Review

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Tin dithiocarbamates: applications and structures

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The uses and potential utility of tin/organotin dithiocarbamate, $^{-}S_2CNR'_2$, compounds are reviewed. Various derivatives exhibit exciting potential as anti-cancer agents, anti-microbial agents and insecticides, e.g. against mosquito larvae. Tin dithiocarbamates have also proven useful as precursors for tin sulfide nanoparticles. There is a wealth of structural data available for such compounds and with the exception of the diorganotin bis(dithiocarbamate) compounds, $R_2Sn(S_2CNR'_2)_2$, compounds for which different structural motifs are evident, there is a certain degree of homogeneity in the molecular structures for each class of compound unless there are additional coordination sites on the R and/or R′ groups. Owing to the strong coordination potential of the dithiocarbamate ligand for tin, supramolecular aggregates involving secondary Sn···S interactions are the exception rather than the norm. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: tin; dithiocarbamate; biological activity; tin sulfide; molecular geometry; crystallography

Introduction

Dithiocarbamate anions of generic formula $^{-}S_2CNR'_2$, Fig. 1, are the best known of an important class of metal-coordinating agents, the 1,1-dithiolates, which also comprise xanthates ($^{-}S_2COR$) and dithiophosphates ($^{-}S_2P(OR)_2$).[1] Dithiocarbamates are generally prepared by the reaction of CS_2 with an amine in the presence of base to yield ammonium or alkali metal salts. Facile reaction with a metal salt, often via simple metathesis, yields the corresponding metal dithiocarbamate. The stability of such complexes is renowned and readily explained by the significant contribution of resonance form (**II**), Fig. 1, to the overall electronic structure, ensuring that this anion is a very effective ligand for metals. There is now a wealth of structural data for metal dithiocarbamates[2,3] promoted in no small part by the many and varied applications of metal dithiocarbamates. Underscoring the affinity of dithiocarbamate ligands for metals, these ligands are known for their use as antidotes for metal poisoning, such as removing excess copper (Wilson's disease)[4] and ameliorating nephrotoxicity associated with platinum-based chemotherapy.[5] Indeed, the oxidized form of diethyldithiocarbamate (**I**, R = Et), i.e. thiuram disulfide or disulfiram (**III**, R = Et), is a drug, Antabuse®, used in the treatment of alcoholism as it interferes with the normal metabolic pathway of alcohol, resulting in a build-up of acetaldehyde and making the patient ill.[6] In addition to other medicinal uses,[7] metal dithiocarbamates are well known for their use in the vulcanization of rubber,[8] as pesticides,[9] and as synthetic precursors for the deposition of metal sulfide nanoparticles.[10]

Tin continues to attract significant attention, again owing to its many and varied applications in fields as diverse as agriculture, biology, catalysis and organic synthesis to name a few.[11] In this review, some of the applications of tin, including organotin, dithiocarbamates are summarized. This review is not meant to be exhaustive but, rather, is designed to highlight recent and exciting advances for this class of compound. As well, their structural characteristics as determined by X-ray crystallographic methods will be surveyed.

Biological Activities

The various applications of organotin compounds in the context of biological activity have been surveyed recently.[12] Organotin compounds have received a great deal of attention in terms of their potential as anti-tumour agents but as yet none have entered clinical trials.[13] Building upon earlier work,[14] a series of phenyltin dithiocarbamates were evaluated for their cytotoxicity against L1210 mouse leukaemia cell lines.[15] It was found that the series of compounds $Ph_{4-n}Sn(S_2CNEt_2)_n$, for $n = 1-3$, gave a 50% growth inhibition ratings of 0.3 μM compared with 0.6 and 1.2 μM for the drugs cisplatin and carboplatin, respectively. Interestingly, the introduction of chloride, as in $PhSn(S_2CNEt_2)_2Cl$ and $Ph_2Sn(S_2CNEt_2)Cl$, resulted in less toxicity, with ratings of 0.4 and 0.08 μM, respectively, but these were still more cytotoxic than the platinum-containing drugs. In a more expansive study, a series of 10 organotin dithiocarbamates were evaluated against a larger panel of human cancer cell lines.[16] Here, the opposite conclusion was found in that compounds of the general formula $(ArCH_2)_2Sn(S_2CNR'_2)Cl$ were more cytotoxic than their counterparts without chloride substituents, i.e. $(ArCH_2)_2Sn(S_2CNR'_2)_2$. The authors of this study suggested that this observation might be related to the ease of hydrolysis of the former.[16] The most cytotoxic compound of the series was $(4\text{-}NC\text{-}C_6H_4CH_2)_2Sn[S_2CN(CH_2CH_2)_2NCH_3]Cl$, with ratings against breast- (MCF-7 and EVSA-T), colon- (WiDr), ovarian- (IGROV) and non-small-cell lung-cancer (M226) cell lines of 8, 14, 34, 11 and 16 ng ml^{-1}, at least an order of magnitude more cytotoxic that exhibited by cisplatin. The organic drug doxorubicin was the other standard, with cytotoxicity ratings intermediate between the organotin compounds and cisplatin.[16]

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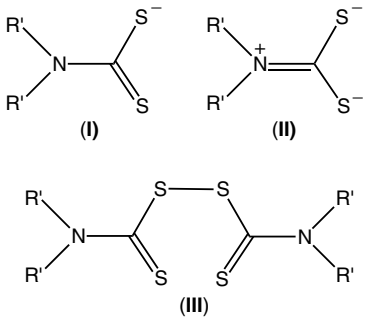

Figure 1. Generic structures for (**I**) the dithiocarbamate anion, (**II**) an important resonance structure for the dithiocarbamate anion, and (**III**) thiuram disulfide.

The potential anti-fungal activity of tin dithiocarbamates has attracted attention in terms of targeting fungi implicated in wood preservation, plant pathogens and in immuno-compromised patients.[17–24] A series of organotin dithiocarbamates analogous to those studied in a cytotoxicity trial described above[15] were also screened for activity against *Candida albicans, Candida tropicalis* and resistant *Candida albicans*.[19] This study showed that, while all organotin dithiocarbamates studied were fungicidal, it was the triphenyltin dithiocarbamate, $Ph_3Sn(S_2CNEt_2)$, and its pyrrolidine derivative that had the lowest minimal inhibitory concentrations.[21] Indeed, in terms of tin-bound substituents, the general trend of potency was Ph_3 > *n*-Bu_2 > Cl_2 > Ph_2 > Ph ~ c-Hex_3. A correlation was found between increasing fungicidal activity and decreasing biosynthesis of ergosterol. Finally, the importance of the presence of tin was illustrated in that all organotin compounds investigated had activities greater than those exhibited by the uncoordinated dithiocarbamate ligands administered on their own,[21] in keeping with earlier observations.[17–19] This observation does not necessarily hold true when considering anti-bacterial activity, where the opposite trend has sometimes been reported.[22–24] For the series of compounds $R_2Sn[S_2CN(CH_2CH_2)_2C(H)CH_3]Cl$, where the dithiocarbamate ligand is derived from 4-methylpiperidine, the R = Ph derivative displayed the greatest anti-fungal activity but it was the R = *n*-Bu species that probably exhibited the better anti-bacterial activity.[22] A series of compounds of the general formula $(SCH_2CH_2S)Sn(S_2CNR'_2)Cl$ have been evaluated against a range of bacteria.[24] While not effective against *E. coli*, some promising activity was found against a range of Gram-positive and Gram-negative bacteria. As with all the trials, usually the commercially available drugs were more active, but investigations continue in order to develop more potent derivatives so to overcome the current and projected problems of organisms developing drug-resistance.

The insecticidal activity of a series of $R_3Sn(S_2CNR'_2)$ compounds, for R = Ph and c-Hex, against the second larval instar of the *Anopheles stepensi* Liston and *Aedes aegypti* (L.) mosquitoes has been reported by the group of Eng *et al*.[25] It is of some interest that these derivatives were effective larvicides. No clear-cut differentiation in activity between the R = Ph and c-Hex derivatives was delineated.[25]

Synthetic Precursors for Tin Sulfides

As mentioned in the Introduction, metal dithiocarbamates have proved extremely useful for the synthesis of metal sulfide nanoparticles, thin films, etc.[10] Tin dithiocarbamates are no exception and their utility in this regard was reviewed in 1994.[26] At that time, it was known that the tin(II) species, $Sn(S_2CNEt_2)_2$, was a useful precursor for the preparation of SnS. Similarly, SnS could be prepared by thermal decomposition of tin(IV) species, $Sn(S_2CNEt_2)_2X_2$ (where X = halide), via X_2SnS intermediates. Less certain was the decomposition pathway of the binary Sn(IV) species, $Sn(S_2CNEt_2)_4$. Degradation was thought to occur through tin(II), i.e. $Sn(S_2CNEt_2)_2$, and thiuram, intermediates. Later work[27] showed that the final product was SnS_2, obtained via dinuclear $[(Et_2NCS_2)_2SnS]_2$, implying that each pair of dithiocarbamate ligands in the precursor $Sn(S_2CNEt_2)_4$ species lost $[Et_2NC(S)]_2S$ via initial elimination of thiuram, as indicated in earlier studies. Further work indicated that, at higher temperatures, $Sn(S_2CNEt_2)_4$ lost two molar equivalents of thiuram to eventually give SnO_2.[27] The same group showed that by chemical vapour deposition of unsymmetrical dithiocarbamate ligands, i.e. where the dithiocarbamate-bound R′ groups are inequivalent, as in $R_3Sn[S_2CN(n\text{-Bu})Me]$ for R = Me and *n*-Bu, both SnS and Sn_2S_3 films could be formed on a glass substrate under ambient conditions with a minimal amount of H_2S present.[28] Mixtures of SnS and Sn_2S_3 are also obtained from the thermal decomposition of $Ph_2Sn[S_2CN(CH_2)_4]_2$, characterized as the toluene solvate, and $Ph_3Sn[S_2CN(CH_2)_4]$, where the dithiocarbamate is derived from pyrrolidine.[29]

Structural Chemistry

With the above applications in mind, it is not surprising that the structural chemistry of tin dithiocarbamate species has received considerable attention over the years. Reflecting this interest, a search of the Cambridge Structural Database (CSD) revealed nearly 200 'hits' for this class of compound.[30] Herein, a systematic survey of the structural characteristics for the binary and other non-organometallic tin dithiocarbamates is presented followed by a description of mono-, di- and tri- organotin dithiocarbamate structures for which fractional atomic coordinates are available in the CSD and that do not suffer from unresolved issues with disorder.[30] Diagrams were produced with arbitrary atomic radii and reported geometric parameters calculated using the DIAMOND programme.[31]

Binary and Non-Organometallic Tin Dithiocarbamate Structures

The first of the structures to be described is the sole example of a tin(II) dithiocarbamate, namely $Sn(S_2CNEt_2)_2$, which has been the subject of two independent investigations (Fig. 2).[32,33] The tin atom is chelated by two asymmetrically coordinating dithiocarbamate ligands which, with the stereochemically active lone-pair of electrons, define a distorted trigonal bipyramidal geometry with the vacant coordination site being in the equatorial plane. Key geometric parameters for this and for other structures described in this section are collated in Table 1. The structure of $Sn(S_2CNEt_2)_2$ is a key example illustrating the strength of chelation afforded by the dithiocarbamate ligands. Thus, in the related tin(II) xanthate structures, $Sn(S_2COR)_2$, intermolecular Sn···S interactions are present that lead to supramolecular chains, but no such interactions are present in $Sn(S_2CNEt_2)_2$.[34a] Other studies have shown the same trends,[34]

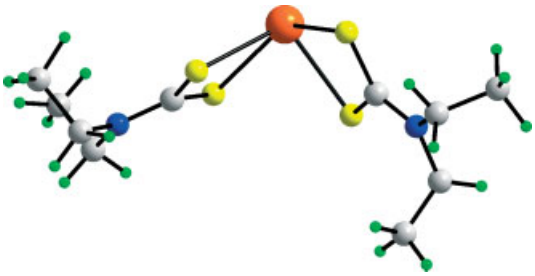

Figure 2. Molecular structure of $Sn(S_2CNEt_2)_2$. Colour code for this and subsequent diagrams: tin, orange; other metal, olive; halide, cyan; sulfur, yellow; oxygen, red; nitrogen, blue; carbon, grey; hydrogen, green.

so that a general observation can be made: the tin dithiocarbamates do not form supramolecular aggregates via Sn···S interactions.

There are two examples of binary tin(IV) dithiocarbamates, i.e. $Sn(S_2CNMe_2)_4$ [33] and $Sn(S_2CNEt_2)_4$,[35] with the former illustrated in Fig. 3. The tin atom is octahedrally coordinated by two chelating ligands and two monodentate dithiocarbamate ligands with the latter occupying mutually *cis*-positions. Distortions from the ideal octahedral are clearly related to the restricted bite angle of the chelating ligands and further, the asymmetry in the Sn–S bond distances formed by the chelating ligand is related to the *trans*-influence exerted by the monodentate ligands, i.e. the longer Sn–S bond distance formed by the chelating ligand is *trans*- to the sulfur atom of the monodentate ligand. The following three structures to be described, $Sn(S_2CNEt_2)_2(SR)_2$ for R = CH_2CF_3, Ph and c-Hex, are of interest in terms of their potential as precursors for the deposition of tin sulfide powders;[27] the R = c-Hex derivative is illustrated in Fig. 4. These structures are clearly related to the binary tin(IV) dithiocarbamates by simple substitution of the monodentate dithiocarbamate with the respective thiolate ligand. A comparison of the geometric parameters describing the binary

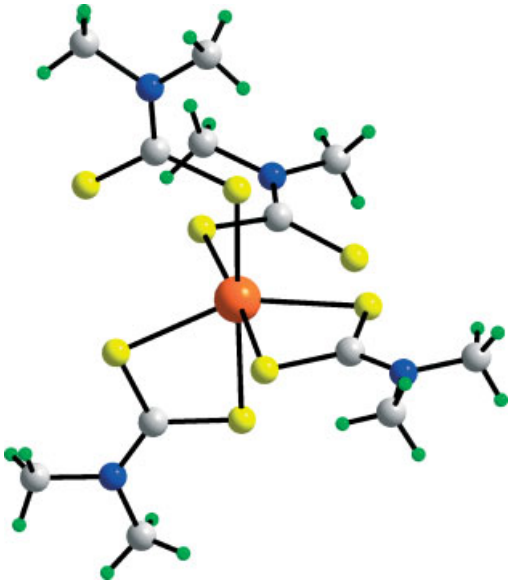

Figure 3. Molecular structure of $Sn(S_2CNEt_2)_4$ highlighting the distorted S_6 octahedral coordination geometry for tin and the *cis*-disposition of the monodentate dithiocarbamate ligands.

tin(IV) species with those of the $Sn(S_2CNEt_2)_2(SR)_2$ compounds shows that the degree of asymmetry in the Sn–S bond distances formed by the chelating ligands is diminished in latter three compounds. Also, the Sn–S bond distances formed by the SR thiolate ligands in $Sn(S_2CNEt_2)_2(SR)_2$ are uniformly shorter than those formed by the monodentate dithiocarbamate ligands. A systematic trend in the bond angles subtended by the SR thiolate ligands in $Sn(S_2CNEt_2)_2(SR)_2$ is also found with the widest angle of 100.68(5)° involving the SR thiolate with the more bulky cyclohexyl groups. Similar structures are found in a series of $Sn(S_2CNR'_2)_2X_2$, X = halide, compounds;[36–40] the R′ = Et, X = Cl derivative is

Table 1. Selected geometric parameters (Å, deg) for binary and non-organometallic tin dithiocarbamate structures

Compound	$Sn-S_{chelate}$	X	Sn–X	X-Sn–X	Ref.
$Sn(S_2CNEt_2)_2$	2.568(3), 2.768(3); 2.578(3), 2.822(2)	–	–	–	[32,33]
$Sn(S_2CNMe_2)_4$	2.511(4), 2.595(4); 2.516(4), 2.707(5)	S	2.500(6); 2.536(5)	91.3(1)	[33]
$Sn(S_2CNEt_2)_4$[a]	2.532(7), 2.553(7)	S	2.503(7)	81.0(1)	[35]
$Sn(S_2CNEt_2)_2(SCH_2CF_3)_2$	2.5534(7), 2.5650(11); 2.5625(8), 2.5773(9)	S	2.4575(9); 2.4745(8)	84.10(3)	[27]
$Sn(S_2CNEt_2)_2(SPh)_2$	2.552(1), 2.639(1); 2.547(2), 2.573(1)	S	2.480(1); 2.473(1)	88.85(4)	[27]
$Sn(S_2CNEt_2)_2[S(c\text{-}Hex)]_2$[a]	2.570(1), 2.618(2)	S	2.450(2)	100.68(5)	[27]
$Sn(S_2CNEt_2)_2Cl_2$	2.501(2), 2.577(2); 2.512(2), 2.570(2)	Cl	2.406(2); 2.394(2)	91.78(9)	[36]
$Sn[S_2CN(n\text{-}Bu)_2]_2Cl_2$	2.502(2), 2.585(2); 2.507(2), 2.547(2)	Cl	2.402(2); 2.380(2)	92.21(7)	[37]
$Sn(S_2CNEt_2)_2Br_2$	2.507(3), 2.589(3); 2.514(3), 2.570(4)	Br	2.557(2); 2.544(3)	92.66(6)	[38]
$Sn(S_2CNR^1)_2Br_2$[a,b]	2.518(2), 2.564(2)	Br	2.711(1)	90.64(3)	[39]
$Sn(S_2CNEt_2)_2I_2$	2.513(4), 2.583(4); 2.518(2), 2.584(3)	I	2.775(3); 2.769(2)	91.14(4)	[40]
$Sn[S_2CN(iBu)_2]_2(L^1)_2$[a,c]	2.576(1), 3.283(3)	$CpFe(CO)_2$	2.557(1)	129.01(4)	[41]
$Sn(S_2CNEt_2)_2L^2$[d]	2.508(2), 2.547(3); 2.542(3), 2.526(3)	I	2.033(5); 2.026(7)	81.3(3)	[42]
$Sn(S_2CNEt_2)_2L^3$[e]	2.526(4), 2.552(4); 2.530(4), 2.582(4)	I	2.135(9); 2.389(4)	83.3(3)	[43]
$\{Sn(S_2CNR^2)_2S\}_2$[f,g,h]	2.569(3), 2.582(3); 2.568(3), 2.609(2)	S	2.446(3); 2.449(3)	91.52(9)	[44]
$\{Sn(S_2CNEt_2)_2S\}_2$[g,i]	2.5676(6), 2.5986(4); 2.5773(6), 2.6076(5)	S	2.4454(4); 2.4550(4)	91.54(2)	[27]

[a] The tin atom is located on a crystallographic two-fold axis of symmetry. [b] NR^1 = morpholine, $N(CH_2CH_2)_2O$. [c] L^1 = the organometallic fragment $CpFe(CO)_2$ where Cp is the cyclopentadienyl anion, see Fig. 6. [d] L^2 = *o*-catecholate, see Fig. 7. [e] L^3 = 1-acetylpropen-1-thiolato-2-olate. [f] NR^2 = 4-methylpiperazine, $N(CH_2CH_2)_2NMe$, see Fig. 8. [g] The molecule is centrosymmetric. [h] Crystallizes as a di-dichloromethane solvate. [i] Crystallizes as a di-chloroform solvate.

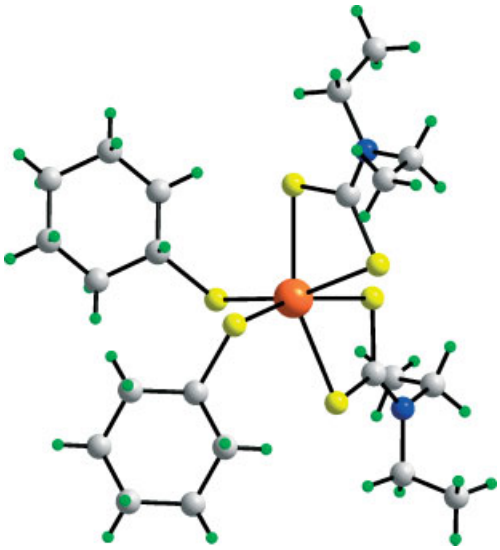

Figure 4. Molecular structure of $Sn(S_2CNEt_2)_2[S(c\text{-}Hex)]_2$ highlighting the distorted S_6 octahedral coordination geometry for tin and the *cis*-disposition of the monodentate thiolate ligands.

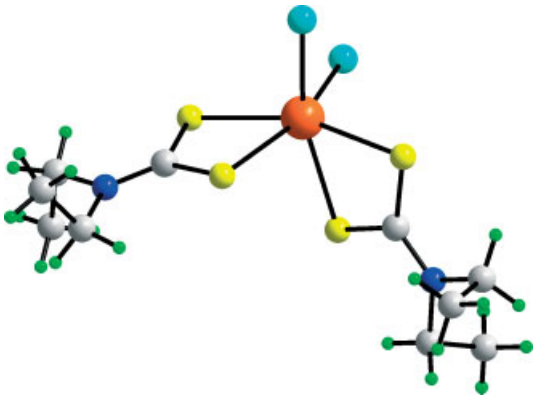

Figure 5. Molecular structure of $Sn(S_2CNEt_2)_2Cl_2$ highlighting the distorted *cis*-Cl_2S_4 octahedral coordination geometry for tin.

shown in Fig. 5. The robustness of this motif is exemplified by the observation that, for the homologous $Sn(S_2CNEt_2)_2X_2$, X = Cl,[36] Br[38] and I,[40] series, except for the expected lengthening of the Sn–X bond distances, there are no systematic trends in the bond distances or angles describing the tin atom geometries. In the same vein, no apparent trends are found to distinguish the structures of $Sn(S_2CNR'_2)_2Cl_2$, R′ = Et [36] and *n*-Bu.[37]

An exceptional structure in this category is found for $Sn(S_2CN(iBu)_2)_2L^1$, where L^1 = the organometallic fragment $CpFe(CO)_2$ (Cp is the cyclopentadienyl anion),[41] depicted in Fig. 6; the molecule has crystallographic two-fold symmetry. The tin atom exists within a skewed trapezoidal bipyramidal geometry with the plane defined by two highly asymmetrically coordinating dithiocarbamate ligands and with the $CpFe(CO)_2$ groups disposed over the weak Sn···S interactions. This motif is closely related to the predominant structural type observed for the diorganotin dithiocarbamates, $R_2Sn(S_2CNR'_2)_2$, as described below. The remaining mononuclear structures to be described have the two; "X" donor atoms linked within a chelating ligand, i.e. $Sn(S_2CNEt_2)_2L^x$, L^2 = *o*-catecholate,[42] Fig. 7, and L^3 = 1-acetylpropen-1-thiolato-2-olate.[43] As these structures follow the trends outlined above, they are not discussed further but their geometric parameters are included in Table 1. The final structures to be described in this section are dinuclear and feature two $Sn(S_2CNR'_2)_2$ units doubly bridged by a pair of sulfide atoms forming a centrosymmetric Sn_2S_2 square; the $\{Sn[S_2CN(CH_2CH_2)_2NMe]_2S\}_2$ derivative[44] is illustrated in Fig. 8. The geometric parameters closely follow those reported for the monomeric $Sn(S_2CNEt_2)_2(SR)_2$ analogues,[27] Table 1.

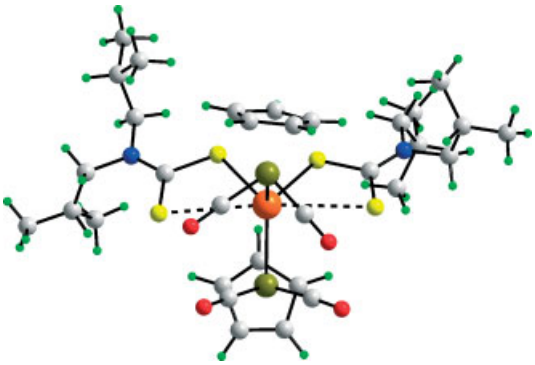

Figure 6. Molecular structure of $Sn[S_2CN(iBu)_2]_2[FeCp(CO)_2]_2$, highlighting the skew-trapezoidal bipyramidal coordination geometry for tin.

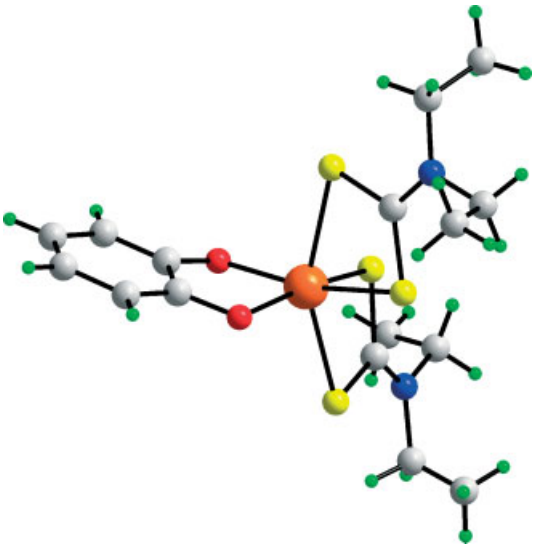

Figure 7. Molecular structure of $Sn(S_2CNEt_2)_2$(*o*-catecholate), highlighting the distorted *cis*-O_2S_4 octahedral coordination geometry for tin.

Monoorganotin Dithiocarbamate Structures

There are five crystal structure determinations that conform to the general formula $RSn(S_2CNR_2)_3$.[45–49] The prototype structure is illustrated in Fig. 9 for $PhSn(S_2CNEt_2)_3$;[49] geometric parameters are collected in Table 2. The structures feature three asymmetrically coordinating dithiocarbamate ligands but with one ligand being decidedly more asymmetric than the remaining two. The coordination geometry is based on a distorted pentagonal bipyramid with the organic substituent and the sulfur atom forming the shortest Sn–S bond occupying the axial positions. There is a high degree of concordance amongst the geometric parameters describing the tin atom geometries in

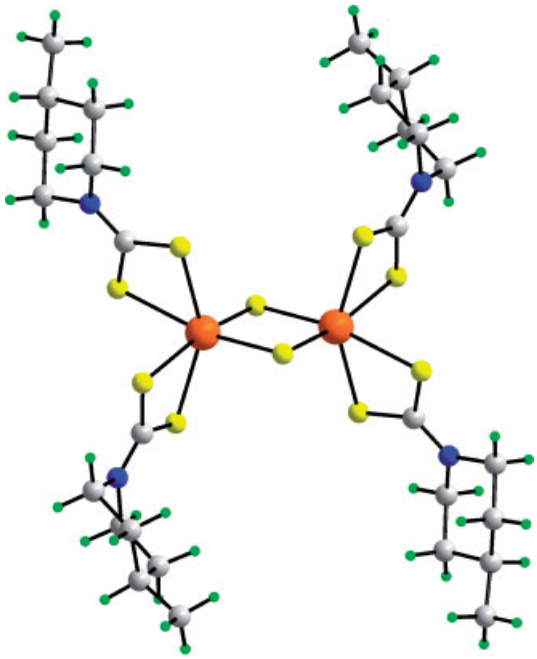

Figure 8. Molecular structure of dinuclear and centrosymmetric $\{Sn[S_2CN(CH_2CH_2)_2NMe]_2S\}_2$, highlighting the distorted S_6 octahedral coordination geometry for tin.

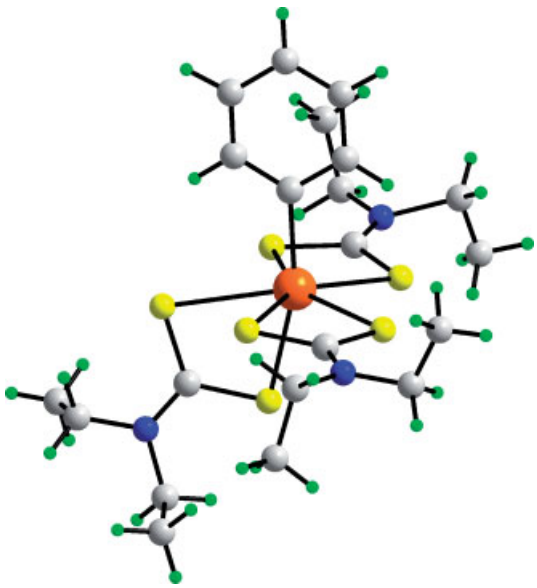

Figure 9. Molecular structure of $PhSn(S_2CNEt_2)_3$, highlighting the distorted pentagonal bipyramidal coordination geometry for tin.

these compounds. The notable exception to this conclusion are the phenyltin derivatives for which there is a clear indication that the Sn–S bond distances are generally shorter and a more symmetric mode of coordination adopted, on average, compared with those in the alkyltin derivatives. This observation is correlated with the somewhat electronegative nature of the phenyl group versus the electropositive alkyl groups. The next series of structures sees the replacement of one dithiocarbamate ligand with a halide, leading to structures with the general formula $RSn(S_2CNR'_2)_2Cl$.

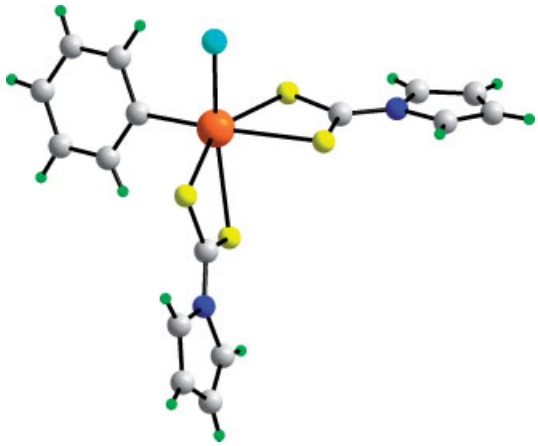

Figure 10. Molecular structure of $PhSn(S_2Cpyrrole)_2Cl$, highlighting the distorted octahedral coordination geometry for tin.

There are 10 structures with the general formula $RSn(S_2CNR'_2)_2Cl$,[50–59] and important tin atom parameters for these are listed in Table 2. The coordination geometry in each case is based on a distorted octahedron with the chloride and organo substituents being approximately *cis*- to each other; the prototype structure of $PhSn(S_2Cpyrrole)_2Cl$ [57] is shown in Fig. 10. The first pair of Sn–S bond distances listed for each compound in Table 2 involves the dithiocarbamate ligand opposite the organic substituent and the second opposite to the chloride. For the latter, the sulfur atoms *trans*- to the chloride always forms the longer Sn–S bond compared with the Sn–S bond *trans*- to a sulfur, consistent with the difference in electronegativity between the chloride and sulfur atoms. The trend is less clear for the first dithiocarbamate as this ligand forms quite symmetric Sn–S bonds in many cases but, in all but one example, the sulfur atom *trans*- to the organic substituent forms the shorter bond than the Sn–S bond *trans*- to a sulfur atom. Further substitution of a dithiocarbamate ligand by another halide leads to compounds of the general formula $RSn(S_2CNR_2)Cl_2$.

Of the eight crystal structure available for compounds conforming to the formula $RSn(S_2CNR_2)Cl_2$,[51,58,60–65] all but one have additional functionality in the tin-bound organic substituents capable of further intramolecular coordination to tin. The exceptional structure of $(n\text{-Bu})Sn(S_2CNEt_2)Cl_2$ [51] is represented in Fig. 11. Here, the tin atom is coordinated by an asymmetrically coordinating dithiocarbamate ligand, the organic substituents and two chlorides to define a five-coordinate, distorted square pyramidal geometry with a *cis*-disposition of the chloride atoms; the value of $\tau = 0.24$ compared with $\tau = 0.0$ for an ideal square pyramidal geometry and $\tau = 1.0$ for an ideal trigonal bipyramid.[66] This geometry leaves an open coordination site and in the crystal structure, centrosymmetrically molecules associate via intermolecular Sn···Cl interactions to form loosely associated dimers, leading to a distorted octahedral geometry about the tin atom, as shown in Fig. 11; the Sn···Cl separation is 3.870(3) Å. The Sn–S distance occupying a position approximately *trans*- to the organic substituents is systematically more tightly bound compared to the sulfur atom *trans*- to the chloride, and the chloride atom not involved in the intermolecular interaction always forms the shorter Sn–Cl bond distance. Selected geometric parameters for this and the remaining $RSn(S_2CNR_2)Cl_2$ structures are collected in Table 2.

The prototype structure for the remaining structures, i.e. $(MeOCH_2CH_2CH_2)Sn(S_2CNEt_2)Cl_2$,[58] is represented in Fig. 12. In

Table 2. Selected geometric parameters (Å, deg) for monorganotin dithiocarbamate structures

Compound	$Sn-S_{chelate}$	C–Sn–S	Reference
$R^xSn(S_2CNR_2)_3$			
$MeSn(S_2CNEt_2)_3$	2.481(1), 2.818(2); 2.618(2), 2.750(2); 2.619(2), 2.773(2)	163.3(3)	[45]
$(n\text{-}Bu)Sn(S_2CNEt_2)_3$	2.491(6), 2.764(8); 2.619(7), 2.822(7), 2.673(8), 2.741(7)	166.3(5)	[46]
$PhSn(S_2CNEt_2)_3$	2.458(2), 2.757(2); 2.569(2), 2.766(3); 2.601(2), 2.676(2)	164.8(1)	[47]
$PhSn[S_2CN(iBu)_2]_3$	2.491(1), 2.729(1); 2.615(2), 2.642(2); 2.709(2), 2.774(2)	166.2(1)	[48]
$R^1Sn(S_2CNEt_2)_3$[a,b]	2.4814(6), 2.7945(5); 2.6110(6), 2.7461(5); 2.6344(5), 2.8115(6)	163.49(6)	[49]
	2.4761(5), 2.7981(6); 2.6069(5), 2.8108(5); 2.6207(6), 2.7476(5)	165.62(6)	

$R^xSn(S_2CNR_2)_2Cl$	$Sn-S_{chelate}$	Sn–Cl	C–Sn–Cl	
$[H_2C{=}(H)C]Sn(S_2CNEt_2)_2Cl$	2.541(4), 2.569(2); 2.517(2), 2.610(2)	2.422(2)	96.1(1)	[50]
$(n\text{-}Bu)Sn[S_2CNEt_2]_2Cl$	2.561(5), 2.587(4); 2.551(4), 2.618(4)	2.464(5)	89.9(5)	[51]
$(n\text{-}Bu)Sn[S_2CN(iPr)_2]_2Cl$	2.548(2), 2.583(2); 2.541(2), 2.641(2)	2.468(2)	96.4(2)	[52]
$(n\text{-}Bu)Sn[S_2CN(iBu)_2]_2Cl$	2.520(2), 2.618(2); 2.558(1), 2.628(2)	2.469(2)	92.2(2)	[53]
$PhSn[S_2CNEt_2]_2Cl$	2.553(1), 2.594(1); 2.528(2), 2.662(1)	2.438(2)	94.12(2)	[54]
$PhSn[S_2CN(n\text{-}Bu)_2]_2Cl$	2.569(4), 2.566(3); 2.514(3), 2.627(3)	2.457(4)	93.8(4)	[55]
$PhSn[S_2CN(iBu)_2]_2Cl$	2.555(1), 2.570(1); 2.533(2), 2.630(2)	2.458(2)	93.3(1)	[56]
$PhSn[S_2C(pyrrole)_2]_2Cl$	2.643(2), 2.580(2); 2.571(2), 2.651(3)	2.411(2)	97.9(1)	[57]
$R^1Sn(S_2CNEt_2)_2Cl$[a]	2.566(2), 2.598(2); 2.569(2), 2.615(2)	2.468(2)	93.3(2)	[58]
$R^2Sn(S_2CNMe_2)_2Cl$[c]	2.540(3), 2.599(4); 2.535(3), 2.635(3)	2.458(4)	93.6(3)	[59]

$R^xSn(S_2CNR_2)Cl_2$	$Sn-S_{chelate}$	Sn–Cl	Sn···O	Cl–Sn–Cl	
$(n\text{-}Bu)Sn(S_2CNEt_2)Cl_2$	2.447(3), 2.631(3)	2.449(4), 2.360(3)	–	94.6(1)	[51]
$R^1Sn(S_2CNEt_2)Cl_2$[a]	2.4728(12), 2.6406(11)	2.4308(11), 2.4128(12)	2.475(3)	94.82(4)	[58]
$R^3Sn(S_2CNMe_2)Cl_2$[d]	2.462(2), 2.657(2)	2.428(2), 2.412(2)	2.437(6)	94.15(8)	[60]
$R^4Sn(S_2CNMe_2)Cl_2$[e]	2.4793(10), 2.6372(16)	2.4231(17), 2.4082(16)	2.394(3)	96.09(6)	[61]
$R^5Sn(S_2CNEt_2)Cl_2$[f]	2.4677(11), 2.6023(12)	2.4280(13), 2.3763(14)	2.532(3)	94.31(5)	[62]
$R^6Sn(S_2CNEt_2)Cl_2$[g]	2.4617(10), 2.6933(9)	2.4055(11), 2.3993(11)	2.374(3)	93.47(4)	[63]
$R^7Sn(S_2CNEt_2)Cl_2$[h]	2.4719(6), 2.6493(6)	2.4509(7), 2.4153(7)	2.4027(17)	97.09(2)	[64]
$R^8Sn(S_2CNEt_2)Cl_2$[i]	2.4644(14), 2.6317(17)	2.4326(18), 2.3874(18)	2.449(5)	93.52(7)	[65]

$R^xSn(S_2CNR_2)L^n$	$Sn-S_{chelate}$	Sn–X	X–Sn–X	
$R^9Sn(S_2CNEt_2)L^1$[j,k]	2.627(2), 2.627(2)	2.018(9) (*O*), 2.018(9) (*O*), 2.323(7) (*N*)	104.3(4) (*O*, *O*)	[67]
$R^{10}Sn(S_2CNEt_2)L^2$[l]	2.493(2), 3.095(2)	2.409(2) (*S*), 2.438(2) (*S*), 2.615(3) (*O*)	114.70(6) (*S*, *S*)	[67]
$\{(n\text{-}Bu)Sn(S_2CNMe_2)L^3\}_2$[m]	2.605(2), 2.638(2)	2.466(3) (*S*), 2.181(5) (*O*), 2.2111(4) (*O*)	69.6(2) (*O*, *O*)	[68]
$\{(n\text{-}Bu)Sn(S_2CNR^1)L^3\}_2$[m,n]	2.606(3), 2.615(2)	2.478(3) (*S*), 2.117(4) (*O*), 2.189(5) (*O*)	70.1(2) (*O*, *O*)	[68]
$\{R^3Sn(S_2CNMe_2)S\}_2$[o]	2.487(4), 2.752(3)	2.381(3) (*S*), 2.509(2) (*S*)	92.53(9) (*S*, *S*)	[69]

[a] $R^1 = CH_2CH_2CH_2OMe$. [b] Two crystallographically independent molecules in the asymmetric unit. [c] $R^2 = CH_2CH_2CH_2C(=O)OMe$. [d] $R^3 = CH_2CH_2C(=O)OMe$. [e] $R^4 = CH_2CH_2C(=O)OEt$. [f] $R^5 = CH_2CH_2C(=O)O(c\text{-}Hex)$. [g] $R^6 = CH_2CH_2C(=O)O\text{-}L\text{-}Menthyl$. [h] $R^7 = C(Me)_2CH_2C(=O)Me$. [i] $R^8 = CH_2CH[C(=O)OMe]CH_2C(=O)OMe$. [j] $R^9 = CH_2CH_2C(=O)OEt$ and $L^1 = OCH_2CH_2N(Me)CH_2CH_2O$. [k] Molecule has mirror symmetry. [l] $R^{10} = CH_2CH_2C(=O)OMe$ and $L^2 = SCH_2CH_2OCH_2CH_2S$. [m] $L^3 = SCH_2CH_2O$. [n] NR^1 = piperidine. [o] Crystallizes as a chloroform di-solvate.

this series of structures, the tin-bound organic substituent carries an oxygen donor, either an ether- (one example) or carbonyl-oxygen (six examples) atom, which forms an intermolecular interaction with the tin atom. So rather than increase its formal coordination number by intermolecular associations, as in the structure of $(n\text{-}Bu)Sn(S_2CNEt_2)Cl_2$,[51] the tin atoms form intramolecular Sn···O interactions instead. In each case, a five-membered SnCCCO chelate ring is formed. The trends observed above for $(n\text{-}Bu)Sn(S_2CNEt_2)Cl_2$ remain but with the chloride atom forming the shorter Sn–Cl distance now opposite the weakly bound oxygen atom. Generally, the Sn–O bond distance formed by the ether-oxygen atom is longer than those formed by the carbonyl-oxygen atom in this series. The only exception is found in the structure of $(c\text{-}HexO(O{=})CCH_2CH_2)Sn(S_2CNEt_2)Cl_2$,[62] i.e. having the bulky cyclohexyl group.

In the next two structures to be described, the two chlorides in $RSn(S_2CNEt_2)Cl_2$ have been replaced by a dinegative, tridentate ligand. In the structure of $[EtO(O{=})CCH_2CH_2]Sn(S_2CNEt_2)[OCH_2CH_2N(Me)CH_2CH_2O]$,[67] which has crystallographic mirror symmetry, Fig. 13, the sulfur atoms of a symmetrically coordinating ligand, forming rather long Sn–S bond distances, are each opposite an alkoxide-oxygen

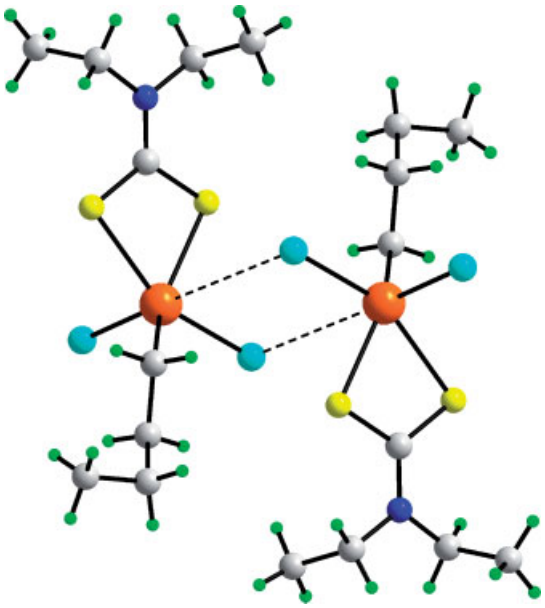

Figure 11. Loosely associated dimer in (*n*-Bu)Sn(S_2CNEt_2)Cl_2, connected through weak intermolecular Sn···Cl interactions.

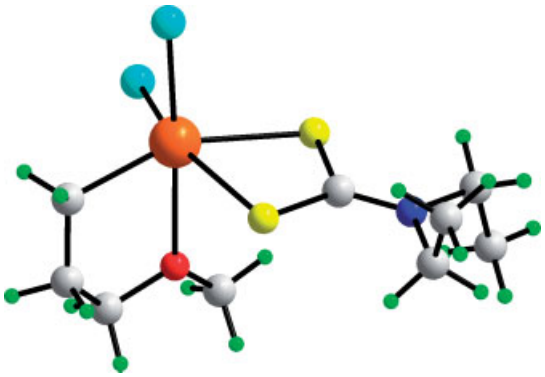

Figure 12. Molecular structure of ($MeOCH_2CH_2CH_2$)Sn(S_2CNEt_2)Cl_2, highlighting the distorted octahedral coordination geometry for tin achieved via an intramolecular Sn–O bond.

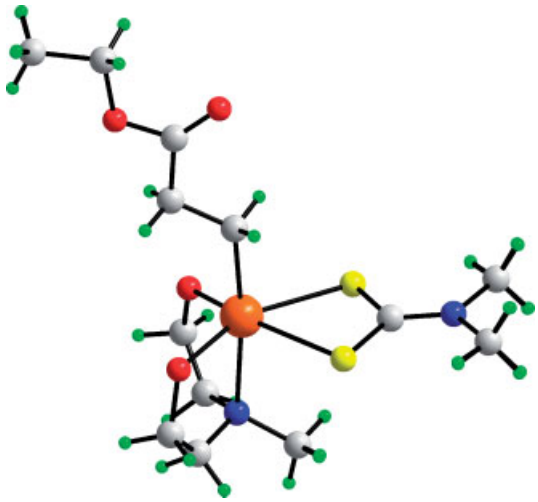

Figure 13. Molecular structure of [EtO(O═)CCH_2CH_2]Sn(S_2CNEt_2)[$OCH_2CH_2N(Me)CH_2CH_2O$], highlighting the distorted octahedral coordination geometry for tin; the molecule has crystallographic mirror symmetry.

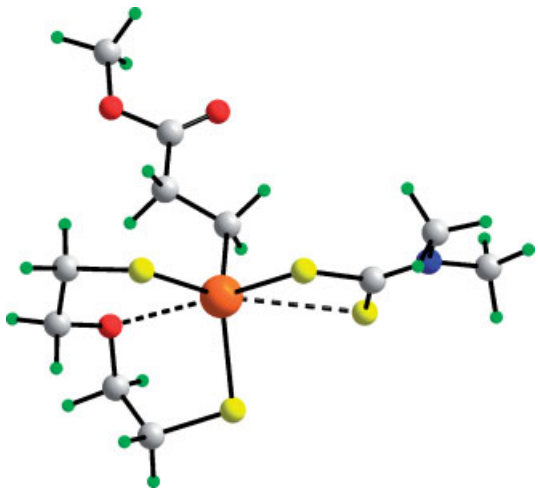

Figure 14. Molecular structure of [MeO(O═)CCH_2CH_2]Sn(S_2CNEt_2)($SCH_2CH_2OCH_2CH_2S$), highlighting the distorted octahedral coordination geometry for tin.

atom. The axial positions in the distorted octahedral geometry are defined by the organic-carbon and amine-nitrogen atoms, derived from the $OCH_2CH_2N(Me)CH_2CH_2O$ dianion. A distinct coordination geometry is found in the analogous compound, [MeO(O═)CCH_2CH_2]Sn(S_2CNEt_2)($SCH_2CH_2OCH_2CH_2S$),[67] Fig. 14. A skewed trapezoidal bipyramidal geometry is found with the trapezoidal plane defined by an asymmetrically coordinating dithiocarbamate ligand, and a thiolate-sulfur and the ether-oxygen atoms of the dinegative $SCH_2CH_2OCH_2CH_2S$ ligand. The organic substituent and the remaining sulfur atom of the $SCH_2CH_2OCH_2CH_2S$ ligand occupy the 'axial' positions in this description.

The remaining monoorganotin dithiocarbamates are dinuclear and centrosymmetric. The structure of [(*n*-Bu)Sn(S_2CNMe_2)(SCH_2CH_2O)]$_2$, where SCH_2CH_2O is a dinegative and tridentate ligand, is shown in Fig. 15.[68] Here, the dithiocarbamate ligand is symmetrically chelating with the sulfur atom opposite the μ_2-alkoxide forming the marginally longer Sn–S bond distance. The structure is constructed about a centrosymmetric Sn_2O_2 core and features octahedral tin atom geometries. The geometric parameters for the piperidyldithiocarbamate derivative are virtually identical, Table 2. The last structure in this category is constructed about a centrosymmetric Sn_2S_2 core, i.e. {[MeO(O═)CCH_2CH_2]Sn(S_2CNMe_2)S}$_2$.[69] The coordination geometry is intermediate between the ideal square pyramidal and trigonal bipyramidal as reflected in the value of τ, i.e. 0.50.[66] There is a weak intramolecular Sn···O contact of 3.197(14) Å involving the carbonyl-oxygen atom but, this is not shown in Fig. 16.

Diorganotin Dithiocarbamate Structures

In terms of crystallographic analyses, the diorganotin dithiocarbamates, $R_2Sn(S_2CNR'_2)_2$, are the best studied and arguably the most interesting in terms of the observed structural diversity. The description of the structural characteristics of the $R_2Sn(S_2CNR'_2)_2$ compounds is followed by those of $R_2Sn(S_2CNR'_2)Cl$. There are

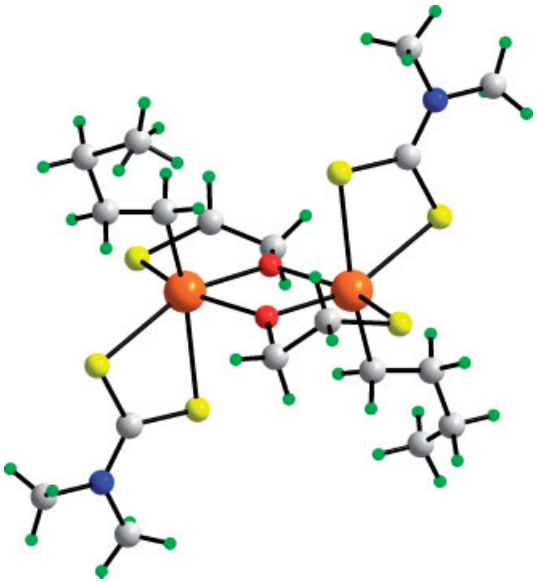

Figure 15. Molecular structure of centrosymmetric and dinuclear $\{(n\text{-Bu})Sn(S_2CNMe_2)(SCH_2CH_2O)\}_2$, highlighting the distorted octahedral coordination geometry for each tin atom.

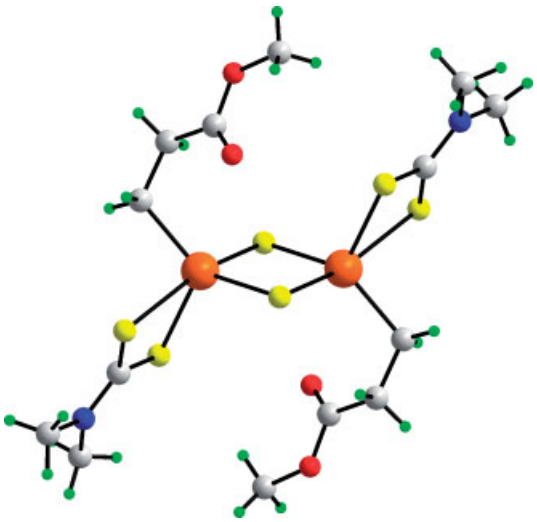

Figure 16. Molecular structure of centrosymmetric and dinuclear $\{[MeO](O{=})CCH_2CH_2]Sn(S_2CNMe_2)S\}_2$; the intramolecular Sn···O contact of 3.197(14) Å is not indicated.

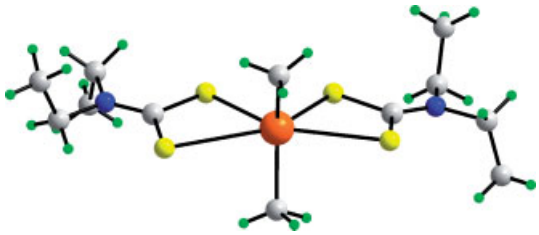

Figure 17. Molecular structure of $Me_2Sn(S_2CNEt_2)_2$, serving as an exemplar of motif I for structures of the general formula $R_2Sn(S_2CNR'_2)_2$.

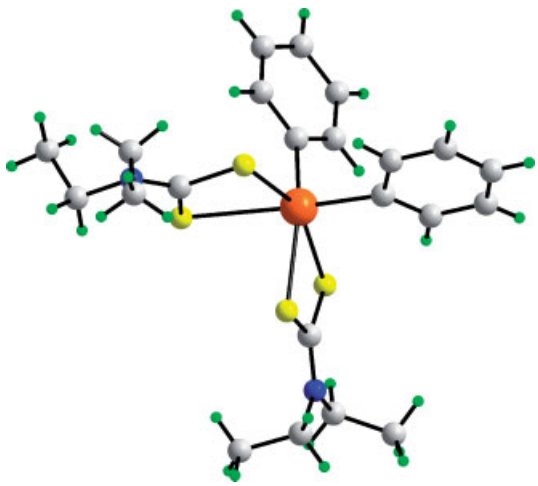

Figure 18. Molecular structure of $Ph_2Sn(S_2CNEt_2)_2$, serving as an exemplar of motif II for structures of the general formula $R_2Sn(S_2CNR'_2)_2$.

also two dinuclear diorganotin dithiocarbamates available in the literature.

There are 42 $R_2Sn(S_2CNR'_2)_2$ compounds in the literature that have been structurally characterized and when taking into account polymorphism, there are about 50 individual structure determinations.[15,16,20,29,57,70–106] A systematic analysis of these structures shows that there are four distinct structural motifs. The most prevalent motif is illustrated in Fig. 17 for $Me_2Sn(S_2CNEt_2)_2$.[71–73] Motif I features two asymmetrically coordinating dithiocarbamate ligands that define a skewed trapezoidal plane and two tin-bound methyl groups that lie over the weaker Sn···S interactions so that the coordination geometry is best described as being skewed trapezoidal bipyramidal. There is a great deal of homogeneity in the geometric parameters describing these structures, Table 3. The short Sn–S bond distances lie in the relatively narrow range 2.48–2.57 Å with the longer distances found in the structures with the more bulky tin-bound groups, e.g. *t*-butyl, cyclohexyl and *o*-$ClC_6H_4CH_2$. The longer distances fall in the range 2.81–3.08 Å. The structures uniformly have the sulfur atoms forming the shorter Sn–S bonds to one side of the SnS_4 plane and hence the skewed-trapezoidal planar description. With one exceptional structure, the S_{short}–Sn–S_{short} bond angles always lie in the range 78–88° and the S_{long}–Sn–S_{long} angles are always in the range 140–154°; normally the values are midway between these extremes. The exceptional structure is that of $(o\text{-}ClC_6H_4CH_2)_2Sn[S_2C(4\text{-methylpiperidine})]_2$,[96] for which the S_{short}–Sn–S_{short} and S_{long}–Sn–S_{long} angles are 95.33(4) and 131.37(4)°, respectively. The presence of an intramolecular Sn···Cl interactions of 3.901(2) Å may be responsible for the widening of the S_{short}–Sn–S_{short} angle and concomitant narrowing of the S_{long}–Sn–S_{long} angle in this structure. However, it should be noted that discerning systematic trends from this class of compound is well known to be fraught with danger.[107]

To illustrate this point, an examination of the trimorphic $Me_2Sn(S_2CNEt_2)_2$ [71–73] system shows that the Sn–S_{short} bond distances lie in the range 2.4877(10)–2.5307(8) Å, Sn–S_{long} 2.916(3)–3.0121(9) Å, S_{short}–Sn–S_{short} angles 81.95(3)–84.29(3)°, S_{long}–Sn–S_{long} 146.62(3)–149.49(3)°, and even the C–Sn–C angle 135.7(2)–142.62(5)°. These variations go well beyond experimental error and point to the influence of crystal packing upon their geometric parameters. Indeed, comparative investigations on organotin compounds, including organotin dithiocarbamates, where experimental, i.e. crystallographic, structures are com-

Table 3. Selected geometric parameters (Å, deg) for $R_2Sn(S_2CNR'_2)_2$

Compound	$Sn-S_{chelate}$	C–Sn–C	Reference
Motif I			
$Me_2Sn(S_2CNMe_2)_2$	2.4975(13), 2.9538(7); 2.5152(9), 3.0606(9)	136.449(9)	[70]
$Me_2Sn(S_2CNEt_2)_2$[a]	2.4877(10), 2.9376(9); 2.515(1), 3.0544(11)	135.7(2)	[71]
$Me_2Sn(S_2CNEt_2)_2$[b,c,d]	2.5209(8), 2.9390(9); 2.5307(8), 3.0121(9)	136.9(1)	[72,73]
	2.5288(9), 2.9546(11)	142.0(1)	
$Me_2Sn(S_2CNEt_2)_2$[e]	2.517(3), 2.961(3); 2.528(2), 2.916(3)	142.62(5)	[73]
$Me_2Sn[S_2CN(CH_2CH_2OH)_2]_2$[f]	2.5126(7), 3.0427(7)	139.3(1)	[74]
$Me_2Sn[S_2CN(Me)c\text{-}Hex]_2$[f]	2.5169(7), 2.9785(6)	137.0(2)	[75]
$Me_2Sn(S_2Cpyrrole)_2$	2.510(2), 3.009(2); 2.532(2), 3.024(2)	135.9(2)	[57]
$Me_2Sn(S_2CNR^1)_2$[g]	2.521(2), 2.918(2); 2.541(2), 2.908(2)	131.2(3)	[76]
$Me_2Sn(S_2CNR^2)_2$[c,h]	2.504(1), 2.892(2); 2.533(2), 3.040(2)	134.0(2)	[77]
	2.520(2), 2.919(2); 2.536(1), 2.917(2)	138.5(2)	
$Me_2Sn(S_2CNR^3)_2$[i]	2.5240(4), 2.9715(4); 2.5190(4), 2.9779(4)	135.64(7)	[78]
$[H_2C{=}(H)C]_2Sn(S_2CNEt_2)_2$	2.495(5), 2.871(5); 2.515(4), 3.078(5)	135.7(8)	[79]
$[H_2C{=}(H)C]_2Sn[S_2CN(Et)c\text{-}Hex]_2$	2.513(5), 3.071(4); 2.523(4), 2.826(5)	133.4(4)	[79]
$[H_2C{=}(H)C]_2Sn(S_2CNc\text{-}Hex_2)_2$	2.514(4), 2.914(3); 2.536(3), 2.914(4)	139.5(4)	[79]
$(n\text{-}Bu)_2Sn(S_2CNEt_2)_2$[c]	2.5089(16), 2.9084(17); 2.5251(15), 3.0478(18)	132.7(2)	[80]
	2.5386(16), 2.9037(15); 2.5494(14); 2.9517(16)	140.8(2)	
$(n\text{-}Bu)_2Sn[S_2CN(nPr)_2]_2$	2.5255(12), 3.0210(13); 2.5287(14), 2.9375(11)	132.6(2)	[81]
$(n\text{-}Bu)_2Sn[S_2CN(iPr)_2]_2$[j]	2.5296(17), 2.9443(18)	131.4(4)	[82]
$(n\text{-}Bu)_2Sn(S_2CNR^4)_2$[k]	2.5338(6), 2.9697(11); 2.5323(9), 2.9834(10)	139.4(1)	[20]
$(n\text{-}Bu)_2Sn(S_2CNR^1)_2$[g,l]	2.477(4), 2.965(5)	147.2(5)	[83]
$(n\text{-}Bu)_2Sn(S_2CNR^5)_2$[l,m]	2.526(3), 3.001(4)	139.7(2)	[84]
$(n\text{-}Bu)_2Sn(S_2CNR^2)_2$[h]	2.5362(14), 2.9189(15); 2.5347(14), 2.9942(16)	135.4(1)	[85]
$(t\text{-}Bu)_2Sn(S_2CNEt_2)_2$[l]	2.5537(15), 2.9539(17)	146.16(7)	[86]
$(c\text{-}Hex)_2Sn(S_2CNMe_2)_2$[l]	2.568(2), 2.914(2)	150.2(3)	[87]
$(c\text{-}Hex)_2Sn[S_2CN(Et)(c\text{-}Hex)]_2$	2.5290(14), 2.9466(15); 2.5394(15), 2.9604(15)	138.0(2)	[88]
$(PhCH_2)_2Sn(S_2CNMe_2)_2$	2.526(2), 2.897(2); 2.531(2), 3.046(2)	135.2(3)	[89]
$(PhCH_2)_2Sn(S_2CNEt_2)_2$	2.5309(9), 2.8940(11); 2.5396(9), 2.9109(10)	145.1(2)	[90]
$(PhCH_2)_2Sn(S_2CNBen_2)_2$	2.520(2), 2.942(2); 2.521(2), 3.004(2)	136.6(2)	[91]
$(PhCH_2)_2Sn(S_2CNR^4)_2$[l]	2.521(1), 2.909(1)	143.5(2)	[92]
$(PhCH_2)_2Sn(S_2CNR^1)_2$[g]	2.540(8), 2.954(8); 2.552(8), 2.966(8)	141.5(6)	[93]
$(PhCH_2)_2Sn(S_2CNR^5)_2$[m]	2.532(2), 2.890(3); 2.539(2), 2.890(3)	139.1(4)	[94]
$(o\text{-}FC_6H_4CH_2)_2Sn(S_2CNR^4)_2$[l]	2.504(2), 2.897(2)	140.1(2)	[95]
$(o\text{-}ClC_6H_4CH_2)_2Sn(S_2CNR^6)_2$[n]	2.5676(13), 2.8675(11); 2.5401(13), 2.8049(12)	150.6(2)	[96]
$(m\text{-}ClC_6H_4CH_2)_2Sn(S_2CNR^7)_2$[o]	2.520(3), 2.840(2); 2.555(2), 2.893(2)	147.7(2)	[97]
$(p\text{-}FC_6H_4CH_2)_2Sn(S_2CNMe_2)_2$	2.526(2), 2.953(2); 2.519(3), 3.002(2)	129.2(2)	[98]
$(p\text{-}ClC_6H_4CH_2)_2Sn(S_2CNMe_2)_2$[l]	2.526(2), 2.933(3)	136.8(1)	[95]
$(p\text{-}ClC_6H_4CH_2)_2Sn(S_2CNR^6)_2$[n]	2.534(2), 2.968(2); 2.550(2), 2.858(3)	146.9(2)	[99]
$(p\text{-}ClC_6H_4CH_2)_2Sn(S_2CNR^6)_2$[l,m]	2.5249(14), 2.9920(16)	139.9(2)	[100]
$(p\text{-}NCC_6H_4CH_2)_2Sn(S_2CNEt_2)_2$	2.524(3), 2.885(3); 2.537(2), 2.879(2)	147.7(3)	[16]
Motif II			
$Ph_2Sn(S_2CNEt_2)_2$[b]	2.558(3); 2.777(3); 2.607(3), 2.632(3)	101.7(3)	[101]
$Ph_2Sn(S_2CNEt_2)_2$[l,p]	2.556(2), 2.659(2)	101.1(3)	[15]
$Ph_2Sn[S_2CN(c\text{-}Hex)_2]_2$	2.567(2), 2.692(2); 2.576(2), 2.678(2)	103.1(3)	[102]
$Ph_2Sn[S_2CN(CH_2CH_2OH)_2]_2$	2.5395(9), 2.8271(9); 2.6063(9), 2.6235(11)	104.9(1)	[103]
$Ph_2Sn[S_2CN(Me)CH_2CH_2OH]_2$	2.5497(14), 2.7474(16); 2.6145(15), 2.6411(17)	102.7(2)	[104]
$Ph_2Sn(S_2CNR^4)_2$[k,q]	2.574(1), 2.950(1); 2.586(2), 2.685(2)	107.6(2)	[29]
Motif III			
$(t\text{-}Bu)_2Sn(S_2CNMe_2)_2$	2.4892(14), 2.7952(9); 2.5727(12), 3.5319(11)	119.1(1)	[105]
Motif IV			
$R^1{}_2Sn(S_2CNMe_2)_2$[r]	2.570(4), 2.847(4); 2.599(4), 2.914(5)	154.4(4)	[106]

[a] Orthorhombic form. [b] Monoclinic form. [c] Two independent molecules in the asymmetric unit. [d] The second molecule has crystallographic two-fold symmetry. [e] Triclinic form. [f] Molecule has crystallographic mirror symmetry. [g] NR^1 = piperidine. [h] NR^2 = 4-methylpiperidine. [i] NR^3 = 4-benzylpiperidine. [j] The tin atom is located on a crystallographic site of symmetry *mm*2. [k] NR^4 = pyrrolidine. [l] Molecule has crystallographic two-fold symmetry. [m] NR^5 = morpholine. [n] NR^6 = 4-methylpiperazine. [o] NR^7 = 4-ethylpiperazine and compound crystallizes as a piperidine hemi-solvate. [p] Tetragonal form. [q] Compound crystallizes as a toluene solvate. [r] R^1 = $CH_2CH_2C(=O)OMe$.

pared with geometry optimized structures obtained from *ab initio* molecular orbital calculations, i.e. theoretical, showed that molecules crystallizing in polymorphs optimize to the same energy minimized structure, and structures with multiple molecules in the asymmetric unit similarly optimize to a single energy minimized structure.[108] The generally applicable conclusion from these studies was that molecular structures were syntactic with their crystalline manifold and adjustments in bond distances and angles were made to accommodate the dictates of crystal packing. In the absence of crystal packing effects, chemically equivalent geometric parameters are equal and, whenever chemically possible, the molecular structures became symmetric.[108]

The second motif for the $R_2Sn(S_2CNR'_2)_2$ compounds is adopted exclusively by the R = Ph derivatives, Table 3. This observation supports the notion that, relative to their alkyl (and vinyl) counterparts, phenyl substituents are less electropositive/more electronegative so that the resulting $Ph_2Sn(S_2CNR'_2)_2$ structures resemble the octahedral *cis*-SnS_4X_2 structures summarized in Table 1. The exemplar structure for motif II is $Ph_2Sn(S_2CNEt_2)_2$, shown in Fig. 18, which highlights the distorted octahedral geometry and the *cis*-disposition of the tin-bound phenyl groups. In fact, this compound crystallizes in two polymorphs, a monoclinic polymorph with no crystallographically imposed molecular symmetry,[101] and a tetragonal polymorph with crystallographic two-fold symmetry.[15] Unrestricted geometry optimization calculations showed that both experimental structures converged to the same energy minimized structure, with two-fold symmetry, so that experimentally distinct geometric parameters observed in the crystal structures were artefacts of the crystal packing and not due to any inherent chemical reason.[108a]

While an electronic reason can be discerned for the appearance of motif II, no obvious reason can be proffered for the appearance of motif III, adopted by one example, namely $(t\text{-Bu})_2Sn(S_2CNMe_2)_2$,[105] shown in Fig. 19. This structure is quite readily related to the skewed trapezoidal bipyramidal geometry for motif I. As a starting point, the structure of the diethyldithiocarbamate analogue, i.e. $(t\text{-Bu})_2Sn(S_2CNEt_2)_2$,[86] is considered. Simply, there is a twist about one of the short Sn–S bonds so that the weakly coordinated dithiocarbamate-sulfur atom is moved to a position approximately orthogonal to the original SnS_4 plane. In so doing, the Sn···S distance expands to 3.5319(11) Å, clearly non-bonding. Both Sn–S bond distances of the remaining chelating dithiocarbamate ligand decrease significantly and the C–Sn–C angle contracts to 119.1(1)°. The resulting coordination geometry is intermediate between square pyramidal and trigonal bipyramidal as seen in the value of $\tau = 0.47$.[66] There are several examples throughout this review where the difference between structures is found solely in the nature of the nitrogen-bound substituent but the structures of $(t\text{-Bu})_2Sn(S_2CNR_2)_2$, R = Me [86] and Et,[105] are the only examples where such a profound difference in the molecular structure is observed.

The fourth and final motif for the $R_2Sn(S_2CNR'_2)_2$ structures is also readily related to motif I. The molecular structure of $[MeO(O{=})CCH_2CH_2)_2Sn(S_2CNMe_2)_2$,[106] is represented in Fig. 20. Here, the tin-bound groups carry additional donor atoms for coordination to tin and one of these in fact forms an intramolecular Sn···O interaction. To a first approximation, the coordination geometry can be thought of as skewed trapezoidal bipyramidal as for motif I. As noted in Fig. 20, the carbonyl-oxygen atom of one

Figure 19. Molecular structure of $(t\text{-Bu})_2Sn(S_2CNMe_2)_2$, the sole example for motif III for structures of the general formula $R_2Sn(S_2CNR'_2)_2$.

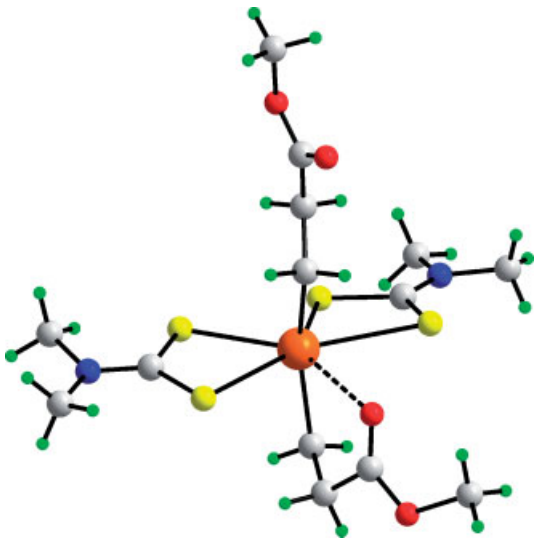

Figure 20. Molecular structure of $[MeO(O{=}C)CH_2CH_2]_2Sn(S_2CNMe_2)_2$, the sole example for motif IV for structures of the general formula $R_2Sn(S_2CNR'_2)_2$.

of the $MeO(O{=})CCH_2CH_2$ groups approaches the tin atom in the SnS_4 plane. The Sn···O separation is 2.75(2) Å and this association results in the formation of a five-membered SnC_3O chelate ring. As expected, there are some geometric consequences of the close association of the carbonyl-oxygen atom. The $S_{long}–Sn–S_{long}$ angle opens up by about 5° compared with the motif I structures but, interestingly, the $S_{short}–Sn–S_{short}$ angle of 81.91(9)° falls in the range of $S_{short}–Sn–S_{short}$ angles, albeit the lower end. This suggests that the sulfur atoms forming $Sn–S_{short}$ bond distances cannot get any closer, no doubt for steric reasons. In order to accommodate the incoming oxygen atom, these sulfur atoms have elongated their Sn–S bonds compared with those of motif I and, concomitantly, one of the $Sn–S_{long}$ distances has contracted [2.847(4) Å] and the other is at the lower end of the $Sn–S_{long}$ range [2.914(5) Å].

The presence of an Sn···O intramolecular interaction in the structure of $[MeO(O{=})CCH_2CH_2]_2Sn(S_2CNMe_2)_2$,[106] raises the question whether any other of the $R_2Sn(S_2CNR'_2)_2$ structures associate in the solid-state via secondary Sn···S interactions.[109] An analysis of the crystal packing for these compounds showed that, in fact, seven out of the 36 structures adopting motif I do in fact

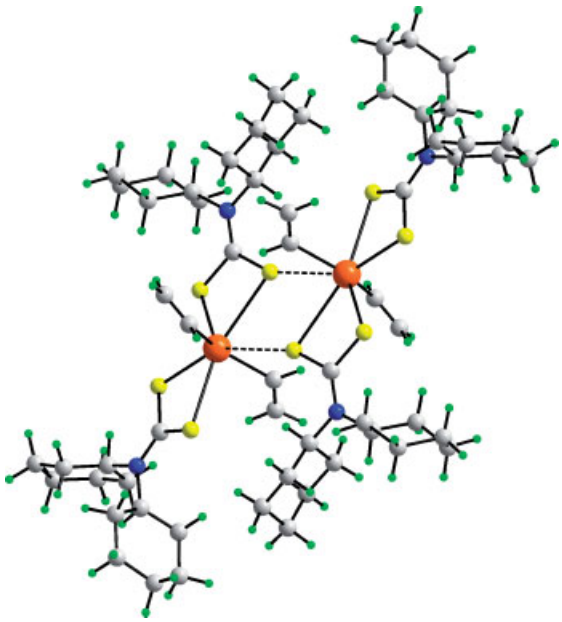

Figure 21. Dimer formation in the structure of $[H_2C{=}(H)C]_2Sn[S_2CN(c\text{-}Hex)_2]_2$, via secondary Sn···S interactions.

form Sn···S contacts with centrosymmetrically related mates. The magnitude of the Sn···S distances vary from long 3.9071(13) Å in $(o\text{-}ClC_6H_4CH_2)_2Sn[S_2C(4\text{-methylpiperidine})]_2$,[97] 3.853(3) Å in $Me_2Sn(S_2CNEt_2)_2$,[73] 3.821(3) Å in $(p\text{-}NCC_6H_4CH_2)_2Sn(S_2CNEt_2)_2$,[16] 3.8162(10) Å in $(PhCH_2)_2Sn(S_2CNEt_2)_2$,[90] 3.765(3) Å in $(p\text{-}ClC_6H_4CH_2)_2Sn[S_2C(4\text{-methylpiperidine})]_2$,[99] 3.662(5) Å in $[H_2C{=}(H)C]_2Sn[S_2CN(c\text{-}Hex)_2]_2$,[79] illustrated in Fig. 21, and 3.638(3) Å in $(m\text{-}ClC_6H_4CH_2)_2Sn[S_2C(4\text{-ethylpiperazine})]_2$.[97] While these interactions are weak they fall within the sum of the van der Waals radii of tin and sulfur, taken as 4.0 Å.[110] While there is a dominance of dibenzyl derivatives in this listing, the lack of systematic trends for such Sn···S secondary interactions is highlighted by the fact that they are observed in the triclinic form of $Me_2Sn(S_2CNEt_2)_2$,[73] but not in the orthorhombic[71] nor monoclinic forms.[72,73]

As noted in Table 3, some of the dithiocarbamate ligands carry hydrogen-bonding functionality so that, while the sulfur atoms of the dithiocarbamate ligands rarely engage in supramolecular aggregation, certainly not to form extended arrays, the substituents might.[111] This is illustrated in Fig. 22 for the structure of $Me_2Sn[S_2CN(CH_2CH_2OH)_2]_2$,[74] where cooperative hydrogen-bonding links the molecules into a supramolecular zig-zag chain.

The second class of mononuclear diorganotin dithiocarbamate structures conform to the general formula $R_2Sn(S_2CNR'_2)X$, where X is usually chloride.[16,22,39,86,97,100,108b,112–132] By contrast to the $R_2Sn(S_2CNR'_2)_2$ structures with four distinct structural motifs, the $R_2Sn(S_2CNR'_2)X$ compounds are decidedly more homogeneous in their structural chemistry. The coordination geometries to be described here for $R_2Sn(S_2CNR'_2)X$ closely resemble that observed for $(t\text{-}Bu)_2Sn(S_2CNMe_2)_2$,[105] motif III for the $R_2Sn(S_2CNR'_2)_2$ structures, in which one of the dithiocarbamate ligands is monodentate. Table 4 summarizes the pertinent structural information for these structures and the prototype structure, namely, $Me_2Sn(S_2CNEt_2)Cl$, is illustrated in Fig. 23. The tin

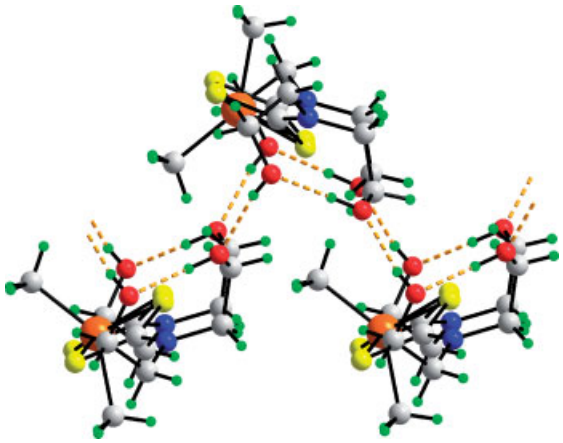

Figure 22. Supramolecular zig-zag chain formation via O-H···O hydrogen (orange-dashed lines) in the structure of $Me_2Sn[S_2CN(CH_2CH_2OH)_2]_2$.

atom is five-coordinated, being chelated by an asymmetrically coordinating dithiocarbamate ligand, a halide and two organic substituents. The Sn–S bond distance approximately *trans*- to the halide atom is always longer than the other Sn–S bond distance. The coordination geometry is almost intermediate between square pyramidal and trigonal bipyramidal with the majority of the structures having a small bias towards the former, at least based on the values of τ [66] collected in Table 4 that generally lie in the range 0.40–0.60. However, there are several structures with values of τ [66] less than 0.40, Table 4. In the structure of $Ph_2Sn(S_2CNMe_2)Br$,[123] $\tau = 0.38$, which contrasts with $\tau = 0.59$ and 0.57 in the structures of $Ph_2Sn(S_2CNEt_2)X$ for X = Cl [86] and I,[124] respectively; however, the different R′ substituents in the dithiocarbamate ligands are noted. Further work is clearly required to elucidate the variations in τ for this series of structures. More tangible explanations are available for the deviation of the coordination geometries towards square pyramidal in each of $[MeO(O{=})CCH_2CH_2]_2Sn(S_2CNMe_2)Cl$,[132] $(o\text{-}FC_6H_4CH_2)_2Sn[S_2C(N(CH_2CH_2)_2NEt)]Cl$[97] and $Me_2Sn(S_2Cpiperidine)Cl$.[114] In $[MeO(O{=})CCH_2CH_2]_2Sn(S_2CNMe_2)Cl$,[132] with $\tau = 0.29$, there are two intramolecular Sn···O contacts formed by the carbonyl-oxygen atoms, i.e. 2.949(5) and 3.147(5) Å, Fig. 24, and in the case of $(o\text{-}FC_6H_4CH_2)_2Sn[S_2C(N(CH_2CH_2)_2NEt)]Cl$,[97] with $\tau = 0.35$, the lower value of τ is due to the presence of an intramolecular Sn···F interaction of 3.518(15) Å. Finally, in the structure of $Me_2Sn(S_2Cpiperidine)Cl$,[114] the presence of intermolecular secondary Sn···S interactions, that lead to the formation of a supramolecular zig-zag chain, Fig. 25, accounts for the variation in coordination geometry. The above notwithstanding, it is likely that it is the more symmetric mode of coordination for the dithiocarbamate ligands in the $R_2Sn(S_2CNR'_2)X$ structures, Table 4, that accounts for the essentially molecular nature of these compounds.

The final two diorganotin structures to be discussed are dinuclear. The structure of $[PhSn(S_2CNEt_2)(S)(CH_2CH_2CH_2)SnPh(S_2CNEt_2)]$,[133] has non-crystallographic two-fold symmetry and a bridging organic ligand connecting the two tin atoms, Fig. 26 and Table 4. Each tin atom is chelated by an asymmetrically chelating dithiocarbamate ligand, a sulfur atom derived from the bridging sulfide atom and two carbon atoms derived from organic substituents. Indeed, this structure can be readily related to the $R_2Sn(S_2CNR')X$ structures just described in

Table 4. Selected geometric parameters (Å, deg) for $R_2Sn(S_2CNR'_2)X$

Compound	Sn–$S_{chelate}$	Sn–X	S–Sn–X	C–Sn–C	τ	Reference
$Me_2Sn(S_2CNMe_2)Cl$	2.482(14), 2.805(14)	2.465(10)	154.59(4)	127.87(3)	0.45	[112]
$Me_2Sn(S_2CNEt_2)Cl$	2.463(2), 2.703(2)	2.479(3)	157.53(8)	127.3(4)	0.50	[108b]
$Me_2Sn[S_2CN(c\text{-}Hex)_2]Cl$	2.464(2), 2.659(2)	2.466(2)	156.79(7)	125.3(3)	0.52	[108b]
$Me_2Sn(S_2CNR^1)Cl$[a]	2.4826(13), 2.7555(12)	2.4598(15)	154.49(4)	125.5(2)	0.48	[113]
$Me_2Sn(S_2CNR^2)Cl$[b]	2.4667(9), 2.7398(14)	2.4853(11)	154.19(3)	126.9(1)	0.46	[22]
$Me_2Sn(S_2CNR^3)Cl$[c]	2.4838(9), 2.7114(8)	2.4929(8)	154.57(2)	130.92(9)	0.39	[114]
$Et_2Sn(S_2CNR^4)Cl$[d]	2.4758(6), 2.6959(6)	2.5243(6)	156.58(2)	123.66(9)	0.55	[115]
$(n\text{-}Bu)PhSn(S_2CNEt_2)Cl$	2.5452(12), 2.7446(17)	2.4491(15)	156.86(3)	127.3(1)	0.49	[116]
$(n\text{-}Bu)_2Sn(S_2CNR^4)Cl$[d,e]	2.4720(5), 2.7315(5)	2.4886(5)	155.11(2)	128.35(8)	0.46	[117]
	2.4690(5), 2.7088(5)	2.4976(5)	155.67(2)	128.12(8)	0.45	
$(t\text{-}Bu)_2Sn(S_2CNMe_2)Cl$	2.4866(11), 2.7418(13)	2.4904(12)	153.06(4)	125.8(7)	0.45	[118]
$(t\text{-}Bu)_2Sn(S_2CNEt_2)Cl$[e]	2.4794(18), 2.7318(18)	2.498(2)	153.19(7)	128.8(3)	0.41	[86]
	2.4824(19), 2.7340(19)	2.505(2)	154.16(7)	128.7(3)	0.42	
$(t\text{-}Bu)_2Sn(S_2CN(c\text{-}Hex)_2)Cl$[e]	2.477(3), 2.744(4)	2.491(4)	152.3(1)	125.4(5)	0.47	[108a]
	2.471(3), 2.722(4)	2.482(4)	152.0(1)	124.0(4)	0.45	
$(t\text{-}Bu)_2Sn(S_2CNR^5)Cl$[f]	2.492(2), 2.767(2)	2.470(2)	150.01(6)	125.1(3)	0.45	[119]
$(t\text{-}Bu)_2Sn(S_2CNR^6)Cl$[g]	2.483(2), 2.751(2)	2.465(3)	152.19(8)	124.5(3)	0.46	[119]
$(t\text{-}Bu)_2Sn(S_2CN(Et)c\text{-}Hex)Cl$	2.479(3), 2.756(3)	2.473(3)	152.58(9)	125.3(3)	0.45	[108b]
$(c\text{-}Hex)_2Sn(S_2CNEt_2)Cl$	2.471(3), 2.768(2)	2.459(2)	155.55(7)	128.5(4)	0.45	[108b]
$(c\text{-}Hex)_2Sn[S_2CN(c\text{-}Hex)_2]Cl$	2.471(3), 2.680(2)	2.493(2)	154.44(6)	124.0(3)	0.51	[108b]
$Ph_2Sn(S_2CNEt_2)Cl$	2.4449(13), 2.7156(15)	2.4404(18)	157.82(6)	117.6(2)	0.59	[86]
$Ph_2Sn[S_2CN(c\text{-}Hex)_2]Cl$	2.440(2), 2.657(2)	2.437(2)	153.57(5)	119.8(2)	0.47	[120]
$Ph_2Sn(S_2CNR^3)Cl$[c]	2.4737(7), 2.6287(7)	2.4766(7)	154.68(2)	114.38(9)	0.51	[121]
$Ph_2Sn(S_2CNR^2)Cl$[b]	2.4614(6), 2.6570(6)	2.4674(8)	153.55(2)	114.61(8)	0.51	[22]
$Ph_2Sn[S_2CN(Et)(c\text{-}Hex)]Cl$	2.459(3), 2.681(3)	2.447(3)	157.3(1)	121.3(4)	0.55	[122]
$Ph_2Sn(S_2CNMe_2)Br$	2.454(2), 2.668(2)	2.6098(12)	156.05(4)	111.9(2)	0.38	[123]
$Ph_2Sn(S_2CNEt_2)I$	2.4504(12), 2.6699(10)	2.8590(5)	155.48(3)	116.9(2)	0.57	[124]
$(C_6H_5CH_2)_2Sn(S_2CNMe_2)Cl$	2.4637(19), 2.707(2)	2.4819(18)	154.03(6)	124.8(3)	0.48	[125]
$(C_6H_5CH_2)_2Sn(S_2CNR^3)Cl$[c]	2.469(2), 2.666(2)	2.494(2)	155.95(6)	120.9(3)	0.52	[126]
$(C_6H_5CH_2)_2Sn(S_2CNR^7)Cl$[h]	2.4738(11), 2.6716(12)	2.5028(12)	156.06(4)	121.1(2)	0.52	[127]
$(C_6H_5CH_2)_2Sn(S_2CNR^8)Cl$[i]	2.466(2), 2.724(3)	2.441(4)	159.45(7)	119.02)	0.58	[128]
$(o\text{-}FC_6H_4CH_2)_2Sn(S_2CNR^5)Cl$[f]	2.4568(15), 2.659(2)	2.459(3)	154.53(7)	116.7(4)	0.35	[97]
$(p\text{-}FC_6H_4CH_2)_2Sn(S_2CNR^8)Cl$[i]	2.466(2); 2.684(2)	2.491(3)	157.30(6)	129.5(2)	0.46	[39]
$(o\text{-}ClC_6H_4CH_2)_2Sn(S_2CNR^9)Cl$[j]	2.4668(14), 2.6981(14)	2.4706(14)	156.66(4)	128.8(2)	0.47	[129]
$(o\text{-}ClC_6H_4CH_2)_2Sn(S_2CNR^5)Cl$[f]	2.4695(16), 2.6614(15)	2.4812(16)	155.83(5)	128.0(2)	0.46	[130]
$(m\text{-}ClC_6H_4CH_2)_2Sn(S_2CNBen_2)Cl$	2.4694(15), 2.6573(14)	2.4716(16)	158.44(5)	116.9(2)	0.53	[16]
$(p\text{-}ClC_6H_4CH_2)_2Sn(S_2CNEt_2)Cl$	2.455(2), 2.672(2)	2.500(2)	156.86(2)	125.8(2)	0.52	[100]
$(p\text{-}ClC_6H_4CH_2)_2Sn(S_2CNR^1)Cl$[a,k]	2.471(3), 2.697(3)	2.468(3)	158.52(7)	118.1(2)	0.49	[131]
$R_2Sn(S_2CNMe_2)Cl$[l]	2.5131(17), 2.6729(13)	2.4895(16)	153.91(5)	136.5(2)	0.29	[132]
$[PhSn(S_2CNEt_2)(S)(CH_2CH_2CH_2)SnPh(S_2CNEt_2)]$	2.4596(18), 2.894(2)	2.4474(13) (*S*)	160.42(5)	119.5(2)	0.68	[133]
	2.4658(17), 2.9573(18)	2.4335(16) (*S*)	160.60(5)	118.8(2)	0.70	
$(t\text{-}Bu)_2Sn[S_2CN(H)CH_2CH_2N(H)CS_2]_2Sn(t\text{-}Bu)_2$[m]	2.459(3), 2.878(3)	2.563(2) (*S*)	155.79(7)	119.53(3)	0.48	[134]

[a] NR^1 = pyrrolidine. [b] NR^2 = 4-methylpiperidine. [c] NR^3 = piperidine. [d] NR^4 = 4-(*p*-nitrophenyl)piperazine. [e] Two independent molecules in the asymmetric unit. [f] NR^5 = 4-ethylpiperazine. [g] NR^6 = 4-benzylpiperazine. [h] NR^7 = piperazine. [i] NR^8 = morpholine. [j] NR^9 = 4-methylpiperazine. [k] Compound crystallizes as a water solvate. [l] R^1 = $CH_2CH_2C(=O)OMe$. [m] Compound crystallizes as a tetrahydrofuran di-solvate.

that X is now a sulfur atom and one of the tin-bound R groups is one end of a bridging organic ligand. The pattern of Sn–S bond distances is consistent with this notion, with the longer distance occupying a position approximately *trans*- to the bridging sulfur atom. The coordination geometries are distinct, however. Based on a comparison of the values of τ, Table 4, the geometries for the tin atoms in the dinuclear compound are decidedly more trigonal bipyramidal. The dinuclear and centrosymmetric structure of $(t\text{-}Bu)_2Sn(S_2CN(H)CH_2CH_2N(H)CS_2)_2Sn(t\text{-}Bu)_2$, isolated as a tetrahydrofuran di-solvate,[134] is shown in Fig. 27; see Table 4 for geometric parameters. This structure features two tin atoms bridged by a pair of bi-functional dithiocarbamate ligands. The coordination geometry comprises one asymmetrically coordinating dithiocarbamate ligand, a monodentate ligand [Sn···S is 3.607(3) Å] and two organic substituents. The coordination geometry is almost identical to that observed for motif III of the $R_2Sn(S_2CNR'_2)_2$ structures, represented by $(t\text{-}Bu)_2Sn(S_2CNMe_2)_2$,[105] Fig. 19.

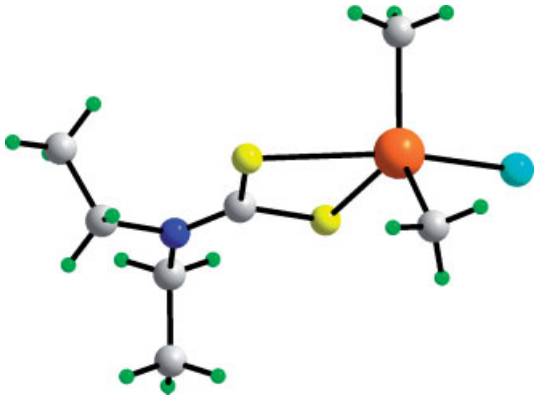

Figure 23. Molecular structure of $Me_2Sn(S_2CNEt_2)Cl$, serving as an exemplar for structures of the general formula $R_2Sn(S_2CNR'_2)X$.

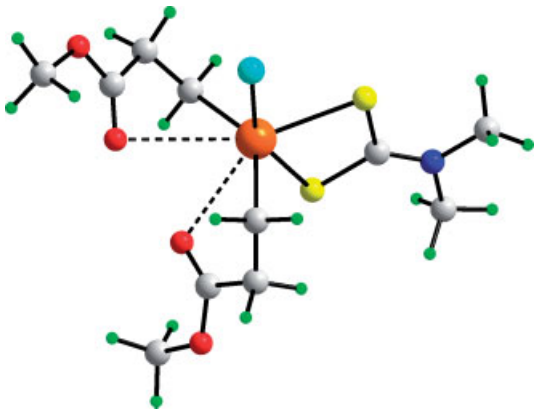

Figure 24. Molecular structure of $[MeO(O{=})CCH_2CH_2]_2Sn(S_2CNMe_2)Cl$, showing the presence of intramolecular Sn···O interactions that are responsible for the deviation of the C_2ClS_2 donor set toward a square pyramidal arrangement.

Triorganotin dithiocarbamate structures

The prototype structure for the majority of structures in this category, i.e. with general formula $R_3Sn(S_2CNR'_2)$, is shown in Fig. 28 for the structure of $Ph_3Sn[S_2CN(CH_2CH_2)_2O]$.[150] Table 5 collects selected geometric parameters for all triorganotin dithiocarbamate structures described herein. Here, the tin atom is coordinated by an asymmetrically coordinating dithiocarbamate ligand and three carbon atoms from the organic substituents. In the more precisely determined structures, the $Sn-S_{short}$ bond distances fall in the narrow range 2.45–2.48 Å. Similarly, the $Sn-S_{long}$ bond distances fall in the range 2.92–3.24 Å. Again, pointing to the influence of crystal packing considerations upon molecular geometry and geometric parameters, no trends are evident although there is a hint that the longer $Sn-S_{long}$ bond distances are generally found with bulky tin-bound substituents, e.g. cyclohexyl, indicating a possible steric influence upon these distances. The coordination geometry is best described as being based on a distorted trigonal bipyramidal geometry with the sulfur atom involved in forming the longer Sn···S bonds occupying one of the axial positions. Based on the values of τ,[66] all but one structure has a coordination environment for tin more closely resembling a trigonal bipyramidal geometry. The exceptional structure is that of $Ph_3Sn[S_2CN(CH_2CH_2)_2NCH_2Ph]$,[149] for which $t = 0.41$. This probably arises as a result of a wide S–Sn–C angle, i.e. 126.5(1)°, involving the more tightly bound

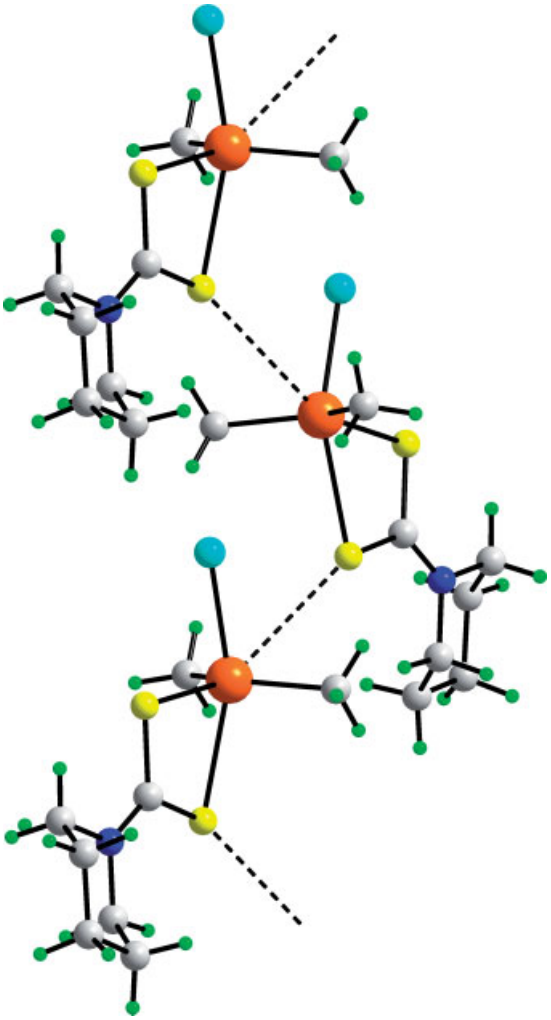

Figure 25. Supramolecular zig-zag chain in the structure of $Me_2Sn(S_2Cpiperidine)Cl$ mediated by secondary Sn···S interactions.

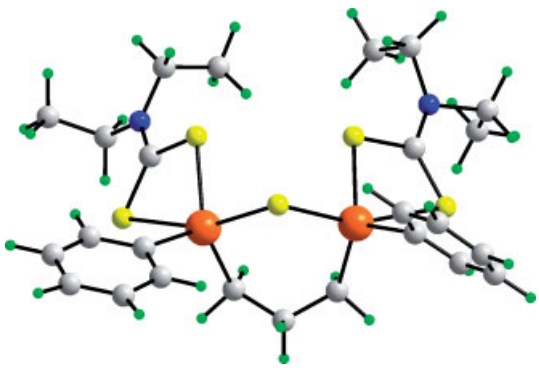

Figure 26. Molecular structure of dinuclear $[PhSn(S_2CNEt_2)(S)(CH_2CH_2CH_2)SnPh(S_2CNEt_2)]$.

sulfur atom, which, in turn, comes about by the relatively close approach of the less tightly bound sulfur atom, i.e. 2.9223(15) Å.

There are two $R_3Sn(S_2CNR'_2)$ structures in which one of the tin-bound R groups carries additional donor atoms capable of coordination to tin. One example, namely $Me_2[2\text{-}(4,4\text{-dimethyl-2-oxazolinyl})\text{-}3\text{-thienyl}]Sn(S_2CNMe_2)$,[158] is

Table 5. Selected geometric parameters (Å, deg) for $R_3Sn(S_2CNR'_2)$

Compound	$Sn-S_{chelate}$	C–Sn···S	τ	Reference
$Me_3Sn(S_2CNMe_2)$[a,b]	2.47(1), 3.33(3)	154(1)	0.56	[135]
	2.47(4), 3.16(3)	153(1)	0.56	
$Me_3Sn(S_2CNMe_2)$[c]	2.47(1), 3.17(1)	156(1)	0.62	[136]
(c-Hex)$_3$Sn[S_2CNH(iBu)]	2.473(3), 3.239(3)	156.7(3)	0.61	[137]
(c-Hex)$_3$Sn[S_2CN(*n*-Bu)$_2$]	2.4679(5), 3.1343(6)	159.36(5)	0.72	[138]
$Ph_3Sn(S_2CNMe_2)$[b,d]	2.460(2), 3.154(2)	155.2(2)	0.61	[139]
	2.4682(18), 3.050(3)	155.4(2)	0.58	
$Ph_3Sn(S_2CNEt_2)$	2.4543(12), 3.1315(11)	155.9(1)	0.58	[15,140]
$Ph_3Sn[S_2CN(n\text{-}Bu)_2]$[b]	2.482(2), 2.945(2)	158.9(2)	0.62	[141]
	2.4703(19), 2.982(3)	159.2(2)	0.67	
$Ph_3Sn[S_2CNMe(n\text{-}Bu)]$	2.4631(10), 3.0840(12)	152.13(6)	0.55	[28]
$Ph_3Sn[S_2CN(Me)(c\text{-}Hex)]$	2.4558(6), 3.0134(7)	158.43(6)	0.70	[142]
$Ph_3Sn[S_2CN(Me)Ph]$	2.4783(14), 3.0161(19)	158.3(2)	0.63	[143]
$Ph_3Sn[S_2CNEt(nPr)]$	2.460(1), 3.095(1)	156.50(6)	0.60	[144]
$Ph_3Sn[S_2CNEt(c\text{-}Hex)]$	2.4758(6), 2.9426(8)	157.11(6)	0.64	[145]
$Ph_3Sn(S_2CNR^1)$[e]	2.4651(15), 3.1059(12)	156.32(9)	0.60	[146]
$Ph_3Sn(S_2CNR^2)$[f,g]	2.482(3), 2.919(2)	156.5(1)	0.59	[147]
$Ph_3Sn(S_2CNR^2)$[f,h]	2.4713(11), 2.9454(10)	158.57(7)	0.65	[140]
$Ph_3Sn(S_2CNR^3)$[i]	2.4649(9), 3.0316(9)	157.25(7)	0.65	[143]
$Ph_3Sn(S_2CNR^4)$[j]	2.4700(11), 3.0124(8)	155.49(9)	0.50	[148]
$Ph_3Sn(S_2CNR^5)$[k]	2.4858(16), 2.9223(15)	154.3(1)	0.41	[149]
$Ph_3Sn(S_2CNR^6)$[l]	2.4635(8), 3.0328(8)	157.10(7)	0.65	[150]
$Ph_2(n\text{-}Bu)Sn(S_2CNMe_2)$	2.467(3), 3.079(3)	158.8(2)	0.71	[151]
$(C_6H_5CH_2)_3Sn(S_2CNR^7)$[m]	2.4808(19), 3.0275(18)	159.4(1)	0.67	[152]
$(C_6H_5CH_2)_3Sn(S_2CNR^8)$[n]	2.4875(7), 3.0527(7)	156.21(8)	0.68	[153]
$(o\text{-}FC_6H_4CH_2)_3Sn(S_2CNR^7)$[m]	2.461(4), 3.035(4)	158.3(2)	0.64	[154]
$(o\text{-}FC_6H_4CH_2)_3Sn(S_2CNR^8)$[b,n]	2.465(4), 3.122(5)	158.6(2)	0.74	[39]
	2.464(4), 3.054(4)	159.9(2)	0.74	
$(o\text{-}ClC_6H_4CH_2)_3Sn(S_2CNR^7)$[m]	2.4664(12), 3.0797(13)	156.90(8)	0.65	[154]
$(o\text{-}ClC_6H_4CH_2)_3Sn(S_2CNR^2)$[f]	2.4519(16), 3.0624(17)	157.4(1)	0.67	[155]
$(o\text{-}ClC_6H_4CH_2)_3Sn(S_2CNR^3)$[i]	2.471(2), 3.0999(17)	156.7(1)	0.61	[155]
$(p\text{-}FC_6H_4CH_2)_3Sn(S_2CNR^7)$[m]	2.470(3), 3.183(4)	156.3(2)	0.66	[156]
$(p\text{-}FC_6H_4CH_2)_3Sn(S_2CNR^4)$[j]	2.4719(10), 3.1262(10)	157.08(9)	0.67	[157]
$Me_2(R^1)Sn(S_2CNMe_2)$[o]	2.5274(11), 3.2678(10)	–	–	[158]
$Ph_2(R^2)Sn(S_2CNMe_2)$[p]	2.560(2), 3.466(3)	–	0.68	[159]
$Ph_3Sn[S_2CN(CH_2CH_2)_2NCS_2]_2SNPh_3$[q,r]	2.4717(17), 3.0659(17)	156.0(1)	0.66	[160]
$(o\text{-}FC_6H_4CH_2)_3Sn[S_2CN(CH_2CH_2)_2NCS_2]_2Sn(CH_2C_6H_4F\text{-}o)_3$[q]	2.457(3), 3.085(2)	156.2(2)	0.64	[161]
$(o\text{-}ClC_6H_4CH_2)_3Sn[S_2CN(CH_2CH_2)_2NCS_2]_2Sn(CH_2C_6H_4Cl\text{-}o)_3$[q]	2.436(4), 3.045(5)	157.8(3)	0.63	[162]
$(PhC(Me)_2CH_2)_3Sn[S_2CN(CH_2CH_2)_2NCS_2]_2Sn(CH_2C(Me)_2Ph)_3$[q]	2.4588(11), 3.3289(10)	158.20(8)	0.71	[163]

[a] Orthorhombic form. [b] Two independent molecules in the asymmetric unit. [c] Monoclinic form. [d] Compound crystallizes as a methanol hemisolvate. [e] NR^1 = pyrrolidine. [f] NR^2 = piperidine. [g] Monoclinic form I. [h] Monoclinic form II. [i] NR^3 = piperazine. [j] NR^4 = 4-methylpiperazine. [k] NR^5 = 4-benzylpiperazine. [l] NR^6 = morpholine. [m] NR^7 = pyrrolidine. [n] NR^8 = morpholine. [o] For structure of R^1 = 2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl, $C_9H_{10}NOS$, see Fig. 29. [p] R^2 = $CH_2CH_2(2\text{-}NC_5H_4)$. [q] Molecule is centrosymmetric. [r] Compound crystallizes as a methanol solvate.

illustrated in Fig. 29 and selected geometric parameters are collected in Table 5. Here, the 2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl group provides an additional nitrogen donor atom, Sn···N is 2.723(3) Å, so that the coordination number of the tin atom is increased to six, based on a skewed trapezoidal bipyramidal geometry. The resultant structure resembles motif I of the $R_2Sn(S_2CNR'_2)_2$ structures in that one of the dithiocarbamate ligands has been replaced by 2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl which provides the C- and N-donor atoms to the trapezoidal plane. The second structure conforming to this type is that of $Ph_2(2\text{-}NC_5H_4CH_2CH_2)Sn(S_2CNMe_2)$,[159] shown in Fig. 30. Here, the dithiocarbamate ligand is monodentate and the Sn–N bond distance is considerably shorter, i.e. 2.486(7) Å, compared with the previous structure. The coordination geometry is based on a trigonal bipyramid with the axial positions being occupied by the more tightly bound sulfur and the nitrogen atoms, the axial S–Sn–N angle is 169.6(2)°.

The four remaining structures to be described are each dinuclear and centrosymmetric.[160–163] The structure of $Ph_3Sn[S_2CN(CH_2CH_2)_2NCS_2]_2SnPh_3$, representative of the four, is shown in Fig. 31, and selected geometric parameters are also collected in Table 5. Each of the structures features the bi-functional, dinegative dithiocarbamate ligand,

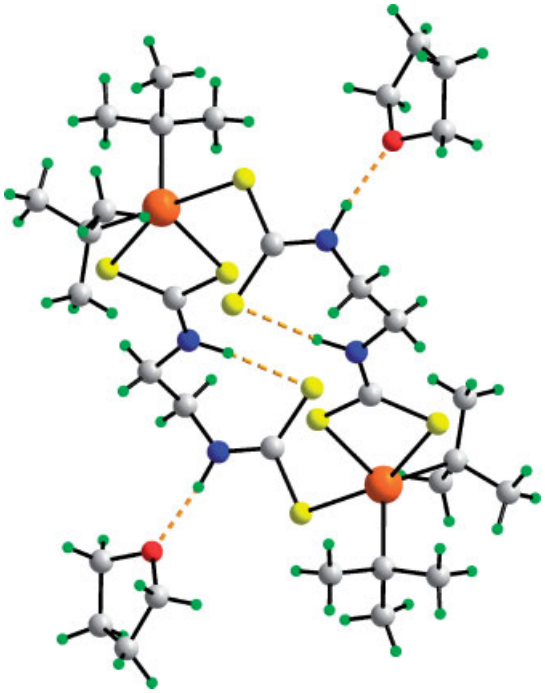

Figure 27. Molecular structure of centrosymmetric $(t\text{-Bu})_2Sn[S_2CN(H)CH_2CH_2N(H)CS_2]_2SN(t\text{-Bu})_2^{\bullet}2$(tetrahydrofuran), featuring a bi-functional dithiocarbamate ligand. Orange dashed bonds represent N–H···O and N–H···S hydrogen bonds.

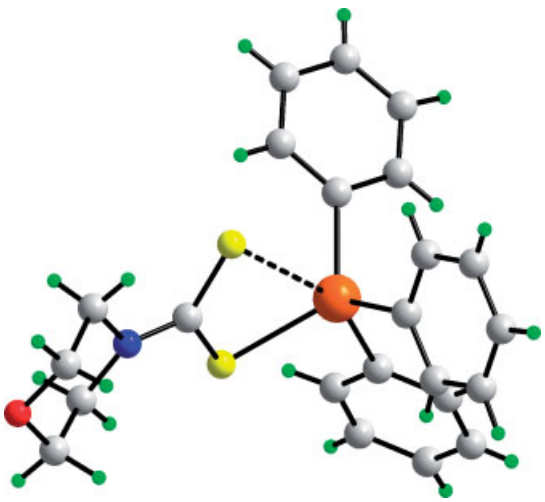

Figure 28. Molecular structure of $Ph_3Sn[S_2CN(CH_2CH_2)_2O]$, serving as an exemplar for structures of the general formula $R_3Sn(S_2CNR'_2)$.

$^{-}S_2CN(CH_2CH_2)_2NCS_2^{-}$, and these bridge the triorganotin centres, defining coordination geometries almost indistinguishable from those described above for mononuclear $R_3Sn(S_2CNR'_2)$, with asymmetrically coordinating dithiocarbamate ligands and approximate trigonal bipyramidal coordination geometries.

Summary and Conclusions

From the foregoing, it is clear that (organo)tin dithiocarbamate compounds have potential medicinal, anti-microbial and agricultural uses. Also, their utility as single-source precursors for the generation of nano-sized tin sulfide particles has been demonstrated. There is a large body of structural data available for these compounds and, generally, for a given combination of R and dithiocarbamate, i.e. $R_{4-n}Sn(S_2CNR'_2)_n$ for $n = 1-4$, there is a reasonable degree of predictability in their solid-state structures. This is due in no small part to the propensity of the dithiocarbamate ligand to form stable chelates with the tin so as to form molecular compounds by precluding supramolecular association via secondary Sn···donor atom interactions. The emphasis of past work has been upon mono-functional dithiocarbamate ligands and the potential exists to develop the structural chemistry of organotin dithiocarbamates to form higher nuclearity aggregates by (i) employing multifunctional dithiocarbamate ligands, and/or (ii) including additional functionality in the R groups of the dithiocarbamate ligands, e.g.

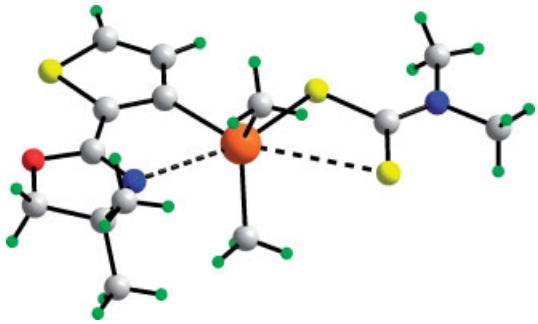

Figure 29. Molecular structure of Me_2[2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl]$Sn(S_2CNMe_2)$, highlighting the skewed trapezoidal bipyramidal geometry for tin.

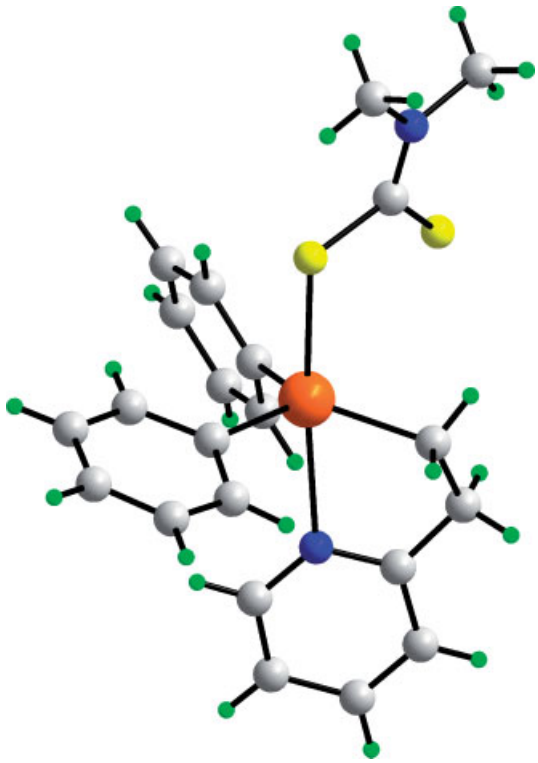

Figure 30. Molecular structure of $Ph_2(2\text{-}NC_5H_4CH_2CH_2)Sn(S_2CNMe_2)$, highlighting the trigonal bipyramidal geometry for tin.

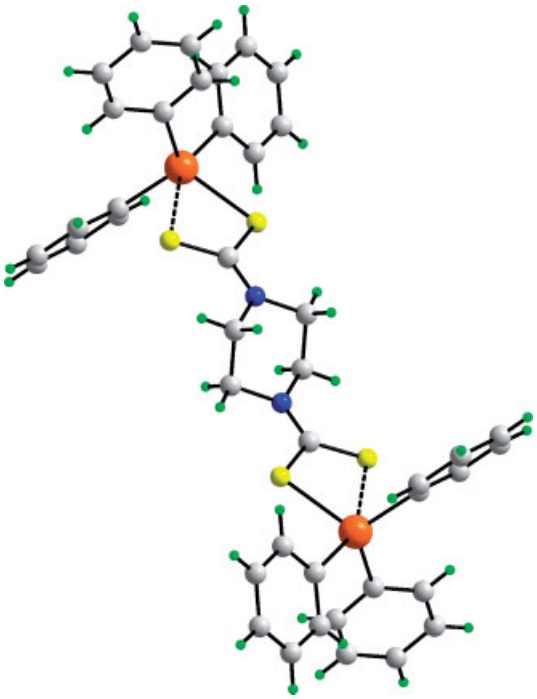

Figure 31. Molecular structure of centrosymmetric $Ph_3Sn[S_2CN(CH_2CH_2)_2NCS_2]_2SNPh_3$, highlighting the distorted trigonal bipyramidal geometry for tin.

groups capable of participating in hydrogen bonding or having additional donor atoms available for additional coordination to tin.

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