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Synthesis, Properties, and Characterization of Some Mixed Ligand Complexes of Tin (IV). (Dialkyldithiocarbamato) (β -Diketonato) (Bromo) Tin (IV)



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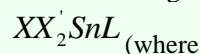
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ABSTRACT

A few mixed ligand complexes of tin(IV) of the type,



$X = Br$, $X' = (C_2H_5)_2 NCS_2$, $(n-C_4H_9)_2 NCS_2$, $HL =$ acetylacetonate, benzoylacetonate, and dibenzoyl methane) have been prepared and characterized. These are generally orange solids and are monomeric. IR, 1H and ^{119}Sn NMR spectral studies suggest six coordination around tin(IV) with a bidentate attachment of both the dithiocarbamate and monodentate attachment of the β -diketonate moieties.



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INTRODUCTION

A considerable number of complexes of tin(IV) have been reported¹⁴⁻¹⁸ in the literature with a variety of ligands¹⁻¹³, yet only a few mixed ligand complexes of tin(IV) have been reported¹⁴⁻¹⁸ so far. Although crystal structure analysis of $Cl_2Sn(S_2CNEt_2)_2$ ¹⁹; $Cl_2Sn(acac)_2$ ⁵; $X_2Sn(S_2COEt_2)^{6,8}$ ($X = Cl, Br, I$), $(S_2CNEt_2)_2Sn(CH_3COCHCSCCH_3)^{15}$ and $(S_2CNEt_2)_2Sn(C_9H_6NO)_2$ ²⁰ have been reported in which tin acquires hexa coordination. During present investigations, we are interested in the properties of new derivatives of tin(IV), $XX'SnL$ ($X = Br, X' = (C_2H_5)_2NCS_2, (\underline{n}-C_4H_9)_2NCS_2, HL =$ acetylacetonone, benzoylacetonone, and dibenzoylmethane) containing more than two different types of ligands.

MATERIALS AND METHODS

Precautions were taken to exclude moisture. Solvents were dried by standard techniques²¹. Molecular weight was determined in chloroform using KNAUER vapor pressure osmometer. Infrared spectra (Nujol and KBr Pellets) were recorded on a Perkin-Elmer 577 spectrophotometer and ¹H and ¹¹⁹Sn NMR spectra on a Jeol FX90Q MHz spectrometer using TMS as the external reference (for ¹H) and tetramethyl tin (for ¹¹⁹Sn) as the external reference.

Sulfur was determined gravimetrically as barium sulfate (Messenger's method)²². Nitrogen and bromide were estimated volumetrically by Kjeldhal's and Vohlard's methods²². Tin was estimated gravimetrically by ignition of a sample with conc. nitric acid followed by weighing as tin (IV) oxide²².

Derivatives of the type, $Sn(S_2CNR_2)_2$ (where $R = C_2H_5$, and $\underline{n}-C_4H_9$) have been prepared by a reported method²³.

All the Mixed ligand complexes have been synthesized by a similar route and hence, the synthesis of only one representative is described below.

Synthesis of $Br_2Sn(S_2CN(C_2H_5)_2)_2$

Bis (diethyl dithiocarbamate)tin(II)(3.45 g, 8.31 mmol) was suspended in ice-cold chloroform, and solution of the bromine (1.45g, 9.08 mmol) in the same solvent was added

dropwise when the color of the bromine disappeared instantaneously. After completing the addition, stirring was continued for 1 hour. The product, dibromo bis (diethyldithiocarbamate) tin(IV) was filtered and dried under reduced pressure. The product was further purified by recrystallization from dichloromethane and *n*-hexane and dried under a vacuum. (Yield 4.55g, 95%)

Anal % found: Sn, 20.47, S, 22.16, N, 4.45 Br, 27.85

Calcd for $Br_2Sn(S_2CN(C_2H_5)_2)_2$; Sn, 20.64; S, 22.30 N, 4.87, Br, 27.79.

Details of the synthesis of other derivatives have been summarized in Table -1.

Table No 1: Synthetic, Analytical, and Physical data for the complexes

S. No.	Reactants	Product (% Yield)	Molecular weight found (Calcd)	Analyses % found (Calcd)				
				Sn	S	N	Br	
	$Br_2Sn(S_2CNR_2)_2$	Na β -diketonate)						
1	1.98 (3.44)	0.45 (3.68)	$BrSn(S_2CN(C_2H_5)_2)_2(CH_3COCHCOCH_3)$ (85)	575 (594.22)	19.46 (19.97)	20.92 (21.58)	4.43 (4.71)	13.29 (13.45)
2	2.10 (3.65)	0.69 (3.75)	$BrSn(S_2CN(C_2H_5)_2)_2(CH_3COCHCOC_6H_5)$ (82)	562 (656.29)	17.86 (18.08)	19.22 (19.54)	4.09 (4.27)	12.01 (12.17)
3	2.02 (3.51)	0.87 (3.53)	$BrSn(S_2CN(C_2H_5)_2)_2(C_6H_5COCHCOC_6H_5)$ (79)	595 (718.37)	16.15 (16.52)	17.54 (17.85)	3.82 (3.90)	11.01 (11.12)
4	2.12 (3.08)	0.40 (3.28)	$BrSn(S_2CN(C_4H_9)_2)_2(CH_3COCHCOCH_3)$ (87)	699 (706.44)	16.62 (16.80)	18.02 (18.15)	3.75 (3.96)	11.22 (11.31)
5	2.06 (3.00)	0.56 (3.04)	$BrSn(S_2CN(C_4H_9)_2)_2(CH_3COCHCOC_6H_5)$ (90)	749 (768.51)	15.32 (15.44)	16.45 (16.69)	3.42 (3.64)	10.31 (10.40)
6	2.16 (3.14)	0.78 (3.17)	$BrSn(S_2CN(C_4H_9)_2)_2(C_6H_5COCHCOC_6H_5)$ (95)	808 (830.58)	14.07 (14.29)	15.31 (15.44)	3.18 (5.37)	9.55 (9.62)

Synthesis of $\text{BrSn}(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_2(\text{CH}_3\text{COCHCOCH}_3)$

Dibromobis(diethyldithiocarbamato)tin(IV), (1.90 g, 3.30 mmol) dissolve in dichloromethane (25ml), was added dropwise to a suspension of sodium acetylacetonate (0.43g, 3.52 mmol) in the same solvent. The mixture was refluxed for 3-4 hours. Sodium bromide formed during the reaction was removed by filtration. The excess solvent was dried under reduced pressure for about 2 hours. The compound was further purified by recrystallization from dichloromethane and n-hexane and finally dried undervalued.

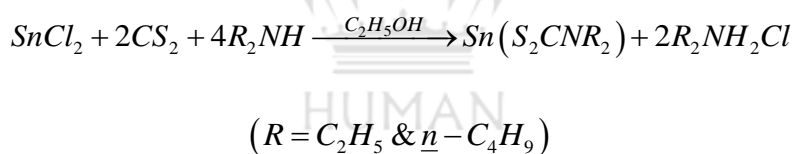
Anal % found: Sn, 19.46; S, 20.51, N, 4.43; Br 13.29;

Calcd for $\text{BrSn}(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_2(\text{CH}_3\text{COCHCOCH}_3)$ Sn, 19.97; S, 21.58; N, 4.47; Br, 13.45.

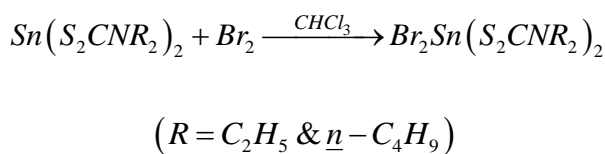
Details of the synthesis of other derivatives have been summarized in Table -1.

RESULTS AND DISCUSSION

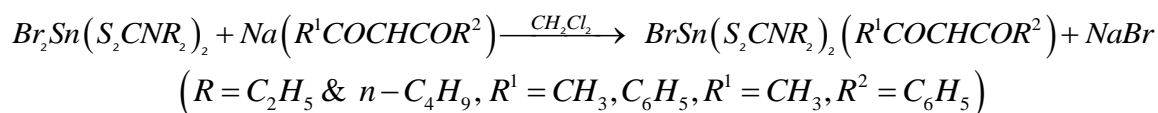
The reaction of stannous chloride with carbon disulfide and secondary amine in 1:2:4 molar ratio in alcohol yields, bis(dialkyldithiocarbamato)tin(II) $\text{Sn}(\text{S}_2\text{CNR}_2)_2$:



Further reaction $\text{Sn}(\text{S}_2\text{CNR}_2)_2$ with a solution of bromine in chloroform in 1:1 (Slight excess) molar ratio yields, dibromo bis (dialkyldithiocarbamato)tin(IV), $\text{Br}_2\text{Sn}(\text{S}_2\text{CNR}_2)_2$ derivatives.



Dibromobis(dialkyldithiocarbamato)tin(IV) reacts with sodium β -diketones in a 1:1 molar ratio in dichloromethane to give products of the type, $\text{BrSn}(\text{S}_2\text{CNR}_2)_2(\text{R}^1\text{COCHCOR}^2)$:



These reactions are quite facile and are completed in 3-4 hours by refluxing the reactants in dichloromethane. sodium bromide formed during the reaction was filtered out. Evaporation of the solvent gave the desired products in almost quantitative yields.

These complexes are orange solids and are soluble in dichloromethane, chloroform, and acetonitrile. They are thermally unstable and decompose even under reduced pressure. The molecular weight determination of these derivatives in chloroform suggests their monomeric nature.

On enhancing the molar ratio(1:2 or excess) of the reactants, only one of the bromine atoms could be substituted by β -diketone moiety even under forcing conditions. Thus, only monosubstituted products could be isolated.

Given the failure to obtain suitable crystals for X-ray structural determination, these have been characterized mainly based on spectral studies (IR and NMR).

IR Spectra

Tentative assignments of IR spectra ($4000-200\text{ cm}^{-1}$) of these complexes have been made based on earlier relevant^{2,14,17,24} reports on dihalobis(dithiocarbamate) tin(IV) and dihalobis (β -diketonato) tin (IV) derivatives (Table -2).

In case of $BrSn(S_2CNR_2)_2(R^1COCHCOR^2)$; the presence of single bands in the region $1495-1510\text{ cm}^{-1}$ and $992-1008\text{ cm}^{-1}$ strongly suggests the bidentate nature of the dithiocarbamate groups^{2,17,24} in the above-mixed ligand complexes of tin(IV), $BrSn(S_2CNR_2)_2(R^1COCHCOR^2)$.

It has been reported that in the spectra of dihalobis(β -diketonato)-tin(IV), the presence of characteristic bands due to $\nu C-O$ and $\nu C-C$ Vibrations at 1515 cm^{-1} and 1530 cm^{-1} indicate bidentate nature of the β -diketonate groups^{14,24}. Whereas in the free ligand C-O band appears in the higher ($1680-1740\text{ cm}^{-1}$) absorption regions.

In the case of mixed ligand complexes of tin(IV), $BrSn(S_2CNR_2)_2(R^1COCHCOR^2)$, the broadband in the region $1680-1705\text{ cm}^{-1}$ has been assigned to C-O vibrations, suggesting monodentate nature of the β -diketonate ligands in these complexes. The absorptions in the region $1520-1535\text{ cm}^{-1}$ may be ascribed to $\nu C-C$ modes.

The asymmetric vC-O stretching vibrations appear in the 1208-1220 cm⁻¹ region while "C-H in-plane" and "out of plane" vibrations have been observed in the regions 1175-1202 cm⁻¹ and 758-773 cm⁻¹ respectively. The bands in the region 475-500 cm⁻¹ might be due to Sn-O stretching modes.

Thus, the IR spectra of $BrSn(S_2CNR_2)_2(R^1COCHCOR^2)$ indicate monodentate nature of the β -diketonate group and bidentate nature of both the dithiocarbamate moieties.

¹H NMR Spectra

The ¹H spectra (table -3) of these complexes show the characteristic resonances due to dithiocarbamate and β -diketonate protons. The resonance positions of different dithiocarbamate moieties have been found to appear in the same range as reported for dihalobis(dialkyl dithiocarbamate) tin(IV) complexes^{17,24}. The integrated proton ratio corresponds to the formula assigned for these complexes.

¹H NMR spectra of $BrSn(S_2CNR_2)_2(R^1COCHCOR^2)$ show single methyl and methine proton resonance in the region δ 2.11-2.14 ppm and δ 6.14-6.82 ppm of the β -diketone moiety. A broad complex multiplet in the region δ 7.15-8.45 ppm has been ascribed to the phenyl proton resonances of the benzoylacetate and dibenzoyl methane moieties. The upfield shifts of methyl protons and downfield shifts of methine proton resonances compared to the dibenzoyl (β -diketonate) tin(IV)² appear to indicate that the β -diketone moieties are behaving as a monodentate ligand.

¹⁹Sn NMR Spectra

The ¹⁹Sn NMR Chemical shifts of some of these derivatives are given in Table -3. The compound, $Cl_2Sn(S_2CN(C_2H_5)_2)_2$ (where a six Coordination around tin(IV) has been proposed based on IR & ¹H NMR spectral studies^{14,25} the ¹⁹Sn NMR Spectra Exhibits a single peak at -179.9 ppm. In the case of mixed ligand complexes of tin(IV), the ¹⁹Sn signals are observed between -175.43 to 179.23 ppm. This observation supports the above inference drawn based on IR and ¹H, NMR spectral studies that there is six coordination around tin(IV) in the above-mixed ligand complexes of tin(IV).

Table no 2: Infrared spectral studies of Bis(dialkyldithiocarbomato) (β -diketonato)BromoTin (IV)

S. No	Compound	$\nu_{\max} (cm^{-1})$		$\nu_{\max} (cm^{-1})$			
		β -diketonate moieties	Dithiocarbamate moieties	ν_{Sn-O}	ν_{Sn-Br}	$\nu_{C \equiv N}$	$\nu_{C \equiv S}$
1	$BrSn(S_2CN(C_2H_5)_2)_2(CH_3COCHCOCH_3)$	1680 s	1528 vs	475 m	322 w	1496 s	1005 s
2	$BrSn(S_2CN(C_2H_5)_2)_2(CH_3COCHCOC_6H_5)$	1702 s	1530 vs	490 s	320 w	1510 s	995 s
3	$BrSn(S_2CN(C_2H_5)_2)_2(C_6H_5COCHCOC_6H_5)$	1705 s	1520 vs	500 m	324 w	1495 s	992 s
4	$BrSn(S_2CN(C_4H_9)_2)_2(CH_3COCHCOCH_3)$	1685 s	1530 vs	485 m	324 w	1498 s	1005 s
5	$BrSn(S_2CN(C_4H_9)_2)_2(CH_3COCHCOC_6H_5)$	1690 s	1525 vs	478 s	322 w	1599 s	1008 s
6	$BrSn(S_2CN(C_4H_9)_2)_2(C_6H_5COCHCOC_6H_5)$	1698 s	1535 vs	495 s	325 w	1495 s	998 s

* vs-very strong, s-strong, m-medium, w-weak

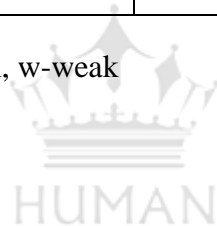


Table no 3: ¹H and ¹¹⁹Sn NMR spectral studies of Bis(dialkyldithiocarbomato) (β-diketonato)BromoTin(IV)

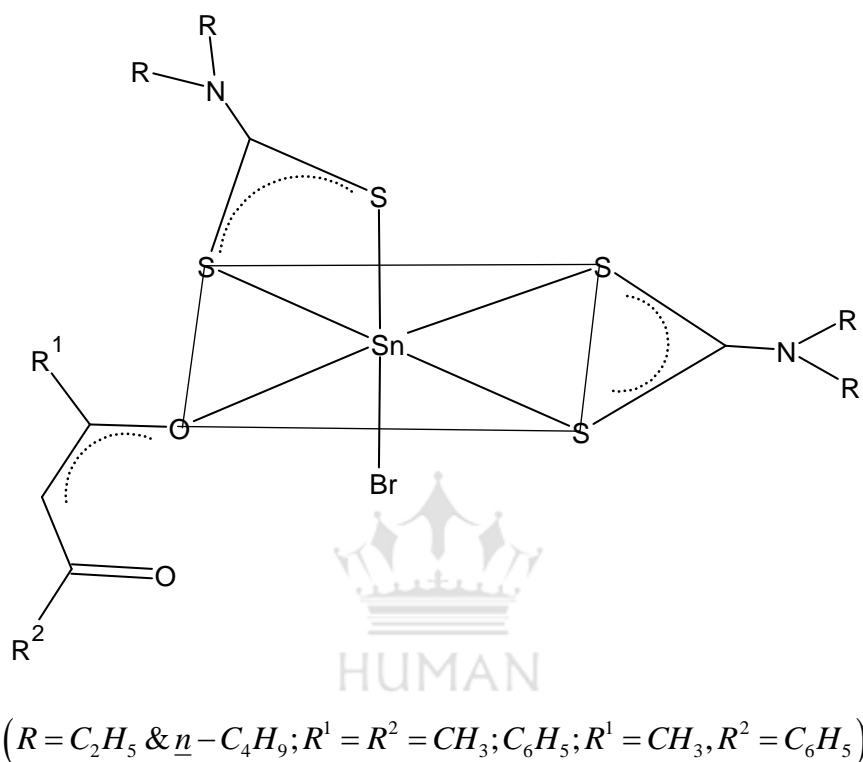
S. No.	Compound	β-diketonate moiety (δ ppm)	Dithiocarbamate moiety (δ ppm)	¹¹⁹ Sn Chemical shift δ ppm in CH ₂ Cl ₂
1	$BrSn(S_2CN(C_2H_5)_2)_2(CH_3COCHCOCH_3)$	2.11 s 6H(-COCH ₃) 6.14 s 1H(-COCH)	1.21 t 6H(-CH ₃) 3.72 q 4H(-CH ₂)	-179.23
2	$BrSn(S_2CN(C_2H_5)_2)_2(CH_3COCHCOC_6H_5)$	2.10 s 3H(-COCH ₃) 6.16 s 1H(-COCH) 7.15-8.45 m 5H(-C ₆ H ₅)	1.23 t 6H(-CH ₃) 3.70 q 4H(-CH ₂)	-
3	$BrSn(S_2CN(C_2H_5)_2)_2(C_6H_5COCHCOC_6H_5)$	5.03 s 1H(-COCH) 7.24-8.21 m 10H(-C ₆ H ₅)	1.26 t 6H(-CH ₃) 3.74 q 4H(-CH ₂)	-
4	$BrSn(S_2CN(C_4H_9)_2)_2(CH_3COCHCOCH_3)$	2.14 s 6H(-COCH ₃) 6.18 s 1H(-COCH)	0.86 t 3H(-CH ₃) 1.25 m 2H(-CH ₂) 1.56 m 2H(-CH ₂) 3.64 m 2H(-CH ₂)	-176.65
5	$BrSn(S_2CN(C_4H_9)_2)_2(CH_3COCHCOC_6H_5)$	2.12 s 3H(-COCH ₃) 6.15 s 1H(-COCH) 7.18-8.36 m 5H(-C ₆ H ₅)	0.84 t 3H(-CH ₃) 1.23 m 2H(-CH ₂) 1.58 m 2H(-CH ₂) 3.61 m 2H(-CH ₂)	-
6	$BrSn(S_2CN(C_4H_9)_2)_2(C_6H_5COCHCOC_6H_5)$	5.08 s 1H(-COCH) 7.28-8.15 m 10H(-C ₆ H ₅)	0.88 t 3H(-CH ₃) 1.28 m 2H(-CH ₂) 1.72 m 2H(-CH ₂) 3.70 m 2H(-CH ₂)	-175.43

* s-singlet, t-triplet, q-quartet, m-multiples

CONCLUSION

Although actual structure can be elucidated only through X-ray studies, the above studies indicate an octahedral geometry for the above monomeric mixed ligand complexes of tin(IV).

$BrSn(S_2CNR_2)_2(R^1COCHCOR^2)$, in which dithiocarbamate ligands behave as bidentate chelating and β -Diketnate group as a monodentate ligand (fig. 1).



(Fig.-1)

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