



through the halogen atoms of adjacent molecules was realized, making one copper atom five coordinate and simultaneously weakening one of the Cu-O bonds (2.3 Å). In this case, there is a weaker antiferromagnetic interaction in 8 than in its analog 5, which must be attributed to the structural effect of weakening the Cu-Cu bridging linkages, since there are no other significant differences between molecules 5 and 8.

Although the magnetic properties of the complexes are very dependent upon temperature, there is no pressure dependence within experimental error, up to 3000 atm, indicating that there is little difference in volume between the singlet and triplet forms of the molecules. This compares interestingly with the lack of volume change on electron pairing in the antiferromagnetic copper(II) acetate²² and the dramatic volume decrease upon electron pairing in ferric dithiocarbamates.^{23,24} At very high pressures (~10⁵ atm), a

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phase change analogous to the tetrahedral → planar transition in CuCl₄²⁻ and CuBr₄²⁻ may be expected.²⁵

In agreement with the pressure effect, the complexes 3 and 4 have different bond angles but essentially the same bond lengths and therefore essentially the same volumes for corresponding molecular fragments despite the fact that 3 contains twice as many triplet state molecules as 4. Thus a single important factor exists between the pairs of copper atoms. This factor is the angular arrangement of the ligand atoms about the copper, and variation of these angles to correspond to tetrahedral distortions from planarity leads to rapid weakening of the interactions.

Purely inductive effects, when the R group is changed, have not been invoked in the discussion, and they are not considered to be large, because changing of R consists of altering a substituent atom three bond distances away from the copper. This is especially so if our conclusion is valid, that it makes little difference whether the substituent X directly on the copper is Cl or Br.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers of this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W. Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy, or \$2.00 for microfiche, referring to code number INORG-74-2013.

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Mossbauer Spectra of *cis*-Dicyanoethylene-1,2-dithiolatotin(IV) Complexes¹

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The Mossbauer spectra of a variety of formally four-, five-, and six-coordinate dicyanoethylene-1,2-dithiolato (mnt) complexes of tin(IV) have been obtained. Evidence is presented for polymeric R₂Sn(mnt) (R = CH₃, C₆H₅) species and for monodentate coordination of the mnt unit in the R₃Sn(mnt)⁻ ion (R = CH₃, C₆H₅). The R₂Sn(mnt)X⁻ (R = CH₃, X = Cl, Br, I; R = C₆H₅, X = Cl) complexes appear to be authentic five-coordinate species. The *cis* configuration is assigned to the R₂Sn(mnt)₂²⁻ (R = CH₃, C₆H₅) ions. The isomer shift of the Sn(mnt)₃²⁻ ion shows a marked cation dependence and is interpreted in terms of distortions in the coordination sphere. The mnt complexes are compared to the corresponding toluedithiolato and dithiocarbamato complexes whenever possible.

Introduction

Recent reports from this laboratory have shown that the *cis*-dicyanoethylene-1,2-dithiolate (mnt)²⁻ ion forms a wide variety of complexes with group IVb metal ions.³⁻⁵ Although

these complexes have been characterized by a variety of techniques,³⁻⁶ several questions concerning the geometrical and electronic structures of the species in question still remain unanswered. Mossbauer spectroscopy has proved to be a useful technique in formulating solutions to problems of this sort for a wide variety of tin compounds.^{7,8} Therefore, we have examined the Mossbauer spectra of a series of Sn^{IV}-mnt complexes in order to understand better the interaction of dithiolato ligands with posttransition elements.

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(2) mnt is an abbreviation of the trivial name maleonitriledithiolate for the dicyanoethylene-1,2-dithiolate ion.

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Experimental Section

Preparative Procedures. All mnt complexes,³⁻⁵ ethanolic solutions of disodium toluene-3,4-dithiolate, Na₂tdt,⁹ the toluene-3,4-dithiolatodimethyltin(IV) complex, (CH₃)₂Sn(tdt),¹⁰ and the chloro-*N,N*-dimethyldithiocarbamatodimethyltin(IV) complex, (CH₃)₂Sn(dtc)Cl,¹¹ were prepared by previously reported procedures. All other reagents and solvents were commercially available and used without further purification.

Bis(tetrabutylammonium) Tris(toluene-3,4-dithiolato)stannate(IV), [(C₄H₉)₄N]₃Sn(tdt)₃.¹² A stirred solution of Na₂tdt (2.00 g, 0.01 mol) in ethanol (100 ml) was treated with tetrabutylammonium chloride (1.95 g, 0.007 mol) and filtered into an ethanolic solution (25 ml) of tin(IV) chloride pentahydrate (1.15 g, 0.003 mol). The resulting yellow solid was isolated by filtration and recrystallized from acetone-ethanol. *Anal.* Calcd for [(C₄H₉)₄N]₃Sn(tdt)₃: C, 60.38; H, 7.74. Found: C, 60.16; H, 8.92.

Measurements. Mossbauer spectra were obtained using a constant-acceleration spectrometer constructed according to the design of Cohen¹³ and incorporating the rapid fly-back modification of Brafman.¹⁴ A single spectrum was accumulated in 256 channels of the Kicksort multichannel analyzer using a barium stannate (BaSnO₃) source obtained from New England Nuclear. The absorbers were contained in an Austin Science Associates nitrogen dewar. Unless otherwise noted, all spectra were obtained in transmission geometry with the source at ambient temperature and the absorber at liquid nitrogen temperature. Velocity was calibrated using 1.0-mil iron foil and isomer shifts are reported relative to BaSnO₃. Spectra were computer fit assuming Lorentzian line shapes. Due to the low intensity (typically 1-3%) of the absorption peaks observed for most of these compounds, the estimated confidence limits are ±0.04 mm/sec.

The mass spectrum was obtained on a Perkin-Elmer RMU-6D spectrometer operating at 80 eV and 130°.

Results and Discussion

Mossbauer parameters for the various tin(IV)-dithiolato complexes are summarized in Table I. Turning first to the (mnt)₃Sn^{IV} moiety, a significant variation in the isomer shift with the identity of the counterion is observed. A similar effect has been observed for the hexahalostannates which contain iodide as a ligand.¹⁵ In both cases, this effect appears to be related to the ease of distortion of the coordination sphere about the tin atom. A molecular structure determination of the (mnt)₃In^{III} complex indicated considerable variation in the indium-sulfur bond lengths.¹⁶ A similar situation is envisioned in the isoelectronic tin(IV) complex with the variation in the tin-sulfur bond lengths being a function of the packing forces, hence the nature of the cation. The infrared spectra of the (mnt)₃Sn^{IV} species indicate a distortion from D₃ symmetry.⁶

The variation in isomer shift for the (mnt)₃Sn^{IV} complexes precludes any quantitative assignment of the mnt group electronegativity. However, it may be estimated⁸ to be in the range of 2.6-2.8 on the Pauling scale. The isomer shift of the (tdt)₃Sn^{IV} complex is in the same general range as the (mnt)₃Sn^{IV} salts. A direct comparison between the two ligands (in the tris complexes) is not possible due to the variation of the isomer shift with the nature of the cation.

The isomer shifts of the dihalo (mnt)₂Sn^{IV} complexes exhibit a linear correlation with the halogen electronegativities

Table I. Mossbauer Data for Dithiolato Complexes

Complex ^a	Γ, ^b mm/sec	δ, ^c mm/sec	Δ, mm/sec
[(C ₆ H ₅) ₄ N] ₂ Sn(mnt) ₃	1.14	1.12	
[(C ₆ H ₅) ₄ N] ₂ Sn(mnt) ₃	1.02	1.23	
[(C ₆ H ₅) ₄ As] ₂ Sn(mnt) ₃	0.96	0.97	
[(C ₆ H ₅) ₄ N] ₂ Sn(tdt) ₃	1.04	1.10	
[(C ₆ H ₅) ₄ N] ₂ Sn(mnt) ₂ Cl ₂ ^d	2.00	0.78	
[(C ₆ H ₅) ₄ N] ₂ Sn(mnt) ₂ Br ₂ ^d	1.38	1.14	
[(C ₆ H ₅) ₄ N] ₂ Sn(mnt) ₂ I ₂ ^d	1.38	1.24	
[(C ₆ H ₅) ₄ N] ₂ Sn(mnt) ₂ (CH ₃) ₂	0.80	1.36	2.46
[(C ₆ H ₅) ₄ N] ₂ Sn(mnt) ₂ (C ₆ H ₅) ₂	0.78	1.22	1.40
[(C ₆ H ₅) ₄ N]Sn(mnt)(CH ₃) ₃	0.86	1.46	2.38
[(C ₆ H ₅) ₄ N]Sn(mnt)(C ₆ H ₅) ₃	0.81	1.26	1.55
[(C ₆ H ₅) ₄ As]Sn(mnt)(CH ₃) ₂ Cl	0.86	1.41	2.47
[(C ₆ H ₅) ₄ P]Sn(mnt)(CH ₃) ₂ Cl	0.84	1.43	2.63
Sn(dtc)(CH ₃) ₂ Cl ^e	0.90	1.45	2.80
[(C ₆ H ₅) ₄ As]Sn(mnt)(CH ₃) ₂ Br	0.80	1.51	2.66
[(C ₆ H ₅) ₄ As]Sn(mnt)(CH ₃) ₂ I	0.82	1.45	2.43
[(C ₆ H ₅) ₄ P]Sn(mnt)(CH ₃) ₂ I	0.93	1.39	2.48
[(C ₆ H ₅) ₄ As]Sn(mnt)(C ₆ H ₅) ₂ Cl	0.76	1.25	2.19
Sn(mnt)(CH ₃) ₂	0.98	1.59	2.93
Sn(mnt)(CH ₃) ₂ ^f	0.82	1.47	3.06
Sn(tdt)(CH ₃) ₂	0.93	1.57	2.53
Sn(mnt)(C ₆ H ₅) ₂	0.81	1.44	2.58

^a Spectra obtained on powders at 77°K. ^b Full width at half-maximum. For spectra showing resolvable quadruple splitting, the figure given is the average of the values for the individual peaks. ^c Relative to BaSnO₃. ^d See text. ^e In good agreement with previously published values: J. C. May, D. Petridis, and C. Curran, *Inorg. Chim. Acta*, 5, 511 (1971). ^f Room-temperature spectrum.

(using Mulliken-Jaffe valence-state electronegativity values¹⁷). The observed shifts are considerably more positive than the corresponding acetylacetates⁷ and slightly greater (for the dibromo and diiodo complexes, which may be subject to cation effects) than the diethyldithiocarbamates.^{18,19} The low values for the acetylacetates confirm the polar nature of these complexes²⁰ compared to the mnt complexes. The large line widths of dihalobis(dicyanoethylene-1,2-dithiolato)tin(IV) complexes suggest unresolved quadrupole splitting. A similar observation, and similar conclusion, was reported¹⁹ for the dihalobis(diethyldithiocarbamato)tin(IV) complexes.

The formally six-coordinate complexes R₂Sn(mnt)₂²⁻ (R = CH₃, C₆H₅) exhibit well-resolved quadrupole splitting. Mossbauer spectroscopy has been applied to the problem of distinguishing between cis and trans isomers in this type of system.²¹⁻²³ Predictions based on a point charge model (assuming idealized geometries) call for the quadrupole splitting of the trans isomer to be twice that of the cis isomer.^{21,24} Furthermore, for those complexes whose geometries have been assigned unambiguously using X-ray crystallography, quadrupole splitting values of approximately 2 mm/sec are associated with cis geometry while quadrupole splitting values of about 4 mm/sec are associated with trans geometries.^{8,21} The data presented in this paper then present an interesting problem in that the magnitude of the quadrupole splitting

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for the bis(dicyanoethylene-1,2-dithiolato)dimethyltin(IV) complex approaches twice that of the corresponding diphenyltin(IV) complex, yet both values are in the range normally associated with the cis configuration.

Six-coordinate diphenyltin(IV) complexes usually exhibit a cis configuration while dimethyltin(IV) complexes adopt either a cis or trans configuration, with the latter predominating.^{21,25} The dimethyltin(IV) unit has a strong tendency to maintain a linear C-Sn-C unit,^{25,26} since this structural feature allows for maximization of s character (and hence bond strength) in the tin-carbon bond. Thus, electronic factors favor formation of the trans isomer. On the other hand, the cis isomer is favored in terms of minimization of nonbonded repulsions on ligand atoms directly bonded to tin.²⁷ A distorted cis isomer with a C-Sn-C angle greater than 90° is even more favorable in this regard. Thus the actual geometry may depend upon a sensitive balance of electronic and steric factors. We will return to the question of distorted structures shortly.

Previous work has shown the dimethyltin(IV)-bis(dicyanoethylene-1,2-dithiolato) complex to have a ¹¹⁹Sn-CH₃ coupling constant (J_{SnCH}) of 78 Hz⁵ which is intermediate between the value of 99 Hz for the *trans*-dimethyltin(IV)-acetylacetonate complex²⁸ and the value of 71 Hz for the distorted *cis*-dimethyltin(IV) oxinate.²⁹ Based on this observation, the tentative suggestion of a cis configuration for the mnt complex was put forward. The proximity of the values for the isomer shifts for the dimethyl- and diphenyltin(IV) complexes also strongly suggests a similar coordination geometry for the two complexes.³⁰ If one were to assign a trans configuration to the dimethyltin(IV) complex, a substantial reduction in quadrupole splitting due to the low electronegativity of the mnt unit would have to be involved. This appears to be an unreasonable assumption in that for a given structure wide variations in the quadrupole splitting with the nature of the ligand are not observed for isostructural organotin compounds.^{30,31} Based on a variety of physical probes, then, the proposed six-coordinate structures for both the diphenyl- and dimethyltin(IV) bis mnt complexes appear to be derived from the idealized cis configuration. Two further structural possibilities must, however, be considered. The first of these is a tetrahedral structure, *e.g.*, one derived from monodentate mnt binding. On the basis of Mossbauer data alone, this possibility seems very strong, since a recent report³² on the Mossbauer spectra of dialkyldithioltin(IV) complexes demonstrates that both the isomer shifts and quadrupole splittings for Me₂Sn(SPh)₂ and Ph₂Sn(SPh)₂ are very close to the values we observe for Me₂Sn(mnt)₂²⁻ and Ph₂Sn(mnt)₂²⁻. We eliminate the possibility that these mnt complexes are four-coordinate on two grounds. As previously mentioned, the nmr coupling constant J_{SnCH} is in the range associated with a cis-octahedral configuration.⁵ Furthermore, as will be discussed below, the formally four-coordinate complex Me₂Sn(mnt) associates in the solid state.

Given this apparent drive to attain coordination numbers greater than 4 it seems unlikely that the formally six-coordinate Me₂Sn(mnt)₂²⁻ would lower its coordination number to the extent necessary to attain tetrahedral geometry.

The remaining structural possibility, and that which we favor, is a severely distorted cis-octahedral configuration involving anisobidentate mnt ligands. In discussing the Mossbauer data for the dialkylbis(diethylthiocarbamato)tin(IV) complexes, Herber, *et al.*,¹⁹ invoked a similar model. Those complexes had quadrupole splittings intermediate between the values expected for cis- and trans-octahedral configurations. Herber chose to discuss the structures in terms of a significant deviation from a 180° C-Sn-C angle, although a similar deviation from a 90° C-Sn-C angle would seem to be an equally good choice. Since both the Mossbauer and nmr data which we observe for Me₂Sn(mnt)₂²⁻ are more compatible with the cis- than the trans-octahedral configuration, we feel that the best description of the structure is one derived by distortion of a cis-octahedral geometry, including opening of the C-Sn-C angle and anisobidentate behavior of the mnt ligands. Our Mossbauer results for Sn(mnt)₃²⁻ indicate that the assumption of anisobidentate behavior for mnt is reasonable, and the steric arguments mentioned previously favor expansion of the C-Sn-C angle. The similarity between the Mossbauer parameters which we observe and those observed³² for R₂Sn(SPh)₂ is then not unexpected, since the limiting case of anisobidentate behavior (*e.g.*, monodentate mnt) and C-Sn-C angle opening is a tetrahedral structure.

There are three idealized geometries which could be considered for complexes of the type R₃Sn(mnt)⁻ (R = CH₃, C₆H₅). These are a polymeric chain of trigonal-planar R₃Sn⁺ units linked by mnt units, a tetrahedral species with a monodentate mnt unit, and a trigonal bipyramid with the mnt ligand bridging axial and equatorial sites. In a previous paper in this series, it was suggested that the polymeric species could be eliminated on the basis of infrared evidence and the tetrahedral species was discarded as unreasonable.⁴ The Mossbauer data in Table I allow us to investigate the stereochemistry of these complexes in more detail.

Quadrupole splittings for R₃SnX compounds where X is a potential electron pair donor exhibit specific ranges for various coordination geometries: *e.g.*, for polymeric species $\Delta > 3.0$ mm/sec,⁸ for tetrahedral species $\Delta = 1.6-2.6$ ^{33,34} (trialkyltin(IV) species at the higher end of the range), and for a trigonal bipyramid with donor atoms in an axial and equatorial site Δ has been predicted to be around 1.55 mm/sec.³⁴ Thus, the magnitude of the quadrupole splitting in the (CH₃)₃Sn^{IV}-mnt complex rules out the polymeric structure (in agreement with the infrared studies⁴) and suggests a tetrahedral configuration, although the probable overlap in likely quadrupole splitting values for the tetrahedral and trigonal-bipyramidal species precludes any definite structural assignments on the basis of this single measurement. The Mossbauer parameters for the R₃Sn(mnt)⁻ (R = CH₃, C₆H₅) ions may be compared to the previously investigated dithiocarbamate complexes.³⁵ The (CH₃)₃Sn^{IV}-dtc complex has been shown by X-ray crystallography to contain a monodentate dithiocarbamate ligand.³⁶ The near equivalence

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of the Mossbauer parameters for the dtc and mnt complexes indicates a monodentate (or nearly monodentate) mnt unit in the $(\text{CH}_3)_3\text{Sn}(\text{mnt})^-$ ion. Furthermore, the observed isomer shift and quadrupole splitting are in the range of the tetrahedral thio and thioacetato derivatives of tributyltin(IV).³⁷ The value of $J_{119, \text{SnCH}}$ for the $(\text{CH}_3)_3\text{Sn}(\text{mnt})^-$ ion is in the range normally associated with four-coordinate trimethyltin(IV) derivatives.⁴ While this may be due to a combination of low s character and rapid intramolecular exchange of axial and equatorial tin-carbon bonds in a five-coordinate species,⁴ it is also consistent with the proposed monodentate mnt moiety.

The diethyldithiocarbamatotriphenyltin(IV) complex has been reported to exhibit monodentate coordination of the dithiocarbamate ligand,³⁸ and the similarity of the Mossbauer parameters for this complex to those of the triphenyltin(IV) mnt complex suggests similar geometries for these complexes. The complication of similar expectations for the quadrupole splittings of the tetrahedral and trigonal-bipyramidal complexes again precludes a definitive structure assignment on the basis of the Mossbauer data alone. The data, particularly when coupled with a comparison to the Mossbauer data for the tetrahedral phenylthiotriphenyltin derivative,³⁷ are at least consistent with a tetrahedral structure. Although a definitive structural assignment must await an X-ray crystallographic determination, on the basis of the available evidence we propose that both the triphenyl- and trimethyltin(IV) mnt complexes are tetrahedral with monodentate mnt ligands.

The problem of bidentate vs. monodentate coordination must also be considered for the $\text{R}_2\text{SnX}(\text{mnt})^-$ complexes. Fitzsimmons and Sawbridge have interpreted the Mossbauer parameters for the analogous dithiocarbamate complexes in terms of monodentate coordination.³⁹ On the other hand, DeVries and Herber suggested an anisobidentate dithiocarbamate, i.e., unequal tin-sulfur bond lengths, for this type of complex.¹⁹ The molecular structure of $(\text{CH}_3)_2\text{Sn}(\text{dtc})\text{Cl}$, as determined by X-ray crystallography, consists of a distorted trigonal bipyramid with equatorial methyl groups, an axial chlorine atom, and the dithiocarbamate group bridging axial and equatorial sites.⁴⁰ The axial tin-sulfur distance is longer than the corresponding equatorial bond length. Thus, the dithiocarbamate moiety exhibits anisobidentate coordination in this complex. This behavior is in accord with the expectations for a trigonal-bipyramidal complex independent of the electronic requirements of the ligand. The Mossbauer parameters of the $\text{R}_2\text{Sn}(\text{mnt})\text{X}$ ($\text{R} = \text{CH}_3$, $\text{X} = \text{Cl}$, Br , I ; $\text{R} = \text{C}_6\text{H}_5$, $\text{X} = \text{Cl}$) ions may also be compared to the corresponding diethyldithiocarbamate complexes.⁴¹ The extensive similarities in the Mossbauer parameters of the dtc and mnt derivatives indicate similar structures for these two series of complexes. The similarities in the nmr and ir parameters⁵ for the dtc and mnt complexes lend support to this assignment.

There is an anomalous trend in the quadrupole splitting constants and isomer shifts in the series $(\text{CH}_3)_2\text{Sn}(\text{mnt})\text{X}$. On going from the chloride to the bromide an increase is observed. However, on going to the iodide a decrease is observed. Similar effects have been reported for some

monoalkylbis(dithiocarbamate) halides, $\text{RSn}(\text{dtc})_2\text{X}$.¹⁸

The formally four-coordinate compounds $\text{R}_2\text{Sn}(\text{mnt})$ ($\text{R} = \text{CH}_3$, C_6H_5) exhibit strong signals at 77°K and the $(\text{CH}_3)_2\text{Sn}(\text{mnt})$ species has a reasonably intense room-temperature spectrum (roughly 30% that of 77°K spectrum). Behavior of this type has been taken to be indicative of a polymeric unit.⁴² The corresponding tdt complex does not exhibit a strong 77°K spectrum, has a substantively lower quadrupole splitting, and is presumed to be monomeric. This observation is in keeping with the large melting point and solubility differences in the two compounds.^{5, 10} The mass spectrum of $(\text{CH}_3)_2\text{Sn}(\text{tdt})$ is composed of fragments from the monomer and one unidentifiable fragment of extremely low intensity (<1%) which may be a ditin fragment.⁴³ The mass spectrum of $(\text{CH}_3)_2\text{Sn}(\text{mnt})$ has significant ditin fragments.⁵ The difference in the two systems can be ascribed to the relative electron-withdrawing capabilities of the two ligands. The more polar tin-sulfur bond in the mnt complex⁴⁴ results in a greater effective positive charge on the tin atom and concomitantly more negative charge on the sulfur atoms. This situation leads to intermolecular association. Polymeric tin(IV) species involving bidentate sulfur donors have been observed in a variety of other systems.^{37, 45} The origin of the difference in quadrupole splitting between the tdt and mnt complexes probably lies in the greater deviation from cubic symmetry in the mnt complex due to the polymeric structure and to the greater charge imbalance in the tin-sulfur bonds in the mnt complex due to the strong electron-withdrawing properties of the mnt ligand. Both the mnt and tdt complexes exhibit substantively larger quadrupole splitting than the dialkyltin(IV) dithiols,¹⁹ which may represent deviations from the tetrahedral angles at the tin atom imposed by the ligand.³⁷ Given the sensitivity of the quadrupole splitting to the nature of the ligand in these complexes, it is of interest to note that the isomer shifts of the mnt and tdt complexes are virtually identical.

In conclusion, we have shown that in conjunction with other spectroscopic data, Mossbauer data allow us to construct some reasonable models for the structures of a large variety of tin(IV) complexes of the mnt ligand. Full conformation of these proposals must, of course, await full structure determination by diffraction methods.

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Registry No. $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Sn}(\text{mnt})_3$, 37523-55-0; $[(\text{C}_4\text{H}_9)_4\text{N}]_2\text{Sn}(\text{mnt})_3$, 31303-19-2; $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{Sn}(\text{mnt})_3$, 31438-61-6; $[(\text{C}_6\text{H}_5)_4\text{N}]_2\text{Sn}(\text{tdt})_3$, 51464-59-6; $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Sn}(\text{mnt})_2\text{Cl}_2$, 38429-12-8; $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Sn}(\text{mnt})_2\text{Br}_2$, 42524-02-7; $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Sn}(\text{mnt})_2\text{I}_2$, 42524-03-8; $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Sn}(\text{mnt})_2(\text{CH}_3)_2$, 37837-96-0; $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Sn}(\text{mnt})_2(\text{C}_6\text{H}_5)_2$, 37837-97-1; $[(\text{C}_2\text{H}_5)_4\text{N}]\text{Sn}(\text{mnt})(\text{CH}_3)_3$, 51391-35-6; $[(\text{C}_2\text{H}_5)_4\text{N}]\text{Sn}(\text{mnt})(\text{C}_6\text{H}_5)_3$, 51391-37-8; $[(\text{C}_6\text{H}_5)_4\text{As}]\text{Sn}(\text{mnt})(\text{CH}_3)_2\text{Cl}$, 51480-93-4; $[(\text{C}_6\text{H}_5)_4\text{P}]\text{Sn}(\text{mnt})(\text{CH}_3)_2\text{Cl}$, 51480-94-5; $[(\text{C}_6\text{H}_5)_4\text{As}]\text{Sn}(\text{mnt})(\text{CH}_3)_2\text{Br}$, 51480-96-7; $[(\text{C}_6\text{H}_5)_4\text{As}]\text{Sn}(\text{mnt})(\text{CH}_3)_2\text{I}$, 51480-98-9; $[(\text{C}_6\text{H}_5)_4\text{P}]\text{Sn}(\text{mnt})(\text{CH}_3)_2\text{I}$, 51480-99-0; $[(\text{C}_6\text{H}_5)_4\text{As}]\text{Sn}(\text{mnt})(\text{C}_6\text{H}_5)_2\text{Cl}$, 51481-01-7; $\text{Sn}(\text{mnt})(\text{CH}_3)_3$, 51391-38-9; $\text{Sn}(\text{tdt})(\text{CH}_3)_2$, 4312-00-9; $\text{Sn}(\text{mnt})(\text{C}_6\text{H}_5)_2$, 51391-39-0.

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(43) Selected monoisotopic mass spectral data based on ¹²⁰Sn: *m/e* 303, $(\text{CH}_3)_2\text{SnS}_2\text{C}_7\text{H}_6^+$ (73%); *m/e* 288, $\text{CH}_3\text{SnS}_2\text{C}_7\text{H}_6^+$ (85%); *m/e* 273, $\text{SnS}_2\text{C}_7\text{H}_6^+$ (100%); *m/e* 241, $\text{SnSC}_7\text{H}_6^+$ (12%); *m/e* 184, SnS_2^+ (6%); *m/e* 152, SnS^+ (9%); *m/e* 122, $\text{C}_7\text{H}_6\text{S}^+$ (84%); *m/e* 121, $\text{C}_7\text{H}_5\text{S}^+$ (84%); *m/e* 120, Sn^+ (26.5%).

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(41) $(\text{CH}_3)_2\text{Sn}(\text{dtc})\text{X}$: $\text{X} = \text{Cl}$, $\delta = 1.43$, $\Delta = 2.80$; $\text{X} = \text{Br}$, $\delta = 1.45$, $\Delta = 2.82$; $\text{X} = \text{I}$, $\delta = 1.53$, $\Delta = 2.84$. $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{dtc})\text{Cl}$: $\delta = 1.28$, $\Delta = 2.21$.¹⁹