  Bull. Chem. Soc. Jpn., 55, 3630—3632 (1982) [Vol. 55, No. 11

Synthesis and Characterization of Tin(IV) Thiocarbamates

Virendra Kumar Gupta, Ravindra Kumar Kanjolia,
and Vishnu Deo Gupta*

Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi-221005, India

(Received January 16, 1982)

Tin(IV) thiocarbamates of the types $SnX_{4-n}(SOCNR_2)_n$, n-$BuSnCl_{3-n}(SOCNEt_2)_n$, and $R'_2Sn(SOCNEt_2)_n$ (where X=Cl, Br, I; R=Me, Et; R′=*n*-Bu, *n*-Pr; n=1—4) were synthesized and characterized by elemental analysis and by molar conductance, molecular weight, and IR and NMR measurements.

The chemistry of metal complexes of thiocarbamate, particularly in association with main group metals, has not thoroughly been investigated in contrast to corresponding dithiocarbamates, only a few reports being made on silicon(IV),[1,2] thallium(I),[3] and some organotin(IV)[4,5] species. The replacement of sulfur by oxygen and the resulting decrease in the chelate bite bring about a remarkable change in the stereochemistry of metal complexes.[6-8] In view of this, we have initiated a detailed and systematic study of metal complexes of thiocarbamate and are reporting here some findings on tin(IV) derivatives.

Experimental

General. All manipulations were carried out under anhydrous conditions in nitrogen atmosphere. Solvents were dried by standard techniques. The sodium and dialkylammonium salts of thiocarbamic acid[9] and tin(IV) halide[10-12] were synthesized by literature procedures. *n*-$BuSnCl_3$ (93 °C/10 mmHg) (1 mmHg=133.322 Pa), *n*-Bu_2SnCl_2 (142 °C/11.0 mmHg), and *n*-Pr_2SnCl_2 (50 °C/1.0 mmHg) were distilled before use. The metal, sulfur, and halogen were estimated gravimetrically. Nitrogen was estimated by Kjeldahl's method. Conductance was measured on a conductivity bridge (Model No. L-370873 from Cambridge Instrument Co., England) at 10^{-3} M (1 M=1 mol dm^{-3}) concentration. Molecular weights of soluble compounds were determined cryoscopically in benzene. Infrared spectra were recorded on a Perkin-Elmer 621 instrument as Nujol mull in the range 4000—200 cm^{-1} and in solution in the range 4000—650 cm^{-1}. NMR spectral studies were carried out on a Varian A-60 spectrometer using tetramethylsilane as the internal standard.

Preparation of Trihalo(thiocarbamato)tin(IV) and Dihalobis(thiocarbamato)tin(IV) Complexes (Table 1). Into a suspension of sodium salt of thiocarbamate in dichloromethane, the stoichiometric amount of tin(IV) halide was added dropwise, and the reaction mixture was allowed to reflux for 12—14 h. The mixture was filtered to remove the separated sodium halide and the volatile materials were removed under reduced pressure. The products were crystallized from acetonitrile/hexane (1:8) and dried at 0.1 mmHg and *ca.* 50 °C for *ca.* 6 h.

Preparation of Chlorotris(diethylthiocarbamato)tin(IV) and Tetrakis(diethylthiocarbamato)tin(IV) Complexes (Table 1). Into a benzene solution of diethylammonium salt of diethylthiocarbamate, the stoichiometric amount of tin(IV) chloride was added dropwise with continuous stirring. The stirring was continued for *ca.* 10 h. The separated diethylammonium chloride was removed by filtration and the volatile materials were removed under reduced pressure. The products were crystallized from benzene/hexane (1:5) and dried at 0.1 mmHg and *ca.* 30 °C for *ca.* 10 h.

Preparation of Butyldichloro(thiocarbamato)tin(IV), Butylchlorobis(thiocarbamato)tin(IV), and Diorganobis(thiocarbamato)tin(IV) Complexes (Table 1). Into an acetone solution of diethylammonium salt of thiocarbamate, the stoichiometric amount of organotin(IV) chloride was added dropwise with continuous stirring. The stirring was continued for *ca.* 6 h. The separated diethylammonium chloride was removed by filtration and the volatile materials were removed under reduced pressure. Viscous liquids thus obtained were dried at 0.1 mmHg and *ca.* 30 °C for *ca.* 6 h.

Preparation of $SnCl_3(C_5H_5N)(SOCNMe_2)$ and $SnX_2(C_5H_5N)(SOCNEt_2)_2$ (X=Cl, I) (Table 1). Into an acetonitrile solution of $SnX_2(SOCNEt_2)_2$ and $SnCl_3(SOCNMe_2)$, an excess of pyridine was added with stirring. The reaction mixture was stirred for *ca.* 6 h and the volatile materials were removed *in vacuo*. The solid products were finally dried at 0.1 mmHg and *ca.* 60 °C for *ca.* 10 h.

Results and Discussion

Thiocarbamatotin(IV), $SnX_{4-n}(SOCNR_2)_n$, and organotin(IV) thiocarbamates, *n*-$BuSnCl_{3-n}(SOCNEt_2)_n$ and $R'_2Sn(SOCNEt_2)_2$, were synthesized according to the following schemes:

$$SnX_4 + \begin{cases} n'(Et_2NCOS^-\overset{+}{N}H_2Et_2) \longrightarrow \\ \qquad SnX_{4-n'}(SOCNEt_2)_{n'} + n'Et_2NH_2X, \\ n(R_2NCOSNa) \longrightarrow \\ \qquad SnX_{4-n}(SOCNR_2)_n + nNaX, \end{cases}$$

$$R'_2SnCl_2 + 2(Et_2NCOS^-\overset{+}{N}H_2Et_2) \longrightarrow R'_2Sn(SOCNEt_2)_2 + 2Et_2NH_2Cl,$$

$$BuSnCl_3 + n(Et_2NCOS^-\overset{+}{N}H_2Et_2) \longrightarrow BuSnCl_{3-n}(SOCNEt_2)_n + nEt_2NH_2Cl.$$

(X=Cl, Br, I; R=Me, Et; R′=*n*-Bu, *n*-Pr; n=1,2; n'=3,4.)

Thiocarbamatotin(IV) derivatives are crystalline solids, insoluble in common organic solvents except acetonitrile, whereas tris and tetrakis derivatives are soluble. Organotin(IV) complexes are viscous liquids, miscible with common organic solvents.

The infrared spectra of all these complexes are dominated by a broad intense band, sometimes split, due to coupled C⋯N and C⋯O stretching vibrations around 1550—70 cm^{-1}, indicating invariably bidentate behavior of the ligand.[4,6,7,13] Medium to strong bands in the regions 560—80 and 380—90 cm^{-1} may be assigned to νSn–O and νSn–S, respectively.[14-16]

Dihalo, dialkyl (molecular weight shows them to be monomeric), and butylchlorobis complexes appear to involve an octahedral geometry. $SnCl_2(SOCNEt_2)_2$ should have a *cis*-structure in the solid state as indi

Table 1. Analytical data of tin(IV) thiocarbamate derivatives

No.	Compound[c]	Appearace[a]	Mp θ_m/°C	Conductivity (MeCN) Ω cm^2 mol^{-1}	Mol wt Found (Calcd)	Found (Calcd)(%) Sn	S	X[f]	N
1	$SnCl_3(SOCNMe_2)$	White	220[d]	73.65	—	35.89 (36.06)	9.49 (9.74)	33.07 (32.34)	4.00 (4.28)
2	$SnCl_3(SOCNEt_2)$	White	158—60	108.90	—	33.95 (33.04)	8.98 (8.97)	29.98 (29.80)	3.82 (3.94)
3	$SnBr_3(SOCNMe_2)$	Light yellow	108—10	40.30	—	25.12 (25.65)	6.56 (6.93)	50.64 (51.84)	2.98 (3.04)
4	$SnBr_3(SOCNEt_2)$	Light yellow	95—97	42.54	—	24.02 (24.18)	6.39 (6.54)	47.86 (48.88)	2.75 (2.87)
5	$SnI_3(SOCNMe_2)$	Brown	102—04	26.55	—	19.45 (19.65)	5.24 (5.31)	62.58 (63.09)	2.12 (2.33)
6	$SnI_3(SOCNEt_2)$	Dark red	72—74	45.02 0.05[b]	—	18.66 (18.78)	5.00 (5.07)	59.12 (60.28)	2.08 (2.23)
7	$SnCl_2(SOCNMe_2)_2$	White	238—40	68.15	—	29.75 (29.81)	16.02 (16.12)	17.61 (17.82)	7.00 (7.07)
8	$SnCl_2(SOCNEt_2)_2$	White	131	40.30	—	25.39 (26.13)	15.29 (14.13)	14.90 (15.63)	6.05 (6.20)
9	$SnBr_2(SOCNMe_2)_2$	Light yellow	166—70	27.61	—	24.18 (24.38)	13.00 (13.17)	32.52 (32.76)	5.58 (5.78)
10	$SnBr_2(SOCNEt_2)_2$	Light yellow	116	16.29	—	21.43 (21.86)	11.71 (11.81)	29.21 (29.45)	5.01 (5.18)
11	$SnI_2(SOCNMe_2)_2$	Dark red	130—32	8.76	—	20.29 (20.42)	10.96 (11.04)	42.60 (43.70)	4.73 (4.85)
12	$SnI_2(SOCNEt_2)_2$	Dark yellow	110—12	8.00 0.03[b]	—	18.50 (18.62)	10.80 (10.06)	38.18 (39.85)	4.30 (4.42)
13	$SnCl(SOCNEt_2)_3$	White	120[d]	20.95	594.4 (550.8)	22.04 (21.54)	17.30 (17.46)	6.30 (6.43)	7.60 (7.66)
14	$Sn(SOCNEt_2)_4$	White	116	8.62	653.6 (647.6)	18.34 (18.32)	19.79 (19.80)	—	8.58 (8.69)
15	n-$BuSnCl_2(SOCNEt_2)$	Brown viscous liquid	e)	44.94 0.48[b]	421.3 (378.2)	31.70 (31.32)	8.11 (8.26)	8.26 (8.46)	3.68 (3.72)
16	n-$BuSnCl(SOCNEt_2)_2$	Brown viscous liquid	e)	25.38	490.2 (475.5)	24.81 (24.94)	13.57 (13.48)	7.20 (7.46)	5.65 (5.92)
17	n-$Bu_2Sn(SOCNEt_2)_2$	Brown viscous liquid	e)	0.91	510.2 (497.3)	23.81 (23.85)	13.51 (12.89)	—	5.43 (5.66)
18	n-$Pr_2Sn(SOCNEt_2)_2$	Viscous liquid	e)	0.91	482.4 (469.3)	25.09 (25.27)	13.73 (13.67)	—	5.89 (6.00)
19	$SnI_2(C_5H_5N)$-$(Et_2NCOS)_2$	Light yellow	150[d]	—	—	16.81 (16.69)	9.18 (9.02)	35.04 (35.72)	5.72 (5.94)
20	$SnCl_2(C_5H_5N)$-$(Et_2NCOS)_2$	White	164—66	—	—	22.28 (22.25)	12.10 (12.03)	13.54 (13.56)	7.78 (7.92)
21	$SnCl_3(C_5H_5N)$-(Me_2NCOS)	White	255	—	—	29.01 (29.07)	7.94 (7.86)	25.96 (26.07)	6.69 (6.90)

a) Solid. b) Molar conductivity in dichloromethane. c) Yield 90%. d) Decomposed. e) Attempted distillation failed. f) X=Cl, Br, I.

cated by the two absorptions at 327 and 315 cm^{-1} due to antisymmetric and symmetric νSn–Cl, respectively.[17] This is further evidenced by ^{1}H NMR spectra (Table 2) of the soluble bis complexes, $SnX_2(SOCNEt_2)_2$, which show two overlapping quartets and triplets perhaps arising from their *cis*-structures and magnetic nonequivalence of the ethyl protons at ambient temperature due to the partial double bond character in C–N providing a restricted rotation.[4,9,13] The complex n-$BuSnCl_2(SOCNEt_2)$ is monomeric and nonionic in dichloromethane involving 5-coordinated tin atom.

Interestingly, in the IR spectra (in solution and in the solid state) of $SnCl(SOCNEt_2)_3$ and $Sn(SOCNEt_2)_4$ (found to be monomeric), an additional broad intense band appears at 1595—1605 cm^{-1} due to the coupled νC⎓N and νC⎓O, indicating also the presence of thiocarbamato moiety bonded to the tin atom through sulfur only.[18–20] This is strongly substantiated by the nature of the ^{1}H NMR spectrum of $Sn(SOCNEt_2)_4$ at ambient temperature which shows two sets of broad peaks of equal intensity, one due to the methylene protons of the two chelating diethylthiocarbamate moiety centered at δ=3.47 (comparable to the values obtained for our other derivatives) and the other at δ=3.00 (evidently separated by 0.47 in δ) owing to the other two ligands having only sulfur atoms bonded to the metal. The methyl protons appear as a complex mixture of triplets. It is evident that the tetrakis complex is octahedral like tetrakis derivatives of dithiocarbamate[21] $Sn(S_2CNEt_2)_4$ and dithiocarbonates[22] $Sn(S_2COEt)_4$. Efforts are being

Table 2. ^{1}H NMR spectra of tin(IV) derivatives in $CDCl_3$

Compound	Resonance	
	Assignment	Chemical shift[a] (δ)
$SnCl_2(SOCNEt_2)_2$	C-CH_3[b]	1.23
		1.33
	N-CH_2[c]	3.43
		3.55
$SnBr_2(SOCNEt_2)_2$	C-CH_3[b]	1.26
		1.35
	N-CH_2[c]	3.45
		3.58
$Sn(SOCNEt_2)_4$	C-CH_3[d]	1.27
	N-CH_2[e]	3.47
	N-CH_2[e]	3.00

a) Shift at 60 MHz relative to tetramethylsilane as the internal reference. b) Centers of two overlapping triplets. c) Centers of two overlapping quartets. d) Centers of complex triplets. e) Centers of broadened quartets.

made to get variable temperature ^{1}H NMR data for establishing the stereochemistry as well as to carry out a single crystal X-ray analysis for determining the full structure.

The conducting behavior of the tin(IV) halothiocarbamates in donor as well as in solvents of high dielectric constant suggests notable deviation from the behavior of the dithiocarbamate analogues in solutions, indicating a poor coordinating ability of the thiocarbamato moiety as ligand towards tin(IV). Dichlorobis(diethyldithiocarbamato)tin(IV) reported earlier[21] has been found to be essentially nonconducting (molar conductance: 3.92 Ω cm^2 mol^{-1}) in acetonitrile, whereas the trihalo- and dihalotin(IV) thiocarbamates exhibit a substantial molar conductance in acetonitrile in the order Cl>Br>I (Table 1) consistent with the general trend.[23] Substitution of the halide by butyl group also decreases the conductance since it lowers down the electrophilicity of the central tin atom. The data suggest the presence of the following solvolytic equilibrium[24] in acetonitrile:

$$SnX_{4-n}(SOCNR_2)_n \overset{MeCN}{\rightleftharpoons} [SnX_{4-(n+1)}(MeCN)(SOCNR_2)_n]^+X^-.$$

In donor solvents like pyridine (with lower dielectric constant), the equilibrium is more towards the right as evidenced by the comparatively much higher value of conductance, for example, of $SnI_2(SOCNEt_2)_2$ in pyridine (50 Ω cm^2 mol^{-1}) than in acetonitrile (8 Ω cm^{-2} mol^{-1}). The spurious conductance due to cationic species with a molecule of the solvent in the coordination sphere is substantiated by the isolation and characterization of pyridine complexes of the types $[SnCl_2(C_5H_5N)(SOCNMe_2)]^+Cl^-$ and $[SnX(C_5H_5N)(SOCNEt_2)_2]^+ X^-$ (X=Cl, I), which give characteristic bands at 690, 753, 1034, 1059, and 1600 cm^{-1} in the IR spectra due to coordinated pyridine.[25]

The authors are grateful to CSIR, New Delhi for a Junior Research Fellowship (VKG) and a Postdoctoral Fellowship (RKK) and to Nitto Kasei for their generous help in supplying us with organotin(IV) chlorides as a gift.

References

1) C. H. Yoder, A. Komoriya, J. E. Kochanowski, and F. H. Suydam, *J. Am. Chem. Soc.*, **93**, 6515 (1971).
2) A. E. Lemire and J. C. Thompson, *J. Am. Chem. Soc.*, **93**, 1163 (1971).
3) R. J. Magee and M. J. O'Connor, *Inorg. Chim. Acta*, **5**, 554 (1971).
4) A. B. Crosby, R. J. Magee, and M. J. O'Connor, *Inorg. Chim. Acta*, **34**, 107 (1979).
5) R. F. Dalton and K. Jones, *J. Chem. Soc., A*, **1970**, 590.
6) B. J. McCormick and B. P. Stormer, *Inorg. Chem.*, **11**, 729 (1972).
7) C. G. Pierpont, R. C. Dickinson, and B. J. McCormick, *Inorg. Chem.*, **13**, 1674 (1974).
8) K. R. M. Springsteen, D. L. Greene, and B. J. McCormick, *Inorg. Chim. Acta*, **23**, 13 (1977).
9) S. L. H. Hawthorne, A. H. Bruder, and R. C. Fay, *Inorg. Chem.*, **17**, 2114 (1978).
10) "Handbook of Preparative Inorganic Chemistry," ed by G. Brauer, Academic Press, New York and London (1963), Vol. I, p. 729.
11) "Handbook of Preparative Inorganic Chemistry," ed by G. Brauer, Academic Press, New York and London (1963), Vol. I, p. 733.
12) T. Moeller and D. C. Edwards, *Inorg. Synth.*, **4**, 119 (1953).
13) S. L. Hawthorne and R. C. Fay, *J. Am. Chem. Soc.*, **101**, 5268 (1979).
14) R. S. Tobias and C. E. Fraddin, *Inorg. Chem.*, **4**, 215 (1965).
15) R. C. Poller, *J. Inorg. Nucl. Chem.*, **24**, 593 (1962).
16) J. L. K. F. DeVries and R. H. Herber, *Inorg. Chem.*, **11**, 2458 (1972).
17) I. R. Beattie, G. P. McQuillan, L. Rule, and W. Webster, *J. Chem. Soc.*, **1963**, 1514.
18) E. M. Krankovits, R. J. Magee, and M. J. O'Connor, *Inorg. Chim. Acta*, **7**, 528 (1973).
19) F. W. Pijipers, A. H. Dix, and J. G. M. van der Linden, *Inorg. Chim. Acta*, **11**, 41 (1974).
20) E. M. Krankovits, R. J. Magee, and M. J. O'Connor, *Aust. J. Chem.*, **26**, 1645 (1973).
21) J. C. May, D. Petridis, and C. Curran, *Inorg. Chim. Acta*, **5**, 511 (1971).
22) C. L. Raston, P. R. Tennant, A. H. White, and G. Winter, *Aust. J. Chem.*, **31**, 1493 (1978).
23) I. R. Beattie, *Quart. Rev. Chem. Soc.*, **17**, 382 (1963).
24) R. A. Walton, *Quart. Rev. Chem. Soc.*, **19**, 126 (1965).
25) N. N. Greenwood and K. Wade, *J. Chem. Soc.*, **1960**, 1130.