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Mössbauer and Related Studies of Tin(IV) Complexes with N,N-Dialkyldithiocarbamic Acids

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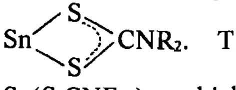
Mössbauer parameters are reported for thirty-two tin(IV) compounds containing N,N–dialkyldithiocarbamate ligands. NMR spectra reveal the bidentate character of the dimethyldithiocarbamate ligand. Mössbauer, NMR and infrared spectra indicate greater tin s–character for Sn–C bonds and weaker Sn–S bonds in seven- than in six-coordinate compounds. The dithiocarbamate ligand effects a greater electron density at the tin nucleus than any other bidentate anionic ligand studied to date.

Introduction

Dithiocarbamates, (dtc), act as bidentate ligands in forming four-membered rings with tin(IV),  The crystal structure of octahedral $Sn(S_2CNEt_2)_4$, which has two free (dangling) C=S groups, reveals two equivalent C–S bond distances in each of the two chelating ligands.[2] Chelation in solution of the dimethyldithiocarbamate ligand with metal atoms is indicated by a chemical shift of about τ 6.60 for the methyl protons, compared to a value of about τ 7.24 in complexes having only one of the sulfur atoms bonded to a metal.[3] NMR data are also useful in evaluating the tin s–character of the Sn–C bond in complexes containing the $Sn–CH_3$ group, from the magnitude of the $^{119}Sn–CH$ coupling constant.[4]

Fitzsimmons and coworkers[5] have concluded from Mössbauer studies of dialkyl- and diphenyltin(dtc)$_2$ complexes that the alkyl groups are *trans* and the phenyl groups *cis* in these complexes. The present study is concerned with establishing five, six and seven-coordination for tin dithiocarbamate complexes, in evaluating the tin s-characater of the tincarbon bonds in a number of these complexes, and in comparing the isomer shifts for $RSnX(dtc)_2$ and $SnX_2(dtc)_2$ with those for complexes having $(^{S}_{O}$, $(^{N}_{O}$, and $(^{O}_{O}$ type chelating ligands.

Experimental Section

Preparation and Purification of Compounds. Di–*n*–butyltin dichloride, diphenyltin dichloride, phenyltin trichloride, methyltin trichloride and trimethyltin chloride were obtained from Alfa Inorganics, Inc. Anhydrous tin(IV) chloride and sodium thiocyanate were Baker Analyzed reagents. Sodium dimethyldithiocarbamate was a Merck product, and sodium diethyldithiocarbamate a Fisher Certified reagent. All solvents were CP grade or better. All precipitated complexes were washed with small portions of the appropriate solvent and dried under vacuum at 56°C.

The $RSn(dtc)_3$ complexes listed in Table I were prepared by adding $RSnCl_3$ in absolute methanol to a filtered solution of the sodium salt of the dialkyldithiocarbamate in the same solvent in a 1:6 ratio. $BuSn(S_2CNEt_2)_3$ and $MeSn(S_2CNEt_2)_3$ were recrystallized from anhydrous diethyl ether.

The $RSnCl(dtc)_2$ complexes precipitated on the addition of methanol solutions of $RSnCl_3$ to methanol solutions ofthe sodium salt of the dialkyldithiocarbamate in a 1:3 ratio. The $RSnX(dtc)_2$ complexes (X = Br, I or NCS) formed on the addition of the $RSnCl(dtc)_2$ complexes in dry acetone to an excess of the sodium halide or pseudohalide in the same solvent. Sodium chloride precipitated and was removed by filtration. After evaporation of the solvent $BuSnBr(S_2CNEt_2)_2$, $BuSnI(S_2CNEt_2)_2$ and $BuSnI(S_2CNMe_2)_2$ were recrystallized from anhydrous diethyl ether. The remaining compounds were washed with anhydrous methanol.

Trimethyl(dimethyldithiocarbamato)tin(IV) was obtained by adding trimethyltin chloride in absolute ethanol to an excess of sodium dimethyldithiocarbamate in the same solvent. Sodium chloride precipitated and was removed by filtration. The solvent was evaporated and the product recrystallized from chloroform. Tetrakis(dimethyldithiocarbamato)tin(IV) and tetrakis(diethyldithiocarbamato)tin(IV) formed as orange precipitates when solutions of tin(IV) chloride in absolute methanol were added to the respective sodium salt of the dialkyldithiocarbamate in a 1:6 ratio.

The $R_2Sn(DTC)_2$ complexes precipitated on the addition of the diorganotin dichlorides in absolute methanol to and excess of the sodium dialkyldithiocarbamates in the same solvent. $Bu_2Sn(S_2CNMe_2)_2$ and $Bu_2Sn(S_2CNEt_2)_2$ were recrystallized from anhydrous

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(1) The Radiation Laboratory is operated by the University of Notre Dame under contract with the Atomic Energy Commission. This is A.E.C. Document No. COO-38-771.

(2) E.O. Schlemper, University of Missouri, private communication.

(3) C. O'Connor, J.D. Gilbert, and G. Wilkins, *J. Chem. Soc.* (A), 84 (1969).

(4) J.R. Homes and H.D. Kaesz, *J. Amer. Chem. Soc.*, *83*, 3903 (1961).

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Table I. Characterization and Mössbauer Data.

	%Carbon		% Hydrogen		Color	Point Melting °C	δ mm/sec	ΔE$_Q$ mm/sec	% Abs 1	% Abs 2
	Calcd	Found	Calcd	Found						
1. (Me)$_3$Sn(SSCNMe$_2$)	25.35	25.40	5.28	5.47		59-60	1.30	2.33	10.0	9.8
2. Sn(SSCNEt$_2$)$_4$	33.75	34.08	5.66	5.86	orange	195(dec)	1.04	*a*	9.8	—
3. Sn(SSCNMe$_2$)$_4$	24.04	24.06	4.00	4.13	orange	216-218	1.06	*b*	8.4	—
4. BuSn(SSCNEt$_2$)$_3$	36.77	37.10	6.30	6.27	yellow	89-91	1.26	1.90	12.5	11.5
5. BuSn(SSCNEt$_2$)$_2$Cl	33.10	32.82	5.71	5.63		92-94	1.21	1.74	12.1	11.7
6. BuSn(SSCNEt$_2$)$_2$Br	30.44	30.58	5.25	5.20	yellow	92-94	1.24	1.73	7.0	6.7
7. BuSn(SSCNEt$_2$)$_2$I	28.05	28.22	4.84	5.10	orange	92-94	1.33	1.76	7.1	6.3
8. BuSn(SSCNMe$_2$)$_3$	29.10	29.34	5.04	5.26	yellow	203-205	1.28	1.94	12.4	12.8
9. BuSn(SSCNMe$_2$)$_2$Cl	26.58	27.56	4.65	4.91		130-132	1.19	1.70	9.7	10.0
10. BuSn(SSCNMe$_2$)$_2$Br	24.19	24.44	4.23	4.41		155-157	1.22	1.70	8.3	8.0
11. BuSn(SSCNMe$_2$)$_2$I	22.10	22.52	3.87	5.43	orange	153-155	1.28	1.66	8.1	7.8
12. MeSn(SSCNEt$_2$)$_3$	33.22	33.19	5.71	5.67	yellow	120-122	1.16	1.97	17.8	17.9
13. MeSn(SSCNEt$_2$)$_2$Cl	28.36	28.48	4.94	5.17		150-152	1.07	1.80	8.7	8.6
14. MeSn(SSCNMe$_2$)$_3$	24.29	24.29	4.25	4.32	yellow	195-196	1.19	1.95	5.6	5.3
15. MeSn(SSCNMe$_2$)$_2$Cl	20.51	20.64	3.66	3.78		214-216	1.09	1.77	6.2	5.7
16. MeSn(SSCNMe$_2$)$_2$Br	18.50	18.62	3.31	3.63		210-212	1.16	1.83	10.7	12.2
17. MeSn(SSCNMe$_2$)$_2$I	16.77	16.90	2.99	3.08	orange	187-189	1.19	1.71	8.6	9.6
18. MeSn(SSCNMe$_2$)(NCS)	22.22	22.21	3.47	3.71		189-191	0.99	1.87	6.5	6.4
19. (Ph)Sn(SSCNet$_2$)$_3$	39.38	39.49	5.47	5.50	yellow	148-150	1.12	1.81	6.1	6.4
20. (Ph)Sn(SSCNEt$_2$)$_2$Cl	36.40	36.13	4.74	4.88		179-181	1.06	1.70	8.6	8.9
21. (Ph)Sn(SSCNMe$_2$)$_3$	32.37	32.79	4.14	4.31	yellow	146-148	1.16	1.84	7.2	6.0
22. (Ph)Sn(SSCNMe$_2$)$_2$Cl	30.54	30.73	3.60	3.70		210-212	1.10	1.69	9.1	9.1
23. (Ph)Sn(SSCNMe$_2$)$_2$Br	27.91	28.69	3.29	3.57		201-203	1.10	1.64	10.6	10.6
24. (Ph)Sn(SSCNMe$_2$)$_2$I	25.58	25.87	3.02	3.00	yellow	190-192	1.15	1.56	6.7	6.6
25. (Ph)Sn(SSCNMe$_2$)$_2$(NCS)	31.58	31.73	3.44	3.33		161-163	0.94	1.64	4.5	4.5
26. (Bu)$_2$Sn(SSCNEt$_2$)$_2$	40.83	41.42	7.18	7.13	yellow	48-50	1.51	2.84	6.2	6.1
27. (Bu)$_2$Sn(SSCNMe$_2$)$_2$	35.52	36.16	6.34	6.56		89-91	1.54	2.98	9.6	10.2
28. (Ph)$_2$Sn(SSCNMe$_2$)$_2$	42.10	42.18	4.29	4.47		230-232	1.07	1.64	5.7	5.5
29. SnCl$_2$(SSCNEt$_2$)$_2$	24.70	25.99	4.14	4.48		213-215	0.78	*c*	13.7	—
30. SnBr$_2$(SSCNEt$_2$)$_2$	20.88	21.29	3.50	3.74	yellow	216-218	0.90	*d*	7.2	—
31. SnI$_2$(SSCNEt$_2$)$_2$	17.95	18.18	3.01	3.09	orange	200-202	1.05	*e*	6.6	—
32. (Ph)$_2$Sn(SSCNEt$_2$)(NCS)	45.18	44.39	4.18	4.20		109-111	1.19	2.43	4.0	—

Line Widths, mm/sec: [a] 0.8; [b] 1.2; [c] 0.92; [d] 0.95; [e] 0.85.

Table II. Tin Proton Coupling Constants J(^{119}Sn—CH) and J(^{117}Sn—CH)

	cps	cps	s-character
MeSn(SSCNEt$_2$)$_3$	119	114	55%
MeSn(SSCNEt$_2$)$_2$Cl	110	105	50%
MeSn(SSCNMe$_2$)$_3$	120	115	56%
MeSn(SSCNMe$_2$)$_2$Cl	110	105	50%
Me$_3$Sn(SSCNMe$_2$)	57	55	27%

diethyl ether.

Dichloro — dibromo — and diiodobis (diethyldithiocarbamato) tin(IV) precipitated on mixing methanol solutions of one part of tin(IV) halide and two parts of sodium diethyldithiocarbamate. Ph$_2$Sn(NCS)(S$_2$CNEt$_2$) precipitated on mixing methanol solutions of diphenyltin diisothiocyanate and sodium diethyldithiocarbamate in a 1:1 ratio. Analyses listed in Table I were performed by Midwest Microlab.

Infrared Spectra. Thes were obtained with Perkin-Elmer spectrometers, Models 421 and 457, in KBr disks.

Mössbauer Spectra. Thes were obtained as described previously,[6] with the absorbers at 80°K and the barium stannate source at room temperature. The spectrometer was calibrated regularly with *n*–Bu$_2$SnCl$_2$. *o*–phenanthroline, having an isomer shift, δ, of 1.57 mm/sec. The values listed in Table I are considered accurate to ±0.05 mm/sec with a relative precision of ±0.03 mm/sec. The spectrum of MeSn(S$_2$CNEt$_2$)$_3$ is illustrated in Figure 1

NMR Spectra. Chemical shfts and coupling constants were obtained using a Varian Model A60 spectrometer at 60 Mc and 42° C. CDCl$_3$ was used as a solvent and TMS as the internal standard. All spectra were obtained locking on the methyl proton resonance of TMS.

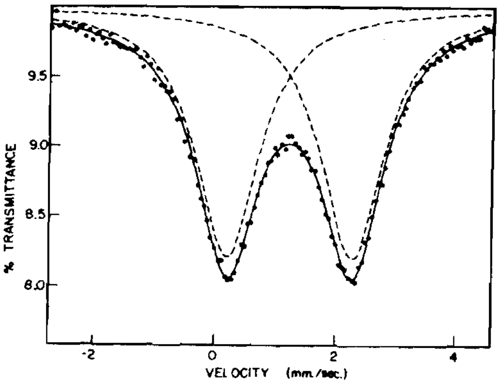

Figure 1. Mössbauer spectrum of methyltris(N,N-diethyldithiocarbamato)tin(IV).

Results and Discussion

Soluble dimethyldithiocarbamato complexes listed

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(6) M.A. Mullins and C. Curran, *Inorg. Chem.*, *7*, 2584 (1968).

in Table I showed PMR absorption at τ 6.52–6.60 and no absorption in the τ 7.24 region, indicating complete chelation in solution. (Compounds 3, 10, 11, 17, 18, 23, 24 and 25 were not sufficiently soluble for measurements.) The absorption area ratio of the $Sn{-}CH_3/N{-}CH_3$ protons in $MeSn(S_2CNMe_2)_3$ is 1:6, a further indication of seven coordination for this tin complex. The crystal structure of $MeSn(S_2CNEt_2)_3$ indicates that the configuration about tin for this molecule is a distorted pentagonal bipyramid having the methyl group axial.[7] It is assumed that the other $RSn(dtc)_3$ complexes are also seven-coordinate in the solid state. The magnitude of the $^{119}Sn{-}CH$ coupling constant for $MeSn(S_2CNEt_2)_3$, Table II, indicates 55% tin-charcter for the Sn–C bond, as compared to 50% for the Sn–C bond in $MeSnCl(S_2CNEt_2)_2$. This suggests a stronger axial Sn–C bond in the seven-coordinate complex than in the octahedral compound. Tha data of Schlemper also reval a significantly shorter Sn–S distance for the axial than for the five equatorial bonds. This is in contrast to the five-cordinate trigonal bipyramid compounds in which the axial bonds are weaker than the equatorial. The quadrupole splitting obtained for $n{-}Bu_2Sn(NCS)_2\cdot$terpyridyl terpyridyl, 4.75 mm/sec, indicates axial alkyl groups in this seven coordinate compound, and the more positive isomer shift obtained for this compound than for $n{-}Bu_2Sn,NCS)_2\cdot$dipyridyl also indicates greater tin s-character for the Sn–C bonds in the seven than in the six-coordinate complex.[8]

Table III. Infrared Absorption Maxima.

	C—N cm^{-1}	C—S cm^{-1}
$BuSn(SSCNEt_2)_3$	1480	997
$BuSn(SSCNEt_2)_2Cl$	1497	988
$BuSn(SSCNMe_2)_3$	1505	982
$BuSn(SSCNMe_2)_2Cl$	1525	970
$MeSn(SSCNEt_2)_3$	1490	998
$MeSn(SSCNEt_2)_2Cl$	1500	990
$MeSn(SSCNMe_2)_3$	1500	981
$MeSn(SSCNMe_2)_2Cl$	1525	972
$(Ph)Sn(SSCNEt_2)_3$	1487	994
$(Ph)Sn(SSCNEt_2)_2Cl$	1500	988
$(Ph)Sn(SSCNMe_2)_3$	1510	983
$(Ph)Sn(SSCNMe_2)_2Cl$	1525	972

Schlemper has observed significantly longer Sn–S distances for the five equatorial bonds in $MeSn(dtc)_3$ than for the six Sn–S bonds in $Sn(dtc)_4$. Further evidence for relatively weak equatorial bonds in seven-coordinate complexes is provided by infrared absorption frequencis listed in Table III. Those in the 1500 cm^{-1} region are associated with the C–N stretching vibration and those between 970 and 1000 cm^{-1} appear to be associated, at least in part, with a C–S stretching mode.[9] It is noted that for each corresponding pair of $RSn(dtc)_3$ and $RSnCl(dtc)_2$ complexes, the frequency of the 1500 cm^{-1} peak is higher and that of the 980 cm^{-1} peak lower for the six-coordinate compound, indicating greater $^{+}N{=}C{-}S^{-}$ character and stronger S–Sn bonds.

Isomer shifts for tin(IV) compounds usually decrease with increasing coordination number for tin. This is associated with increasing number of electron pairs. As examples, the isomer shifts of 8–hydroxyquinoline,[10] picolinic acid,[11] and tropolone[12] complexes are: $SnCl_2(ox)_2$ 0.34 mm/sec, $SnCl(ox)_3$ 0.11 mm/sec; $SnCl_2(pic)_2$ 0.31 mm/sec, $SnCl(pic)_3$ 0.15 mm/sec; $SnCl_2(trop)_2$ 0.28 mm/sec, $SnCl(trop)_3$ 0.12 mm/sec. In contrast, the isomer shifts for the $RSn(dtc)_3$ complexes are more positive than for the corresponding $RSnCl(dtc)_2$ and $RSnBr(dtc)_2$ compounds, Table I. This indicates that the weaker tin share of bonding electrons in the seven-coordinate complexes is outweighed by the greater s-character for the Sn–C bonds (in line with the NMR data), in which the tin atom has a relatively large share of the bonding electrons. As the axial bonds appear to have more s-character than equatorial bonds in the seven-coordinate complexes, the Mössbauer data suggest that the phenyl group in $PhSn(dtc)_3$ is also axial; isomer shifts increase from $PhSn(dtc)_2X$ to $PhSn(dtc)_3$.

Unlike the dithiolato complexes, the oxinates show a decrease in isomer shift from $BuSnCl(ox)_2$, 0.84 mm/sec to $BuSn(ox)_3$, 0.69 mm/sec.[13] This may reflect the weaker tin share of the electrons of the three Sn–O and there Sn–N bonds as compared to the six Sn–S bonds, which predominates over any increase in tin s-character of the Sn–C bond in the seven-coordinate complex.

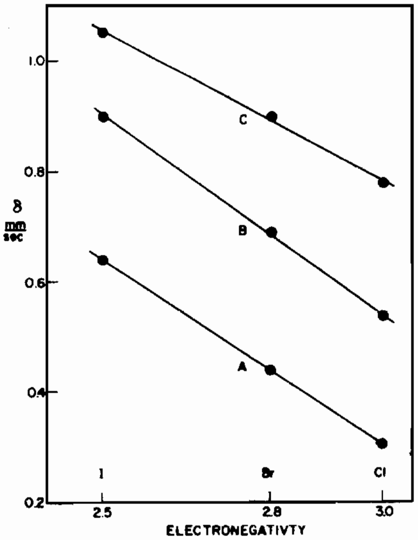

Figure 2. Variation of isomer shift with halogen electronegativity for A, $SnX_2(picolinate)_2$; B, $SnX_2(2\text{-}Spy0)_2$; C, $SnX_2(S_2CNEt_2)_2$.

Isomer shifts listed in Table I for the $RSnX(dtc)_2$ compounds show the expected increase from NCS to

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[7] E.O. Schlemper, private communication.

[8] J.C. May and C. Curran, Abstracts of the 160th meeting of the American Chemical Society, Chicago, Illinois, September, 1970, Phys 180.

[9] F. Bonati and A. Ugo, *J. Organometal. Chem.*, *10*, 257 (1967).

[10] K.M. Ali, D. Cunningham, M.J. Frazer, J.D. Donaldson, and B.J. Senior, *J. Chem. Soc.* (A), 2836 (1969).

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[12] J. May, unpublished work, this Laboratory.

[13] R.C. Poller and J.N.R. Ruddick, *J. Chem. Soc.* (A), 2273 (1969).

I for each series of compounds. Previous results[6] have indicated that the NCS group effects a lower s-electron density at the tin nucleus than does chlorine in octahedral R_2SnX_2 . dipy and R_2SnX_2 . *o*–phen complexes. In Figure 2 the isomer shifts for $SnX_2(S_2CNEt_2)_2$, $SnX_2(2\text{–}SpyO)_2$[14] and SnX_2(picolinate)$_2$ are plotted against halogen electronegativity. These complexes have $(^{S}_{S}$, $(^{S}_{O}$ and $(^{N}_{O}$ ligands, respectively. It is evident that the dithio ligands effect the greatest electron density at the tin nucleus. Isomer shifts for complexes containing $(^{O}_{O}$ type ligands, kojic acid and 8–hydroxyquinoline N–oxide, which have been obtained in this Laboratory, are the same as those for the corresponding picolinates and oxinates, within experimental error, indicating a similar electron release by the oxygen and pyridine nitrogen atoms in forming dative bonds with tin(IV. Absorptions at 310 and 288 cm^{-1} in the infrared spectrum of $SnCl_2$(dtc)$_2$ (not present in the spectra of the dibromo and diiodo compounds) are assigned to antisymmetric and symmetric Cl–Sn–Cl stretching vibrations, indicating a *cis* configuration in line with the interpretation of Bonati and Ugo.[9] It is of interest that the isomer shift of six-coordinate tin in $Sn(S_2CNEt_2)_4$, 1.04 mm/sec, is more positive than that of $(NH_4)_2SnBr_6$, 0.80 mm/sec.[15]

Absorption at 2045 cm^{-1} by solid $Ph_2Sn(S_2CNEt_2)$(NCS) indicates no –NCS– bridging and therefore five-coordination for tin. The isomer shift for this compound, 1.19 mm/sec, is intermediate between the value 1.35 mm/sec for four coordinate Ph_2SnCl_2[6] and 1.07 mm/sec for six coordinate tin in $Ph_2Sn(S_2CNMe_2)_2$. These are pertinent examples of the usual decrease in electron density at the tin nucleus with increasing coordination number. Exceptions to this general trend include the increase in δ from $R_2SnX_3^-$ to $R_2SnX_4^{2-}$, associated with changes in C–Sn–C bond angles and s-character,[16] and seven-coordinate complexes with axial Sn–C bonds.

NMR absorption in $DCCl_3$ by $Me_3Sn(S_2CNMe_2)$ at τ 6.52 indicates chelation, in contrast to the structure of monoclinic crystals of the solid,[17] which reveals Sn–S distances of 2.47 and 3.16 A. The weak "non-bonded" interaction with the second sulfur atom is, however, sufficient to distort the C–Sn–C angles from the tetrahedral values. The infrared absorption in the CN stretching region is at 1493 cm^{-1} in both a KBr disk and a chloroform solution, compared to a range of 1478 – 1490 cm^{-1} for complexes with dangling sulfur atoms.[3] The isomer shift for $Me_3Sn(S_2CNMe_2)$ is 1.30 mm/and the quadrupole splitting 2.33 mm/sec. These compare with corresponding values of 1.43 and 3.32 mm/sec. for Me_3SnCl,[18] and indicate a significant interaction of the tin with the second sulfur atom of dithiocarbamate ligand in the solid complex.

Acknowledgement. The A–60A NMR instrument used in this investigation was acquired under National Science Foundation equipment Grant No. GP 6875.

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(18) J.C. Hill, R.S. Drago, and R.H. Herber, *J. Amer. Chem. Soc.*, *91*, 1644 (1969).