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SOME DIORGANOTIN DITHIOCARBAMATES

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Abstract—Some new diorganotin dithiocarbamates of the formula $R_2Sn(dtc)_2$, (R = phenyl, benzyl, methyl, butyl, dtc. = dibutyl, diethyl, morpholine-, phenyl-, dimethyl- and piperidine dithiocarbamates) are described. The analytical, conductance, dipole moment, IR, proton magnetic resonance and electronic spectra data suggest an ester type structure with a monodentate dithiocarbamate moiety. Results obtained from thermogravimetric and differential thermal analysis are briefly discussed.

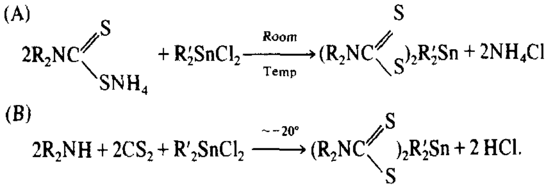
INTRODUCTION

The dithiocarbamate group in organotin derivatives can be monodentate[1] or bidentate[2, 3]. In some dialkyltin(IV) dithiocarbamates where geometry at the tin atom is intermediate between tetrahedral and octahedral arrangements, the presence of an isobidentate dithiocarbamate group has been suggested[4–5]. It was considered of interest to synthesize and establish the structure of some dithiocarbamates of the formula $R_2Sn(dtc)_2$, (R = phenyl, benzyl, methyl, butyl, dtc. = dibutyl-, diethyl-, morpholine-, phenyl-, dimethyl- and piperidine dithiocarbamates).

EXPERIMENTAL

Reagents. Ammonium salts of N-phenyl- and N,N-, dibutyl-, dithiocarbamic acids and ammonium morpholine or piperidine carbodithioates were prepared by the published method[6]. Dimethyl-, dibenzyl- and dibutyltin dichlorides were obtained from Alfa Inorganics (U.S.A.). Diphenyltin dichloride was prepared by the published method[7]. Solvents and amines were purified and dried before use by conventional methods.

Preparation of diorganotin (IV) bis dithiocarbamates. Diorganotin(IV) bis dithiocarbamates have been prepared either by the substitution (A) or insertion (B) reactions represented below:



(A)

$$2R_2NC\begin{matrix}\nearrow S\\ \searrow SNH_4\end{matrix} + R_2'SnCl_2 \xrightarrow[\text{Temp}]{\text{Room}} (R_2NC\begin{matrix}\nearrow S\\ \searrow S\end{matrix})_2R_2'Sn + 2NH_4Cl$$

(B)

$$2R_2NH + 2CS_2 + R'_2SnCl_2 \xrightarrow{\sim -20^\circ} (R_2NC\begin{matrix}\nearrow S\\ \searrow S\end{matrix})_2R_2'Sn + 2\,HCl.$$

Corresponding compounds with primary amines are similarly prepared.

Typical details of the two methods are described below.

Diphenyltin (IV) bis(morpholine N-carbodithioate). (A) To a suspension of ammonium morpholine N-carbodithioate (20 mmole) in 10 ml methanol was added a solution of diphenyltin dichloride (10 mmole) in 15 ml of the same solvent. The mixture was stirred at room temperature for about 1 hr and filtered. On distilling off the excess methanol white crystalline diphenyltin(IV) bis (morpholine-N-carbodithioate) was obtained. It was recrystallised from diethyl ether and dried in vacuum. M.p. 154–55°, yield 76%.

(B) To a mixture of diphenyltin dichloride (10 mmole) and carbon disulfide (10 ml) methanol, morpholine (20 mmole) in the same solvent was added dropwise at ~ –20°C and the mixture stirred for 2 hr. Excess of methanol was distilled off at reduced pressure and the residual yellow liquid on treatment with excess of diethyl ether yielded white crystalline diphenyltin bis (morpholine N-carbodithioate). It was recrystallised from diethyl ether and dried in vacuum. M.p. 154–55°, yield 70%.

Analysis. Carbon and hydrogen analysis were done by microanalytical techniques at the Central Drug Research Institute, Lucknow. The results of analysis are presented in Table 1.

Instrumentation. IR spectra of the solid compounds were recorded in Nujol between CsI plates in the region 4000–300 cm^{-1} using a Perkin-Elmer 521 spectrophotometer. Liquid samples were examined neat. Proton magnetic resonance spectra were measured at room temperature (30°C) with a Varian A 60 D spectrometer in deutrochloroform. Electronic spectra of solution in chloroform, in the concentration range 0.04–0.16×10^{-3}, were recorded with a Perkin-Elmer 202 spectrometer using a 1 cm quartz cell. The electrolytic conductance of 10^{-3} M solutions in nitrobenzene was measured using a Philips conductivity assembly PR 9500. Molecular weights were determined cryoscopically in benzene using a Beckmann thermometer of accuracy ∓0.01.

RESULTS AND DISCUSSION

The elemental analysis, melting point and molecular weight of the compounds are listed in Table 1. All the products are crystalline with sharp m.ps except dibutyltin and diphenyltin bis (dibutyl dithiocarbamates) which are liquid. They are stable at room temperature, unaffected by atmospheric oxygen and moisture and are soluble in common organic solvents except methanol and ethanol in which they dissolve sparingly. The molecular weights of the compounds in benzene and the conductance measurement indicate the covalent nature of the compounds and absence of ionic species in solution. The thermogravimetric analysis of the compounds shows that they are stable upto 100°C. On further heating decomposition starts and eventually it yields an involatile residue of tin metal. On differential thermal analysis the intense endothermic peak at 165°C for diphenyltin(IV) bis (morpholine-N-carbodithioate) may be due to melting of the compound while the exothermic peak at 294° may be attributed to change in phase of the intermediate products. The electric dipole moment values of the compounds obtained by Guggenheim's method[8] are in the range (2.10–3.32 D) which support the presence of a monodentate dithiocarbamate group.

IR spectra. The IR absorption frequencies of diagnostic value in relation to the bonding are given in Table 2.

A comparasion of the C–N stretching modes in different diorganotin(IV) morpholine dithiocarbamates shows that it is sensitive to the nature of organic group attached to the metal atom. The presence of relatively more electron releasing groups causes a gradual lowering of the C–N bond order in the sequence, aryl > alkyl. There is also a shift in the C–N bond stretching frequencies with change in the organic group at the

Table 1. Experimental data for $R_2Sn(dtc)_2$

No	R	Compound dtc.	Solvent % yield.	M.p. (°C)	Mol. wt Found (calcd)	Analysis % Found (Calcd) Sn	C	H
1.	Ph	Dibutyl	Acetone 55	Oily	675 (681)	17.45 (17.47)	52.84 (52.86)	6.63 (6.75)
2.	Ph	Morpholine	Acetone 78	154–56	576 (597)	19.88 (19.93)	44.20 (44.22)	4.32 (4.36)
3.	Ph	Phenyl	Methanol 63	142–44	597 (609)	19.55 (19.54)	51.21 (51.23)	3.61 (3.61)
4.	Bz	Dimethyl	Methanol 88	161–62	538 (541)	21.97 (21.99)	44.36 (44.36)	4.80 (4.80)
5.	Bz	Morpholine	Acetone 72	135–36	593 (625)	19.02 (19.04)	46.00 (46.08)	4.75 (4.80)
6.	Me	Morpholine	Acetone 68	148–50	468 (473)	25.16 (25.16)	30.42 (30.44)	4.63 (4.63)
7.	Bu	Dimethyl	Methanol 86	89–91*	452 (473)	25.15 (25.16)	35.51 (35.51)	6.30 (6.34)
8.	Bu	Morpholine	Acetone 78	165–66	537 (557)	21.35 (21.36)	38.78 (38.78)	6.07 (6.10)
9.	Bu	Piperidine	Benzene 76	85	547 (553)	21.48 (21.51)	43.43 (43.41)	6.88 (6.87)
10.	Bz	Diethyl	Methanol 86	80	565 (597)	19.86 (19.93)	48.24 (48.25)	5.61 (5.69)
11.	Bu	Dibutyl	Benzene 72	Oily	635 (641)	18.54 (18.56)	48.68 (48.67)	8.41 (8.42)

†Ref. [16].

Table 2. Characteristic IR bands (cm^{-1}) of $R_2Sn(dtc)_2$

No.†	νC$\simeq$N	νC=S	νC–S	νSn–C	Out-of-plane ring bending and skeletel modes of vibrations	νSn–S
1.	1510 vs	1023 s	1000 s			
2.	1478 vs	1020 vs	998 vs	—	—	—
3.	1450 s	1005 m	1000 m	—	—	
4.	1481 vs	1028 m	999 vs	562 m	434 vs 430 sh	355 vs 395 vs
5.	1468 vs	1022 vs	998 vs	—	—	—
6.	1463 vs	1023 s	1000 vs	555 m 515 w	430 vs	360 vs
7.	1478(br, vs)	1015 m	984 vs	611 w	463 vs 442 s	375 vs
8.	1460 vs	1025 vs	999 vs	615 m 500 w	435 vs 430 sh	365 s
9.	1493 vs	1032 vs	996 vs	—	—	—
10.	1479 s	1020 vs	1005 m	—	—	—
11.	1475 vs	1010 w	980 s	—	—	—

†Number refers to compounds in Table 1.

nitrogen atom in the order:

alkyl > heterocycle > aryl.

The high electron releasing ability of the alkyl group shifts the C–N bond order to a high value. For heterocyclic carbodithioates, the small negative shift as compared to alkyl dithiocarbamates may be due to the rigid heterocyclic system which shows a comparatively smaller tendency to release electron[9]. The negative shift is more prominent in the case of morpholine carbodithioates compared with piperidine carbodithioates due to the presence of the electronegative oxygen atom at the *p*-position.

Whether the dithiocarbamate moiety is monodentate or bidentate is reflected in the C–S stretching frequency[10]. The presence of two bands around $1000\,cm^{-1}$ due to C–S and C=S stretching modes indicates a monodentate dithiocarbamate group in the compound[1, 11]. Unlike the C–N stretching frequencies, C–S stretchings are not significantly affected by change in the nature of the organic groups either at the tin or the nitrogen atoms.

Far IR spectra. The spectra of a few compounds were recorded up to $300\,cm^{-1}$ and a band at $373 \pm 12\,cm^{-1}$ is assigned to the Sn–S stretching mode in agreement with previous reports[12]. This absorption is significantly affected by the nature of the organic groups attached to the metal atom. Thus like νC–N an electron releasing alkyl group strengthens the bond and shifts the absorption to a higher frequency while electron withdrawing aryl groups cause a negative shift in the absorption.

Electronic spectra. The absorption maxima (λ max) and the molar absorptivities (log ϵ) of the compounds are

Table 3. Electronic spectra of $R_2Sn(dtc)_2$

No.†	λ max (nm)	Log ε
2.	255	4.27
	287	3.57
7.	257	4.22
	278	4.21
8.	265	4.06
	285	3.30

†Nos. refer to Table 1.

Table 4. ^{1}HNMR spectra of $R_2Sn(dtc)_2$ at ~30°C

No.†	Assignment τ^b (ppm)
1.	2.00–2.50 (m, 10, Ar–H)
	6.34 (t, 4, N–CH_2)
	8.04–9.24 (m, 14, rest aliphatic H)
6.	5.91 (t, 4, O–CH_2)
	6.3 (t, 4, N–CH_2)
	8.5 (S, 6, Sn–CH_3)

†Nos. refer to Table 1.

b, center of signals, s, singlet, t, triplet, m, multiplet.

collected in Table 3. The electronic spectra of solutions of the compounds in chloroform show two bands at 259 ± 8 nm and 284 ± 6 nm due to intraligand transitions. The former band is assigned to the $\pi \rightarrow \pi^*$ transition in the CS_2 group[13]. The presence of single strong absorption at ~255 nm suggests a monodentate dithiocarbamate moiety in the compounds[14].

Proton magnetic resonance spectra. ^{1}HNMR data listed in Table 4 indicate that all the compounds show two groups of signals due to R_2Sn and NR_2 protons. The latter gives two sets of signals. The presence of two sets of NR_2 signals in the compounds suggests that the two alkyl groups bonded to the nitrogen atom become magnetically non equivalent due to a high rotation barrier around C–N bond[15]. The spectra and their integration agree well with the proposed stoichiometry of the compounds. The data collected above support the conclusion that both the dithiocarbamate groups in the derivatives examined are monodentate and the tin atom is tetracoordinated.

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