

Coordination Chemistry of Organotin(IV) Dithiocarbamate Complexes

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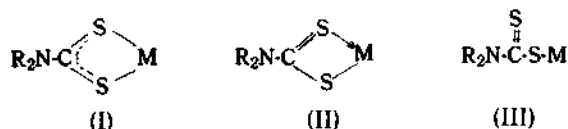
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Coordination chemistry of organotin(IV) dithiocarbamate complexes has been examined in terms of far infrared and ^{119}Sn -NMR spectroscopies. Although the Sn-S stretching vibrational bands of the complex could not be correlated with the bonding nature of the dithiocarbamate ligand, ^{119}Sn chemical shifts were sensitive enough to distinguish clearly the coordination number of tin, and as such the bonding mode of the dithiocarbamate ligand could be identified to be monodentate or bidentate. Thus the ^{119}Sn -NMR study on new cyclohexyltin(IV) dithiocarbamate complexes along with the known complexes suggests that the bonding mode of the dithiocarbamate ligands and the consequent coordination number of tin are determined mainly by the inductive effects of the organic groups attached to the tin atom.

Introduction

Numerous organotin(IV) dithiocarbamate complexes have been subjected to X-ray crystallographic studies¹⁻¹⁴ in order to understand the coordination chemistry of organotin complexes. Depending on the coordination mode of dithiocarbamate ligand, the local geometry around tin(IV) atom is variable, and as such the coordination number of tin atom ranges from 4 to 7.

It is well known that the dithiocarbamate ligand of organotin(IV) dithiocarbamates may coordinate to tin(IV) atom in three different ways,^{15,16} that is, as bidentate(I), anisobidentate(II) or monodentate(III). In the anisobidentate mode the



two metal to sulfur bonds are not equivalent. Bonati and Ugo¹⁷ attempted to correlate the C-S stretching vibrational mode appearing in the range 950-1050 cm^{-1} with bonding type of the $-\text{CS}_2$ moiety, and thus proposed that a single symmetrical peak in this region is indicative of bidentate coordination whereas splitting of the peak indicates monodentate or anisobidentate bonding. However, in recent years the validity of the Bonati-Ugo method was questioned by Kellner, *et al.*,¹⁸ who has proved that the $\nu(\text{C-S})$ band can not be used for discerning the bonding type of $-\text{CS}_2$ moiety due to its intraligand coupling with the $\nu(\text{R-N})$ modes.

On the other hand, Otera^{19,22} recently has shown that ^{119}Sn -NMR may be used as a tool for characterizing the tin coordination of organotin(IV) compounds including dithiocarbamate ligands since the ^{119}Sn chemical shift is strongly dependent on the coordination number of tin atom.

In this paper the coordination chemistry of various organotin(IV) dithiocarbamates will be examined by means of ^{119}Sn -NMR and far IR spectroscopy reflecting the stretching frequencies of Sn-X bonds where X represents coordinating atoms.

Experimental

Reagent grade chemicals for syntheses were used without further purification. Chemical analyses were carried out by

the Chemical Analysis Laboratory at KAIST. The far infrared spectra in the 300-700 cm^{-1} region were measured both in KBr pellets and in Nujol mull between CsI cell with a Perkin-Elmer 283B spectrophotometer. ^{119}Sn -NMR spectra with complete proton noise decoupling were measured on Bruker AM-200 spectrometer operating at 74.63 MHz in pulse mode with Fourier transform at ambient temperature. The deuterated solvent(CDCl_3) was used as internal lock. The chemical shifts were relative to external neat tetramethyltin (TMT).

Preparation of $\text{Cy}_2\text{Sn}(\text{mdtc})_2$. A solution of 3.58g (20 m mole) sodium N,N-dimethyldithiocarbamate(Na-mdtc) dissolved in 100 ml of ethanol was added dropwise to a solution of 4.45g (100 m mole) dicyclohexyltin(IV)dibromide(Cy_2SnBr_2) in 50 ml of chloroform, and the mixture was stirred for 30 min. The NaBr formed was removed by filtration. The filtrate was evaporated to yield $\text{Cy}_2\text{Sn}(\text{mdtc})_2$ (86%) which was recrystallized from chloroform-petroleum ether mixture(1:1). Anal. Calcd. for $\text{C}_{18}\text{H}_{34}\text{N}_2\text{S}_4\text{Sn}$: C, 41.15; H, 6.52; N, 5.33. Found: C, 41.08; H, 6.58; N, 5.35.

Preparation of $\text{Cy}_2\text{SnBr}(\text{mdtc})$. 1.79g (10 m mole) Na-mdtc in ethanol was treated with 4.45g (10 m mole) Cy_2SnBr_2 in chloroform in the same method as used for preparation of $\text{Cy}_2\text{Sn}(\text{mdtc})_2$. An off-white solid product was obtained in 88% yield. Anal. Calcd. for $\text{C}_{15}\text{H}_{28}\text{NS}_2\text{BrSn}$: C, 37.14; H, 5.82; N, 2.89. Found: C, 37.10; H, 5.86; N, 2.91.

Preparation of $\text{Cy}_3\text{Sn}(\text{mdtc})$. Reaction of Tricyclohexyltin bromide(Cy_3SnBr) with the mdtc ligand in the mole ratio of 1:1 according to the same method for $\text{Cy}_2\text{Sn}(\text{mdtc})_2$, followed by recrystallization from chloroform, resulted in white crystalline solid with 90% yield. Anal. Calcd. for $\text{C}_{21}\text{H}_{39}\text{NS}_2\text{Sn}$: C, 51.65; H, 8.05; N, 2.87. Found: C, 51.50; H, 8.11; N, 2.91.

Preparation of $(\text{Cy}_3\text{Sn})_2(\text{ebdte})$. A solution of 1.82g(5 m mole) disodium ethylenebis(dithiocarbamate)($\text{Na}_2\text{-ebdte}$) in 100 ml of ethanol was added dropwise to a solution of 4.48g(10 m mole) Cy_3SnBr in 100 ml of chloroform. After the reaction mixture was cooled to about 0°C, the NaBr formed was removed by filtration. The filtrate was evaporated to yield a solid product(85%) which was recrystallized from a chloroform-n-hexane mixture(1:1). Anal. Calcd. for $\text{C}_{40}\text{H}_{72}\text{N}_2\text{S}_4\text{Sn}_2$: C, 50.75; H, 7.62; N, 2.96. Found: C, 50.46; H, 7.47; N, 2.89.

Preparation of $(t\text{-Bu})_2\text{SnCl}(\text{mdtc})$. Na-mdtc was reacted with di-*t*-butyltin(IV) dichloride($(t\text{-Bu})_2\text{SnCl}_2$) in equimolar ratio by the same procedure for the preparation of

Table 1. Local Geometries of Tin and Far IR Bands of Organotin(IV) Dithiocarbamate Complexes

Compounds	Local geometry* of Tin	$\nu(\text{Sn-C})$, cm^{-1}	$\nu(\text{Sn-S})$, cm^{-1}	$\nu(\text{Sn-Cl})$, cm^{-1}
$\text{Me}_3\text{Sn}(\text{mdtc})^1$	Th	560(s) 545(s)	356(s)	--
$\text{Me}_2\text{Sn}(\text{mdtc})_2^2$	Oh	560(s) 540(s)	355(s)	--
$\text{Me}_2\text{SnCl}(\text{mdtc})^3$	Tbp	555(s) 515(s)	395(s)	268(s)
$\text{Me}_2\text{Sn}(\text{edtc})_2^4$	Oh	556(s) 540(s)	378(s) 360(s)	--
$\text{MeSn}(\text{edtc})_3^5$	Pbp	552(s)	375(s) 350(s)	--
$\text{Sn}(\text{mdtc})_4^6$	Oh	--	375(s)	--
$(t\text{-Bu})_2\text{Sn}(\text{mdtc})_2^9$	Tbp	560(s) 545(s)	370(s) 348(s)	--
$[(t\text{-Bu})_2\text{Sn}(\text{ebdtc})]_2 \cdot 4\text{THF}^8$	Tbp	545(m) 510(m)	370(s) 330(m)	--

* Th, Tetrahedron; Oh, Octahedron; Tbp, Trigonalbipyramid; Pbp, Pentagonalbipyramid

$\text{Cy}_2\text{SnBr}(\text{mdtc})$. The resulting solid obtained in 94% yield was recrystallized from dichloromethane to yield an off-white crystalline solid. Anal. Calcd. for $\text{C}_{11}\text{H}_{24}\text{NS}_2\text{ClSn}$: C, 34.00; H, 6.23; N, 3.60. Found: C, 34.24; H, 6.19; N, 3.62.

Other known organotin(IV) dithiocarbamates employed in this study were prepared according to the literature methods: $\text{MeSn}(\text{mdtc})_3^5$, $\text{MeSn}(\text{edtc})_3^5$ (edtc = diethyldithiocarbamate), $\text{Me}_2\text{Sn}(\text{mdtc})_2^2$, $\text{Me}_2\text{Sn}(\text{edtc})_2^2$, $\text{Me}_2\text{SnCl}(\text{mdtc})^3$, $\text{Me}_3\text{Sn}(\text{mdtc})^1$, $(t\text{-Bu})_2\text{Sn}(\text{ebdtc}) \cdot 4\text{THF}^8$, $(t\text{-Bu})_2\text{Sn}(\text{mdtc})_2^9$, and $\text{Sn}(\text{mdtc})_4^6$.

Results and Discussion

Among the organotin(IV) and tin(IV) dithiocarbamates which have already been structurally known by X-ray crystallography, selected compounds were examined in the far infrared region in order to see if there is any correlation between Sn-X stretching modes where X represents coordinating atoms and the bonding type of the dithiocarbamates.

In Table 1 are given the far infrared bands of Sn-X skeleton vibrations of the selected dithiocarbamates showing relatively simple vibrations in this region. The vibrational spectra of SnC_3 - and SnC_2 -moieties in trimethyltin and dimethyltin derivatives have already been studied in detail.^{24,25} If the Sn-C stretching modes appearing in the 500-600 cm^{-1} region are observed as two peaks, the configuration of SnC_3 group is nonplanar or that of SnC_2 is nonlinear. However, if only one Sn-C stretching band appears, the configuration of SnC_3 group is planar or that of SnC_2 is linear. All the di- and trialkyltin(IV) dithiocarbamates in the table exhibited two $\nu(\text{Sn-C})$ bands, which is consistent with their known structures but does not give any informations on the whole coordination feature of tin atom. Instead, the vibrational pattern of Sn-S bonds is the key for determination of coordination number of tin. Theoretically, in a chelated dithiocarbamate-tin bonding structure two symmetric and asymmetric Sn-S stretching vibrations are expected whereas only one Sn-S stretching band is expected in a monodentate dithiocarbamate-

Table 2. ^{119}Sn Chemical Shifts, $\delta(^{119}\text{Sn})$, and Coordination Numbers of Dithiocarbamate-tin(IV) Complexes

Compounds	$\delta(^{119}\text{Sn})$, ppm	Coord. No.	Ref.
Me_4Sn	0	4	(28)
Me_3SnCl	+166	4	(28)
Me_2SnCl_2	+137	4	(28)
$\text{Me}_3\text{Sn}(\text{mdtc})$	+25	4	(29)
$\text{Me}_2\text{SnCl}(\text{mdtc})$	-204	5	(29)
$\text{Me}_2\text{SnCl}(\text{edtc})$	-201	5	(29)
$\text{Me}_2\text{SnBr}(\text{edtc})$	-233	5	(28)
$(t\text{-Bu})_2\text{Sn}(\text{mdtc})_2$	-255	5	(22)
$\text{Me}_2\text{Sn}(\text{mdtc})_2$	-338	6	(29)
$\text{Me}_2\text{Sn}(\text{edtc})_2$	-333	6	(29)
$\text{Ph}_2\text{Sn}(\text{mdtc})_2$	-501	6	(29)
$\text{MeSn}(\text{mdtc})_3$	-786	7	(21)
$\text{PhSn}(\text{mdtc})_3$	-695	7	(21)

te-tin bonding structure. The assignments of $\nu(\text{Sn-S})$ bands in the table could be made easily, since the Sn-S stretching frequencies ranging from 360 to 420 cm^{-1} are distinguishable from Sn-C stretching frequencies.^{26,27} The appearance of a single Sn-S stretching frequency in the tetrahedral tin compound, $\text{Me}_3\text{Sn}(\text{mdtc})$, is in accordance with its X-ray structural data¹ showing that the dithiocarbamate ligand in the compound acts as monodentate. However, the appearances of a single Sn-S stretching band in the chelated dithiocarbamate complexes, $\text{Me}_2\text{Sn}(\text{mdtc})_2^2$, $\text{Me}_2\text{SnCl}(\text{mdtc})^3$ and $\text{Sn}(\text{mdtc})_4^6$ can hardly be explained. Furthermore, the observed pattern of Sn-S stretching vibrations does not reflect coexistence of two different bonding modes of dithiocarbamate ligands in a molecule of such complexes as $\text{Sn}(\text{mdtc})_4^6$, $[(t\text{-Bu})_2\text{Sn}(\text{ebdtc})]_2 \cdot 4\text{THF}^8$ and $(t\text{-Bu})_2\text{Sn}(\text{mdtc})_2^9$. Consequently, it may be concluded that the far infrared spectra of Sn-C and Sn-S stretching vibrations can hardly be used for discerning the bonding type of dithiocarbamate-tin(IV) complexes.

Contrary to such unpredictable results of the infrared data, the ^{119}Sn -NMR spectroscopy has been found to be useful for elucidation on the nature of coordination in the dithiocarbamate-tin(IV) complexes. It is known that the ^{119}Sn chemical shift, $\delta(^{119}\text{Sn})$, is sensitive to the chemical environments of the tin atom.²⁸ In particular, Otera, *et al.*,¹⁹⁻²¹ have found that $\delta(^{119}\text{Sn})$ is strongly dependent on the coordination number of tin atom and thus $\delta(^{119}\text{Sn})$ moves upfield by 60-150 ppm with a change of the coordination number of tin from 4 to 5, by 130-200 ppm from 5 to 6, and approximately 150-300 ppm from 6 to 7. In Table 2 reported $\delta(^{119}\text{Sn})$ values relative to SnMe_4 of organotin(IV) dithiocarbamate complexes are listed depending on their coordination number, and it is seen from the plotted Figure 1 that there is an approximate linear relationship between the $\delta(^{119}\text{Sn})$ values and the coordination numbers of the complexes. Although, for each of the same coordination number, some wide ranges of $\delta(^{119}\text{Sn})$ values are observed depending on the different organic and dithiocarbamate groups, fortunately the $\delta(^{119}\text{Sn})$ values of dithiocarbamate-tin(IV) complexes with different coordination numbers do not overlap with each other. Of course, such a relationship is valid for dithiocarbamate-tin(IV) complexes, and will break if dithiocarbamate ligand is replaced by other anionic ligands with different

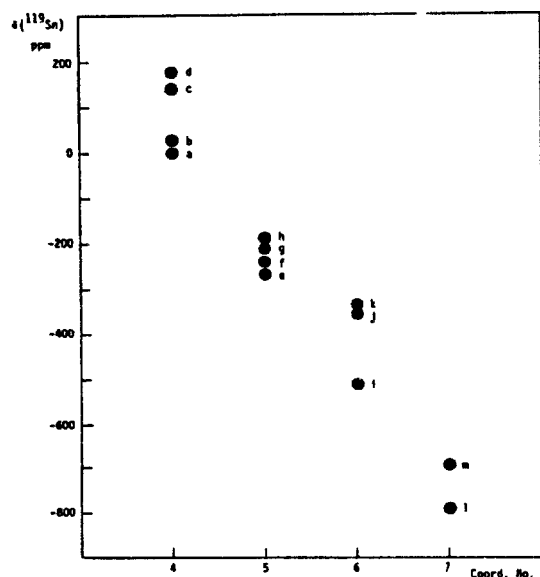


Figure 1. ^{119}Sn chemical shifts vs coordination number of Me_4Sn (a), $\text{Me}_3\text{Sn}(\text{mdtc})(\text{b})$, $\text{Me}_2\text{SnCl}_2(\text{c})$, $\text{Me}_3\text{SnCl}(\text{d})$, $(\text{t-Bu})_2\text{Sn}(\text{mdtc})_2(\text{e})$, $\text{Me}_2\text{SnBr}(\text{edtc})(\text{f})$, $\text{Me}_2\text{SnCl}(\text{mdtc})(\text{g})$, $\text{Me}_2\text{SnCl}(\text{edtc})(\text{h})$, $\text{Ph}_2\text{Sn}(\text{mdtc})_2(\text{i})$, $\text{Me}_2\text{Sn}(\text{mdtc})_2(\text{j})$, $\text{Me}_2\text{Sn}(\text{edtc})_2(\text{k})$, $\text{MeSn}(\text{mdtc})_3(\text{l})$, $\text{PhSn}(\text{mdtc})_3(\text{m})$.

Table 3. $\delta(^{119}\text{Sn})$ Values of Cyclohexyltin(IV) Dithiocarbamate Complexes

Compounds	Solvent	$\delta(^{119}\text{Sn})$, ppm	Coord. No.
$\text{Cy}_2\text{Sn}(\text{mdtc})_2$	CHCl_3	-374	6
$\text{Cy}_2\text{SnBr}(\text{mdtc})$	CHCl_3	-239	5
$(\text{t-Bu})_2\text{SnCl}(\text{mdtc})$	CHCl_3	-224	5
$\text{Cy}_3\text{Sn}(\text{mdtc})$	CHCl_3	-20	4
$(\text{Cy}_3\text{Sn})_2(\text{ebdtc})$	CHCl_3	-1	4

donor atoms.

We have already seen in Table 1 and 2 that the dithiocarbamate ligand acts as a chelating ligand or as a monodentate. In particular, it is interesting that both types of coordination of dithiocarbamate ligands coexist in $(\text{t-Bu})_2\text{Sn}(\text{mdtc})_2$ resulting in a pentacoordinate structure unlike the similar compounds $\text{Me}_2\text{Sn}(\text{mdtc})_2$ and $\text{Me}_2\text{Sn}(\text{edtc})_2$ of octahedral six coordinate structure. Otera, *et al.*,²² pointed out that t-butyl group reduces the acceptor property of tin by means of both inductive and steric effects. In order to evaluate the effect of alkyl groups on the nature of coordination in dithiocarbamatotin(IV) complexes, new complexes involving cyclohexyl group close to t-butyl group in bulkiness but median between methyl and t-butyl group in inductive effect, were prepared, and their ^{119}Sn chemical shifts measured are listed along with their coordination number deduced in Table 3.

From Table 2 or Figure 1 $\delta(^{119}\text{Sn}) = -374$ for $\text{Cy}_2\text{Sn}(\text{mdtc})_2$ indicates that the tin atom in the complex is hexa-coordinated and thus both dithiocarbamate ligands act as chelating ligand. The $\delta(^{119}\text{Sn})$ values of $\text{Cy}_2\text{SnBr}(\text{mdtc})$ and $(\text{t-Bu})_2\text{SnCl}(\text{mdtc})$ imply that they are both five-coordinate complexes also with chelating dithiocarbamate ligands. However, the $-\text{CS}_2$ moiety acts as monodentate in both tricyclohexyltin(IV) dithiocarbamate complexes in the table since their $\delta(^{119}\text{Sn})$ values clearly indicate that their coordination numbers are 4.

Such results suggest that the acceptor property of tin toward sulfur donor atom is strongly dependent upon the inductive effect of organic groups on the tin atom. Thus trialkyltin(IV) compounds seem not to allow more than one sulfur-coordination to tin whereas monoalkyltin(IV) compounds are capable to accept even six sulfur donor atoms resulting in seven-coordinate complexes. Since many six-coordinate $(\text{t-Bu})_2\text{Sn}(\text{IV})$ -complexes are known,²² the inductive effect by t-butyl groups in $(\text{t-Bu})_2\text{Sn}(\text{IV})$ -complexes seems to play a major role in reduction of the acceptor property of tin to afford only three sulfur donor atoms while four sulfur-tin bondings are allowed in dimethyl- and dicyclohexyltin(IV) compounds. Such a strong electronic effect on the acceptor property of tin is probably due to difficult availability of energetically high empty 5d orbitals, which is characteristic of main group elements in their coordination chemistry.

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Spectral and Thermal Studies of Transition Metal PSSA Ionomers

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Transition metal PSSA ionomers containing Co(II), Ni(II), Cr(III), Ru(III), and Rh(III) are investigated by IR, Far-IR, UV-Vis and DSC. Reliable IR Spectroscopic criteria are established for assessing the degree of ion-exchange of PSSA ionomers and the local structures around metal cations in them. In the hydrated transition metal PSSA ionomers, the ionic groups are solvated by water molecules and there is no significant interactions between sulfonate group and metal cations. The visible spectra indicated that metal cations are present as $[M(H_2O)_6]^{n+}$ with Oh symmetry. Their T_g values increase as the extent of ionic site concentration increases, but there is no direct dependence of T_g on the nature of metal cations or their oxidation states. Thus, the water content in PSSA ionomer is found to have dominant influence on T_g of hydrated transition metal PSSA ionomers. Dehydration of the hydrated transition metal PSSA ionomers results in direct interaction between ionic groups and significant color changes of the ionomers due to the changes of the local structures around metal cations. On the base of spectral data, their local structures are discussed. In case of dehydrated 12.8 and 15.8 mol % transition metal PSSA ionomers, no glass transition is observed in 25-250 °C region and this is believed to arise from the formation of highly cross-linked structures caused by direct coordination of sulfonate groups of metal cations. In the 6.9 mol % transition metal PSSA ionomers, the glass transition is always observed whether they are hydrated or dehydrated and this is thought to be caused by the sufficient segmental mobility of the polymer backbone.

Introduction

Ionomers are a relatively new class of amorphous materials based on organic polymers that are functionalized with ionic groups such as SO_3^- or COO^- .¹⁻⁵ These materials have been under intensive study in recent years because of their potential applications such as gas separation materials, heterogeneous catalytic supports and solid state ionic electrolytes for use in batteries.⁶⁻¹⁰

Sulfonated linear polystyrene(PSSA) which is among the typical ionomers was developed by Lundberg and coworkers at EXXON^{11,12} and related research on these PSSA ionomers has been focused on the questions of whether ionic domains form, what structures exist in them, how they depend on ionic site concentrations or on the nature of cations and how their properties, especially, their glass transition temperatures vary with cations, anionic site concentrations and thermal history. In 1984, Mattera and Risen carried out a series of systemic spectroscopic studies and reported the dependence of properties of the PSSA ionomers on the ionic site concentrations and the nature of the metal cations in alkali and alkaline earth metal PSSA ionomers, in which cation site attractions are coulombic in nature.¹³ Also, some interesting catalytic reactivity of rhodium and ruthenium metals, con-

tained within the ionic domain of PFSA and PSSA ionomers, was reported recently.^{14,15,16}

However, there has been no reports about the study of the metal site interactions and the effect of transition metal on the thermal property of transition metal PSSA ionomers, which is believed to be important for the development of ionomer supported catalyst system.

In this background, several PSSA ionomers containing Co(II), Ni(II), Cr(III), Ru(III), and Rh(III) ions at different ionic site concentration have been investigated by various spectroscopic methods and the differential scanning calorimetry. The results are reported in this paper.

Experiments

The sulfonated linear polystyrene(PSSA) ionomers were kindly provided by Dr. R.D. Lundberg of the EXXON Research and Engineering Co. who developed the materials.¹⁷ Their chemical composition can be represented as follows:

