$_2$CNEt$_2$)$_2$ which shows four coordinate tin.[3] The four coordination of tin, considered along with the presence of a valence shell lone pair, suggests that tin may incorporate valence *d* orbitals in bonding.[14]

We have assigned bands at 368 and 381 cm^{-1} as the Sn–S stretches in III and IV, indicating perhaps a slightly stronger DTC–Sn coordination in the diethyl derivative as expected from inductive considerations attributed to the different alkyl groups. The difference may well be too small for valid conclusions to be drawn, however.

One possible method by which to assess such inductive differences is via photoelectron spectra (ESCA).[15] Table IV lists the observed binding energies of selected tin and sulfur orbitals in the free elements[15] and in the compounds III and IV. The apparent binding energy of a particular orbital in an atom varies with the partial atomic charge, the higher the (positive)charge the higher the observed binding energy. Thus, by comparing binding energies in free elements and compounds, one can determine the sign and relative magnitude of the charge on a given atom. Thus, the binding energies of the tin 3d(3/2, 5/2) pair are 494.0 and 485.0 eV (Table IV). The binding energies of both these electrons increase when tin is involved in either of the DTC complexes, reasonably suggesting that the tin is experiencing a (relatively) positive oxidation state. Similarly the sulfur 2*p*(1/2, 3/2) binding energies decrease for the same comparison, suggesting sulfur is in a relatively negative oxidation state.

In principle comparison of tin or sulfur binding energies in the two complexes could indicate which have higher or lower oxidation states. The spectra data in Table IV, however, have a reproducibility of about ±1 eV, so the observed small differences in the binding energies in III and IV are probably not significant. It would thus appear that the complexes are electronically very similar.

Acknowledgement

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TABLE IV. Photoelectron (ESCA) Spectra of Sn(DTC)$_2$ Complexes.

Species	Binding Energy (eV)[a]			
	3*d*(3/2)	3*d*(5/2)	2*p*(1/2)	2*p*(3/2)
Sn^0	494.0[b]	485.0[b]	–	–
S^0	–	–	165.0[b]	164.0[b]
$Sn[S_2CN(CH_3)_2]_2$	495.0	486.4	163.3	163.3
$Sn[S_2CN(C_2H_5)_2]_2$	495.3	487.1	163.1	163.1

[a] Reproducibility ± 1 eV. [b] Reference 15.

We also appreciate the use of a thermogravimetry instrument belonging to W. W. Wendlandt and of an ESCA instrument at the Johnson Space Center, Houston, Texas.

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