Synthesis and Molecular Structure of Tin(IV) 1-Pyrrolecarbodithioates

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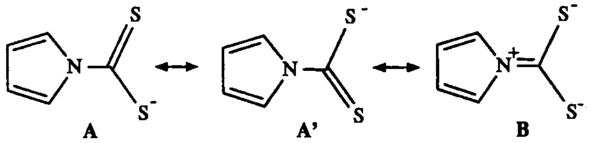
The 1-pyrrolecarbodithioate complexes of tin, $PhSnCl(S_2CNC_4H_4)_2$ (**1**) and $Sn(S_2CNC_4H_4)_4$ (**2**) have been synthesized and characterized by IR and NMR spectra (^1H, ^{13}C and ^{119}Sn). $\delta^{119}Sn$ suggests hexacoordination for **1** and an even higher coordination number for **2**. X-ray structure determinations of these as well as of $Me_2Sn(S_2CNC_4H_4)_2$ (**3**) have shown that **3** is one of the few known examples with a skew-trapezoidal bipyramidal configuration. **1** attains approximately a *cis*-octahedral geometry with two bidentate carbodithioate ligands with the Cl atom and the phenyl group in *cis* position. Complex **2** possesses two bidentate ligands while the other two are essentially anisobidentate leading to a structure between an octahedraon and a dodecahedron.

Despite extensive synthetic and structural reports on metal dialkyldithiocarbamates[1,2] $(R_2NCS_2)_nM$ those containing an aromatic R_2N group received much less attention. Work by Bereman and coworkers[3,4] on their transition metal complexes mark the beginning in that direction. Among the few known aromatic dithiolate complexes, those with the pyrrole ligand are especially interesting. And this ligand can be described with the canonical contribution **A** and **B** to its ground state. In this case a positive charge at the nitrogen atom would increase considerably the contribution of the dianionic electronic structure **B**. In addition, this ligand can act as bidentate, anisobidentate, or unidentate.



From a recent study of the complete series of tin(IV) 1-pyrrolecarbothioates[5], $R_{4-n}Sn(SOCNC_4H_4)_n$, an interesting trend has been witnessed for the bonding pattern of this asymmetrical sulfur-containing ligand. There is a change from an essentially unidentate to an anisobidentate behavior tending to become bidentate with concomitant increase in the Sn-O interaction as *n* increases. This also reflects the stereoelectronic effect responsible for the molecular structure. It is not clear, however, wether in reference to a typical non-transition metal centre such as tin(IV) these evident features are the consequence of an oxygen-sulfur donor combination of the potentially bidentate ligand and/or the nature of the central tin atom. In this paper, we report on the synthesis of two new tin(IV) 1-pyrrolecarbodithioate complexes, $PhSnCl(S_2CNC_4H_4)_2$ (**1**) and $Sn(S_2CNC_4H_4)_4$ (**2**) as well as on their crystal and molecular structures and, in addition, also on the structure of $Me_2Sn(S_2CNC_4H_4)_2$ (**3**)[6].

Results and Discussion

Contrary to an earlier report[6] the chlorophenyltin complex **1**, $PhSnCl(S_2CNC_4H_4)_2$, is invariably the product of the reaction of $PhSnCl_3$ with potassium 1-pyrrolecarbodithioate as shown in eq. (1). Despite the failure to substitute the third Cl atom of $PhSnCl_3$ by the ligand, the formation of the tetrakis complex **2** according to eq. (2) turned out to be facile.

$$PhSnCl_3 + 2\,KS(S)CNC_4H_4 \rightarrow \underset{\mathbf{1}}{PhSnCl(S_2CNC_4H_4)_2} + 2\,KCl \qquad (1)$$

$$SnCl_4 + 4\,KS(S)CNC_4H_4 \rightarrow \underset{\mathbf{2}}{Sn(S_2CNC_4H_4)_4} + 4\,KCl \qquad (2)$$

As was to be expected all these new compounds display IR absorption bands typical for the $C_4H_4NCS_2^-$ ligand[6]. The Sn−S stretching vibration[7] is observed in **1** at 351 and in **2** at 356 cm^{-1}. An additional band at 301 cm^{-1} in **1** may be assigned to ν(Sn−Cl) or ν(Sn−C(Ph))[7,8]. We consider the former as the more likely alternative.

More information related to the structure of the complexes and the bonding situation was expected from NMR data. Thus the ^1H-NMR spectra of **1** and **2** show two triplets due to pyrrole protons. Thus, the ligands are chemically equivalent. In the case of **2** the triplets resulting from the α-H atoms get mixed up with the multiplet signal of the phenyl group bonded to the tin atom. According to this observation the dithioate ligand must rotate freely either around the CN or the CS bond assuming an unidentate behavior. This result is corroborated by the ^{13}C-NMR spectra which reveal three resonances for the ligand, two resulting from the pyrrole unit and the other from the CS_2N group. In **1** additional four lines are observed for the phenyl group suggesting that this group rotates freely. The ^{13}C-NMR data, therefore, do not allow to draw any additional conclusions related to details of the structure of the complexes.

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However, it is known that the ^{119}Sn-NMR signal moves upfield with increasing coordination number for the tin centre in the organotin(IV) compounds with similar ligands. The ^{119}Sn-NMR spectrum of **3** shows an absorption at $\delta = -267$ which is intermediate between those of four-coordinated diorganotin(IV) dithiolates[9,10] (δ ranges from -120 to 144) and of six-coordinated dimethyltin(IV) bis-β-diketonates[11,12] (δ^{119}Sn $= -356$) suggesting pentacoordination at the tin atom. δ^{119}Sn for **1** is found at $\delta = -378$ corresponding to hexacoordinated Sn. The tetrakis complex **2** absorbs at a much higher field with $\delta = -729$ consistent with a coordination at the tin atom higher than six, most likely eight. These shifts can only be explained by assuming a bidentate behavior of the ligand $C_4H_4NCS_2^-$. Moreover, the data for **1** are only in accord with the phenyl group and the Cl atom in *trans* position. However, the NMR data allow no conclusion regarding details of bonding and conformation of the complexes under consideration. Therefore, crystals of the complexes were subjected to an X-ray structure determination.

The unit cell of **3**, shown in Figure 1, consists of discrete mononuclear molecules. There is an intermolecular sulfur-sulfur contact of 3.551 Å between atoms S(4) and S(3)′ of another molecule indicated by dashed lines. Intramolecular bond lengths of **3** are summarized in Table 1 together with those of the other complexes. The molecular structure of **3** (Figure 2) shows a rather unsymmetrical environment for the tin atom. One sulfur atom of each ligand is covalently bonded with an averaged distance of 2.521 Å (0.08 Å longer than the sum of the covalent radii, 2.44 Å) while the other one is located at an average distance of 3.016 Å. This may be considered as a weak coordinative bond corresponding to an anisobidentate ligand. The four sulfur atoms lie almost in a plane constituting a trapezoid. The two methyl groups are skewed with an angle CSnC′ = 135.9(2)° towards the edge constituted by the distant sulfur atoms of the trapezoid, and the S_4 plane is almost perpendicular with it. The bond angles subtended at the tin atom by the methyl carbons and S(2) and S(4) atoms range from 105.4 – 107.5° demonstrating that the tin – carbon bonds are symmetrically bent towards the longer tin – sulfur bonds. This is obviously a consequence of repulsion between the bonding electron pairs around the central tin atom. Evidently these angles are close to the tetrahedral angle. However, the interligand angle S(2)SnS(4) happens to be only 83.4(1)°. The coordination polyhedron around the tin centre can be considered to be approximately skew-trapezoidal bipyramidal. However, the symmetric approach of the two sulfur atoms one from each ligand (tending to become bidentate) is perhaps responsible for the angle deformation and explicitly reflects an intramolecular transition of a tetrahedron to an octahedron. This and two earlier reported[13] bis-chelates $Me_2Sn(RCSCHCOR)_2$ are the first few examples of a skew-trapezoidal bipyramidal structure[14] with two equivalent ligands and two bidentate ones.

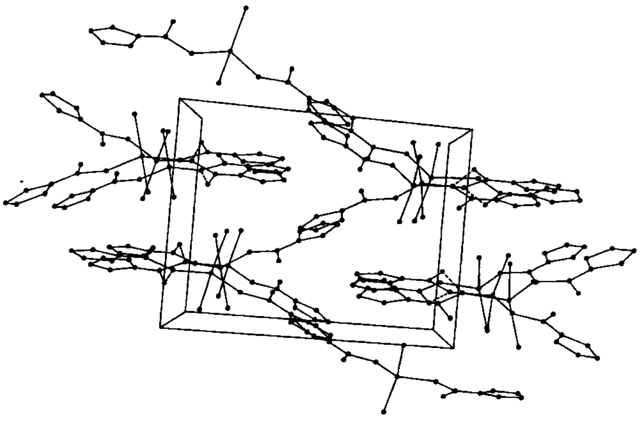

Figure 1. Plot of the unit cell of **3**. View down the *b* axis. Short intermolecular contacts are depicted with broken lines

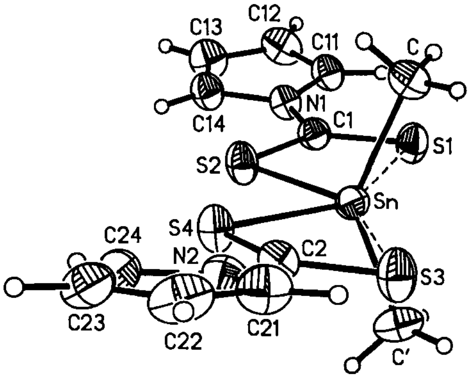

Figure 2. ORTEP plot of a molecule of **3**. Selected bond angles [°]: Sn(2) – Sn – S(4) 83.4(1), S(2) – Sn – C(A) 105.7(2), S(2) – Sn – C(B) 106.4(2), S(4) – Sn – C(A) 170.5(1), S(4) – Sn – C(B) 105.4(1), C – Sn – C′ 135.9(2), Sn – S(2) – C 94.1(2), Sn – S(4) – C′ 94.4(2), S(1) – C(1) – S(2) 123.1(3), S(3) – C(2) – S(4) 121.5(3)

Table 1. Selected bond distances of the molecules of **1** – **3**

	3	**1**	**2** A	**2** B
Sn-S(1)	3.025(1)	2.649(1)	2.414(4)	2.593(5)
Sn-S(2)	2.533(1)	2.570(1)	3.186(4)	2.703(4)
Sn-S(3)	3.008(1)	2.643(1)	2.586(4)	2.439(4)
Sn-S(4)	2.509(1)	2.580(1)	2.667(4)	3.173(4)
S(1)-C(1)	1.659(4)	1.697(5)	1.741(9)	-
S(2)-C(1)	1.714(4)	1.710(4)	1.652(10)	-
S(3)-C(2)	1.659(5)	1.694(5)	1.721(9)	-
S(4)-C(2)	1.736(5)	1.697(5)	1.687(9)	-
C(1)-N(1)	1.387(6)	1.365(5)	1.390(12)	-
C(2)-N(2)	1.362(6)	1.361(6)	1.356(11)	-
Sn-C/C(3)	2.104(5)	2.139(5)		
Sn-C'	2.132(5)	-		
Sn-Cl	-	2.411(1)		
Sn-S(5)	-	-	2.427(4)	2.574(4)
Sn-S(6)	-	-	3.292(4)	2.799(5)
Sn-S(7)	-	-	2.602(4)	2.416(4)
Sn-S(8)	-	-	2.709(4)	3.187(4)

The stereodistribution of the C_2SnS_4 core in **3** is comparably similar to the $C_2SnO_2S_2$ core of the corresponding 1-pyrrolecarbothioate complex[5]; the position of the two weakly coordinated oxygens is occupied by the distant sulfur atoms in **3**. The interligand bond angle S(2)SnS(4) is sharper by ≈10° in comparison to the monothio analog perhaps due to the S(2)–S(4) interaction (3.356 Å) and longer bite of the dithiocarbamates. In both anisobidentate ligands each shorter tin–sulfur bond is associated with a longer carbon–sulfur bond (aver. 1.659 Å) and vice versa (longer C–S, 1.725 Å); this is in consonance with the bonding asymmetry of the ligands. The C–N bond lengths (aver. 1.374 Å) is longer than the corresponding distance of 1.31 Å reported[14] for $Me_2Sn(S_2CNMe_2)_2$ emphasizing a diminished contribution of the dianionic canonical contribution **B**.

In transition metal dithiocarbamates[1,2], sulfur–metal distances are almost of equal length. On the contrary, there are two sets of intranuclear distances in diorganotin bisdithiocarbamates[15]. The central tin atom in $RSnCl(S_2CNC_4H_4)_2$ complexes with a chlorine atom replacing one organo group should display enhanced acceptor strength due to the presence of the more electronegative Cl atom in comparison to the organo group in $R_2Sn(S_2CNC_4H_4)_2$. This should strengthen the bonding interaction of the weakly coordinated sulfur of the ligand moiety. As such the increased acidity of the tin centre should spread over both the coordination sites of the NCS_2 skeleton. The examination of the molecular structure of $PhSnCl(S_2CNC_4H_4)_2$ (**1**) described henceforth, corroborates this. The crystal structure consists of four molecules in the monoclinic unit cell (Figure 3). As indicated by the dashed lines, there are only two significant intermolecular interactions in the solid state, namely between N(2) and S(4)′ (3.275 Å) in addition to the contact between Cl and S(4)′ (3.564 Å). The molecular structure of **1** is portrayed in Figure 4. As was to be expected six atoms are arranged in the coordination sphere of the tin centre. An approximate equatorial plane is defined by atoms Cl, C(3), S(1), and S(3); the other sulfur atoms S(4) and S(2) of two NCS_2 ligand cores occupy the axial positions. This provides an octahedral configuration around the tin with phenyl and chloride in *cis* position. Although the equatorial angles vary between 81.6 and 98.4°, these do not deviate too much from the ideal 90°, while the *trans* angle, S(4)SnS(2) is only 152.3(1)° rather than 180°. Much of the distortions from the ideal octahedron can be attributed to the short ligand bite angle (aver. 68.8°) of the carbodithioate group.

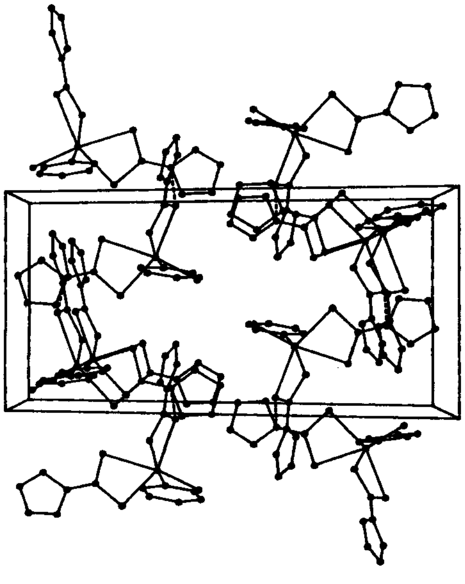

Figure 3. Plot of the unit cell of **1**. View down the *b* axis. Short intermolecular contacts are shown with dashed lines

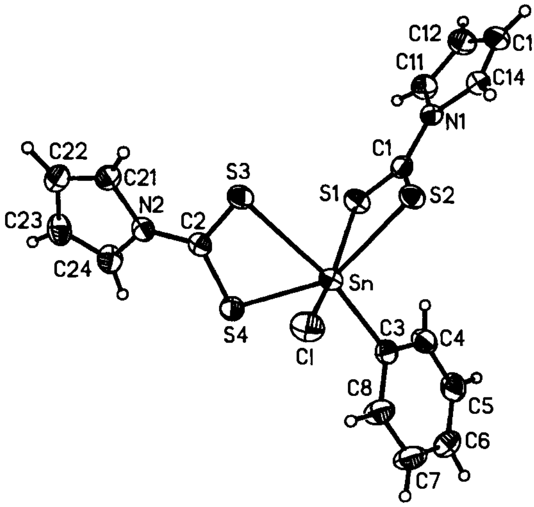

Figure 4. ORTEP plot of a molecule of **1**. Selected bond angles [°]: S(1)–Sn–S(2) 69.1(1), S(1)–Sn–S(3) 81.6(1), S(1)–Sn–S(4) 92.5(1), S(1)–Sn–C(3) 96.5(1), S(1)–Sn–Cl 160.9(1), S(1)–C(1)–S(2) 120.7(3), S(2)–Sn–S(4) 152.3(1), S(2)–Sn–C(3) 97.6(1), S(2)–Sn–Cl 95.5(1), S(3)–Sn–S(4) 68.5(1), S(3)–Sn–C(3) 165.8(1), S(3)–Sn–Cl 86.8(1), S(4)–Sn–Cl 97.3(1), S(4)–Sn–C(3) 97.6(1), Sn–S(1)–C(1) 84.0(1), Sn–S(2)–C(1) 86.2(2), Sn–S(3)–C(2) 84.7(2), Sn–S(4)–C(2) 86.6(2)

The two Sn–S bond lengths (Table 1) of each ligand such as Sn–S(1) [2.649(1)Å] and Sn–S(2) [2.570(1) Å] differ again by approximately 0.08 Å; the equatorial ones are longer than the axial bonds. The geometry of both $C_4H_4NCS_2$ ligands in **1**, although chemically not equivalent, show the same structural parameters within the limits of standard deviations. Thus the C–S bonds are to be considered as equal and the distance average, 1.699 Å, suggests significant multiple bonding. The CN bonds are short (average 1.363 Å) but somewhat longer than a true CN double bond. This can be described by contributions of the various canonical forms **A** and **B** to the electronic ground state configuration with contribution by **A** dominating. Not unexpected, the pyrrole plane lies almost coplanar with the NCS_2 plane, the prerequisite for strong CN π-bonding. The Sn–C distance of 2.139(5) Å falls into the normal range. The molecule **1** has only C_1 symmetry in the solid state. It is somewhat surprising that the Sn–S bonds *trans* to the Cl atom or the phenyl group are almost of equal length (average 2.646 Å). A "*trans*" effect is obviously not operative.

Complex **2** crystallized from dichloromethane/*n*-hexane and kept 0.5 mol of the solvent in its crystal lattice. As deduced from its U_{ij} values, the Cl atoms are highly vibrationally and rotationally mobile. Although the structure revealed only discrete molecules with no unusually short contacts its tin atom showed fairly large U_{ij} values as compared with the thermal parameters for the sulfur atoms. This suggested disorder for the tin position. Indeed, subsequent refinement with two tin positions of equal occupancy led to rapid convergence in the final cycles of refinement. As a consequence of this disorder, particularly of the solvent molecule, we arrived at a final *R* much higher than to be expected for structures containing a tin atom. Figure 5 depicts the two molecules resulting from disorder, e.g. both have the same ligand shell but two different positions for the tin centre. Consequently, Table 1 lists two sets of bonding parameters[16].

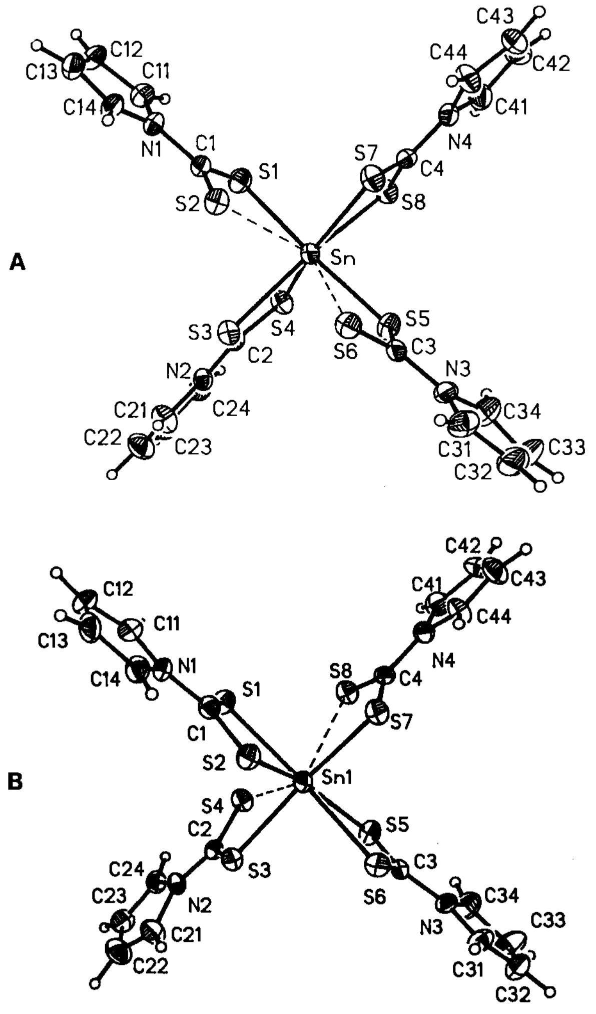

Figure 5. ORTEP plot of the two (disordered) molecules of **2**. Note the identical orientation of the ligands. Dashed lines represent interactions of the anisobidentate ligands with the tin centre. Selected bond angles [°], standard deviations for angles subtended at tin are 0.1°. Molecule A: S(1)−Sn−S(3) 165.0, S(1)−Sn−S(4) 85.4, S(1)−Sn−S(5) 91.8, S(1)−Sn−S(7) 93.3, S(1)−Sn−S(8) 85.5, S(3)−Sn−S(4) 68.7, S(3)−Sn−S(5) 91.8, S(3)−Sn−S(7) 135.9, S(4)−Sn−S(5) 83.3, S(4)−Sn−S(7) 155.3, S(4)−Sn−S(8) 87.8, S(5)−Sn−S(7) 92.9, S(4)−Sn−S(8) 87.8, S(5)−Sn−S(7) 92.9, S(5)−Sn−S(8) 84.1, S(7)−Sn−S(8) 76.6, Sn−S(1)−C(1) 100.3(3), Sn−S(3)−C(2) 86.2(3), Sn−S(4)−C(2) 84.3(3), Sn−S(5)−C(3) 103.2(3), Sn−S(7)−C(4) 86.8(3), Sn−S(8)−C(4) 84.1(3). − Molecule B: S(1)−Sn1−S(2) 67.9, S(1)−Sn1−S(3) 92.5, S(1)−Sn1−S(5) 136.6, Sn(1)−Sn1−S(6) 157.1, S(1)−Sn1−S(7) 93.5, S(2)−Sn1−S(3) 84.4, S(2)−Sn1−S(5) 155.5, S(2)−Sn1−S(6) 85.8, S(2)−Sn1−S(7) 84.3, S(3)−Sn(1)−S(5) 91.8, S(3)−Sn1−S(6) 85.8, S(3)−Sn1−S(7) 164.2, S(5)−Sn1−S(6) 66.4, S(5)−Sn1−S(7) 93.8, S(6)−Sn1−S(7) 83.0, Sn1−S(1)−C(1) 86.2(3), Sn1−S(2)−C(1) 84.4(3), Sn1−S(3)−C(2) 100.4(3), Sn1−S(5)−C(3) 88.9(3),Sn1−S(6)−C(3) 82.2(3), Sn1−S(7)−C(4) 100.8

The structure of **2** consists of two different kinds of chelating dithio ligands, two being truly bidentate and two anisobidentate. Six sulfur atoms occupy the vertices of a distorted octahedron. The two more distant sulfur atoms approach the opposite edges defined by equatorial sulfur atoms leading to a (distorted) dodecahedral arrangement. The *trans* orientation of the anisobidentate ligands makes the complex **2** conspicuously different from the earlier reported tetrakis-dithiocarbamates $Sn(S_2CNEt_2)_4$[17] and $Sn(S_2CNMe_2)_4$[18] as well as even its monothio analogue, $Sn[S(O)CNC_4H_4]_4$[5], where invariably the two unidentate ligands occupy a *cis* position. It seems that the *cis* orientation sequence is not as essential as anticipated[18] for binding four bidentate ligands to tin(IV).

Among the two sets of ligands in **2**, there are considerable variations in the tin−sulfur bond distances. In the anisobidentate ligands (Figure 5A) the bonds Sn−S(1) [2.414(4)Å] and Sn−S(5) [2.427(4) Å] appear to be shorter than the sum of the covalent single bond radii (2.44 Å). This would be even shorter than the corresponding distances reported for $Sn(S_2CNEt_2)_4$[17] (average 2.502 Å) and for $Sn(S_2CNMe_2)_4$[18] (average 2.500 Å). The other sulfur atoms weakly coordinates with an average distance of 3.238 Å. This is distinctly shorter than the analogous bond lengths found for $Sn(S_2CNEt_2)_4$[16] (3.89 Å) and $Sn(S_2CNMe_2)_4$[17] (3.58 Å). In the two bidentate chelating ligands the tin−sulfur distances vary from 2.586(4) Å for Sn−S(3) to 2.709(4) Å for Sn−S(8). These distances are comparable to the corresponding Sn−S bond lengths in the other two tetrakis-dithiocarbamates.

The SSnS bond angles deviate considerably from 90°. Due to the acute bite angle (average 68.1°) of the two bidentate ligands, the other two equatorial bond angles S(3)SnS(7) [135.9(1)°] and S(4)SnS(8) [87.8(1)°] are at much variance. The *trans* angle S(1)SnS(5) is 165.0(1)°. In the ligand geometry, the intrachelate angle subtended at the sulfur in the anisobidentate ones (average 101.7°) closes up considerably on chelation (average 85.3°). The four-membered chelate rings are almost planar and so are their corresponding pyrrole units. The two chelating and the two anisobidentate ligands also maintain planarity among themselves. The interplanar angles defined by the planes through Sn,S(1),S(2) and Sn,S(3),S(4) or between the planes Sn,S(5),S(6) and Sn,S(7),S(8) are 89.3 and 90.4°, respectively. This demonstrates that the anisobidentate ligands stand perpendicular to the bidentate ones.

A known tetrakis-bidentate dodecahedral tin complex is $Sn(NO_3)_4$[19]. $Sn(OAc)_4$[20] is considered to be an example with pseudododecahedral geometry, its Sn−O bonds are longer and more variable. Otherwise the molecule would be overcrowded. This is accounted for in terms of the longer bite of the acetate unit (2.23 Å) as compared to 2.14 Å for nitrate. As a result of this, $[Sn(OAc)_5]^-$ attains only a pentagonal bipyramidal coordination[21]. The much longer bite distance of chelating dithiocarbamates (2.9 Å) leads to essentially octahedral tetrakis-dithiocarbamates including the present complex **2**. Nevertheless, owing to the much closer proximity of the other two sulfur atoms of the unidentate ligands to tin, the molecular structure of **2** may be considered a transition from hexacoordination to octacoordination.

Conclusions

Although the ^{119}Sn-NMR resonances of **1**–**3** are in accordance with the penta-, hexa-, and octacoordination at the tin atoms, the high symmetry of the ligand arrangement as suggested by the ^{1}H- and ^{13}C-NMR resonances do not correspond with the structure observed in the solid state. Rotation around the C–N bond will not be explicable for **1**. It is therefore more likely and more reasonable from the structures in the solid state that all these molecules are fluxional in solution by opening Sn–S bonds allowing the ligand to rotate around the remaining Sn–S bond. Although a rather small movement of the tin atom in **2** will readily transform the molecule shown in Figure 5A to the molecule depicted in Figure 5B. This kind of fluxionality would not be in accord with the ^{13}C-NMR data since all four ligands are equivalent on the NMR time scale in solution. It will be interesting to see if dithio ligands with a different bite angle will be able to achieve octacoordination at tin(IV) giving rise to true dodecahedral or square-antiprismatic geometry.

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Experimental

All experimental manipulations were carried out under strictly anhydrous conditions in a nitrogen atmosphere. – Potassium 1-pyrrolecarbodithioate[22] and $Me_2Sn(S_2CNC_4H_4)_2$[6] were prepared by the literature procedures. $PhSnCl_3$ (b.p., 75°C/10 Torr) and $SnCl_4$ (b.p. 114°C) were distilled before use. The preparation and characterization of $Me_2Sn(S_2CNC_4H_4)_2$ has been described earlier[6]. – Elemental analyses (C, H, N): Perkin-Elmer analyzer. – IR: Perkin-Elmer 783 spectrometer, range 4000–200 cm^{-1}, nujol mull, CsI plates. – NMR: Jeol FX 90Q spectrometer at 25°C in $CDCl_3$, TMS as internal standard for ^{1}H and ^{13}C and Me_4Sn in sealed capillary for ^{119}Sn as external reference.

Chlorophenylbis(1-pyrrolecarbodithioato)tin(IV) (**1**): Phenyltin trichloride (1.04 g), dissolved in dichloromethane (20 ml), was added to the suspension of $KS_2CNC_4H_4$ (1.81 g) in dichloromethane (30 ml) with continuous stirring at ambient temp. Stirring was continued for about 8 h, and the yellow solid formed was filtered off. It was dried and crystallized from CH_2Cl_2/MeOH. Yield: 1.57 g of **1** (89%), m.p. 167–70°C. – IR (cm^{-1}): 1335 ν(C–N), 995 ν(C–S), 351 ν(Sn–S), 351 ν(Sn–Cl) or ν(Sn–C(Ph)) 301. – δ^{1}H: 6.27 (β-H, t), 6.95–7.85 (α-H and Ph, m). – δ^{31}C: 209.4 (CS), 123.0, 117.1 (pyrrole carbons), 131.5, 130.1, 129.7, 128.9 (Ph). – δ^{119}Sn: –378.0 (s).

$C_{15}H_{13}ClN_2S_4Sn$ (503.7)	Calcd.	C 37.2	H 2.5	N 5.4
	Found	C 37.8	H 2.4	N 5.7

Table 2. Data concerning unit cell, data collection, structure solution and refinement. Two check reflections were measured after every 48 intensity measurements. Intensities were Lp-corrected and for absorption (ψ scans). The structures were solved by Direct Methods and all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the final refinements using a riding model

Crystal Data	**3**[a]	**1**[b]	**2**[a]
Formula	$C_{12}H_{14}N_2S_4$	$SnC_{16}H_{13}ClN_2S_4$	$SnC_{20}H_{16}N_4S_8Sn \cdot 0.5CH_2Cl_2$
M_w	433.2	515.7	730.0
a [Å]	12.116(2)	9.946(2)	10.738(5)
b [Å]	19.389(1)	9.935(2)	10.862(6)
c [Å]	13.792(2)	20.332(4)	13.180(14)
α [°]	90.0	90.0	89.16(7)
β [°]	103.03(4)	103.86(2)	79.97(7)
γ [°]	90.0	90.0	88.26(4)
V [Å^3]	1691.3(4)	1949.7(7)	1513(2)
$d_{calc.}$[Mg/m^3]	1.701	1.757	1.602
Z	4	4	2
Space Group	$P2_1/a$	$P2_1/n$	P1bar
$\mu_{MoK\alpha}$ [cm^{-1}]	19.79	18.66	14.85
F(000)	856	1016	726
Size [mm]	0.4x0.5x0.45	0.2x0.2x0.5	0.15x0.28x0.55
Data Collection and Structure Solution			
2Θ-range	2-50, h k +/-l	2-50, h k +/-l	3-50, +/-h +/-k+/-l
Scan speed [°/min]	1.8-29.3	1.8-29.3	2-29.3
Reflect. meas.	3258	3694	8385
Reflect. indep.	2926	3254	5361
Reflect. obs. (3σI)	2536	2893	3914
Max/min transm.	0.355/0.330	0.550/0.467	0.538/0.493
Variables	172	217	319
R	0.0393	0.0249	0.0913
R_w	0.0778	0.0248	0.1407
g	0.0116	0	0.0216
Δ_{max}[e/Å^3]	0.51	0.275	2.94

[a] From dichloromethane/*n*-hexane. – [b] From dichloromethane/methanol.

Table 3. Fractional atomic coordinates (× 10^4 Å) and equivalent isotropic thermal parameters (× 10^3 Å^2) of compound **1**

	x	y	z	U_{eq}
Sn	9130(1)	3065(1)	8370(1)	41(1)
Cl	10642(1)	1023(1)	9342(1)	62(1)
S(1)	8095(1)	2881(1)	7109(1)	50(1)
S(2)	9488(1)	273(1)	7516(1)	46(1)
S(3)	11351(1)	3301(1)	8170(1)	49(1)
S(4)	9313(1)	4492(1)	8834(1)	51(1)
C(1)	8713(3)	1393(4)	6901(2)	41(1)
N(1)	8601(3)	1083(3)	6235(1)	43(1)
C(11)	8081(4)	1925(4)	5677(2)	56(1)
C(12)	8083(5)	1223(5)	5115(2)	68(2)
C(13)	8577(4)	-84(5)	5305(2)	60(2)
C(14)	8900(4)	-165(4)	5978(2)	50(1)
C(2)	10755(3)	4631(4)	8541(2)	40(1)
N(2)	11465(3)	5822(3)	8608(1)	45(1)
C(21)	12715(4)	6081(4)	8421(2)	52(1)
C(22)	13036(4)	7372(5)	8543(2)	60(2)
C(23)	11999(5)	7967(4)	8814(2)	67(2)
C(24)	11058(4)	7025(4)	8851(2)	60(2)
C(3)	7193(4)	1540(4)	8593(2)	45(1)
C(4)	5965(4)	1522(5)	8096(2)	58(2)
C(5)	4731(4)	1276(5)	8271(2)	68(2)
C(6)	4702(5)	1059(5)	8930(3)	74(2)
C(7)	5901(5)	1084(6)	9423(2)	79(2)
C(8)	7147(4)	1315(5)	9260(2)	64(2)

Tetrakis(1-pyrrolecarbodithioato)tin(IV) (**2**): Tin tetrachloride (0.72 g), dissolved in dichloromethane (25 ml), was added to a suspension of potassium 1-pyrrolecarbodithioate (2.0 g) in dichloromethane (20 ml) with constant stirring at 25°C. Stirring was continued for 12 h. The reddish-yellow solid which had separated was filtered off and crystallized from CH_2Cl_2/*n*-hexane and dried in vacuo. Yield: 1.74 g of **2** (92%), m.p. 130–132°C. – IR (cm^{-1}): 1340 ν(C–N), 996 ν(C–S), 356 ν(Sn–S). – δ^{1}H: 7.56 (β-H, t), 6.38 (α-H, t). – δ^{13}C: 207.6 (CS), 112.7, 116.9 (pyrrole carbons). – δ^{119}Sn: –729.2 (s).

$C_{20}H_{16}N_4S_8Sn$ (687.5)	Calcd.	C 34.9	H 2.3	N 8.1
	Found	C 33.2	H 2.4	N 8.2

X-Ray Structure Determinations were performed by using a Nicolet R3m four-circle diffractometer operating with a graphite monochromator and Mo-K_α radiation, λ = 0.71069 Å, for data collection at 25°C. The SHELXTL PLUS program package was applied in calculations. Crystallographic data and details of the data collection and X-ray structure determinations are summarized in Table 2, Fractional atomic coordinates in Tables 3–5[23].

Table 4. Fractional atomic coordinates (× 10^4 Å) and equivalent isotropic thermal parameters (× 10^3 Å^2) of compound **2**

	x	y	z	U_{eq}
Sn	4121(2)	2528(2)	2659(1)	38(1)
Sn(1)	4090(2)	2639(2)	3139(2)	44(1)
S(1)	1987(3)	1866(3)	2699(2)	49(1)
S(2)	2283(3)	2429(2)	4833(2)	47(1)
C(1)	1396(9)	1971(8)	4013(7)	41(3)
S(3)	4759(2)	577(2)	3617(2)	43(3)
S(4)	4802(3)	669(2)	1363(2)	47(1)
C(2)	5020(8)	-121(8)	2432(6)	35(3)
S(5)	6315(3)	3083(3)	2143(2)	50(1)
S(6)	5740(3)	3486(2)	4384(2)	49(1)
C(3)	6724(9)	3554(7)	3260(7)	38(3)
S(7)	3393(3)	4776(2)	3166(2)	49(1)
S(8)	3744(3)	3924(2)	1014(2)	49(1)
C(4)	3343(8)	5032(8)	1889(7)	39(3)
N(1)	148(7)	1624(7)	4295(6)	43(3)
C(11)	-637(10)	1249(10)	3656(9)	57(4)
C(12)	-1791(10)	964(10)	4261(13)	68(5)
C(13)	-1620(12)	1162(10)	5326(13)	79(5)
C(14)	-465(10)	1547(9)	5314(9)	55(4)
N(2)	5437(7)	-1314(6)	2379(5)	39(2)
C(21)	5745(12)	-2015(10)	3233(9)	64(4)
C(22)	6074(13)	-3142(11)	2865(11)	72(5)
C(23)	6037(11)	-3168(10)	19817(10)	64(4)
C(24)	5649(10)	-2080(10)	1532(9)	53(4)
N(3)	7923(7)	4047(7)	3161(6)	45(3)
C(31)	8486(11)	4473(11)	3973(12)	63(4)
C(32)	9605(13)	4831(12)	3626(12)	77(5)
C(33)	9837(12)	4676(16)	2548(11)	90(6)
C(34)	8751(11)	4206(12)	2284(11)	70(5)
N(4)	2975(7)	6189(7)	1602(6)	45(3)
C(41)	2940(11)	6624(11)	649(9)	62(4)
C(42)	2566(11)	7831(12)	692(10)	66(4)
C(43)	2356(12)	8188(11)	1692(12)	77(5)
C(44)	2568(11)	7179(9)	2285(8)	55(4)
Cl(1)	1378(15)	431(14)	8612(12)	169(5)
Cl(2)	950(15)	2179(14)	10114(12)	163(5)
C	893(39)	1641(33)	8983(29)	115(1)

Table 5. Fractional atomic coordinates (× 10^4 Å) and equivalent isotropic thermal parameters (× 10^3 Å^2) of compound **3**

	x	y	z	U_{eq}
Sn	1612(1)	2462(1)	8583(1)	47(1)
S(1)	647(1)	1861(1)	6412(1)	65(1)
S(2)	2998(1)	1611(1)	7612(1)	60(1)
S(3)	1229(1)	3401(2)	10545(1)	71(1)
S(4)	3301(1)	2378(1)	10021(1)	59(1)
C	1341(5)	4406(5)	8164(4)	75(2)
C'	575(5)	878(5)	8795(4)	72(2)
C(1)	1984(3)	1407(4)	6535(3)	50(1)
N(1)	2331(3)	816(4)	5752(2)	52(1)
C(11)	1648(4)	454(5)	4850(3)	61(2)
C(12)	2272(5)	-169(6)	4314(3)	73(2)
C(13)	3391(5)	-190(6)	4879(4)	75(2)
C(14)	3429(4)	372(5)	5758(3)	64(2)
C(2)	2559(4)	2897(5)	10889(3)	52(1)
N(2)	3131(3)	2859(4)	11859(3)	53(1)
C(21)	2656(5)	3049(6)	12685(4)	71(2)
C(22)	3471(6)	2899(6)	13513(4)	78(2)
C(23)	4485(7)	2569(4)	13215(5)	79(3)
C(24)	4273(6)	2541(4)	12227(5)	60(2)

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[15] Obviously the bond lengths and angles associated with the ligands are only the average of the two types of coordination displayed by the dithioate ligand in the molecular structure. Therefore, the bonding parameters around the C atom of the pyrrolecarbodithioate group represent also only an average situation.

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[23] Additional data related to the present X-ray structure determinations have been deposited with Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, and may be requested by quoting the depository number CSD-56174, the name of the authors and the literature citation.

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CAS Registry Numbers

1: 139943-18-3 / **2**: 139943-19-4 / **2** · 0.5 CH_2Cl_2: 139943-20-7 / **3**: 131400-86-7 / $KS_2CNC_4H_4$: 62641-74-1 / $PhSnCl_3$: 1124-19-2 / $SnCl_4$: 7646-78-8