CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY,
RUTGERS UNIVERSITY, NEW BRUNSWICK, NEW JERSEY 08903

Mössbauer Spectroscopy of Organometallics. Structure and Bonding in Organotin(IV) Dithiocarbamates

BY J. L. K. F. deVRIES AND R. H. HERBER*

Received February 24, 1972

A number of organotin(IV) diethyldithiocarbamate and related compounds have been examined by ^{119}Sn Mössbauer and infrared spectroscopy. The two sulfur atom containing monovalent anionic ligand is found to act as an anisobidentate moiety in a number of these compounds with one strong and one weak bonding interaction between the metal atom and the nearest neighbor sulfur atoms accounting for the observed spectroscopic properties. From isomer shift–electronegativity systematics a group electronegativity of ~5.7 on the Mulliken–Jaffe scale is deduced for alkyl groups bonded to Sn(IV). From the temperature dependence of the recoil-free fraction and the Gol'danskii–Karyagin asymmetry in $(CH_3)_2Sn[S_2CN(C_2H_5)_2]_2$ it is concluded that this compound is monomeric with an essentially isotropic amplitude of vibration of the metal atom in the temperature range 78–150°K. Proton nuclear magnetic resonance data for this compound are consistent with the anisobidentate nature of the sulfur-bonded ligand in this compound.

I. Introduction

Because of their unusual magnetic properties, the dithiocarbamate complexes of the transition metals have received a good deal of attention in recent years,[1] and a number of X-ray diffraction studies of such compounds have been reported.[2] In general, the monovalent anionic ligand acts as a bidentate moiety in these species in the solid state, with two equivalent (or nearly equivalent) metal–sulfur bond distances being observed. In the bis(dithiocarbamate) complexes of Fe(III) and Co(II), the four sulfur atoms form the base of a rectangular pyramid, while the metal atom sits ~0.5–0.6 Å above the basal plane. The ligands are essentially planar to the alkyl groups attached to the nitrogen atom and can be described in terms of a carbon–nitrogen double bond.

A rather different bonding situation obtains in the case of trimethyltin(IV) dithiocarbamate for which X-ray data of both the orthorhombic and monoclinic crystal modifications have been reported.[3] In these two cases—which involve essentially identical molecular configurations—the methyldithiocarbamate ligand interacts with the metal primarily through a single Sn–S bond of normal covalent length (2.47 ± 0.01 Å), with a second considerably weaker interaction through a long (3.16 ± 0.01 Å) Sn–S bond. The C–Sn–C bond angles in the trimethyltin fragment of the molecule are approximately tetrahedral, ranging from 100 ± 1 to 119 ± 1° in the two cases reported.

In view of the structural and bonding information which can be derived from ^{119}Sn Mössbauer effect studies, it was decided to examine a series of tin(IV) dithiocarbamate complexes and to relate the systematics of such an investigation to the information derivable from more conventional spectroscopies. An earlier study by Fitzsimmons[4] had shown that anomalous quadrupole splitting values are observed for compounds of the type R_2SnL_2 (R = alkyl or phenyl; L = methyl-, ethyl-, or phenyldithiocarbamate). A more detailed Mössbauer spectroscopic study of 32 organotin dithiocarbamates has recently been reported by May, Petridis, and Curran,[5] who assigned a bidentate function to the ligand and assigned a cis octahedral configuration to diphenyltin(IV) dithiocarbamates and a trans octahedral configuration to dibutyl- and dimethyltin(IV) dithiocarbamates, irrespective of the nature of the organic groups bonded to the ligand nitrogen atom.

The present work was undertaken to explore in a more detailed fashion the structures of organotin(IV) dithiocarbamate complexes, to elucidate the bonding character of the two ligand sulfur atoms to the metal center in these compounds, and to explore the Mössbauer parameter systematics in these materials.

II. Experimental Section

Preparation of the Complexes SnXY(dtc)$_2$.—The X = Y = Cl, Br, and I complexes were prepared according to literature methods from SnX_4 and commercially available Na(dtc)·$3H_2O$ in ethanol–chloroform solution. Impure samples of the corresponding fluorine complex (X = Y = F) were prepared from SnF_4 and gave consistent infrared and Mössbauer spectra but poor analytical results. On purification, only the sodium salt of the free ligand could be recovered. The experimental data obtained for the crude product $SnF_2(dtc)_2$ sample are indicated by parentheses in the data summaries below. An attempted synthesis of the fluorine complex from AgF and $SnI_2(dtc)_2$ was unsuccessful. The X = Y = dtc complex was obtained from freshly prepared dithiocarbamate and an ethanol solution of $SnCl_4$.[6] The X = Y = C_6H_5, CH_3, C_3H_7, *i*-C_4H_9, and *n*-C_4H_9 compounds were synthesized from SnX_2Cl_2 and Na(dtc)·$3H_2O$ in ethanol solution by a method similar to the $Sn(CH_3)_2(dtc)_2$ preparation reported earlier.[7] The complexes for X = Cl, Y = CH_3, *n*-C_4H_9, C_6H_5, and X = Br, Y = *n*-C_4H_9 were prepared according to the method of Honda, *et al.*,[8] and this method was also used in the preparation of SnX_2Y(dtc) from SnX_2Cl_2. The preparation of $(C_6H_5)_3$Sn(dtc) and $(C_6H_5)_2$Sn(dtc)Cl has been described by Kupchik and Calabretta.[9]

The identity of the products of the synthetic procedures has been confirmed from their infrared spectra and elemental analysis. *Anal.* Calcd for $Sn(Et_2dtc)_2$: C, 28.92; H, 4.85; N,

---

[1] G. D. Thorn and R. A. Ludwig, "The Dithiocarbamates and Related Compounds," Elsevier, Amsterdam, 1962; A. H. White, *et al.*, *Aust. J. Chem.*, **17**, 294 (1964); H. H. Wickman and A. M. Trozzolo, *Inorg. Chem.*, **7**, 63 (1968), and references therein.

[2] P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 668 (1962); B. F. Hoskins, R. L. Martin, and A. H. White, *Nature (London)*, **211**, 627 (1966).

[3] G. M. Sheldrick and W. S. Sheldrick, *J. Chem. Soc. A*, 490 (1970); G. M. Sheldrick, W. S. Sheldrick, R. F. Dalton, and K. Jones, *ibid.*, 493 (1970).

[4] B. W. Fitzsimmons, *Chem. Commun.*, 1485 (1968).

[5] J. C. May, D. Petridis, and C. Curran, *Inorg. Chim. Acta*, **5**, 511 (1971).

[6] F. Bonati, G. Minghetti, and S. Cenini, *ibid.*, **2**, 375 (1968); F. Bonati and R. Ugo, *J. Organometal. Chem.*, **10**, 257 (1967).

[7] F. Bonati and R. Ugo, *ibid.*, **10**, 257 (1967); F. Bonati, S. Cenini, and R. Ugo, *ibid.*, **9**, 935 (1967).

[8] M. Honda, M. Komura, Y. Kawasaki, T. Tanaka, and R. Okawara, *J. Inorg. Nucl. Chem.*, **30**, 3231 (1968).

[9] E. J. Kupchik and P. J. Calabretta, *Inorg. Chem.*, **4**, 973 (1965).

6.75; S, 30.88. Found: C, 28.66; H, 4.67; N, 6.57; S, 30.59. Calcd for $(C_3H_7)_2Sn(Et_2dtc)_2$: C, 38.33; H, 6.83. Found: C, 38.71; H, 6.54.

Mössbauer Measurements.—The Mössbauer parameters were extracted from spectra taken with a constant-acceleration spectrometer of the BTL type described earlier,[10] using a barium stannate source at room temperature. The spectrometer was calibrated periodically using the four inner lines of the magnetic hyperfine spectrum of ^{57}Fe in NBS standard reference material 99.99% metallic iron,[11] 0.8 mil thick which gives an uncorrected line width of about 0.23 mm/sec. All isomer shifts are referred to the center of a room-temperature $BaSnO_3$–$BaSnO_3$ spectrum and are directly comparable (to better than ±0.005 mm/sec, well within the experimental errors quoted in the present paper) to room-temperature SnO_2 isomer shifts as well as to liquid nitrogen $BaSnO_3$ isomer shifts. Routine samples were mounted as thin layers of microcrystalline powders, sandwiched between aluminum foils, using a standard copper sample holder which attaches directly to the copper cold finger of a liquid nitrogen dewar, the temperature of which was monitored using a calibrated thermocouple. The temperature-dependent Mössbauer parameters were obtained using a liquid helium variable-temperature dewar, the temperature of which could be monitored using a platinum and carbon resistance thermometer and a copper–constantan thermocouple. Either the Mössbauer data were analyzed manually using a statistical curve-fitting procedure or data reduction was effected using a computer program which assumes a lorentzian line shape and treats line position, intensity, and width as independent parameters in a multiple-iteration least-squares fitting procedure. An excess of 5×10^5 counts was scaled per channel in these spectra.

Infrared Measurements and Related Spectroscopies.—Ir spectra were recorded using a Perkin-Elmer 225 spectrometer at ambient temperature. Samples were mounted as ~0.8% by weight in KBr pellets. The tin-sulfur band region (200–500 cm^{-1}) was scanned at speeds of ~10 cm^{-1} min^{-1} and showed no deterioration of the samples with time. Proton nmr spectra were recorded using a Varian T-60 spectrometer on CCl_4 or D_3C-$COCD_3$ solution, using TMS as an internal standard. Both ir and nmr measurements were made at room temperature.

III. Results and Discussion

The numerical parameters extracted from the liquid nitrogen temperature Mössbauer spectra are summarized in Table I and a representative spectrum is shown in Figure 1. For those compounds for which a direct comparison is possible, the present data are in satisfactory agreement with the earlier values reported by Curran, *et al.*,[5] despite the rather different method used for spectrometer calibration in the two studies. The spectra of the dialkyltin(IV) bis(dithiocarbamates), the monoalkyl(or aryl)tin bis(dithiocarbamate) halides, and dialkyltin mono(dithiocarbamate) halides consist of well-resolved doublets indicating a lack of cubic symmetry of the charge distribution around the metal atom in these compounds. In contrast, the spectra of the tin bis(dithiocarbamato)dihalide compounds (**6**–**9**) as well as those of the tetrakis(methyl- and -ethyldithiocarbamate) compounds (**18**, **19**) consist—as a first approximation—of a single resonance maximum, indicative of cubic (or nearly cubic) charge distribution symmetry around the metal atom. A more detailed examination of the line widths observed for the four dihalide compounds (**6**–**9**) shows a systematic increase in the line width (full width at half-maximum) as the electronegativity of the halogen increases from I to F, indicative of an increasing unresolved quadrupole hyperfine interaction involving the metal atoms in these compounds.

TABLE I

MÖSSBAUER AND INFRARED DATA[a]

No.	Compd[b]	IS,[c,d] mm/sec	QS,[d] mm/sec	Γ,[e] mm/sec	ν_{Sn-S}, cm^{-1}
1	$(CH_3)_2SnL_2$	1.51	3.04	0.97	363.8 ± 0.3
2	$(C_3H_7)_2SnL_2$	1.54	2.82	0.83	370.3 ± 1.0
3	$(i\text{-}C_4H_9)_2SnL_2$	1.57	2.92	0.97	365.2 ± 1.0
4	$(n\text{-}C_4H_9)_2SnL_2$	1.56	2.91	1.14	368.2 ± 1.0
5	$(C_6H_5)_2SnL_2$	1.13	1.74	1.14	374.3 ± 0.4
6	SnL_2I_2	1.12	0	1.19	375.5 ± 0.8
7	SnL_2Br_2	0.95	0	1.42	379.8 ± 0.5
8	SnL_2Cl_2	0.74	0	1.60	382.0 ± 0.5
9	$(SnL_2F_2$	0.19	0	2.05	)
10	$(CH_3)SnL_2Cl$	1.09	1.76		375.7 ± 0.5
11	$(n\text{-}C_4H_9)SnL_2Cl$	1.21	1.73		373.8 ± 1.2
12	$(C_6H_5)SnL_2Cl$	1.12	1.66		377.0 ± 0.5
13	$(n\text{-}C_4H_9)SnL_2Br$	1.27	1.80		373.0 ± 1.0
14	$(CH_3)_2SnLCl$	1.43	2.80		392.2 ± 0.5
15	$(CH_3)_2SnLBr$	1.45	2.82		391.3 ± 0.4
16	$(i\text{-}C_4H_9)_2SnLCl$	1.53	2.84		
17	$(C_6H_5)_2SnLCl$	1.28	2.21		
18	SnL_4	1.10	0	1.22	379.8 ± 0.3
19	SnL'_4	1.16	0	1.25	
20	$(C_6H_5)_3SnL$	1.30	1.71		

[a] The Mössbauer measurements were carried out at 81 ± 2°K; the infrared measurements were carried out on 0.8% by weight samples in KBr pellets, at a scan speed of ~10 cm^{-1} min^{-1}. [b] L = diethyldithiocarbamate, L′ = dimethyldithiocarbamate. [c] With respect to $BaSnO_3$ at room temperature. [d] ±0.04 mm/sec. [e] Line width (full width at half-maximum), average of all components of the spectrum.

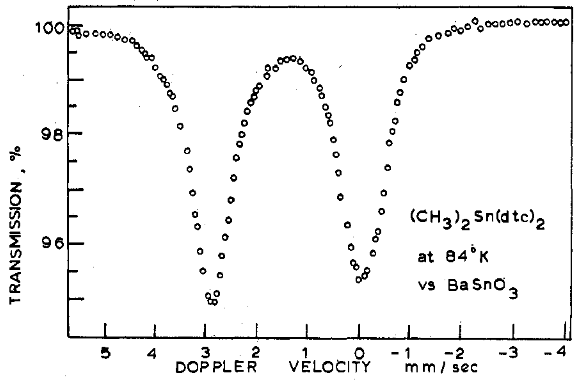

Figure 1.—Mössbauer spectrum of dimethyltin(IV) bis(diethyldithiocarbamate) at 84°K. The intensity asymmetry arises from a crystal orientation effect and is temperature independent.

(a) **Isomer Shift Systematics in $Sn(dtc)_2XY$.**—The isomer shifts observed in the spectra of these compounds, all of which fall well within the range characteristic of Sn(IV) species, vary in a systematic manner with the donor properties of the ligands attached to the metal atom. An early observation[12] concerning the isomer shift systematics of Sn(IV) compounds was that in the case of tetrahedral tetrahalogen complexes there is a linear relationship between the isomer shift (IS) and the ligand electronegativity (χ_L). Subsequently this observation was extended[13,14] to both the simple and mixed octahedral hexahalogen compounds which show a very similar relationship between the two parameters. Moreover, although the absolute values for the IS parameter for corresponding tetrahedral SnX_4 and octahedral SnX_6^{2-} differ significantly, d(IS)/dχ is

---

(10) See for example N. Benzcer-Koller and R. H. Herber in "Chemical Applications of Mossbauer Spectroscopy," V. I. Gol'danskii and R. H. Herber, Ed., Academic Press, New York, N. Y., 1968, Chapter 2.

(11) J. J. Spijkerman, J. R. DeVoe, and J. C. Travis, *Nat. Bur. Stand. (U. S.), Spec. Publ.*, **No. 260-20** (1970); see also R. H. Herber in "Mossbauer Effect Methodology," Vol. 7, I. Gruverman, Ed., Plenum Press, New York, N. Y., 1971.

(12) V. I. Gol'danskii, *At. Energy Rev.*, **4**, 3 (1963); M. Cordey-Hayes, *J. Inorg. Nucl. Chem.*, **26**, 915 (1964).

(13) R. H. Herber and H.-S. Cheng, *Inorg. Chem.*, **8**, 2145 (1969).

(14) C. A. Clausen and M. L. Good, *ibid.*, **9**, 817 (1970).

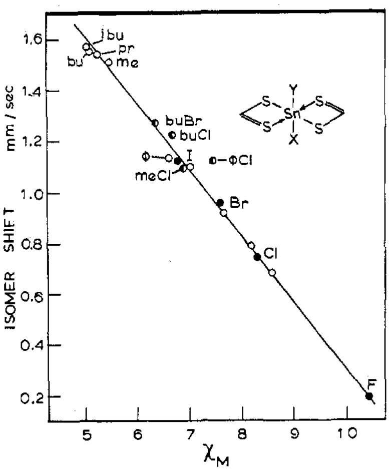

Figure 2.—Isomer shift (with respect to $BaSnO_3$)–electronegativity correlation for compounds of the type $SnXY(dtc)_2$ discussed in the text.

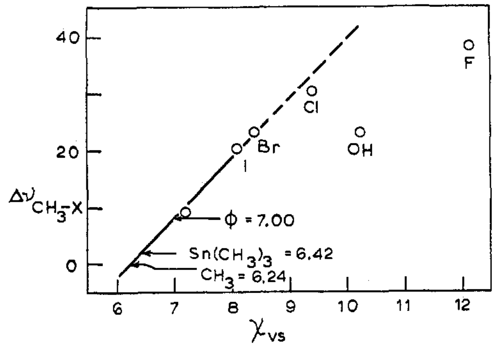

Figure 3.—Correlation between the methyl–tin asymmetric stretching frequency in compounds of the type $(CH_3)_3SnX$ and the ligand electronegativity (valence state). The linear relationship has been calibrated from the data for X = Cl, Br, I, and H. The data points for X = F and OH do not lie on the curve due to the polymeric structure of these species.

essentially the same for the two series of compounds. By using the χ_L values for the monoatomic halogen ligands to calibrate the isomer shift–electronegativity correlation, it is possible to use these systematics to estimate group electronegativities for polyatomic ligands, and this method has been used previously[15] to estimate χ_L for the pseudohalogen ligands N_3^-, SCN^-, CN^-, and NCO^-. The data reported in the present study (Table I) permit an extension of these correlations to achieve an estimate of the group electronegativity of alkyl and aryl groups bonded to an $Sn^{IV}(dtc)_2$ moiety as shown in Figure 2. The isomer shift–electronegativity correlation can be calibrated using the Mulliken–Jaffe valence-state electronegativity values[16] for the monatomic halogen ligands (filled circles) and extrapolating these data for the compounds of the type $Sn(dtc)_2X_2$ (X = halogen, alkyl) to encompass the isomer shift values for the dialkyl derivatives. From such an extrapolation the values $\chi_{CH_3} = \chi_{n\text{-Bu}} = 5.70$ and $\chi_{i\text{-Bu}} = 5.65$ are obtained.

There are two qualitative checks on the validity of this procedure. The first of these is one of internal consistency since the data points for the mixed compounds of the type $Sn(dtc)_2XY$ (X = halogen, Y = alkyl) fall nearly on the linear correlation plot when the observed isomer shift is plotted against the average X,Y electronegativity. Second, the methyl group electronegativity extracted from the Mössbauer data can be compared with that extracted from pertinent infrared data, specifically the asymmetric methyl stretching frequency for compounds of the type $(CH_3)SnX$ (X = halogen, CH_3, etc.). A plot of the difference between the $\nu_{CH_3\,asym}$ for tetramethyltin and the corresponding frequency for $(CH_3)_3SnX$ is plotted against the Mulliken–Jaffe electronegativity in Figure 3. The group electronegativity for CH_3 extracted from these data is 6.24 in reasonable agreement with the value extracted from the Mössbauer data. Similarly, $\chi_{C_6H_5}$ is seen to be ~7.5 from the Mössbauer data and ~7.0 from the infrared results. This modest agreement is only indicative of the fact that changes in the isomer shift, infrared frequency, and group electronegativity are all manifestations of the changes in s-electron population (and concomitant changes in the 5p population by hybridization of the orbitals) of the tin–ligand bond due to changes in covalency, and no greater quantitative character of the electronegativity parameter should be read into these correlations.

(b) Quadrupole Splitting Systematics in $Sn(dtc)_2XY$.—As noted above, the Mössbauer resonance spectra of the compounds in which X = Y = I, Br, Cl, or F consist of systematically broadened single maxima, consistent with either a tetrahedral or an octahedral configuration corresponding to the action of the dithiocarbamate ligand as a monodentate or bidentate moiety, respectively. On the basis of these data, no conclusions concerning the stereochemistry (coordination number) of the metal atom can be drawn. Such evidence is, however, available from the data for the compounds in which X = Y = alkyl, which show well-resolved quadrupole splittings (QS) in the range $2.82 < {}^1/_2e^2qQ < 3.04$ mm/sec. From the extensive data compilation available in the literature (see for example that by Zuckerman[17] or by Gol'danskii, *et al.*[18]) it is seen that for octahedral *trans*-dialkyltin(IV) compounds having axial symmetry such as $(CH_3)_2SnF_2$, $(CH_3)_2Sn(NCS)_2$, $(CH_3)_2Sn(acac)_2$, etc., for which the configurational assignment is based on unambiguous X-ray diffraction data, the observed quadrupole splittings lie in the range $3.5 < {}^1/_2e^2qQ < 4.6$ mm/sec. On the other hand, the corresponding cis compounds result in resonance spectra for which $1.5 < {}^1/_2e^2qQ < 2.2$ mm/sec, in agreement with the predictions of the point-charge model which show that QS(trans) = 2QS(cis). Clearly the observed quadrupole splittings for the dialkyltin bis(dithiocarbamates) are smaller than those observed for axially symmetric trans octahedral complexes of the type R_2SnX_4 and larger than those observed for the analogous cis configurations. The other geometry which suggests itself is that of a distorted tetrahedral configuration in which the two dithiocarbamate ligands act as unidentate moieties with a single tin–sulfur σ bond, leaving the second sulfur atom in each ligand in a nonbonding orientation. Such a

---

[15] K. L. Leung and R. H. Herber, *Inorg. Chem.*, **10**, 1020 (1971).

[16] H. H. Jaffe, *J. Phys. Chem.*, **67**, 1501 (1963); J. E. Huheey, *ibid.*, **69**, 3284 (1965), and references therein; J. E. Huheey and J. C. Watts, *Inorg. Chem.*, **10**, 1553 (1971).

[17] J. J. Zuckerman, *Advan. Organometal. Chem.*, **9**, 21 (1970).

[18] V. I. Gol'danskii, V. V. Khrapov, O. Yu. Okhlobystin, and V. Ya Rochev, "Chemical Applications of Mossbauer Spectroscopy," V. I. Gol'danskii and R. H. Herber, Ed., Academic Press, New York, N. Y., 1968, Chapter 6.

structure can, however, be ruled out on the basis of recent data[19] on dialkyltin(IV) bisthiols obtained in this laboratory. The observed quadrupole splittings for $(CH_3)_2Sn(SCH_2C_6H_5)_2$, $(CH_3)_2Sn(SC_{12}H_{25})_2$, and $(C_4H_9)_2Sn(SC_{12}H_{25})_2$ are 1.65, 1.59, and 1.58 mm/sec, respectively, at ~80°K, and it is concluded that this magnitude of the QS parameter is properly associated with a distorted tetrahedral structure for dialkyltin compounds having two tin–sulfur σ bonds.

Returning now to the bonding action of the dithiocarbamate ligand, the present data can be understood in terms of two different tin–sulfur interactions per ligand: one of these is a normal tin–sulfur σ bond involving a tin–sulfur distance of ~2.5 Å, while the other sulfur atom is located at ~3 Å from the metal atom and reflects a considerably weaker bonding interaction between the metal and the ligand. Under these conditions it is probable that the C–Sn–C bond angle will depart significantly from 180° and C_{2v} symmetry no longer obtains in these compounds. This behavior is to be contrasted with the bidentate nature of the ligand–transition metal interaction in which two essentially equivalent metal–sulfur bond lengths (and hence bonding interactions) have been reported.

The *anisobidentate* (from the Greek meaning unequal, and referring to the interaction between a metal and a bidentate ligand having two identical atoms involved in unequal bonding situations) character of the dtc ligand is also evident from the infrared spectra of these compounds, as shown in Figure 4. In addition to the characteristic Sn—S stretching frequency at about 380 cm^{-1}, the spectra of both the X = Y = alkyl and X = Y = halogen compounds show the characteristic infrared bands assigned to the C=S stretching frequency at ~985 cm^{-1} and a ligand mode at ~909 cm^{-1}. While the Sn—S vibrational frequency is dependent on the nature of the other ligands attached to the metal atom, the C=S and ligand modes in the 900–1000-cm^{-1} region are relatively insensitive to changes in the other ligands attached to the metal atom.

Both the isomer shift parameter and the Sn–S vibrational frequency reflect the charge density around the metal atom, and it is thus not too surprising that there is a reasonably linear correlation of these two parameters not only with each other (Figure 5) but also with the electronegativity of the X and Y ligands as is inferred from the isomer shift systematics referred to above (Figure 6). From this latter figure it is seen that $d\nu/d\chi$ is positive, indicating that as the halogen becomes more electronegative and thus stabilizes a larger positive charge on the metal atom, the tin–sulfur vibrational frequency shifts to higher values as the chalcogen atom transfers more of its charge to the metal atom.

Finally, in the context of the anisobidentate action of the dtc ligand in the dialkyltin(IV) compounds, it is interesting to note that the quadrupole splitting observed for $(C_6H_5)_2Sn(dtc)_2$ is only 1.74 mm/sec (see Table I) consistent with the values for the diphenyl-, dibenzyl-, and dibutyldithiocarbamate complexes of diphenyltin(IV) reported by Fitzsimmons,[4] as well as the data reported by Parish and Platt[20] in their review of isomer shift systematics in substituted organotin(IV)

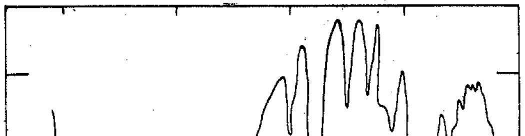

Figure 4.—Portion of the infrared spectrum of dimethyltin(IV) bis(diethyldithiocarbamate).

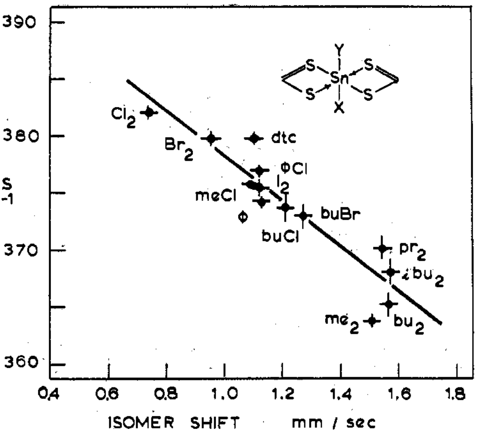

Figure 5.—Correlation between the Sn–S infrared frequency and the Mössbauer isomer shift for a series of tin(IV) bis(diethyldithiocarbamate) compounds discussed in the text.

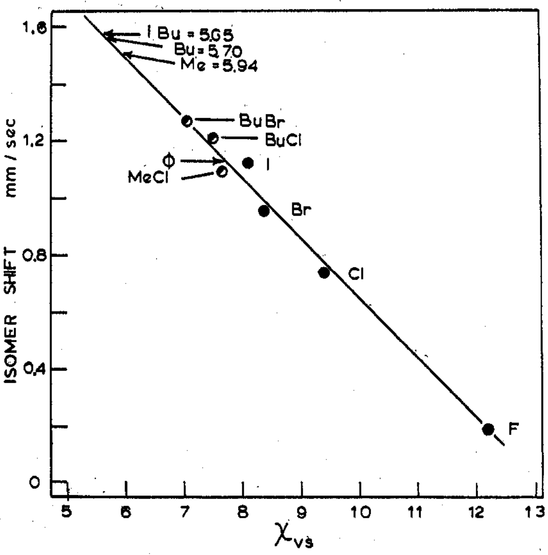

Figure 6.—Correlation betwen the isomer shift (from $BaSnO_3$) and ligand electronegativity for the compounds of the type $Sn^{IV}XY(dtc)_2$ discussed in the text. Where X = Y, the ligand electronegativity has been extracted from the extrapolation of the data for X = Y = F, Cl, Br, I. Where X ≠ Y, the average of the two ligand electronegativities has been used to fix the point on the horizontal axis.

---

[19] C. H. Stapfer and R. H. Herber, to be submitted for publication.

[20] R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, **4**, 589 (1970).

compounds. As noted above these values are very close to those observed[19] for dialkyltin(IV) compounds in which there are two tin–sulfur σ bonds leading to a distorted tetrahedral configuration about the metal atom. It should be noted, however, that the QS observed for $(C_6H_5)_2Sn(dtc)_2$ is close to half that observed for the analogous dialkyltin(IV) species and may thus be indicative of a cis configuration of the two aryl groups, since a point-charge model calculation demands QS(cis) = $^1/_2$QS(trans) if all bond distances and angles remain invariant under the symmetry change. It is clear from the present results that the interaction between the metal atom and the two sulfur atoms of the ligand moiety involves two rather different orbital overlaps, and it is not surprising that the anisobidentate nature of the ligand leads to a quadrupole interaction which approaches that due to a distorted tetrahedral diaryltin(IV) bis(sulfur-bonded ligand) structure.

Further support for the structure of the dimethyltin(IV) bis(dithiocarbamate) can be inferred from the nuclear magnetic resonance data summarized in Table II. As expected, the methylene protons of the ligand ethyl group are more sensitive to variations in the nature of the metal–ligand bond than are the methyl protons of the ligand. The chemical shift of the CH_2 protons lies intermediate between that observed for the sodium salt of the ligand (in which the C=S bond is preserved and the ligand acts as a monodentate entity) and that observed for the nickel(II) complex (in which the ligand is acting as a symmetrical bidentate moiety with two essentially equal metal–sulfur interactions). Again, these data support the anisobidentate nature of the dithiocarbamate ligand in the organotin compound. It should be noted, however, that these data refer to solution (rather than neat solid) species and that, at the present time, little is known concerning the integrity of the compound when neat solid and solution species are involved.

Table II

Nuclear Magnetic Resonance Data[a]

	Na^+L^- (acetone-d_6)	$(CH_3)_2SnL_2$-(CH_2Cl_2)	$(CH_3)_2SnL_2$-(acetone-d_6)	NiL_2-(CH_2Cl_2)
CH_3	1.20	1.26	1.27	1.19
CH_2	4.13	3.85	3.90	3.59
$CH_3(Sn)$		1.55	1.44	
		J Values, Hz		
$^{119}Sn–H$		43 ± 1	43 ± 1	
$^{117}Sn–H$		41 ± 1	40 ± 1	

[a] The proton shifts are given in ppm from TMS. $CH_3(Sn)$ refers to the protons of the methyl group bonded to the tin atom.

(c) **Temperature Dependence of the Mössbauer Parameters in $(CH_3)_2Sn(dtc)_2$.**—From the temperature dependence of the area under the resonance curve and the temperature dependence of the relative intensity of the two components of the quadrupole-split Mössbauer spectrum, it is possible to extract two further pieces of information concerning the intermolecular bonding forces and stereochemistry of dimethyltin bis(dithiocarbamate).

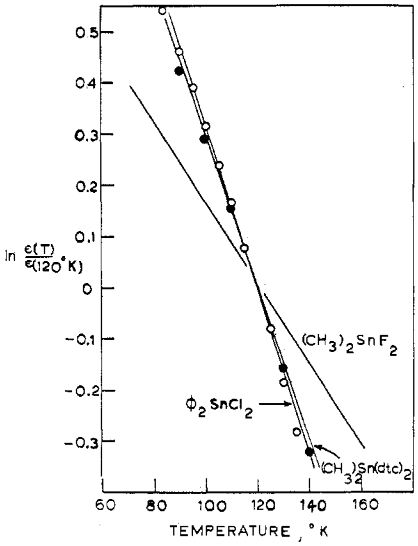

Figure 7.—Normalized ln (resonance effect magnitude) plotted as a function of temperature for dimethyltin(IV) bis(diethyldithiocarbamate), diphenyltin dichloride, and dimethyltin(IV) difluoride. The slopes of the curves are related to the strength of the intermolecular bonding in these compounds. The data have been normalized to the 120°K values to effect intersample comparison.

The anisobidentate nature of the dithiocarbamate ligand makes possible one additional architecture for the R_2Sn^{IV} complexes under discussion which needs to be examined. In this structure, the dtc ligand would act as a bridging moiety between two adjacent metal atoms, giving rise to a polymeric structure for the neat solid. The existence of such a polymeric configuration can be examined by a comparison of the temperature dependence of the recoil-free fraction of the ^{119}Sn resonance in the compound in question with that observed in appropriate monomeric and polymeric model compounds. For a thin absorber ($t \propto n\sigma_0 f_a < 1$) the temperature dependence of the recoil-free fraction in the absorber, $f_a(T)$, is identical with the temperature dependence of the area under the resonance curve $A_a(T)$, a parameter which can be readily extracted from the appropriate Mössbauer data. Moreover, normalization of such data to a common temperature (in the present case 120°K) permits direct comparison of the temperature dependence of the area parameter between different samples. From the simple Debye theory of solids it is inferred[21] that a plot of ln $A(T)$ against temperature will be a linear function in the high-temperature limit, and such data have been used previously to extract a "Mössbauer temperature" for a variety of organometallic and related compounds. The slope d ln A/dT can be related to the strength of the intermolecular bonding forces; under comparable conditions, the smaller this temperature dependence the larger is the sum of all of the intermolecular bonding forces which influence the vibrational spectrum of the metal atom. The temperature dependence of the area under the resonance curve (normalized to the 120°K data point) for $(CH_3)_2Sn(dtc)_2$ is given in Figure 7, together with corresponding data for $(C_6H_5)_2SnCl_2$ and $(CH_3)_2SnF_2$. A recent X-ray diffraction study[22] of diphenyltin dichloride (mol wt 343) has shown that the solid consists of discrete molecular units composed of distorted tetrahedral entities. The Sn–Cl distance in adjacent molecules is 3.77 Å, as compared

---

[21] See for example R. H. Herber, *Symp. Faraday Soc.*, **No. 1** (1968); S. C. Chandra and R. H. Herber, "Mossbauer Effect Methodology," Vol. 5, I. Gruverman, Ed., Plenum Press, New York, N. Y., 1970.

[22] P. T. Greene and R. F. Bryan, *J. Chem. Soc. A*, 2549 (1971).

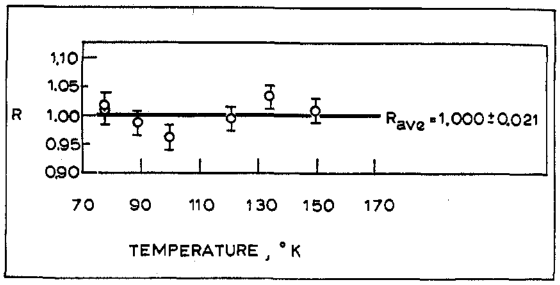

Figure 8.—Gol'danskii–Karyagin asymmetry in $(CH_3)_2Sn^{IV}(dtc)_2$. The data have been corrected for temperature-independent crystal orientation effects and departure of the spectrometer base line from linearity due to solid angle effects. The vibrational amplitude is isotropic within the quoted 2% experimental error.

to the normal Sn–Cl bonding distance of 2.346 Å, and hence significant bridging behavior of the halogen atoms can be ruled out. In this context, this molecule can be considered as an appropriate model compound for a monomeric Sn(IV) organometallic entity. In contrast, the diffraction data[23] for $(CH_3)_2SnF_2$ show unambiguously the presence of strong intermolecular bonding forces in which the halogen atoms serve as bridging groups to give a two-dimensional polymeric solid. A detailed Mössbauer study of this compound has been reported earlier.[24]

From the data summarized in Figure 7 it is seen that d ln $A(T)/dT$ for $(CH_3)_2Sn(dtc)_2$ is nearly the same as that for $(C_6H_5)_2SnCl_2$ (the slope ratio is 1.14:1) and significantly larger than that observed for $(CH_3)_2SnF_2$. From these results—as well as those[15] for such polymeric species as $(CH_3)_2Sn(acac)_2$, $(CH_3)_2Sn(SCN)_2$, and related five-coordinate polymeric organotin compounds[25]—it is clear that there is no significant intermolecular bonding in the bis(dithiocarbamate) species and that consequently the ligand is bonded to a single metal atom and acts as an anisobidentate entity to a single metal atom as has already been inferred from the QS data cited above. This monomeric nature of the dialkyltin(IV) bis(dithiocarbamates) in the solid state is in agreement with and extends the molecular weight data of Bonati, *et al.*,[7] in which the nature of the solute was determined in $CHCl_3$ and C_6H_6 solutions.

This conclusion is further supported by the absence of a temperature-dependent asymmetry in the relative intensity of the two components of the quadrupole doublet spectrum. It has been amply demonstrated in previous studies[24,25] that when a tin atom is the central atom in a molecule which possesses axial symmetry and in which there is a significant anisotropy of the vibrational amplitude parallel and perpendicular to the symmetry axis, the Mössbauer spectra will reflect a temperature-dependent asymmetry in the intensity ratio of the quadrupole-split doublet (the so-called Gol'danskii–Karyagin effect[26]). As shown in Figure 8, and summarized numerically in Table III, there is no significant temperature dependence of this intensity ratio in the spectra of $(CH_3)_2Sn(dtc)_2$ in the temperature range 78–150°K. Although these data do not by themselves rule out other structural possibilities (since a coincidental balancing of bonding forces could obtain even in a distorted tetrahedral or regular trans octahedral configuration to give rise to an isotropic vibrational amplitude distribution about the metal atom), they are again consistent with the distorted quasioctahedral structure postulated above for the dialkyltin(IV) bis(dithiocarbamate) ligands which is expected to reduce the difference in the strength of the bonding interaction between the metal and the two sulfur atoms on the one hand and the metal and the alkyl groups on the other. Moreover, the departure from cylindrical symmetry due to the nonlinearity of the C–Sn–C interactions referred to above will also reduce the ellipticity of the vibrational amplitude of the metal atom. The observed consequence of this effect is to lead (within the experimental errors of the present measurements) to a spherically symmetric (isotropic) vibrational motion of the metal atom with respect to the center of the molecular geometry.

TABLE III

TEMPERATURE DEPENDENCE OF THE GOL'DANSKII–KARYAGIN ASYMMETRY RATIO (R) FOR $(CH_3)_2Sn(dtc)_2$[a]

Temp, °K	$R = I_+/I$	Temp, °K	$R = I_+/I$
78	1.016	121	0.993
78	1.007	134	1.030
89	0.985	150	1.007
100	0.960		

[a] The raw data have been corrected for temperature-independent crystal orientation effects and solid angle instrumental departure from base line linearity. The average value over the interval 78° ≤ T ≤ 150° is $R = 1.000 \pm 0.021$.

(d) **Bonding and Structure of Monoalkyltin(IV) Bis(dithiocarbamate) Compounds.**—The data on compounds of the type $RSnL_2X$ summarized in Table I can be rationalized on the basis of the preceding discussion concerning the nature of the dithiocarbamate ligand. The magnitude of the quadrupole splitting parameter which is observed (~1.7 mm/sec) does not permit an unambiguous structural assignment to be made, since model compounds for monoalkyltin species with three- and five-coordinating ligands have not been studied in detail. From the fact that the isomer shift of $RSnL_2X$ is just intermediate between the isomer shifts observed for R_2SnL_2 and SnL_2X_2, it may be concluded that the nature of the ligand L is identical in the three cases. On this basis a working hypothesis may be adopted that the dithiocarbamate ligand in the monoalkyltin(IV) species exists as the same kind of anisobidentate moiety as has been postulated present in the dialkyltin(IV) compounds.[27]

(e) **Bonding and Structure of Tetrakis(dithiocarbamato)tin(IV).**—The absence of a resolvable quadrupole splitting for the tetrakis(dimethyl- and -diethyl dithiocarbamato)tin(IV) is indicative of a (nearly) cubic symmetry charge distribution around the metal atom in these two compounds. The qualification arises from the observation that the line width, which is

---

(23) E. O. Schlemper and W. C. Hamilton, *Inorg. Chem.*, **5**, 995 (1966).

(24) R. H. Herber and S. C. Chandra, *J. Chem. Phys.*, **52**, 6045 (1970).

(25) R. H. Herber, S. C. Chandra, and Y. Hazony, *ibid.*, **53**, 3330 (1970).

(26) V. I. Gol'danskii, *et al.*, *Dokl. Akad. Nauk SSSR*, **147**, 127 (1962); *Dokl. Phys. Chem.*, **147**, 766 (1963).

(27) After this paper had been submitted for publication, the authors received a communication from Professor E. O. Schlemper, pertaining to the results of an X-ray diffraction study of $C_4H_9Sn(dtc)_3$ and $CH_3Sn(dtc)_3$ confirming the essential correctness of this hypothesis. The diffraction data clearly indicate the *anisobidentate* nature of the bis(ethyldithiocarbamate) ligand in these compounds, and a complete discussion of the X-ray data is to be published. We are grateful to Professor Schlemper for making these data available to us prior to publication.

observed even for moderately thin samples (~1.2 mm/sec), is broader than would be expected for an ideally cubic compound and suggests a small departure from such an idealized geometry, presumably due to the steric requirements of the ligands.

A crystal structure study of the tetrakis(*N*,*N*-diethyldithiocarbamato)tin(IV) has been published by Harreld and Schlemper,[28] who found a distorted octahedral environment around the tin atom with two monodentate and two bidentate ligands evident from the metal–sulfur bond distances. The departure from regular O_h symmetry is significant in this molecule in which the S–Sn–S bond angle is 70.6° for the chelated ligand and 99.7° for the S–Sn–S angle between the chelated and monodentate ligands. Finally, it is interesting to note that the S–Sn–S bond angle involving the two monodentate ligands is 81.1°, thus placing these two groups nearly cis with respect to each other, rather than in the trans position which might have been expected. The Sn–S bond distance for the nonbonded sulfur atom is 3.9 Å (compared to a van der Waals contact of 3.7 Å) and hence the monodentate ligand cannot be considered as anisobidentate in this structure.

The line broadening observed in the Mössbauer spectra (*vide supra* and Table I) reflects this departure from cubic symmetry and suggests a similarity between the structure of the tetrakis(*N*,*N*-dimethyldithiocarbamato) compound and the structure studied by Harreld and Schlemper. From the isomer shift–electronegativity correlation[12] the mean ligand–sulfur electronegativity is seen to be about 8.75 on the Jaffe–Mulliken scale, intermediate between the electronegativity of bromide and chloride bonded to Sn(IV). Beyond observing the internal consistency of this value for a tin–sulfur bonding interaction little further information can be extracted with confidence from the present data.

IV. Summary

The present study has served to elucidate the structure and bonding in a series of organotin(IV) dithiocarbamates by the use of infrared, nmr, and Mössbauer spectroscopies. In dialkyltin(IV) bis(dithiocarbamate) complexes the ligand acts as an anisobidentate moiety, the two sulfur atoms interacting unequally with the central metal atom to give rise to significantly distorted octahedral configurations about the tin atom. Mössbauer studies over the temperature range 78–150°K have shown that in $(CH_3)_2Sn(dtc)_2$, the solid is composed of monomolecular units and no evidence for intermolecular bridging by the sulfur-containing ligand in the solid is noted in the data. The metal atom vibration is essentially isotropic in this molecule over the indicated temperature range. In the case of the tetrakis(dimethyldithiocarbamate and -diethyldithiocarbamate) complexes of Sn(IV), there is no resolvable quadrupole splitting extractable from the Mössbauer data—although there is a noticeable line broadening observed in the spectra—and thus the charge distribution about the metal atom must be nearly ideally cubic, arising from the distorted octahedral ligand configuration about the metal atom involving two isobidentate and two monodentate ligands bonded to the central atom as indicated by published diffraction data. The present study has also permitted the evaluation of group electronegativities for alkyl and aryl groups bonded to Sn(IV), as well as for the ethyldithiocarbamate ligand in a series of structurally related compounds.

Acknowledgment.—This research has been supported in part by the U. S. Atomic Energy Commission under Contract At(11-1) 3513, and the present paper constitutes Document CH-3513-82. This support is gratefully acknowledged. The authors are also indebted to Dr. C. H. Stapfer for a number of illuminating discussions and for his permission to cite experimental data prior to publication.

---

[28] C. S. Harreld and E. O. Schlemper, *Acta Crystallogr., Sect. B*, **27**, 1964 (1971).

CONTRIBUTION FROM LABORATORIO CNR AND ISTITUTO DI CHIMICA
GENERALE ED INORGANICA DELL'UNIVERSITÁ DI FIRENZE, 50132 FLORENCE, ITALY

Single-Crystal Electronic Spectra of a $NiPI_3$ Chromophore

BY I. BERTINI,* D. GATTESCHI, AND F. MANI

Received February 2, 1972

Single-crystal polarized spectra of tetraphenylarsonium triiodo(triphenylphosphine)nickelate(II), $[(C_6H_5)_4As][NiI_3\{P(C_6H_5)_3\}]$, have been recorded between 380 and 77°K. The $NiPI_3$ chromophore has an approximate C_{3v} symmetry; however, the observed polarization properties cannot be accounted for by axial symmetry. The band intensities are found to be temperature dependent. This has been discussed on the basis of a temperature dependent population of levels arising from low symmetry and spin–orbit coupling effects on the ^3E ground level.

Introduction

The technique of single-crystal polarized electronic spectroscopy has developed as a useful tool in gaining specific information about the electronic structure of the metal complexes.[1,2] However only a few high-spin nickel(II) complexes have been investigated.[3–7] Among the pseudotetrahedral chromophores, only

---

[1] N. S. Hush and R. J. M. Hobbs, *Progr. Inorg. Chem.*, **10**, 259 (1968).

[2] B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).

[3] R. A. Palmer and T. S. Piper, *Inorg. Chem.*, **5**, 864 (1966).

[4] C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, **40**, 792 (1964).

[5] R. Dingle and R. A. Palmer, *Theor. Chim. Acta*, **6**, 249 (1966).

[6] R. A. Palmer and C. R. Taylor, *Inorg. Chem.*, **10**, 2546 (1971).

[7] M. Gerloch, J. Kohl, J. Lewis, and W. Uhrland, *J. Chem. Soc. A*, 3269 (1970).