

PROGRESS IN INORGANIC CHEMISTRY

Edited by

KENNETH D. KARLIN

DEPARTMENT OF CHEMISTRY
JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND

VOLUME 53



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**Progress in
Inorganic Chemistry**

Volume 53

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**Progress in
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Volume 53**

Main Group Dithiocarbamate Complexes

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I. INTRODUCTION

Main group dithiocarbamate complexes find wide-ranging applications in materials and separation science, and have potential use as chemotherapeutics, pesticides, and fungicides. The literature on main group dithiocarbamates as a whole has not been reviewed extensively since the 1970s (1, 2) despite the large number of publications that have appeared subsequently. From an inorganic chemistry stand point, dithiocarbamates are highly versatile ligands toward main group metals. They can stabilize a variety of oxidation states and coordination geometries, and seemingly small modifications to the ligand can lead to significant changes in the structure–behavior of the complexes formed. This chapter focuses primarily on structural aspect of main group dithiocarbamate complexes, covering the essential literature from 1978 to 2003. For the purposes of this chapter, the zinc triad of elements is not considered as being main group: Zinc dithiocarbamate complexes are covered in chapter 2 of this volume on transition metal dithiocarbamates by Hogarth.

The structural parameters of the dithiocarbamate ligands themselves are not modified significantly on coordination to main group elements. Distances (Å) and angles (°) are in the range: C–N(R₂) = 1.24–1.52 (1.33 mean);

C—S = 1.52–1.82 (1.72 mean); SCS = 110.1–128.9 (118.6 mean). The two C—S distances are often slightly different, indicating some charge localization: as one would expect, the shorter C—S are generally associated with the S atom that is least strongly associated with the metal center. The SCS bond angle generally increases in line with the size of the metal to which the dithiocarbamate is coordinated.

Extensive use has also been made of infrared (IR) spectroscopy for the characterization of dithiocarbamate complexes. Particular diagnostic use has been made of the C—N(R₂) and C=S stretching modes, which fall typically in the range 1500 ± 50 and $980 \pm 50 \text{ cm}^{-1}$, respectively. The occurrence of more than one C=S stretching band has been used to imply a monodentate or highly anisobidentate bonding mode for the dithiocarbamate ligand; however, this is not unambiguous and should not be relied upon.

II. *s*-BLOCK METALS

The dithiocarbamates of the *s*-block elements, prepared by reaction of the appropriate amine and CS₂ in the presence of the metal cation, are water soluble, ionic compounds. The structures of a number of hydrated compounds have been determined by X-ray crystallography (3–26). Although there are some exceptions (see below), data show that, except for the heavier metal ions, there is generally little or no direct interaction between metal ion and the essentially planar dithiocarbamate anion in the solid state. Structural data show that the C—S bond distances of the free dithiocarbamate moieties lie in the range 1.65–1.81 Å; one C—S bond is often significantly shorter than the other, indicating some localization of the negative charge. The C—N distances and SCS angles lie in the range 1.32–1.43 Å and 117.0–128.9°, respectively. The SCS bond angle generally decreases with increasing steric bulk of the N substituents, as a result of intermolecular S···H—C interactions.

Under anhydrous conditions, dithiocarbamates can coordinate to lighter *s*-block metal ions. Insertion of CS₂ into the Be—N bonds of bis(diisopropylamino)beryllium yields the corresponding bis(diisopropylidithiocarbamate)beryllium compound (27). The four S atoms of the two dithiocarbamate ligands coordinate to Be, giving a distorted tetrahedral geometry at the metal ion. The ⁹Be nuclear magnetic resonance (NMR) spectrum of [Be(S₂CN*i*-Pr₂)₂] in cyclohexane displays a single resonance at δ 1.55, typical of four-coordinate Be, indicating that the solid-state structure is retained in solution. Similarly, lithiation of diphenylamine followed by reaction with CS₂ in tetrahydrofuran (THF) gives Ph₂NCS₂Li·2THF, in which the diphenyldithiocarbamate anion chelates the Li⁺ ion (Fig. 1) (28a).

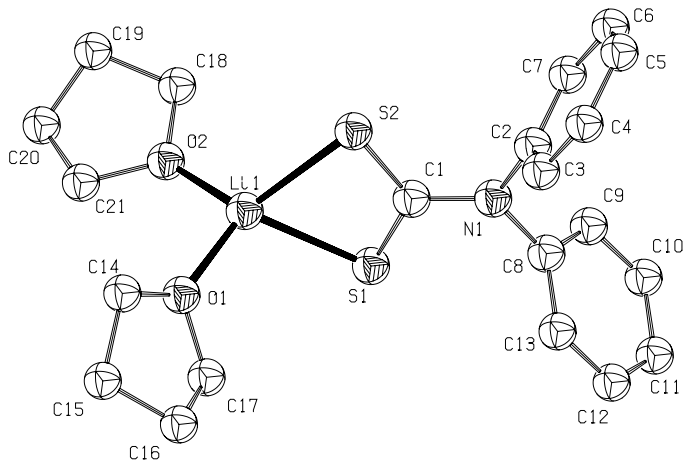


Figure 1. The ORTEP plot of $[\text{Li}(\text{S}_2\text{CNPh}_2)(\text{THF})_2]$. *Note:* ORTEP and PLUTON plots were drawn using the PLATON software, with arbitrary displacement parameters. In all cases hydrogen atoms have been omitted for clarity. (See Refs. 28b and 28c.)

III. GROUP 13 (III A)

A. Boron and Aluminum

Main group dithiocarbamate complexes are generally prepared by reaction of the appropriate metal halide with the parent (hydrated) group 1 (I A) metal or ammonium dithiocarbamate salt. Few dithiocarbamate complexes of boron and aluminum have therefore been reported: aluminum and boron halides are susceptible to hydrolysis, and hydroxide substitution is generally unfavorable.

Aminoboranes react readily with CS_2 to form the dithiocarbamate complexes $[\text{BR}(\text{S}_2\text{CNR}'_2)_2]$ or $[\text{BR}(\text{NR}_2)(\text{S}_2\text{CNR}'_2)]$, where R is an organic substituent (29), while the corresponding reactions with diboranes give complexes of the types $[\text{B}_2\text{R}_2(\text{S}_2\text{CNR}'_2)_2]$ and $[\text{B}_2(\text{S}_2\text{CNR}_2)_4]$ (30). No detailed structural studies appear to have been carried out on these complexes, but ^{11}B NMR spectra of the diboron complexes each display two signals, indicating that they exist as a mixture of two coordination isomers in solution (30). Reaction of boron trichloride with sodium dimethyldithiocarbamate gives either $[\text{BCl}_2(\text{S}_2\text{CNMe}_2)]$ or $[\text{B}(\text{S}_2\text{CNMe}_2)_3]_2$, depending on the reaction conditions (31). The product of the reaction of BRCl_2 with sodium dimethyldithiocarbamate depends on the nature of the R group: if R = butyl or phenyl, the dithiocarbamate complexes $[\text{BRCl}(\text{S}_2\text{CNR}_2)]$ result, but when R = methyl, CS_2 elimination occurs, yielding

the corresponding aminoborane (31). Elimination of CS_2 also occurs on addition of sodium dimethyldithiocarbamate to the dialkyl compounds, BR_2Cl (31).

In the cluster compound $[\mu\text{-}2,7\text{-}(\text{S}_2\text{CNEt}_2)\text{-}7\text{-}(\text{PMe}_2\text{Ph})\text{-}nido\text{-}7\text{-PtB}_{10}\text{H}_{11}]$, the dithiocarbamate ligand bridges the Pt–B bond, forming an exopolyhedral five-membered PtSCSB ring (32). The B–S bond length (1.90 Å) is comparable to other B–S bonds in boron cluster compounds and indicates a bond order between one and two.

Only five aluminum dithiocarbamate complexes have so far been reported, namely, $[\text{Al}(\text{S}_2\text{CNR}_2)_3]$ [R = methyl (Me), ethyl (Et), isopropyl (*i*-Pr), or benzyl (Bz)] (33–35) and $[\text{AlCl}(\text{S}_2\text{CNEt}_2)_2]$ (33). The homoleptic tris(dithiocarbamate) complexes are mononuclear, with the hexacoordinated aluminum atom displaying a distorted octahedral geometry, in both the solid state and in solution. The dithiocarbamate ligands are bound in an essentially isobidentate fashion. The unusually long Al–S bond lengths (2.38–2.40 Å), similar to the analogous Ga–S distances, have been attributed to the relative “hardness” of Al compared to S. The complex $[\text{AlCl}(\text{S}_2\text{CNEt}_2)_2]$ has not been characterized crystallographically, but solution molecular mass measurements and ^{27}Al NMR data indicate the Al atom is hexacoordinate, suggesting a dimeric structure in which the Al atoms are presumed to be chloride bridged (33).

Dithiocarbamates have been shown to inhibit the corrosion of Al in aqueous sodium chloride solution (36), probably via the formation of a dithiocarbamate species at the surface of the metal, and have also been used as complexing agents for the extraction and quantitative determination of Al (37).

B. Gallium, Indium, and Thallium

1. Homoleptic and Mixed Bidentate Ligand Complexes

A large number of monomeric tris(dithiocarbamate) complexes (Table I) is known for the heavier group 13 (III A) elements, Ga(III) (34, 38–44), In(III) (35, 38, 40–43, 45–49), and Tl(III) (50–54), in which the MS_6 core possesses approximate D_3 symmetry rather than O_h symmetry because of the small bite angle of the dithiocarbamate ligands (55). The dithiocarbamate ligands are bound in a quasiisobidentate fashion, with only small, but in some cases chemically significant, differences in the M–S bond lengths. These differences tend to be greater in the Ga complexes than in either the In or Tl complexes.

The ambient temperature solution NMR spectra of the tris(dithiocarbamate) complexes, including those of Al (see above), show the complexes to be fluxional on the NMR chemical shift time scale. The stereodynamics can be quite complex with several different processes possible, namely, (1) a metal-centered rearrangement of the ligand polyhedron, (2) reversible ligand dissociation, (3) restricted rotation about the single N–C bonds of (bulky) N substituents,

TABLE I
 Group 13 (III A) Homoleptic Dithiocarbamate Complexes

Complex	M-S (Å)	References
[B(S ₂ CNMe ₂) ₃]		31
[B ₂ (S ₂ CNMe ₂) ₄]		30
[Al(S ₂ CNMe ₂) ₃]		33
[Al(S ₂ CNEt ₂) ₃]		34
[Al(S ₂ CN <i>i</i> -Pr ₂) ₃]		35
[Al(S ₂ CNBz ₂) ₃]		34
[Ga(S ₂ CNH ₂) ₃]		38
[Ga(S ₂ CNMe ₂) ₃]		34, 38, 39, 42
[Ga(S ₂ CNEt ₂) ₃]	2.40–2.46	34, 38, 40
[Ga(S ₂ CN <i>n</i> -Pr ₂) ₃]		38
[Ga(S ₂ CN <i>i</i> -Pr ₂) ₃]		42
[Ga(S ₂ CN <i>n</i> -Bu ₂) ₃]		38
[Ga{S ₂ CN(Et)Ph} ₃]		38
[Ga{S ₂ CN(Me)Ph} ₃]		41
[Ga(S ₂ CNBz ₂) ₃]		34, 41
[Ga{S ₂ CN(CH ₂) ₄ } ₃]	2.41–2.47	42
[Ga{S ₂ CN(CH ₂) ₅ } ₃]		38
[Ga{S ₂ CN(CH ₂) ₄ NMe} ₃]		43
[Ga{S ₂ CN(CH ₂ CH ₂) ₂ O} ₃]	2.42–2.45	43
[Ga{S ₂ CN(Me)Hex} ₃]		44
[In(S ₂ CNH ₂) ₃]		38
[In(S ₂ CNHMe) ₃]		38
[In(S ₂ CNMe ₂) ₃]	2.58–2.61	47
[In(S ₂ CNEt ₂) ₃]	2.58–2.61	38, 40
[In{S ₂ CN(Me) <i>n</i> -Bu} ₃]		48
[In{S ₂ CN(Me)Hex} ₃]		48
[In(S ₂ CN <i>i</i> -Pr ₂) ₃]	2.58–2.62	35, 46
[In{S ₂ CN(CH ₂) ₄ } ₃]	2.58–2.61	46
[In(S ₂ CNMePh ₂) ₃]		41
[In(S ₂ CNBz ₂) ₃]		41
[In{S ₂ CN(CH ₂) ₅ } ₃]	2.58–2.59	45
[In{S ₂ CN(CH ₂ CH ₂) ₂ O} ₃]	2.58–2.62	43
[In{S ₂ CN(CH ₂ CH ₂) ₂ NMe} ₃]	2.57–2.58	43, 49
[Ti(S ₂ CNMe ₂) ₃]	2.61–2.68	51, 52, 54 ^a
[Ti(S ₂ CNEt ₂) ₃]	2.67	51, 54 ^a
[Ti(S ₂ CN <i>n</i> -Pr ₂) ₃]		54 ^a
[Ti(S ₂ CNBu ₂) ₃]		54 ^a
[Ti(S ₂ CNBz ₂) ₃]		54 ^a
[Ti{S ₂ CN(CH ₂) ₅ } ₃]		54 ^a
[Ti(S ₂ CNMe ₂) ₂]	2.99–3.44	56, 57, 60, 64, 65
[Ti(S ₂ CNEt ₂) ₂]	3.07–3.62	53, 56, 57, 62, 64, 65
[Ti(S ₂ CN <i>n</i> -Pr ₂) ₂]	2.88–4.37	56, 57, 58, 64, 65
[Ti(S ₂ CN <i>i</i> -Pr ₂) ₂]	2.98–3.04	57, 59
[Ti(S ₂ CN <i>n</i> -Bu ₂) ₂]	2.97–3.16	56, 57, 63, 64, 65
[Ti(S ₂ CN <i>i</i> -Bu ₂) ₂]	2.97–3.47	61
[Ti{S ₂ CN(<i>i</i> -C ₅ H ₁₁) ₂ }]		57
[Ti{S ₂ CN(Me)Ph}]		65

TABLE I (Continued)

Complex	M-S (Å)	References
[Tl(S ₂ CNBz ₂)]		65
[Tl{S ₂ CN(CH ₂) ₅ }]		64
[Tl{S ₂ CN(CH ₂) ₄ O}]		65

^a Reference 54 also reports mixed dithiocarbamate complexes of the type [Tl(S₂CNR₂)₂(S₂CNR'₂)].

or (4) restricted rotation about the (S₂)C–N partial double bond (34, 35, 41, 46, 52). It is not always easy to distinguish between these processes and it is possible that two or more can occur simultaneously. The energy barriers observed (<60 kJ mol⁻¹) are rather low for rotation about the (S₂)C–N partial double bond and Fay and co-worker (35) demonstrated unambiguously that restricted rotation occurs about the N–C(*i*-Pr) single bonds rather than about the (S₂)C–N bond in the [M(S₂CNi-Pr₂)₃] complexes (M = Al or In) at and below ambient temperatures: Contributions to the measured rate constants from (S₂)C–N bond rotation process are negligible. Synthetic studies of some Tl^{III} complexes (54) indicate that the dithiocarbamate ligands are labile: mixed-ligand complexes, [Tl(S₂CNR₂)₂(S₂CNR'₂)], are rapidly formed on mixing simple, “symmetric” dithiocarbamate complexes. Rates of formation of the mixed-ligand complexes are greater in polar solvents, indicating the formation of a [Tl(S₂CNR₂)₂]⁺ intermediate, consistent with a ligand dissociation pathway and lending support for a dynamic ligand dissociation–recombination process, at least in the case of Tl(III).

Unlike the lighter members of the group, which only form M(III) dithiocarbamate complexes, a number of homoleptic thallium(I) dithiocarbamates has been reported (56–65). In the solid state, [Tl₂(S₂CNR₂)₂] dimers are linked by intermolecular Tl–S coordination to form polymeric structures (56–63). Although the basic dimeric structure is similar in each case (see below), the way in which they are linked differs, depending on the nature of the N-substituents: The balance between the coordination requirements of Tl and the packing forces determines the precise crystal structure. The dimeric units have a distorted octahedral structure, shown in Fig. 2, with the two Tl atoms axial and the four S atoms, which form an almost planar parallelogram, equatorial. Tl···Tl distances vary between 3.47 and 4.00 Å. When the interdimer Tl···S coordination is considered, the Tl atoms may be five-, six-, or even seven-coordinate, leading to the formation of either extended chains or layers.

The basic dimeric structure of the Tl(I) dithiocarbamates (see Fig. 2) appears to be retained in solution (56, 57); consequently they have lower motilities than their monomeric Tl(III) analogues, enabling mixtures of to be readily separated (65). Dithiocarbamate ligands have thus been used for the separation and extraction of (toxic) Tl(I) from Tl(III), as well as other metal ions (64–70).

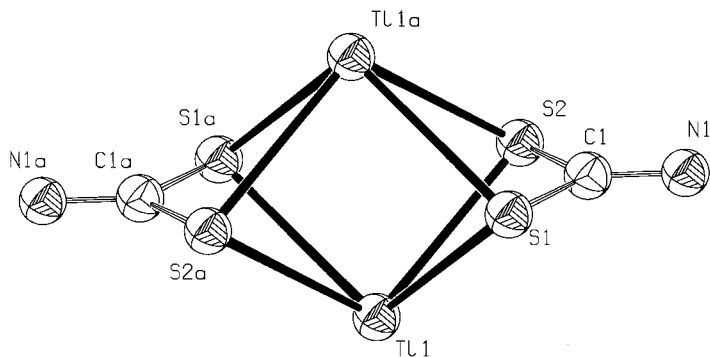
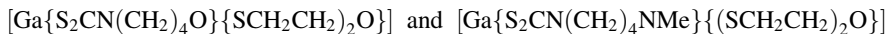
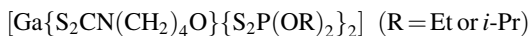


Figure 2. The ORTEP plot of the dimeric unit in the Tl(I) complexes $[\text{Tl}_2(\text{S}_2\text{CNR}_2)_2]$. The N substituents are omitted for clarity.

The complexes



prepared by adding stoichiometric quantities of the appropriate ligands to GaCl_3 , appear to be the only complexes in which two different types of bidentate ligand (including a dithiocarbamate) are coordinated to the group 13 (III A) metal center (43).

2. Nonhomoleptic Complexes

Complexes of the type $[\text{MCl}_2(\text{S}_2\text{CNR}_2)]$, $[\text{MR}_2(\text{S}_2\text{CNR}'_2)]$, $[\text{MCl}(\text{S}_2\text{CNR}_2)_2]$, and/or $[\text{MR}(\text{S}_2\text{CNR}'_2)_2]$ ($\text{R} = \text{alkyl, aryl, or Cp}$) are known for all group 13 (III A) elements (Table II). The most numerous are the diorganometal complexes (51, 71–77), which have found use as single source precursors for the chemical vapor deposition of M_xS_y thin films (75–77). The complexes are generally monomeric in both the solid state and in solution. X-ray crystallographic studies of $[\text{InR}_2(\text{S}_2\text{CNET}_2)]$ [$\text{R} = \text{Me}$ (75), Et (75), or $t\text{-Bu}$ (77)], $[\text{In}t\text{-Bu}_2(\text{S}_2\text{CNMe}_2)]$ (77), and $[\text{TlPh}_2(\text{S}_2\text{CNET}_2)]$ [Fig. 3(a)] (72) show that the metal ions possess a highly distorted tetrahedral geometry. With the exception of $[\text{InMe}_2(\text{S}_2\text{CNET}_2)]$ and $[\text{In}t\text{-Bu}_2(\text{S}_2\text{CNMe}_2)]$, which show a small but chemically significant difference in the two M–S distances, the dithiocarbamate ligands are bound in an essentially isobidentate fashion. In contrast, the molecular units in $[\text{TlMe}_2(\text{S}_2\text{CN}n\text{-Pr}_2)]$ (74) are linked by two intermolecular $\text{Tl}\cdots\text{S}$ interactions, giving a well-ordered spiral arrangement, while in

TABLE II
 Group 13 (III A) Alkyl- and Chlorodithiocarbamate Complexes

Complexes	M–S (Å)	References
[BMe(S ₂ CNMe ₂) ₂]		31
[BPh(S ₂ CNMe ₂) ₂]		31
[B <i>n</i> -BuCl(S ₂ CNMe ₂) ₂]		31
[BPhCl(S ₂ CNMe ₂) ₂]		31
[BCl ₂ (S ₂ CNMe ₂) ₂]		31
[AlCl(S ₂ CNEt ₂) ₂]		33
[GaMe ₂ (S ₂ CNEt ₂) ₂]		75
[GaEt ₂ (S ₂ CNEt ₂) ₂]		75
[Ga <i>t</i> -Bu ₂ (S ₂ CNMe ₂) ₂]		77
[Ga <i>t</i> -Bu ₂ (S ₂ CNEt ₂) ₂]	2.38, 2.43	77
[Ga <i>t</i> -Bu ₂ (S ₂ CN <i>n</i> -Pr ₂) ₂]		77
[Ga(C ₅ H ₁₁) ₂ (S ₂ CNEt ₂) ₂]		75
[GaMe ₂ {S ₂ CNMe(CH ₂) ₃ NMe ₂ } ₂]		76
[GaEt ₂ {S ₂ CNMe(CH ₂) ₃ NMe ₂ } ₂]		76
[Ga(CH ₂ CHMe ₂) ₂ {S ₂ CNMe(CH ₂) ₃ NMe ₂ } ₂]		76
[Ga(C ₅ H ₁₁) ₂ {S ₂ CNMe(CH ₂) ₃ NMe ₂ } ₂]		76
[GaCl ₂ {S ₂ CN(CH ₂ CH ₂) ₂ O} ₂]		43
[GaCl ₂ (4-MePy) ₂ (S ₂ CNMe ₂) ₂]	2.45, 2.49	80
[GaCl ₂ (4-MePy) ₂ (S ₂ CNEt ₂) ₂]	2.48, 2.48	81
[Ga <i>t</i> -Bu(S ₂ CNMe ₂) ₂]		77
[Ga <i>t</i> -Bu(S ₂ CNEt ₂) ₂]		77
[Ga <i>t</i> -Bu(S ₂ CN <i>n</i> -Pr ₂) ₂]	2.31–2.60	77, 78
[Ga(O <i>i</i> -Pr)(S ₂ CN <i>n</i> -Pr ₂) ₂]	2.31–2.57	78
[GaCl(S ₂ CNMe ₂) ₂]	2.21–2.43	42
[GaCl(S ₂ CN <i>i</i> -Pr ₂) ₂]		42
[GaCl{S ₂ CN(CH ₂) ₅ } ₂]		42
[GaCl{S ₂ CN(CH ₂ CH ₂) ₂ O} ₂]		43
[InMe ₂ (S ₂ CNMe ₂) ₂]		71
[InMe ₂ (S ₂ CNEt ₂) ₂]		75
[InEt ₂ (S ₂ CNEt ₂) ₂]	2.56, 2.68	75
[In(C ₅ H ₁₁) ₂ (S ₂ CNEt ₂) ₂]		75
[InMe ₂ {S ₂ CNMe(CH ₂) ₃ NMe ₂ } ₂]		75
[InEt ₂ {S ₂ CNMe(CH ₂) ₃ NMe ₂ } ₂]	2.59, 2.79	75
[In(CH ₂ CHMe ₂) ₂ {S ₂ CNMe(CH ₂) ₃ NMe ₂ } ₂]		75
[In(C ₅ H ₁₁) ₂ {S ₂ CNMe(CH ₂) ₃ NMe ₂ } ₂]		75
[InCl ₂ {S ₂ CN(CH ₂ CH ₂) ₂ O} ₂]		43
[InMe(S ₂ CNMe ₂) ₂]		71
[InEt(S ₂ CNMe ₂) ₂]		71
[InCl(S ₂ CN <i>i</i> -Pr ₂) ₂]	2.38–2.56	42
[GaCl{S ₂ CN(CH ₂ CH ₂) ₂ O} ₂]		43
[TiMe ₂ (S ₂ CNHEt ₂) ₂]		74
[TiMe ₂ (S ₂ CNH <i>n</i> -Pr) ₂]		74
[TiMe ₂ (S ₂ CN <i>n</i> -Pr ₂) ₂]	2.70, 2.80	74
[TiMe ₂ (S ₂ CN <i>n</i> -Bu ₂) ₂]		74
[TiMe ₂ (S ₂ CN <i>sec</i> -Bu ₂) ₂]		74
[TiMe ₂ {S ₂ CNMe(CH ₂) ₂ OH} ₂]		74

TABLE II (Continued)

Complexes	M-S (Å)	References
[TlMe ₂ (S ₂ CNMe ₂)]		51
[TlMe ₂ (S ₂ CNEt ₂)]		51
[TlMe ₂ (S ₂ CNPh ₂)]		51
[TlPh ₂ (S ₂ CNEt ₂)]	2.72, 7.72	51, 72
[TlCp ₂ {S ₂ CN(Me)Cy}]		73
[TlCp ₂ {S ₂ CN(Et)Cy}]		73
[TlCp ₂ {S ₂ CN(Me)Cy}]		73
[TlCp ₂ {S ₂ CN(<i>i</i> -Pr)Cy}]		73
[Tl(C ₉ H ₇){S ₂ CN(Me)Cy}]		73
[Tl(C ₉ H ₇){S ₂ CN(Et)Cy}]		71
[Tl(C ₉ H ₇){S ₂ CN(<i>i</i> -Pr)Cy}]		73
[Tl(C ₁₃ H ₉) ₂ {S ₂ CN(Me)Cy}]		71
[Tl(C ₁₃ H ₉) ₂ {S ₂ CN(Et)Cy}]		71
[Tl(C ₁₃ H ₉) ₂ {S ₂ CN(<i>i</i> -Pr)Cy}]		73
[Tl(<i>p</i> -tolyl)(S ₂ CNEt ₂) ₂]	2.55–2.80	79

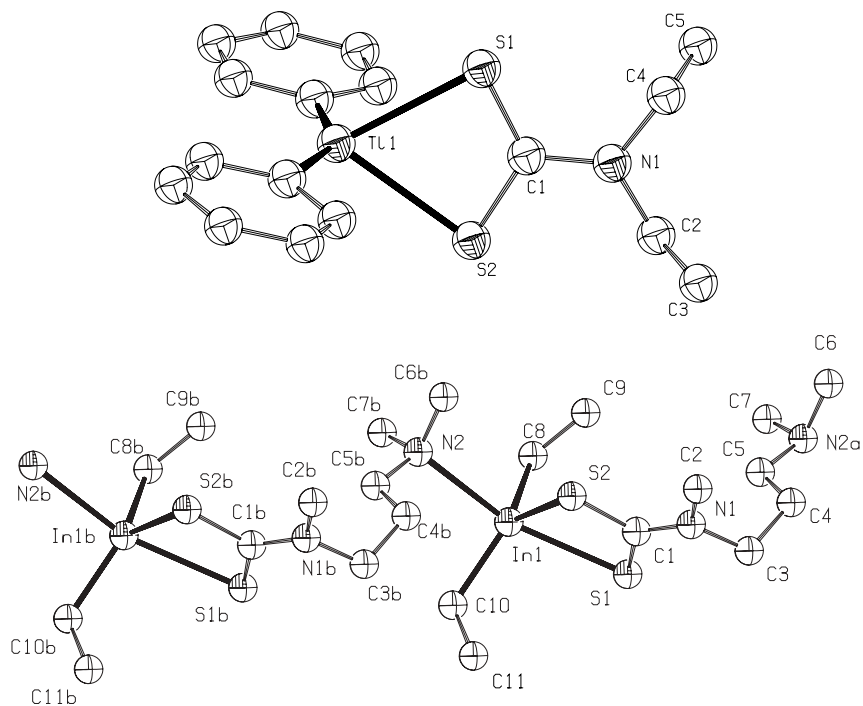


Figure 3. The ORTEP plots of (a) [TlPh₂(S₂CNEt₂)] and (b) [InEt₂{S₂CN(Me)(CH₂)₃NMe₂}], showing a section of the polymeric chain.

[InEt₂{S₂CNMe(CH₂)₃NMe₂}] (76) the molecular units are linked by intermolecular In–N bonds (2.66 Å), forming a chain polymer [Fig. 3(b)].

Although less common than the dialkylmetal dithiocarbamate complexes, several monoalkyl bis(dithiocarbamate) complexes have been reported (31, 71, 77–79). The complexes [Gat-Bu(S₂CNR₂)₂] (R = Me, Et, or *n*-Pr), were isolated as minor products during the synthesis of the dialkyl complexes [Gat-Bu₂(S₂CNR₂)] from the reaction of [Gat-Bu₂(μ-Cl)]₂ with sodium dithiocarbamate salts (77). Interestingly, these monoalkyl complexes are only formed during the initial synthesis: The dialkylmetal complexes cannot be converted to the corresponding monoalkyl complexes.

The X-ray molecular structures of [Gat-Bu(S₂CN*n*-Pr₂)₂] (78), [Ga(O*i*-Pr)(S₂CNEt₂)₂] (78) and [Tl(*p*-tolyl)(S₂CNEt₂)₂] (79) show that the metal ions possess a distorted trigonal-bipyramidal geometry, with the alkyl or aryl group occupying an axial position. The dithiocarbamate ligands bind in an anisobidentate fashion. The precise geometry at the metal atom is determined primarily by the steric bulk of the alkyl ligand, as measured by the Tolman cone angles: cone angles <94° favor a square-based pyramidal structure, while cone angles >94° shift the geometry toward trigonal bipyramidal (78). These structures lie on the unusual two-step “Texas” pseudo-rotation pathway between true square-based pyramidal and trigonal-bipyramidal structures rather than the more usual one-step Berry pseudo-rotation pathway.

The monochloro bis(dithiocarbamate) complexes of gallium and indium, [MCl(S₂CNR₂)₂] (42, 43), closely resemble the corresponding monoalkyl complexes; however, the geometry at the metal atom tends toward square pyramidal rather than trigonal bipyramidal, because of the smaller cone angle of Cl. The dichloro complexes, [MCl₂(S₂CNR₂)] (M = Ga or In) (43) have not been well characterized. Solution molecular mass measurements of the corresponding boron complexes, [BCl₂(S₂CNR₂)], indicate that they are monomeric (31): By analogy, the gallium and indium complexes have therefore also been assumed to be monomeric in solution. Reaction of Ga₂Cl₂ with tetramethyl- or tetraethylthiuram disulfide in 4-methylpyridine solvent yields [GaCl₂(4-Mepy)₂(S₂CNR₂)] [R = Me (80) or Et (81) and py = pyridine (ligand)]. X-ray crystallography shows that the Ga atoms are in a distorted octahedral coordination environment, with chloride ligands *cis* each other, *trans* the dithiocarbamate S atoms.

IV. GROUP 14 (IV A)

The carbon compounds of dithiocarbamates, dithiocarbamic acid esters, are generally classified as organic compounds and, as such, fall outside the scope of this chapter.

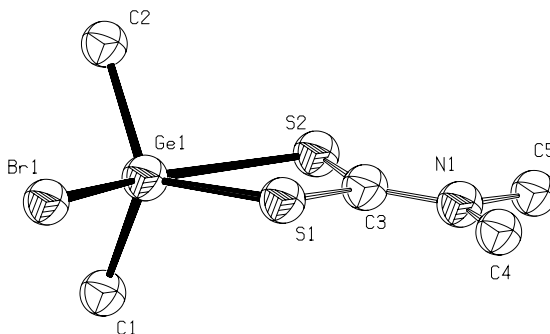


Figure 4. The ORTEP plot of $[\text{GeMe}_2\text{Br}(\text{S}_2\text{CNMe}_2)]$.

A. Silicon and Germanium

Although silicon dithiocarbamate complexes remain rare, complexes of the type $[\text{SiR}_2(\text{S}_2\text{CNR}_2)_2]$ ($\text{R} = \text{Me}$ or Ph) have been reported recently (82). Spectroscopic data for the complexes (IR and NMR) have been interpreted in terms of a tetracoordinate silicon atom, with the two dithiocarbamate ligands monodentate.

The homoleptic germanium dithiocarbamate complex $[\text{Ge}\{\text{S}_2\text{CN}(i\text{-Pr})\text{Cy}\}_4]$ ($\text{cy} = \text{cyclohexyl}$), was reportedly prepared by the reaction of GeCl_4 with an excess of the sodium dithiocarbamate salt (83). However, attempts to prepare $[\text{Ge}(\text{S}_2\text{CNMe}_2)_4]$ similarly were unsuccessful (84). The diorganogallium bis(dithiocarbamate) complexes, $[\text{GeR}_2(\text{S}_2\text{CNR}_2)_2]$, have been prepared by reaction of GeR_2Cl_2 with the appropriate sodium dithiocarbamate salt (84, 85); an X-ray crystallographic study of $[\text{GeMe}_2(\text{S}_2\text{CNMe}_2)_2]$ reveals that the Ge atom lies at the center of a distorted octahedron, with the four S atoms in the equatorial plane (84). In the $[\text{GeMe}_2\text{X}(\text{S}_2\text{CNMe}_2)]$ complexes ($\text{X} = \text{Cl}$, Br , or I) the Ge atom is in a distorted trigonal-bipyramidal coordination environment with the dithiocarbamate ligand bound in an anisobidentate fashion (86–88). The structure of $[\text{GeMe}_2\text{Br}(\text{S}_2\text{CNMe}_2)]$ is shown in Fig. 4. Complexes of general formula $[\text{GeR}_3(\text{S}_2\text{CNR}_2)]$ ($\text{R} = \text{alkyl}$ or phenyl) have also been prepared (84, 89, 90); solution NMR data indicate they are essentially isostructural with the $[\text{GeMe}_2\text{X}(\text{S}_2\text{CNMe}_2)]$ complexes.

B. Tin and Lead

1. Homoleptic Complexes

Homoleptic dithiocarbamate complexes are known for tin(II), tin(IV), and lead(II). The tin(II) complexes, $[\text{Sn}(\text{S}_2\text{CNR}_2)_2]$, are best prepared by reaction of

SnCl_2 with the sodium salt of the appropriate dithiocarbamic acid (91–93). The complexes are monomeric in the solid state (92), with the dithiocarbamate bound in an anisobidentate fashion, but molecular weight measurements suggest they may be polymeric in solution (93). In the solid state molecular structure, the geometry at Sn is best considered as highly distorted trigonal bipyramid, with the stereochemically active lone pair of electrons equatorial and the two long Sn–S bonds displaced away from the lone pair in pseudo-axial positions.

The tetrakis(dithiocarbamate)tin(IV) complexes are of interest because of the different bonding modes of the dithiocarbamate ligands, which may be monodentate, anisobidentate, or isobidentate (94, 95). The geometry at Sn depends on the binding modes adopted. In $[\text{Sn}(\text{S}_2\text{CNMe}_2)_4]$ the Sn atom is essentially six coordinate, with two of the dithiocarbamate ligands anisobidentate and two monodentate: The nonbonding Sn \cdots S distances are 3.44 and 3.64 Å (94). In contrast, in $[\text{Sn}\{\text{S}_2\text{CN}(\text{CH}_2)_4\}_4]$ two of the ligands are essentially isobidentate and two highly anisobidentate (Sn–S = 2.42 and 3.24 Å); if the long Sn–S contacts are included, the tin is best considered as displaying a distorted dodecahedral arrangement (Fig. 5) (95). The very low frequency shift of the ^{119}Sn NMR signal in tetrakis(1-pyrrolidinedithiocarbamate)tin(IV) ($\delta = -729$, relative to SnMe_4) indicates that the Sn atom is at least six and possibly seven coordinate in solution. Ambient temperature solution proton NMR (^1H) and ^{13}C NMR spectra indicate that the four ligands are equivalent on the NMR chemical

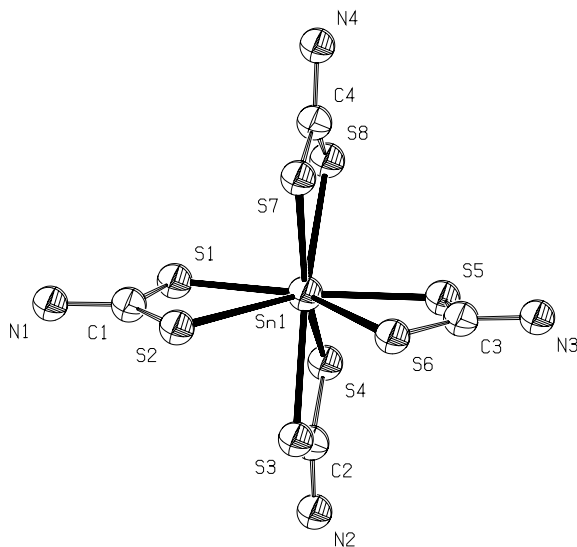


Figure 5. The ORTEP plot of $[\text{Sn}\{\text{S}_2\text{CN}(\text{CH}_2)_4\}_4]$, showing dodecahedral arrangement at tin. The N substituents omitted for clarity.

shift time scale, with an effective plane of symmetry bisecting the SCS angle. These observations are consistent with a fluxional process that involves reversible cleavage of the Sn—S bonds.

The bis(dithiocarbamate) complexes of lead(II), $[\text{Pb}(\text{S}_2\text{CNR}_2)_2]$, have been studied quite extensively, revealing a number of interesting structural variations (96–101). The basic molecular geometry at lead is that of a distorted square pyramid, with the four S atoms of the (usually) anisobidentate ligands forming the base and the stereochemically active lone pair of electrons apical, consistent with the results of quantum chemical calculations (102). However, secondary $\text{Pb} \cdots \text{S}$ intermolecular interactions in the solid state increase the coordination number at lead to between 5 and 8, depending on the number of interactions. The crystal structure of bis(dimethyldithiocarbamate)lead comprises $[\text{Pb}(\text{S}_2\text{CNMe}_2)_2]$ units stacked along the crystallographic c axis (96). Within the stack, each Pb atom has a long contact with two S atoms ($\text{Pb} \cdots \text{S} = 3.36 \text{ \AA}$) of the unit directly above, giving a pseudo-six-coordinate metal center. The crystal structure of $[\text{Pb}\{\text{S}_2\text{CN}(\text{Et})i\text{-Pr}\}_2]$ comprises polymeric chains of bis(dithiocarbamate)lead units, also linked by bridging S atoms; however, the bridging S atoms are from different monomer units (one above and one below) (98). A rather different situation is found in bis(pyrrrolidinedithiocarbamate)lead (99), where all four S atoms form long-range interactions with a second $[\text{Pb}(\text{S}_2\text{CN}(\text{CH}_2)_4)_2]$ unit. The coordination environment at lead is that of a distorted square antiprism, with staggered faces. The lone-pair points through the square face formed by the four S atoms of the next monomeric unit, toward the lead atom. The $\text{Pb} \cdots \text{Pb}$ distance is 3.89 \AA , suggesting some weak metal–metal bonding (Fig. 6). The bulky N substituents in bis(dipropyldithiocarbamate)lead give rise to a notably different, centrosymmetric tetrameric structure with pentacoordinate Pb atoms (97). The tetramer possesses a $\text{Pb}_2(\text{S}_2\text{CN}i\text{-Pr}_2)_4$ core, in which the two Pb atoms are bridged by S atoms from different

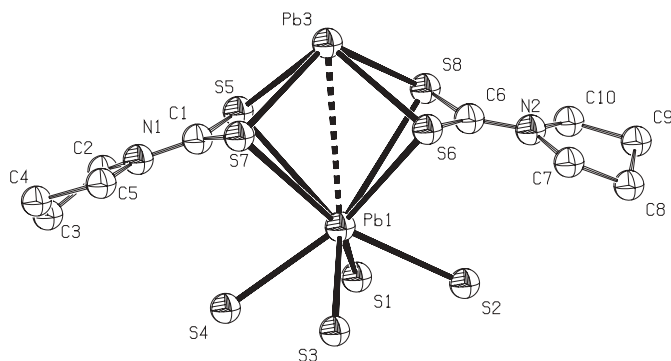


Figure 6. The ORTEP plot of $[\text{Pb}\{\text{S}_2\text{CN}(\text{CH}_2)_4\}_2]$, showing a section of the polymeric chain.

dithiocarbamate ligands. Two further $[\text{Pb}(\text{S}_2\text{CN}n\text{-Pr}_2)_2]$ monomer units bind to the Pb_2S_4 core via single Pb—S bridges, completing the tetrameric structure.

The NMR and molecular mass measurements indicate that, while they retain the same basic molecular structures, the $[\text{Pb}(\text{S}_2\text{CNR}_2)_2]$ complexes tend to polymerize in solution (93, 103). The NMR and electrochemical studies also show that the dithiocarbamate ligands are highly labile in solution (103, 104).

The homoleptic dithiocarbamate complexes of both Sn and Pb have been investigated recently as possible single source precursors for the deposition of metal sulfide materials (98, 105, 106) and dithiocarbamates have also been used for the extraction of lead from environmental samples (107).

2. Nonhomoleptic Complexes

Although nonhomoleptic complexes of Sn have been extensively studied because of their considerable structural diversity and potential applications, for example, in chemotherapy, those of lead are rare. The complex $[\text{Pb}(\text{phen})(\text{S}_2\text{CNEt}_2)_2]$ (phen = 1,10-phenanthroline) is one of only a few examples of a nonhomoleptic lead(II) dithiocarbamate complex (108). The geometry at Pb (Fig. 7) is best considered as distorted trigonal bipyramidal, with the bridging S atoms occupying axial positions.

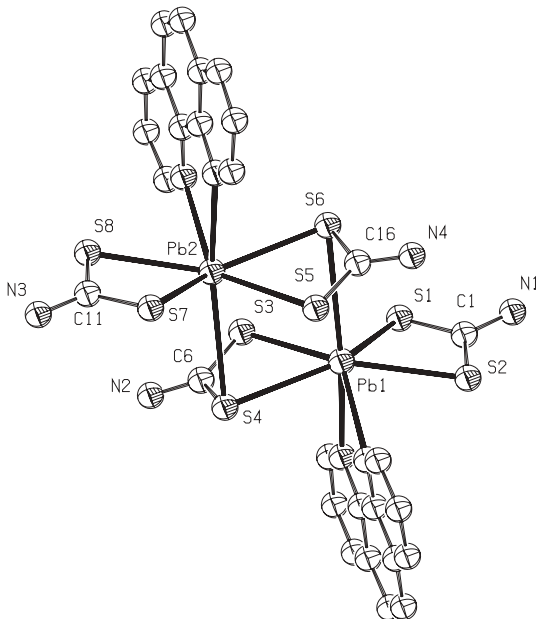


Figure 7. The ORTEP plot showing the dimeric structure of $[\text{Pb}(\text{phen})(\text{S}_2\text{CNEt}_2)_2]$. The N substituents of the dithiocarbamates and atom labels of the phen ligands have been omitted for clarity.

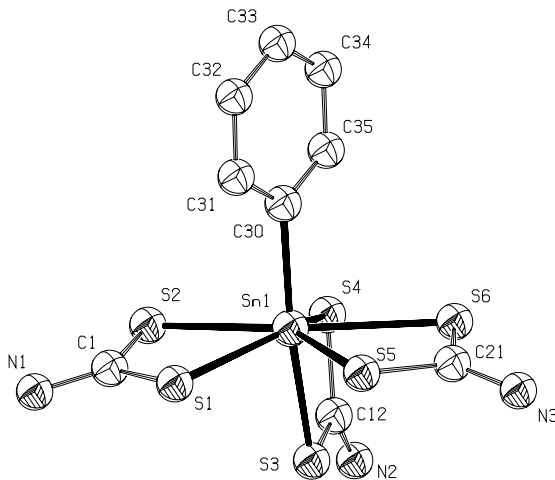


Figure 8. The ORTEP plot of $[\text{SnR}(\text{S}_2\text{CNR}_i\text{-Bu}_2)_3]$ showing the distorted pentagonal bipyramidal coordination of tin in the complexes $[\text{SnR}(\text{S}_2\text{CNR}_2)_3]$ and $[\text{SnX}(\text{S}_2\text{CNR}_2)_3]$. The N substituents are omitted for clarity.

The majority of tin(IV) dithiocarbamate complexes are of the general type $[\text{SnR}_{4-n-m}\text{X}_n(\text{S}_2\text{CNR}_2)_m]$ (where R = alkyl or aryl; X = halide; $n = 0, 1, 2, 3$; $m = 1, 2$, or 3). In the tris(dithiocarbamate) complexes $[\text{SnR}(\text{S}_2\text{CNR}_2)_3]$ and $[\text{SnX}(\text{S}_2\text{CNR}_2)_3]$ (109–121), the Sn atom is in a distorted pentagonal bipyramidal coordination environment, with the unidentate ligand axial (Fig. 8). The dithiocarbamate ligand that spans the axial (ax)–equatorial (eq) positions is highly anisobidentate [$\text{Sn}-\text{S}(\text{ax}) \approx 2.48 \text{ \AA}$; $\text{Sn}-\text{S}(\text{eq}) \approx 2.77 \text{ \AA}$]; usually the two equatorial dithiocarbamates are also anisobidentate, but to a much lesser degree. The solution ^{119}Sn NMR chemical shift of $[\text{SnPh}(\text{S}_2\text{CNEt}_2)_3]$ is strongly temperature dependent: $\delta = -813$ (ambient); $\delta = -888$ (-100°C) (115). Nuclear magnetic resonance data thus indicate a dynamic process, which involves the exchange of dithiocarbamate ligands, leading to a decrease in the effective coordination number of Sn at ambient temperature. Solid-state ^{13}C and ^{119}Sn NMR data (115, 117) are consistent with the X-ray structure (115); it is noteworthy that the ^{119}Sn SSNMR chemical shift (-894 ppm) is to slightly lower frequency of that in solution at -100°C , suggesting that the lower temperature limit of the fluxional process is only a little below -100°C .

A large number of bis(dithiocarbamate)tin(IV) complexes of general formula $[\text{SnR}_n\text{X}_{2-n}(\text{S}_2\text{CNR}_2)_2]$ (R = alkyl or aryl; X = halogen or pseudo-halogen; $n = 0, 1$, or 2) have been reported (89, 95, 111–115, 117, 119, 122–167). In the majority of cases, the geometry at tin is best described as a highly distorted octahedron or skew-trapezoidal bipyramid, with asymmetrically coordinated

dithiocarbamate ligands. Although the CSnC bond angle in the $[\text{SnR}_2(\text{S}_2\text{CNR}_2)_2]$ complexes is highly variable ($\sim 100\text{--}150^\circ$), there is no obvious trend with respect to the steric bulk of the organic Sn substituents; however, if one or both of the organic groups is substituted for a halogen, the bond angle (RSnX or XSnX) decreases to $\sim 89\text{--}96^\circ$, suggesting that the Lewis acidity of the metal center is an important factor.

Three crystalline modifications of $[\text{SnMe}_2(\text{S}_2\text{CNET}_2)_2]$ are known (141, 163), namely, triclinic, monoclinic, and orthorhombic; except for the small variability in the CSnC bond angles the molecular structures are chemically identical in the three forms, and differ little from the other dimethyltin(IV) bis(dithiocarbamate) complexes that have been structurally characterized (95, 125, 143, 152). The *tert*-butyl complexes $[\text{Snt-Bu}_2(\text{S}_2\text{CNMe}_2)_2]$ (150), $[(\text{Snt-Bu}_2)_2\{\mu\text{-S}_2\text{CN}(\text{H})(\text{CH}_2)_2\text{N}(\text{H})\text{CS}_2\}]$ (124), and $[\text{Snt-Bu}_2(\text{S}_2\text{CNET}_2)_2]$ (153) show some interesting structural differences. The molecular structure of $[\text{Snt-Bu}_2(\text{S}_2\text{CNET}_2)_2]$ is very similar to that of the dimethyltin(IV) bis(dithiocarbamate) complexes, but in $[\text{Snt-Bu}_2(\text{S}_2\text{CNMe}_2)_2]$ one of the dithiocarbamates is essentially monodentate (Sn-S (long) = 3.53 Å) and the geometry at Sn is best described as a distorted trigonal bipyramid, with the two *t*-Bu groups equatorial; in this respect, $[\text{Snt-Bu}_2(\text{S}_2\text{CNMe}_2)_2]$ is structurally more akin to the triorganotin(IV) dithiocarbamates. The Sn atoms in the centrosymmetric dimeric complex $[(\text{Snt-Bu}_2)_2\{\mu\text{-S}_2\text{CN}(\text{H})(\text{CH}_2)_2\text{N}(\text{H})\text{CS}_2\}]_2$ (Fig. 9) are also five coordinate: one end of the ligand is bidentate, while the other is monodentate. The chelating dithiocarbamate ligand spans *ax/eq* positions and is highly anisobidentate (Sn-S = 2.459 and 2.878 Å).

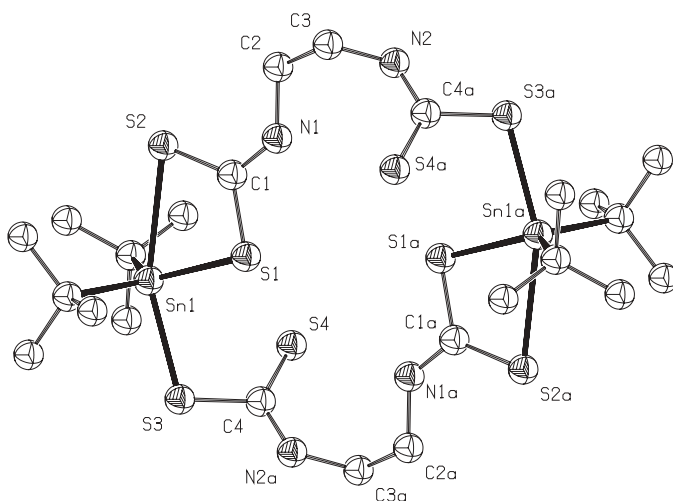


Figure 9. The ORTEP plot of $[(\text{Snt-Bu}_2)_2\{\mu\text{-S}_2\text{CN}(\text{H})(\text{CH}_2)_2\text{N}(\text{H})\text{CS}_2\}]_2$.

The complex $[\text{SnPh}_2(\text{S}_2\text{CNEt}_2)_2]$ has been shown to exist in at least two polymorphs, namely, monoclinic (122, 152) and tetragonal (117). In the monoclinic form, one dithiocarbamate is anisobidentate and the other almost isobidentate, while in the tetragonal form, both are asymmetrically coordinated; the degree of asymmetry in the tetragonal polymorph is about one-half that observed for the anisobidentate dithiocarbamate in the monoclinic form [$\Delta\text{Sn}-\text{S} = 0.10 \text{ \AA}$ (tetragonal) and 0.24 \AA (monoclinic)].

The effects of the dithiocarbamate N substituents on the structures of the phenyl and vinyl complexes $[\text{SnPh}_2(\text{S}_2\text{CNR}_2)_2]$ and $[\text{Sn}(\text{CHCH}_2)_2(\text{S}_2\text{CNR}_2)_2]$ have been investigated by Tiekink and Hall (159, 160) and appear to be small as far as the tin-dithiocarbamate bonding is concerned. In contrast, the effects of the ancillary organic ligands are quite marked: The greater the electronegativity of the ligands, the more symmetrical the bonding of the dithiocarbamate. The reduction in the asymmetry is presumably due to the increased Lewis acidity of the metal center. The effect of the organic groups on the CSnC bond angle is considerable: The average CSnC angle in the phenyl complexes is 102.4° , which contrasts with 136.2° in the vinyl complexes. The reasons for the difference in the bond angle are not immediately obvious, although it is clear from crystallographic data for other bis(dithiocarbamate)tin(IV) complexes that the CSnC angle generally decreases as the electronegativity of the substituents increases.

The $[\text{SnRCl}(\text{S}_2\text{CNR}'_2)_2]$ complexes are structurally similar to the dialkyl analogues (95, 117, 126, 128–131); the Sn atom is in a highly distorted octahedral coordination environment, with the two dithiocarbamate ligands bidentate. Although the dithiocarbamate ligands are anisobidentate, the asymmetry in the bonding is reduced considerably [$\Delta\text{Sn}-\text{S}(\text{ave}) \approx 0.06 \text{ \AA}$], compared to that observed in the dialkyl complexes, because the Lewis acidity of the metal center is increased by the presence of the more electronegative chloride ligand: The CSnX bond angle is also reduced.

Reaction of anhydrous tin(II) chloride with sodium diethyldithiocarbamate under aerobic conditions gives the tin(IV) bis(dithiocarbamate) complex, $[\text{SnCl}_2(\text{S}_2\text{CNEt}_2)_2]$ (157). The mechanism probably involves the initial formation of $[\text{Sn}(\text{S}_2\text{CNEt}_2)_2]$, followed by aerial oxidation to yield tetraethylthiuram disulfide, which then oxidatively adds to another molecule of SnCl_2 , giving the final product, accounting for the reaction yield (50%, relative to SnCl_2). In a separate experiment, it was shown that tetramethylthiuram disulfide reacts directly with SnCl_2 , yielding $[\text{SnCl}_2(\text{S}_2\text{CNEt}_2)_2]$, providing further evidence in support of the proposed mechanism. Interestingly, reaction of $[\text{SnCl}_2(\text{S}_2\text{CNEt}_2)_2]$ with 2-thiouracil in dimethyl sulfoxide (DMSO) yields the dithioester $\text{CH}_2(\text{S}_2\text{CNEt}_2)_2$ (167). The X-ray structure of $[\text{SnCl}_2(\text{S}_2\text{CNEt}_2)_2]$ reveals that the Sn atom is in a distorted octahedral coordination environment (156, 157), with the two dithiocarbamate ligands chelating in an almost symmetric fashion ($\Delta\text{Sn}-\text{S} \approx 0.06 \text{ \AA}$). The two chloride ligands are cis

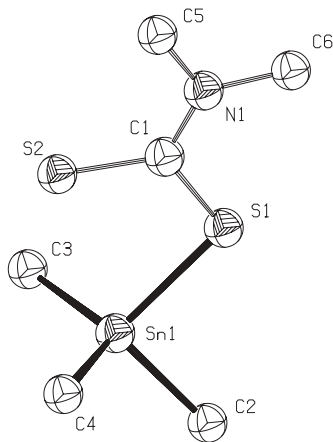


Figure 10. The ORTEP plot of $[\text{SnMe}_3(\text{S}_2\text{CNMe}_2)]$ showing the distorted tetrahedral coordination geometry of tin in the $[\text{SnR}_3(\text{S}_2\text{CNR}_2)]$ complexes.

($\text{ClSnCl} = 91.8^\circ$). The other dihalide complexes that have been characterized crystallographically are structurally analogous (133, 134, 140, 168).

The mono(dithiocarbamate) complexes $[\text{SnR}_{3-n}\text{X}_n(\text{S}_2\text{CNR}_2)]$ ($\text{R} = \text{alkyl or aryl}$; $\text{X} = \text{halide}$; $n = 0, 1, 2, \text{ or } 3$) have also been studied extensively (112–114, 116, 117, 119, 131, 140, 153, 169–188). In the triorganyl complexes the dithiocarbamate ligands tend toward monodentate coordination and the geometry at tin is probably best considered as (distorted) tetrahedral rather than pentagonal bipyramidal (Fig. 10); the average $\text{Sn}-\text{S}$ distances are 2.46 Å (short) and 3.04 Å (long). Substitution of one or more of the organic groups by Cl reduces the asymmetry [$\text{Sn}-\text{S}(\text{short}) = 2.46 \text{ \AA}$, $\text{Sn}-\text{S}(\text{long}) = 2.71 \text{ \AA}$], such that the dithiocarbamate should be considered as anisobidentate. The geometry at Sn is thus best described as a highly distorted trigonal bipyramid, with the dithiocarbamate bridging *ax-eq* positions; the long $\text{Sn}-\text{S}$ bond is axial. The reduction in the asymmetry of the $\text{Sn}-\text{S}$ bonding presumably arises because the presence of the electronegative chloride ligand increases the Lewis acidity of the metal center. Although there appears to be some correlation of the Sn dithiocarbamate bonding parameters with both the Lewis acidity of the metal center and the basicity of the dithiocarbamate N substituents in the gas phase, no such correlation is found in the solid state: Crystal packing factors are therefore thought to have a significant effect on the solid-state structures (180).

Molloy et al. (116) prepared a series of triorganotin(IV) dithiocarbamate complexes of general formula $[\text{SnPh}_2\text{R}(\text{S}_2\text{CNR}'_2)]$ ($\text{R} = 2\text{-(2-pyridyl)ethyl}$, $\text{R}' = \text{Me or Et}$; $\text{R} = 2\text{-(4-pyridyl)ethyl}$, $\text{R}' = \text{Me}$; $\text{R} = 2\text{-(2-oxo-}N\text{-pyrrolidinyl)ethyl}$, $\text{R}' = \text{Me}$), and Das (176) reported the analogous complexes

[SnMe₂R(S₂CNMe₂)] [R = 2-(4,4-dimethyl-2-oxazoliny)-3-thienyl or 3-(2-pyridyl)-2-thienyl] and [Sn(*p*-tolyl)₂R(S₂CNMe₂)] [R = 3-(2-pyridyl)-2-thienyl]. In the complexes of 2-(2-pyridyl)ethyl, 2-(4,4-dimethyl-2-oxazoliny)-3-thienyl and 3-(2-pyridyl)-2-thienyl, the N donor of the organic ligand is coordinated to the metal in both the solid state and in solution. The dithiocarbamate is monodentate (the nonbonding Sn···S distance is ~3.27–3.47 Å). In contrast, the carbonyl oxygen in the 2-(2-oxo-*N*-pyrrolidiny)ethyl complex does not interact significantly with the metal, and the dithiocarbamate is weakly bidentate.

The N donor of the pyridyl ring of the 2-(4-pyridyl)ethyl ligand, R, in [SnPh₂R(S₂CNMe₂)] cannot coordinate to the metal center in an intramolecular sense: Spectroscopic data suggest that the complex is monomeric in solution and polymeric, with intermolecular coordination of N, in the solid state. The dithiocarbamate appears to be monodentate both in the solid state and in solution.

3. Mixed-Ligand and Ester Complexes

Ester tin(IV) dithiocarbamate complexes of general formula [SnX_{3-n}(ester)(S₂CNR₂)_n] and [SnX_{2-n}(ester)₂(S₂CNR₂)_n] (where X = Cl or pseudo-halide; *n* = 1 or 2) have been studied in some detail (151, 189–191). The dithiocarbamate ligands are usually bound in an anisobidentate fashion both in the solid state and solution. The ester may be monodentate (Sn–C coordination only) or bidentate (Sn–C and Sn–O coordination). Solution NMR data (¹¹⁹Sn and ¹H) indicate that the Sn atom in the monoester mono(dithiocarbamate) complexes [Sn(CH₂CH₂COOR)(S₂CNMe₂){(XCH₂CH₂)₂Y}] (R = Me or Et, X = O or S, Y = O, S or NMe) (192) is essentially six coordinate in solution: The ester group appears to be monodentate (Sn–C coordination only), irrespective of the (XCH₂CH₂)₂Y ligand, which is always terdentate. X-ray structural data show clearly how the bonding of the dithiocarbamate ligand is influenced by the ancillary ligand, (XCH₂CH₂)₂Y; it is isobidentate in [Sn(CH₂CH₂COOR)(S₂CNMe₂)(OCH₂CH₂)₂NMe] (i.e., X = O, Y = NMe), but highly anisobidentate, with one exceptionally long Sn–S contact (3.09 Å), in [Sn(CH₂CH₂COOR)(S₂CNMe₂)(SCH₂CH₂)₂O] (i.e., X = S, Y = O). In the former case, both dithiocarbamate S atoms are trans O, while in the latter, one is trans O and the other trans S; the long Sn–S(dithiocarbamate) contact is trans S and is presumably a consequence of the strong trans influence of S.

Reaction of the diester tin monohalide complex, [SnCl(CH₂CH₂COOMe)₂(S₂CNMe₂)], with sodium sulfide (190) gives the known products [Sn(CH₂CH₂COOMe)₃]₂S₃ and [Sn(CH₂CH₂COOMe)₂(S₂CNMe₂)₂]. The corresponding reaction of the monoester tin dihalide complexes, [SnCl₂{CH₂CH₂COOMe}(S₂CNMe₂)] and [SnCl₂{CH₂CH(COOMe)CH₂COOMe}(S₂CNMe₂)] yields the pentacoordinate dimers, [Sn(ester)(S₂CNMe₂)S]₂,

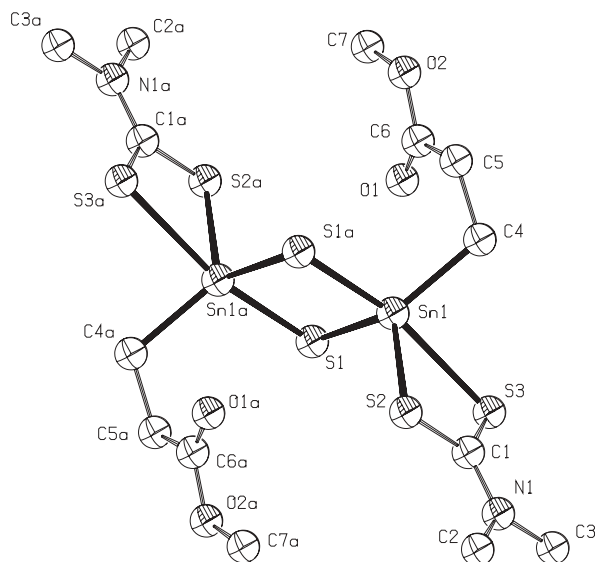


Figure 11. The ORTEP plot of $[\text{Sn}\{\text{CH}_2\text{CH}_2\text{COOMe}\}(\text{S}_2\text{CNMe}_2)\text{S}]_2$, showing the Sn_2S_2 ring found in the $[\text{Sn}(\text{ester})(\text{S}_2\text{CNMe}_2)\text{S}]_2$ complexes.

which possess a Sn_2S_2 four-membered ring in the solid state and in solution (Fig. 11) (193). Prolonged reflux of tetrakis(4-methylpiperidinedithiocarbamate)tin(IV) in dichloromethane yields $[\{\text{Sn}\{\text{S}_2\text{CN}(\text{CH}_2)_4\text{CHMe}\}\text{S}\}_2]$, which also possesses a Sn_2S_2 ring (194), as does $[\text{Sn}(\text{S}_2\text{CNET}_2)_2\text{S}_2]$, which is the initial product of the decomposition of $[\text{Sn}(\text{S}_2\text{CNET}_2)_4]$ (106). In all three cases, the dithiocarbamate ligands are bound in a bidentate fashion.

Reaction of $[\{\text{SnPh}(\text{S}_2\text{CNET}_2)\}_2(\text{CH}_2)_3]$ with Na_2S gives $[\{\text{SnPh}(\text{S}_2\text{CNET}_2)\}_2(\text{CH}_2)_3(\mu\text{-S})]$, which possesses a SnC_3SnS six-membered metallocycle (195). The X-ray structure (Fig. 12) reveals that the dithiocarbamate ligands are bound to the tin atoms in an anisobidentate fashion. The phenyl groups are cis. The solid state ^{119}Sn NMR spectrum displays two signals at -149 and -169 ppm, consistent with five-coordinate tin atoms; the two signals are due to the presence of cis and trans isomers in the polycrystalline material, which are also present in solution.

The addition of sodium acetylacetonate to $[\text{SnBr}_2(\text{S}_2\text{CNET}_2)_2]$ is reported to initially give the expected product, $[\text{SnBr}(\text{S}_2\text{CNET}_2)_2\{\text{MeC}(\text{O})\text{CHC}(\text{O})\text{Me}\}]$, although it has not been characterized fully. On prolonged standing in solution, orange, crystalline $[\text{Sn}(\text{S}_2\text{CNET}_2)_2\{\text{OC}(\text{Me})\text{CSC}(\text{O})\text{Me}\}]$, which possesses a five-membered $\text{SnOC}=\text{CS}$ ring, was isolated (196). The source of the *additional* S atom is not clear, although it has been suggested that it might be derived from

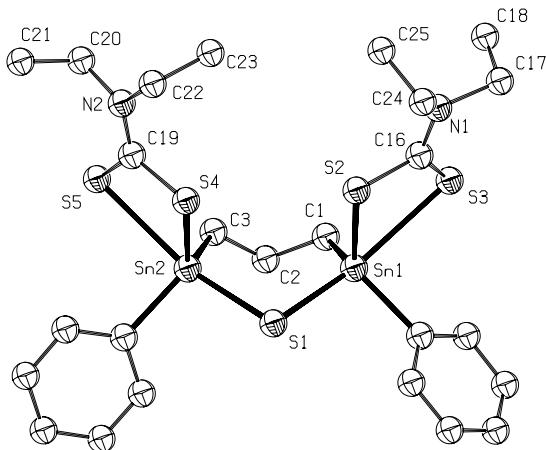


Figure 12. The ORTEP plot of $[\{\text{SnPh}(\text{S}_2\text{CNEt}_2)_2\}_2(\text{CH}_2)_3(\mu\text{-S})]$. The phenyl C atom labels have been omitted for clarity.

tetraethylthiuram disulfide, which is known to be produced as a side product in the bromination of tin(II) dithiocarbamates (197); the starting material, $[\text{SnBr}_2(\text{S}_2\text{CNEt}_2)_2]$, was prepared by bromination of $[\text{Sn}(\text{S}_2\text{CNEt}_2)_2]$. The closely related catecholate complex, $[\text{Sn}(\text{S}_2\text{CNEt}_2)_2(o\text{-C}_6\text{H}_4\text{O}_2)]$, which possesses a five-membered $\text{SnOC}=\text{CO}$ ring, is prepared by oxidative addition of tetraethylthiuram disulfide to $[\text{Sn}(o\text{-C}_6\text{H}_4\text{O}_2)]$ (198). In both complexes, the dithiocarbamate ligands are bound in an essentially isobidentate fashion, with the tin atoms in a distorted octahedral coordination environment.

The complexes 2-*n*-butyl-2-(dimethyldithiocarbamate)-1,3,2-oxathiaannolane (Fig. 13) and 2-*n*-butyl-2-(piperidylthiocarbamate)-1,3,2-oxathiaannolane (199) are dimeric in the solid state, with the Sn atoms adopting a highly distorted octahedral geometry: Notably, the Sn atoms are O bridged rather than S bridged. However, the ^{119}Sn NMR spectra of the complexes points toward them being monomeric in solution: The ^{119}Sn chemical shifts (-251 and -230 , respectively) are consistent with the Sn atom being five coordinate and, importantly, no Sn—Sn scalar couplings are observed.

4. Spectroscopic Studies

As has already been alluded to, the solution-state structures of tin(IV) dithiocarbamate complexes have been studied extensively using ^{119}Sn NMR (95, 106, 111, 112, 115–117, 119, 121, 131, 134, 143, 146–148, 153, 157, 171, 176, 181, 189–193, 198, 199). Although it is often difficult to ascertain the exact coordination of the tin atom unambiguously, because of the anisobidenticity of

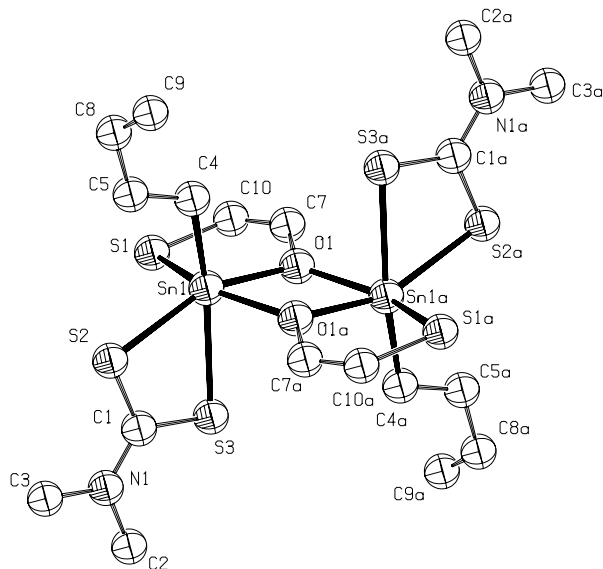


Figure 13. The ORTEP plot of 2-*n*-butyl-2-(dimethyldithiocarbamate)-1,3,2-oxathiastannolane.

the dithiocarbamate ligands and the latent fluxional behavior of many of the complexes, ^{119}Sn chemical shifts give a reasonable guide to the coordination number within a particular series of compounds: the higher the coordination number the lower the resonance frequency (Table III). From Table III, it is also apparent that, as the electronegativity of the tin substituents increases, the asymmetry in the Sn—S(dithiocarbamate) bonding decreases, leading to an increase in the effective coordination number of Sn, causing the chemical shift to move to lower frequency.

Hydrogen-1 and ^{13}C NMR spectroscopy can also be used to probe the structures of the diorganotin(IV) complexes in solution; the magnitudes of the $^1J_{\text{SnC}}$ and $^2J_{\text{SnH}}$ scalar coupling constants have been shown empirically to depend on the CSnC bond angle, θ (141, 200).

The ^{119}Sn Mössbauer spectra of a number of tin dithiocarbamate complexes have been reported (89, 91, 94, 108, 118, 147, 178, 180): Data are collected in Table IV. The Mössbauer spectral parameters have been used to infer the coordination number of the Sn atom. The isomer shift (IS) of tin species decreases as the *s*-electron density at the Sn atom decreases; thus the isomer shift would generally be expected to decrease on increasing coordination number or increasing electronegativity of the ligands. These two factors are difficult to separate, since the anisobidenticity of dithiocarbamate ligands generally decreases as the Lewis acidity of the metal moiety increases.

TABLE III
 Solution ^{119}Sn NMR Data for Tin Dithiocarbamate Complexes

Complex ^a	$\delta(^{119}\text{Sn})$	References
[SnI ₂ (S ₂ CNEt ₂) ₂]	-1861	134
[SnBr ₂ (S ₂ CNEt ₂) ₂]	-1092	134
[SnPh(S ₂ CNEt ₂) ₃]	-813	115
[Sn <i>n</i> -Bu{S ₂ CN(Me) <i>n</i> -Bu} ₃]	-807	119
[SnPh(S ₂ CNEt ₂) ₃]	-807	117
[Sn(MeO ₂ CCH ₂ CH ₂)(S ₂ CNMe ₂) ₃]	-804	189
[Sn{S ₂ CN(Me) <i>n</i> -Bu} ₄]	-786	106
[Sn(S ₂ CNEt ₂) ₄]	-766	106
[SnMe(S ₂ CNEt ₂) ₃]	-752	115
[Sn(S ₂ CNEt ₂) ₂ S] ₂]	-736	106
[Sn{S ₂ CN(CH ₂) ₅ } ₄]	-729	95
[SnPhBr(S ₂ CNEt ₂) ₂]	-704	115
[SnPh(S ₂ CNMe ₂) ₃]	-695	111
[SnPh{S ₂ P(OEt ₂)}(S ₂ CNEt ₂) ₂]	-689	115
[Sn(PhS) ₂ (S ₂ CNEt ₂) ₂]	-666	106
[Sn(CF ₃ CH ₂ S) ₂ (S ₂ CNEt ₂) ₂]	-661	106
[SnPh{S ₂ CN(Me) <i>n</i> -Bu} ₃]	-655	119
[SnPhCl(S ₂ CNEt ₂) ₂]	-650	117
	-647	115
[Sn(CyS) ₂ (S ₂ CNEt ₂) ₂]	-649	106
[Sn(<i>o</i> -C ₆ H ₄ O ₂)(S ₂ CNEt ₂) ₂]	-647	198
[SnPh(S ₂ COEt)(S ₂ CNEt ₂) ₂]	-645	115
[SnMe{S ₂ CN(Me) <i>n</i> -Bu} ₃]	-605	119
[SnCl(MeO ₂ CCH ₂ CH ₂)(S ₂ CNMe ₂) ₂]	-605	189
[SnMeCl(S ₂ CNEt ₂) ₂]	-598	115
[SnCl ₂ (S ₂ CNEt ₂) ₂]	-519	157
[SnPh ₂ {S ₂ CN(Me) <i>n</i> -Bu} ₂]	-505	119
[SnPh ₂ (S ₂ CNEt ₂) ₂]	-502	117
	-501	112
	-499	153
[SnPhBr ₂ (S ₂ CNEt ₂) ₂]	-472	115
[SnMe ₂ L ¹ (S ₂ CNMe ₂) ₂]	-466	147
[SnMe ₂ L ¹ (S ₂ CNEt ₂) ₂]	-463	147
[Sn(MeO ₂ CCH ₂ CH ₂) ₂ (S ₂ CNMe ₂) ₂]	-439	190
[SnPhBrCl(S ₂ CNEt ₂) ₂]	-419	115
[Sn(CH ₂ CH ₂ CO ₂ Me){(OCH ₂ CH ₂) ₂ NMe}(S ₂ CNMe ₂) ₂]	-418	192
[SnCl ₂ {CH ₂ CH(CO ₂ Me)CH ₂ CO ₂ Me}(S ₂ CNMe ₂) ₂]	-405	191
[SnCl ₂ (CH ₂ CH ₂ CO ₂ Me)(S ₂ CNMe ₂) ₂]	-386	189
[SnPh{S ₂ CN(CH ₂) ₄ } ₃]	-378	121
[SnPhCl{S ₂ CN(CH ₂) ₅ } ₂]	-378	95
[SnPhCl(S ₂ CNMe ₂) ₂]	-361	111, 112, 147
[SnPhCl ₂ (S ₂ CNEt ₂) ₂]	-355	115
[SnPhCl ₂ {S ₂ CN(CH ₂) ₅ }]	-354	181
[SnMe ₂ {S ₂ CN(Me) <i>n</i> -Bu} ₂]	-349	119
[SnPhCl ₂ {S ₂ CN(CH ₂) ₄ NMe}]	-349	181
[SnPhCl ₂ {S ₂ CN(CH ₂) ₄ O}]	-349	181
[SnPh ₂ Br(S ₂ CNEt ₂) ₂]	-343	153

TABLE III (continued)

Complex ^a	$\delta(^{119}\text{Sn})$	References
[<i>Sn</i> <i>n</i> -Bu ₂ {S ₂ CN(Me) <i>n</i> -Bu ₂ }	-341	119
[SnMe ₂ (S ₂ CNMe ₂) ₂]	-338	112, 146, 147
[SnMe ₂ {S ₂ CN(CH ₂) ₄ CHMe} ₂]	-336	143
[SnMe ₂ (S ₂ CNEt ₂) ₂]	-336	153
	-333	112, 146, 147
[<i>Sn</i> <i>n</i> -Bu ₂ (S ₂ CNEt ₂) ₂]	-336	153
[SnMe ₂ {S ₂ CN(CH ₂) ₅ } ₂]	-335	143
[SnMe ₂ {S ₂ CN(CH ₂) ₄ NMe} ₂]	-330	143
[SnPh ₂ Cl(S ₂ CNEt ₂)]	-327	153
	-325; -340	117
[SnPhCl ₂ {S ₂ CN(CH ₂) ₄ CHMe}]	-326	181
[SnMe ₂ {S ₂ CN(CH ₂) ₄ O} ₂]	-325	143
[<i>Sn</i> <i>n</i> -BuCl ₂ {S ₂ CN(CH ₂) ₄ CHMe}]	-299	181
[SnMeCl ₂ (S ₂ CNEt ₂)]	-296	115
[<i>Sn</i> <i>n</i> -BuCl ₂ {S ₂ CN(CH ₂) ₅ } ₂]	-293	181
[<i>Sn</i> <i>n</i> -BuCl ₂ (S ₂ CNEt ₂)]	-285	131
[<i>Sn</i> <i>n</i> -BuCl ₂ {S ₂ CN(CH ₂) ₄ NMe}]	-283	181
[<i>Sn</i> <i>n</i> -BuCl ₂ {S ₂ CN(CH ₂) ₄ O}]	-273	181
[SnMe ₂ {S ₂ CN(CH ₂) ₄ } ₂]	-267	121
[<i>Sn</i> <i>n</i> -Bu ₂ (S ₂ CNEt ₂) ₂]	-262	148
	-239	153
[Sn(CH ₂ CH ₂ CO ₂ Me) ₂ Cl(S ₂ CNMe ₂)]	-259	190
[<i>Sn</i> <i>n</i> -Bu ₂ (S ₂ CNMe ₂) ₂]	-255	148
[{ <i>Sn</i> <i>n</i> -Bu(SCH ₂ CH ₂ O)(S ₂ CNMe ₂) ₂ }]	-251	199
[{Sn{CH ₂ CH(CO ₂ Me)CH ₂ CO ₂ Me}(S ₂ CNMe ₂)S} ₂]	-246	191
[{Sn(CH ₂ CH ₂ CO ₂ Me)(S ₂ CNEt ₂)S} ₂]	-233; -235	193
[{ <i>Sn</i> <i>n</i> -Bu(SCH ₂ CH ₂ O){S ₂ CN(CH ₂) ₅ } ₂]	-231	199
[Sn(CH ₂ CH ₂ CO ₂ Me)(S ₂ CNMe ₂)S] ₂]	-230; -232	193
[<i>Sn</i> <i>n</i> -Bu ₂ Cl(S ₂ CNEt ₂)]	-217	153
[Sn(<i>p</i> -tolyl) ₂ (L ²)(S ₂ CNMe ₂)]	-211	176
[SnPh ₂ L ³ (S ₂ CNMe ₂)]	-202	116
[SnMe ₂ Cl(S ₂ CNEt ₂)]	-201; -204	112, 153
[<i>Sn</i> <i>n</i> -Bu ₂ Cl(S ₂ CNEt ₂)]	-200	153
[SnPh ₂ L ⁴ (S ₂ CNEt ₂)]	-198	116
[Sn{CH ₂ CH ₂ CO ₂ Me}{(OCH ₂ CH ₂) ₂ S}(S ₂ CNMe ₂)]	-196	192
[SnPh ₃ (S ₂ CNEt ₂)]	-192	112, 117, 153
[SnPh ₃ {S ₂ CN(CH ₂) ₅ }]	-191	171
[SnPh ₃ {S ₂ CN(CH ₂) ₂ CHMe(CH ₂) ₂ }]	-191	171
[SnPh ₃ {S ₂ CN(Me) <i>n</i> -Bu}]	-190	119
[SnPh ₂ L ³ (S ₂ CNEt ₂)]	-183	116
[SnPh ₃ {S ₂ CN(CH ₂) ₂ O(CH ₂) ₂ }]	-182	171
[Sn(CH ₂ CH ₂ CO ₂ Me){(SCH ₂ CH ₂) ₂ O}(S ₂ CNMe ₂)]	-178	192
[SnPh ₃ {S ₂ CN(CH ₂) ₂ NMe(CH ₂) ₂ }]	-176	171
[SnMe ₂ (L ³)(S ₂ CNMe ₂)]	-174	176
[SnCl ₂ {S ₂ CN(CH ₂) ₄ } ₂]	-140	121
[SnMe ₂ (L ⁵)(S ₂ CNMe ₂)]	-139	176
[SnPh ₃ {S ₂ CN(CH ₂) ₄ }]	-131	121
[SnPh ₂ L ⁶ (S ₂ CNMe ₂)]	-128	116

TABLE III (continued)

Complex ^a	$\delta(^{119}\text{Sn})$	References
[SnMe ₃ {S ₂ CN(CH ₂) ₂ CHMe(CH ₂)}]	17	171
[SnMe ₃ {S ₂ CN(CH ₂) ₅ }]	20	171
[SnMe ₃ {S ₂ CNEt ₂ }]	21	153
[Sn <i>n</i> -Bu ₃ {S ₂ CN(Me) <i>n</i> -Bu}]	21	119
[SnMe ₃ {S ₂ CN(Me) <i>n</i> -Bu}]	22	119
[SnMe ₃ {S ₂ CN(CH ₂) ₂ NMe(CH ₂) ₂ }]	23	171
[SnMe ₃ {S ₂ CNMe ₂ }]	25	112
[SnMe ₃ {S ₂ CN(CH ₂) ₂ O(CH ₂) ₂ }]	34	171

^aChemical shifts reported in ppm relative to SnMe₄ as an external standard. Data quoted at ambient temperature. L¹ = 1-(2-pyridylazo)-2-naphtholate. L² = 3-(2-pyridyl)-2-thienyl. L³ = 2-(2-oxo-*N*-pyrrolidiny)ethyl. L⁴ = 2-ethylpyridine. L⁵ = 2-(4,4-dimethyl-2-oxazoliny)-3-thienyl. L⁶ = 4-ethylpyridine.

Examination of Table IV shows no reliable correlation of the isomer shift with coordination number in organotin dithiocarbamate complexes.

The magnitude of quadrupole splitting (QS) and the QS/IS ratio (ρ) have also been used as a diagnostic probe for the geometry at tin (higher magnitudes being associated with higher coordination numbers), but again data collected in Table IV show no reliable correlation for the organotin dithiocarbamate complexes. However, for the diorganotin compounds, the QS can be correlated with the CSnC bond angle, provided a point-charge model is applicable and that the contribution of the organic ligands to the electric field-gradient is negligible (89).

V. GROUP 15 (V A)

Homoleptic and mixed-ligand dithiocarbamate complexes of the heavier group 15 (V A) elements have been studied extensively and show considerable structural diversity. The dithiocarbamate ligand tends to act in an unsymmetrical chelating fashion to the smaller members of the group, with one of the two M—S bonds appreciably shorter than the other. As the size of the metal increases, the asymmetry in the M—S bond lengths diminishes and there is an increasing tendency for polynuclear species to form via either halide and/or S bridges; halide bridges are favored whenever possible. The arsenic, antimony and bismuth complexes of dithiocarbamates together with other 1,1-dithiolate ligands have been reviewed previously (201).

A. Nitrogen and Phosphorus

The nitrogen compounds [N(SiMe₃)₂(S₂CNR₂)] (R = Me, Et, *i*-Pr, or Bz) (202–204) have been prepared via three routes, namely, (1) reaction of

TABLE IV
 Tin-119 Mössbauer Data for Tin Dithiocarbamate Complexes

Complex ^a	IS	QS	ρ	Reference
[{Sn(S ₂ CNEt ₂) ₂ S}] ₂	0.97	0.66	0.68	108
[SnPh{S ₂ CN(Me) <i>n</i> -Bu}] ₃	1.11	1.81	1.63	121
[SnMe{S ₂ CN(Me) <i>n</i> -Bu}] ₃	1.13	1.92	1.7	121
[Sn(<i>p</i> -tolyl) ₂ (L ¹)(S ₂ CNMe ₂)]	1.16	2.47	2.13	178
[SnPh ₂ {S ₂ CN(CH ₂) ₄ } ₂]	1.2	1.7	1.42	91
[SnPh ₃ {S ₂ CN(Me) <i>n</i> -Bu}]	1.23	1.79	1.46	121
[Sn <i>n</i> -Bu{S ₂ CN(Me) <i>n</i> -Bu}] ₃	1.25	1.84	1.47	121
[SnPh ₂ {S ₂ CN(Me) <i>n</i> -Bu}] ₂	1.26	2.13	1.69	121
[SnPh ₂ {2-(2-py)CH ₂ CH ₂ }(S ₂ CNEt ₂)]	1.27	2.35	1.85	118
[SnPh ₂ {2-(2-py)CH ₂ CH ₂ }(S ₂ CNMe ₂)]	1.27	2.55	2.01	118
[SnPh ₂ {2-(4-py)CH ₂ CH ₂ }(S ₂ CNMe ₂)]	1.27	2.55	2.01	118
[SnMe ₃ {S ₂ CN(Me) <i>n</i> -Bu}]	1.27	2.14	1.69	121
[SnMe ₂ (L ²)(S ₂ CNMe ₂)]	1.27	2.59	2.04	178
[SnHex ₂ (S ₂ CNEt ₂) ₂]	1.29	3.02	2.34	147
[SnPh ₃ {S ₂ CN(CH ₂) ₄ }]	1.3	1.9	1.46	91
[SnPh ₂ {2-(2-Oxo- <i>N</i> -pyr)CH ₂ CH ₂ }(S ₂ CNMe ₂)]	1.3	2.18	1.68	118
[SnMe ₂ (L ¹)(S ₂ CNMe ₂)]	1.31	2.71	2.07	180
[Sn <i>n</i> -Bu ₃ {S ₂ CN(Me) <i>n</i> -Bu}]	1.39	2.19	1.58	121
[SnMe ₂ {S ₂ CN(Me) <i>n</i> -Bu}] ₂	1.4	2.89	2.06	121
[SnHex ₂ (S ₂ CNi-Pr ₂) ₂]	1.4	2.83	2.02	147
[SnHex ₂ {S ₂ CN(Me)Ph}] ₂	1.42	2.89	2.04	147
[Sn <i>n</i> -Bu ₃ {S ₂ CN(CH ₂) ₄ }]	1.44	1.94	1.35	91
[SnMe ₂ {S ₂ CN(CH ₂) ₄ } ₂]	1.44	2.84	1.97	91
[SnHex ₂ (S ₂ CNMe ₂) ₂]	1.45	2.96	2.04	147
[Sn <i>n</i> -Bu ₂ (S ₂ CNMe ₂) ₂]	1.49	2.93	1.97	147
[SnHex ₂ {S ₂ CN(CH ₂) ₂ O(CH ₂) ₂ } ₂]	1.51	2.89	1.91	147
[Sn <i>n</i> -Bu ₂ {S ₂ CN(Me) <i>n</i> -Bu}] ₂	1.52	2.89	1.9	121
[Sn <i>n</i> -Bu ₂ {S ₂ CN(Me)Ph}] ₂	1.55	2.68	1.73	147
[SnBz ₂ {S ₂ CN(CH ₂) ₄ } ₂]	1.58	2.45	1.55	91
[SnOct ₂ {S ₂ CN(CH ₂) ₄ } ₂]	1.58	2.92	1.85	91
[Sn <i>n</i> -Bu ₂ (S ₂ CNEt ₂) ₂]	1.59	2.71	1.7	147
[Sn <i>n</i> -Bu ₂ {S ₂ CN(CH ₂) ₄ } ₂]	1.65	2.46	1.49	91
[SnEt ₂ {S ₂ CN(CH ₂) ₄ } ₂]	1.65	2.83	1.72	89
[Sn <i>n</i> -Bu ₂ (S ₂ CNi-Pr ₂) ₂]	1.66	2.61	1.57	147
[Sn <i>n</i> -Bu ₂ {S ₂ CN(CH ₂) ₂ O(CH ₂) ₂ } ₂]	1.69	2.93	1.73	147
[Sn(S ₂ CNEt ₂) ₂]	1.92	1.05	0.55	94

^a IS = Isomer shift, QS = quadrupole splitting, ρ = (QS/IS). Data reported in mm s⁻¹. L¹ = 2-(4,4-dimethyl-2-oxazolynyl)-3-thienyl. L² = 3-(2-pyridyl)-2-thienyl.

N(SiMe₃)₂Br with the sodium salt of the appropriate dithiocarbamate, (2) reaction of Na[N(SiMe₃)₂] with thiuram disulfides, and (3) reaction of (SiMe₃)₂NMgBr with thiuram disulfides (202). The X-ray molecular structures show that the dithiocarbamates are essentially monodentate [N—S(short) \approx 1.66 Å; N—S(long) \approx 3.05 Å] with the amino nitrogen and dithiocarbamate coplanar (203). A variable temperature NMR study of the dimethyldithiocarbamate

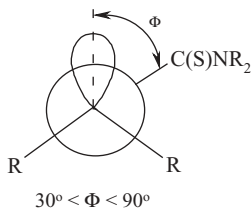


Figure 14. Newman projection showing the *gauche* arrangement of the P–S–C=S moiety in the complexes $[\text{PR}_2(\text{S}_2\text{CNR}'_2)]$.

complex indicates that the barrier to $(\text{S}_2)\text{C}-\text{N}(\text{Me}_2)$ bond rotation is 58 kJ mol^{-1} at 371 K (204), which is similar to magnitudes observed in other main group and transition metal complexes.

Although phosphorus dithiocarbamate compounds, which are generally prepared by insertion of CS_2 into P–N bonds or by reaction of dithiocarbamate salts with phosphorus chlorides, have been known for >100 years, they have received relatively little attention recently (205–213). The structures of $[\text{P}(\text{S}_2\text{CNMe}_2)_3]$ (205), $[\text{P}(\text{S}_2\text{CNEt}_2)_3]$ (206), $[\text{PPh}(\text{S}_2\text{CNEt}_2)_2]$ (207, 208), and $[\text{PPh}_2(\text{S}_2\text{CNEt}_2)]$ (207) have been determined crystallographically; in all four cases the dithiocarbamate ligand is essentially monodentate (P–S = 2.12–2.18 Å), with only weak secondary interactions between the P atom and the second S(=C) atom (P··S = 2.88–3.18 Å; cf. 3.74 Å for the sum of the van der Waals radii). The P–S–C=S moiety adopts a *gauche* arrangement (Fig. 14) as a consequence of repulsions between the stereochemically active lone pair and the S(–P) atom, and the secondary P··S interactions (207). The ^{31}P NMR spectrum of $[\text{P}(\text{S}_2\text{CNMe}_2)_3]$ shows a single chemical shift at ca. –63 ppm suggesting the phosphorus atom has a coordination number >3 (205); this presumably arises because the P atom undergoes metallotropic shifts between the dithiocarbamate S atoms, via a pseudo-bidentate transition state.

The complex $[\text{P}(\text{S})\text{Ph}_2(\text{S}_2\text{CNEt}_2)]$ adopts a similar structure to $[\text{PPh}_2(\text{S}_2\text{CNEt}_2)]$, but the secondary P··S interaction is weaker (3.315 Å) and the angle, ϕ (see Fig. 14), is increased significantly (to 106.4°) as a result of greater steric interactions between the dithiocarbamate and the bulky sulfide ligand attached to the PPh_2 moiety (209). The analogous ethoxide complexes, $[\text{P}(\text{S})(\text{OEt})_2(\text{S}_2\text{CNR}_2)]$ have been shown to display both antifungal and antiviral activity (210), although they are less active than classical organophosphorus reagents.

Bicyclic $\text{P}_4\text{S}_3\text{I}_2$ reacts with $[\text{SnPh}_3(\text{S}_2\text{CNR}_2)]$ or dithiocarbamic acids in the presence of dimethylamine to give $[\text{P}_4\text{S}_3\text{I}(\text{S}_2\text{CNR}_2)]$ or $[\text{P}_4\text{S}_3(\text{S}_2\text{CNR}_2)_2]$, depending on the stoichiometry (211). The dithiocarbamate ligands are bound in an essentially monodentate fashion, but variable temperature ^{31}P NMR

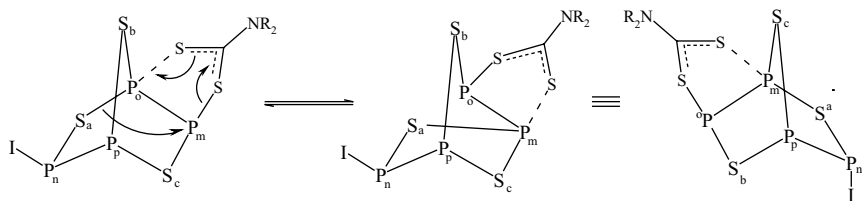


Figure 15. The skeletal rearrangement observed in $[P_4S_3I(S_2CNR_2)]$.

indicates that the P_4S_3 bicyclic skeleton undergoes an unusual rearrangement (Fig. 15) in solution via the formation of a bidentate (bridging) mode in the transition state.

B. Arsenic, Antimony, and Bismuth

1. Homoleptic Complexes

The homoleptic tris(dithiocarbamate) complexes $[M(S_2CNR_2)_3]$ ($M = As, Sb, \text{ or } Bi$) have been studied extensively (93, 212–245). The arsenic complexes are mononuclear with three short As–S bonds (As–S = 2.31–2.39 Å) that are essentially cis each other, and three long As–S bonds (As–S = 2.77–2.94 Å). Valence bond sum (VBS) calculations show that the valency of the As atom is, as expected, close to three (224). The geometry at arsenic in the $[As(S_2CNR_2)_3]$ is best described as a distorted octahedron with the stereochemically active lone pair directed along the pseudo threefold axis, capping the triangular face defined by the three weakly coordinated S atoms (Fig. 16) (222–224, 230).

As with other main group homoleptic dithiocarbamate complexes, those of antimony have been prepared traditionally by the reaction of $SbCl_3$ with the appropriate dithiocarbamate salt or by insertion of CS_2 into Sb–amide bonds. However, the condensation of Sb_2O_3 with dithiocarbamic acids has been shown to be a more facile route (221). The complexes are monomeric, nonelectrolytes in solution (213), but may be either monomeric or dimeric, with weak $Sb-S \cdots Sb$ bridges, in the solid state. Thus, for example, while tris(diethanoldithiocarbamate)antimony(III) is monomeric (223), tris(diethyldithiocarbamate)antimony(III) is a centrosymmetric dimer in the solid state, with one S from a dithiocarbamate of each $Sb(S_2CNEt_2)_3$ moiety bridging: $(Sb)S \cdots Sb = 3.47 \text{ \AA}$ (217). The reasons for the differences in behavior are not clear; there are no stabilizing interactions between the hydroxyl groups and the metal center in the diethanoldithiocarbamate complex, for example, and there are no obvious steric restrictions to dimerization. In both cases, the lone pair is stereochemically active. The local geometry around Sb is best considered as distorted trigonal

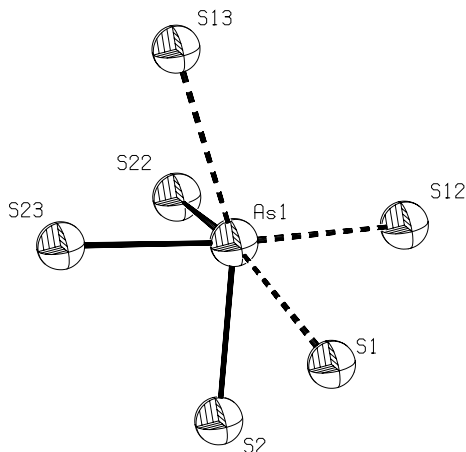


Figure 16. The ORTEP plot of the coordination sphere of As in the tris(dithiocarbamate) complexes $[\text{As}(\text{S}_2\text{CNR}_2)_3]$. The stereochemical active lone-pair caps the triangular face made by the three weakly bound S atoms, which are indicated by the dashed lines.

prismatic and distorted dodecahedral, respectively. The dithiocarbamate ligands are anisobidentate, with the three short Sb—S bonds essentially at right angles to each other: Sb—S(short) = 2.47–2.74 Å; Sb—S(long) = 2.83–3.00 Å. The shortest Sb—S contact is to the apical S atom.

The homoleptic bis(dimethyldithiocarbamate) cations $[\text{Sb}(\text{S}_2\text{CNMe}_2)_2]^+$ and $[\text{M}(\text{S}_2\text{CN}n\text{-Bu}_2)_2]^+$ (M = As or Sb) have also been prepared (246–248). The dithiocarbamate ligands are bonded in an asymmetric fashion ($\Delta\text{Sb—S} \approx 0.16$ Å). The metal is in a pyramidal coordination environment with the lone pair of electrons apical. In $[\text{Sb}(\text{S}_2\text{CNMe}_2)_2][\text{CF}_3\text{SO}_3]$, weak $\text{Sb} \cdots \text{S}$ interactions lead to the cation possessing a dimeric structure, with a center of symmetry, in the solid state: there are also weak interactions between one of the Sb atoms and an oxygen atom of the triflate group (247).

Although $[\text{Bi}\{\text{S}_2\text{CN}(\text{Me})\text{CH}_2\text{CH}_2\text{OH}\}_3]$ (224), $[\text{Bi}\{\text{S}_2\text{CN}(i\text{-Pr})\text{CH}_2\text{CH}_2\text{OH}\}_3]$ (225) and $[\text{Bi}\{\text{S}_2\text{CN}(\text{Me})(\text{Hex})\}_3]$ (240) are monomeric in the solid state, the tris(dithiocarbamate) complexes, $[\text{Bi}(\text{S}_2\text{CNR}_2)_3]$, are generally S-bridged dimers: The Bi—S \cdots Bi bridges are appreciably stronger than in the Sb analogues. The coordination environments of the Bi atoms can vary quite appreciably and the exact structure depends on the nature of the dithiocarbamate. In $[\text{Bi}_2\{\text{S}_2\text{CN}(\text{CH}_2\text{CH}_2\text{OH})_2\}_6]$ the metal atoms are bridged by four S atoms, so that the geometry at the Bi is described best as a distorted square antiprism (Fig. 17) (223, 227), while in $[\text{Bi}_2\{\text{S}_2\text{CN}(\text{Et})n\text{-Bu}\}_6]$ (228) the two Bi atoms are bridged by only two S atoms. The bonding of the nonbridging dithiocarbamate ligands to the metal center is considerably less asymmetric than in the corresponding arsenic or antimony complexes.