CHAPTER 1

Main Group Dithiocarbamate Complexes

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CONTENTS

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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(R_2) = 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(R_2) and C=S stretching modes, which fall typically in the range 1500 ± 50 and $980 \pm 50\,cm^{-1}$, 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 CS_2 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 CS_2 into the Be—N bonds of bis(diisopropylamino)beryllium yields the corresponding bis(diisopropyldithiocarbamate)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 ^{9}Be nuclear magnetic resonance (NMR) spectrum of [Be(S_2CN*i*-$Pr_2)_2$] 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 CS_2 in tetrahydrofuran (THF) gives $Ph_2NCS_2Li \cdot 2THF$, in which the diphenyldithiocarbamate anion chelates the Li^+ ion (Fig. 1) (28a).

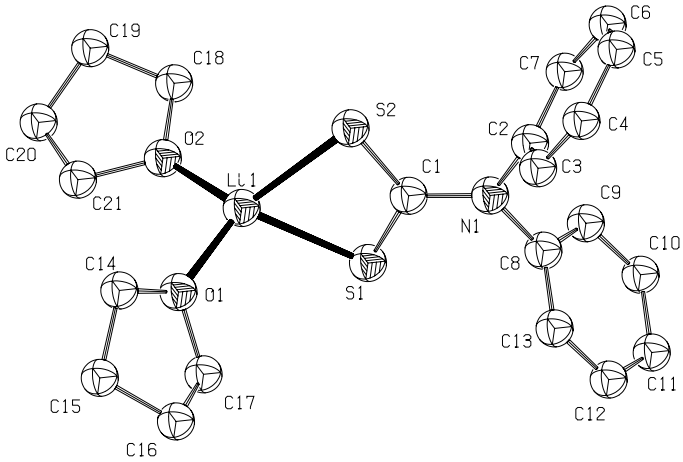

Figure 1. The ORTEP plot of $[Li(S_2CNPh_2)(THF)_2]$. *Note*: ORTEP and PLUTON plots were drawn using the PLATON software, with arbitrary displacement parameters. In all cases hydrogen atoms have been omitted for clarity. (See Refs. 28b and 28c.)

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 $[BR(S_2CNR'_2)_2]$ or $[BR(NR_2)(S_2CNR'_2)]$, where R is an organic substituent (29), while the corresponding reactions with diboranes give complexes of the types $[B_2R_2(S_2CNR'_2)_2]$ and $[B_2(S_2CNR_2)_4]$ (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 $[BCl_2(S_2CNMe_2)]$ or $[B(S_2CNMe_2)_3]_2$, 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 $[BRCl(S_2CNR_2)]$ 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 [μ-2,7-(S_2CNEt_2)-7-(PMe_2Ph)-*nido*-7-$PtB_{10}H_{11}$], 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, [$Al(S_2CNR_2)_3$] [R = methyl (Me), ethyl (Et), isopropyl (*i*-Pr), or benzyl (Bz)] (33–35) and [$AlCl(S_2CNEt_2)_2$] (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 [$AlCl(S_2CNEt_2)_2$] 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
$[B(S_2CNMe_2)_3]$		31
$[B_2(S_2CNMe_2)_4]$		30
$[Al(S_2CNMe_2)_3]$		33
$[Al(S_2CNEt_2)_3]$		34
$[Al(S_2CN\textit{i}\text{-}Pr_2)_3]$		35
$[Al(S_2CNBz_2)_3]$		34
$[Ga(S_2CNH_2)_3]$		38
$[Ga(S_2CNMe_2)_3]$		34, 38, 39, 42
$[Ga(S_2CNEt_2)_3]$	2.40–2.46	34, 38, 40
$[Ga(S_2CN\textit{n}\text{-}Pr_2)_3]$		38
$[Ga(S_2CN\textit{i}\text{-}Pr_2)_3]$		42
$[Ga(S_2CN\textit{n}\text{-}Bu_2)_3]$		38
$[Ga\{S_2CN(Et)Ph\}_3]$		38
$[Ga\{S_2CN(Me)Ph\}_3]$		41
$[Ga(S_2CNBz_2)_3]$		34, 41
$[Ga\{S_2CN(CH_2)_4\}_3]$	2.41–2.47	42
$[Ga\{S_2CN(CH_2)_5\}_3]$		38
$[Ga\{S_2CN(CH_2)_4NMe\}_3]$		43
$[Ga\{S_2CN(CH_2CH_2)_2O\}_3]$	2.42–2.45	43
$[Ga\{S_2CN(Me)Hex\}_3]$		44
$[In(S_2CNH_2)_3]$		38
$[In(S_2CNHMe)_3]$		38
$[In(S_2CNMe_2)_3]$	2.58–2.61	47
$[In(S_2CNEt_2)_3]$	2.58–2.61	38, 40
$[In\{S_2CN(Me)\textit{n}\text{-}Bu\}_3]$		48
$[In(S_2CN(Me)Hex\}_3]$		48
$[In(S_2CN\textit{i}\text{-}Pr_2)_3]$	2.58–2.62	35, 46
$[In\{S_2CN(CH_2)_4\}_3]$	2.58–2.61	46
$[In(S_2CNMePh_2)_3]$		41
$[In(S_2CNBz_2)_3]$		41
$[In\{S_2CN(CH_2)_5\}_3]$	2.58–2.59	45
$[In\{S_2CN(CH_2CH_2)_2O\}_3]$	2.58–2.62	43
$[In\{S_2CN(CH_2CH_2)_2NMe\}_3]$	2.57–2.58	43, 49
$[Tl(S_2CNMe_2)_3]$	2.61–2.68	51, 52, 54[a]
$[Tl(S_2CNEt_2)_3]$	2.67	51, 54[a]
$[Tl(S_2CN\textit{n}\text{-}Pr_2)_3]$		54[a]
$[Tl(S_2CNBu_2)_3]$		54[a]
$[Tl(S_2CNBz_2)_3]$		54[a]
$[Tl\{S_2CN(CH_2)_5\}_3]$		54[a]
$[Tl(S_2CNMe_2)]$	2.99–3.44	56, 57, 60, 64, 65
$[Tl(S_2CNEt_2)]$	3.07–3.62	53, 56, 57, 62, 64, 65
$[Tl(S_2CN\textit{n}\text{-}Pr_2)]$	2.88–4.37	56, 57, 58, 64, 65
$[Tl(S_2CN\textit{i}\text{-}Pr_2)]$	2.98–3.04	57, 59
$[Tl(S_2CN\textit{n}\text{-}Bu_2)]$	2.97–3.16	56, 57, 63, 64, 65
$[Tl(S_2CN\textit{i}\text{-}Bu_2)]$	2.97–3.47	61
$[Tl\{S_2CN(\textit{i}\text{-}C_5H_{11})_2\}]$		57
$[Tl\{S_2CN(Me)Ph\}]$		65

TABLE I (*Continued*)

Complex	M—S (Å)	References
$[Tl(S_2CNBz_2)]$		65
$[Tl\{S_2CN(CH_2)_5\}]$		64
$[Tl\{S_2CN(CH_2)_4O\}]$		65

[a] Reference 54 also reports mixed dithiocarbamate complexes of the type $[Tl(S_2CNR_2)_2(S_2CNR'_2)]$.

or (4) restricted rotation about the $(S_2)C—N$ 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 $(S_2)C—N$ 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 $(S_2)C—N$ bond in the $[M(S_2CNi\text{-}Pr_2)_3]$ complexes (M = Al or In) at and below ambient temperatures: Contributions to the measured rate constants from $(S_2)C—N$ bond rotation process are negligible. Synthetic studies of some Tl^{III} complexes (54) indicate that the dithiocarbamate ligands are labile: mixed-ligand complexes, $[Tl(S_2CNR_2)_2(S_2CNR'_2)]$, 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 $[Tl(S_2CNR_2)_2]^+$ 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, $[Tl_2(S_2CNR_2)_2]$ 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).

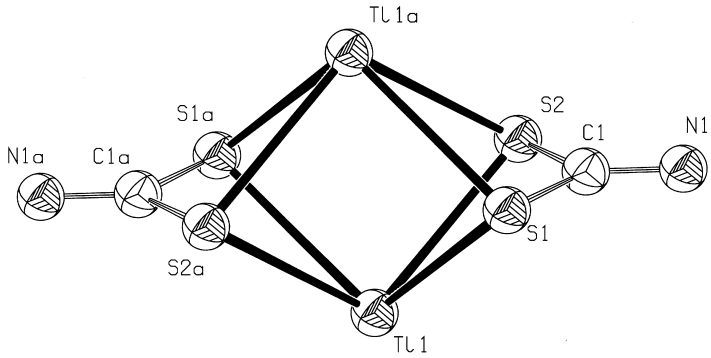

Figure 2. The ORTEP plot of the dimeric unit in the Tl(I) complexes $[Tl_2(S_2CNR_2)_2)]$. The N substituents are omitted for clarity.

The complexes

$[Ga\{S_2CN(CH_2)_4O\}\{S_2P(OR)_2\}_2]$ (R = Et or *i*-Pr)
$[Ga\{S_2CN(CH_2)_4O\}\{SCH_2CH_2)_2O\}]$ and $[Ga\{S_2CN(CH_2)_4NMe\}\{(SCH_2CH_2)_2O\}]$

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 $[MCl_2(S_2CNR_2)]$, $[MR_2(S_2CNR'_2)]$, $[MCl(S_2CNR_2)_2]$, and/or $[MR(S_2CNR'_2)_2]$ (R = 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 $[InR_2(S_2CNEt_2)]$ [R = Me (75), Et (75), or *t*-Bu (77)], $[In$*t*$-Bu_2(S_2CNMe_2)]$ (77), and $[TlPh_2(S_2CNEt_2)]$ [Fig. 3(*a*)] (72) show that the metal ions possess a highly distorted tetrahedral geometry. With the exception of $[InMe_2(S_2CNEt_2)]$ and $[In$*t*$-Bu_2(S_2CNMe_2)]$, 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 $[TlMe_2(S_2CN$*n*$-Pr_2)]$ (74) are linked by two intermolecular Tl···S interactions, giving a well-ordered spiral arrangement, while in

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

Complexes	M–S (Å)	References
$[BMe(S_2CNMe_2)_2]$		31
$[BPh(S_2CNMe_2)_2]$		31
$[B$*n*$\text{-}BuCl(S_2CNMe_2)]$		31
$[BPhCl(S_2CNMe_2)]$		31
$[BCl_2(S_2CNMe_2)]$		31
$[AlCl(S_2CNEt_2)_2]$		33
$[GaMe_2(S_2CNEt_2)]$		75
$[GaEt_2(S_2CNEt_2)]$		75
$[Ga\ t\text{-}Bu_2(S_2CNMe_2)]$		77
$[Ga\ t\text{-}Bu_2(S_2CNEt_2)]$	2.38, 2.43	77
$[Ga\ t\text{-}Bu_2(S_2CN$*n*$\text{-}Pr_2)]$		77
$[Ga(C_5H_{11})_2(S_2CNEt_2)]$		75
$[GaMe_2\{S_2CNMe(CH_2)_3NMe_2\}]$		76
$[GaEt_2\{S_2CNMe(CH_2)_3NMe_2\}]$		76
$[Ga(CH_2CHMe_2)_2\{S_2CNMe(CH_2)_3NMe_2\}]$		76
$[Ga(C_5H_{11})_2\{S_2CNMe(CH_2)_3NMe_2\}]$		76
$[GaCl_2\{S_2CN(CH_2CH_2)_2O\}]$		43
$[GaCl_2(4\text{-}MePy)_2(S_2CNMe_2)]$	2.45, 2.49	80
$[GaCl_2(4\text{-}MePy)_2(S_2CNEt_2)]$	2.48, 2.48	81
$[Ga$*t*$\text{-}Bu(S_2CNMe_2)_2]$		77
$[Ga$*t*$\text{-}Bu(S_2CNEt_2)_2]$		77
$[Ga$*t*$\text{-}Bu(S_2CN$*n*$\text{-}Pr_2)_2]$	2.31–2.60	77, 78
$[Ga(O$*i*$\text{-}Pr)(S_2CN$*n*$\text{-}Pr_2)_2]$	2.31–2.57	78
$[GaCl(S_2CNMe_2)_2]$	2.21–2.43	42
$[GaCl(S_2CN$*i*$\text{-}Pr_2)_2]$		42
$[GaCl\{S_2CN(CH_2)_5\}_2]$		42
$[GaCl\{S_2CN(CH_2CH_2)_2O\}_2]$		43
$[InMe_2(S_2CNMe_2)]$		71
$[InMe_2(S_2CNEt_2)]$		75
$[InEt_2(S_2CNEt_2)]$	2.56, 2.68	75
$[In(C_5H_{11})_2(S_2CNEt_2)]$		75
$[InMe_2\{S_2CNMe(CH_2)_3NMe_2\}]$		75
$[InEt_2\{S_2CNMe(CH_2)_3NMe_2\}]$	2.59, 2.79	75
$[In(CH_2CHMe_2)_2\{S_2CNMe(CH_2)_3NMe_2\}]$		75
$[In(C_5H_{11})_2\{S_2CNMe(CH_2)_3NMe_2\}]$		75
$[InCl_2\{S_2CN(CH_2CH_2)_2O\}]$		43
$[InMe(S_2CNMe_2)_2]$		71
$[InEt(S_2CNMe_2)_2]$		71
$[InCl(S_2CN$*i*$\text{-}Pr_2)_2]$	2.38–2.56	42
$[GaCl\{S_2CN(CH_2CH_2)_2O\}_2]$		43
$[TlMe_2(S_2CNHEt_2)]$		74
$[TlMe_2(S_2CNH$*n*$\text{-}Pr)]$		74
$[TlMe_2(S_2CN$*n*$\text{-}Pr_2)]$	2.70, 2.80	74
$[TlMe_2(S_2CN$*n*$\text{-}Bu_2)]$		74
$TlMe_2(S_2CN$*sec*$\text{-}Bu_2)]$		74
$[TlMe_2\{S_2CNMe(CH_2)_2OH\}]$		74

TABLE II (*Continued*)

Complexes	M–S (Å)	References
$[TlMe_2(S_2CNMe_2)]$		51
$[TlMe_2(S_2CNEt_2)]$		51
$[TlMe_2(S_2CNPh_2)]$		51
$[TlPh_2(S_2CNEt_2)]$	2.72, 7.72	51, 72
$[TlCp_2\{S_2CN(Me)Cy\}]$		73
$[TlCp_2\{S_2CN(Et)Cy\}]$		73
$[TlCp_2\{S_2CN(Me)Cy\}]$		73
$[TlCp_2\{S_2CN(i\text{-}Pr)Cy\}]$		73
$[Tl(C_9H_7)\{S_2CN(Me)Cy\}]$		73
$[Tl(C_9H_7)\{S_2CN(Et)Cy\}]$		71
$[Tl(C_9H_7)\{S_2CN(i\text{-}Pr)Cy\}]$		73
$[Tl(C_{13}H_9)_2\{S_2CN(Me)Cy\}]$		71
$[Tl(C_{13}H_9)_2\{S_2CN(Et)Cy\}]$		71
$[Tl(C_{13}H_9)_2\{S_2CN(i\text{-}Pr)Cy\}]$		73
$[Tl(p\text{-tolyl})(S_2CNEt_2)_2]$	2.55–2.80	79

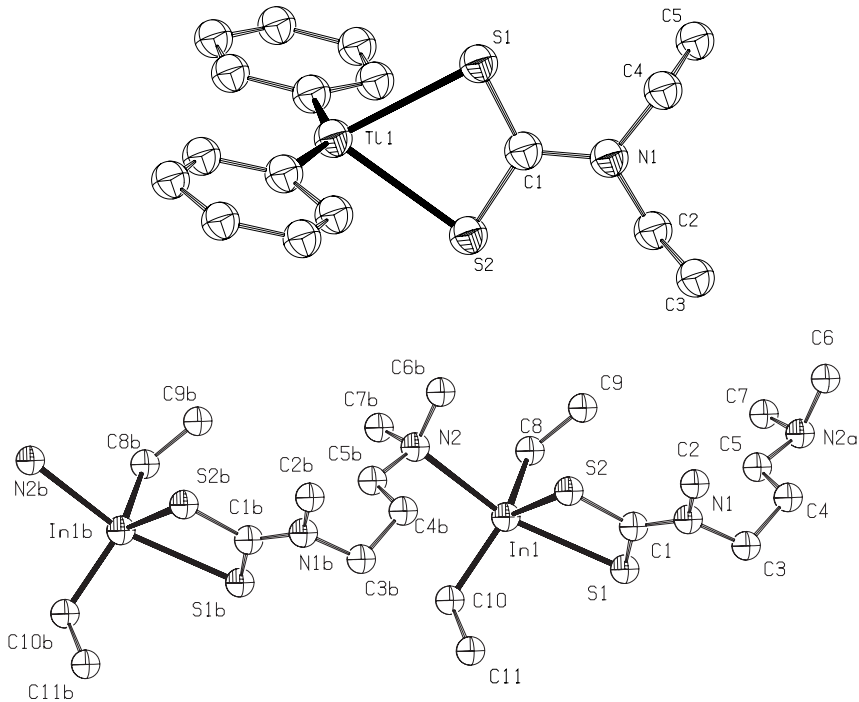

Figure 3. The ORTEP plots of (*a*) $[TlPh_2(S_2CNEt_2)]$ and (*b*) $[InEt_2\{S_2CN(Me)(CH_2)_3NMe_2\}]$, showing a section of the polymeric chain.

$[InEt_2\{S_2CNMe(CH_2)_3NMe_2\}]$ (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 $[Ga\textit{t}\text{-}Bu(S_2CNR_2)_2]$ (R = Me, Et, or *n*-Pr), were isolated as minor products during the synthesis of the dialkyl complexes $[Ga\textit{t}\text{-}Bu_2(S_2CNR_2)]$ from the reaction of $[Ga\textit{t}\text{-}Bu_2(\mu\text{-}Cl)]_2$ 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 $[Ga\textit{t}\text{-}Bu(S_2CN\textit{n}\text{-}Pr_2)_2]$ (78), $[Ga(O\textit{i}\text{-}Pr)(S_2CNEt_2)_2]$ (78) and $[Tl(\textit{p}\text{-tolyl})(S_2CNEt_2)_2]$ (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 $<94^\circ$ favor a square-based pyramidal structure, while cone angles $>94^\circ$ 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, $[MCl(S_2CNR_2)_2]$ (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, $[MCl_2(S_2CNR_2)]$ (M = Ga or In) (43) have not been well characterized. Solution molecular mass measurements of the corresponding boron complexes, $[BCl_2(S_2CNR_2)]$, 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 Ga_2Cl_2 with tetramethyl- or tetraethylthiuram disulfide in 4-methylpyridine solvent yields $[GaCl_2(4\text{-}Mepy)_2(S_2CNR_2)]$ [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.

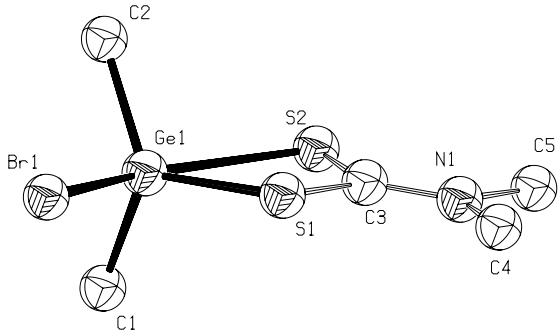

Figure 4. The ORTEP plot of $[GeMe_2Br(S_2CNMe_2)]$.

A. Silicon and Germanium

Although silicon dithiocarbamate complexes remain rare, complexes of the type $[SiR_2(S_2CNR_2)_2]$ (R = 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 $[Ge\{S_2CN(i\text{-}Pr)Cy)\}_4]$ (cy = cyclohexyl), was reportedly prepared by the reaction of $GeCl_4$ with an excess of the sodium dithiocarbamate salt (83). However, attempts to prepare $[Ge(S_2CNMe_2)_4]$ similarly were unsuccessful (84). The diorganogallium bis(dithiocarbamate) complexes, $[GeR_2(S_2CNR_2)_2]$, have been prepared by reaction of GeR_2Cl_2 with the appropriate sodium dithiocarbamate salt (84, 85); an X-ray crystallographic study of $[GeMe_2(S_2CNMe_2)_2]$ 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 $[GeMe_2X(S_2CNMe_2)]$ complexes (X = 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 $[GeMe_2Br(S_2CNMe_2)]$ is shown in Fig. 4. Complexes of general formula $[GeR_3(S_2CNR_2)]$ (R = alkyl or phenyl) have also been prepared (84, 89, 90); solution NMR data indicate they are essentially isostructural with the $[GeMe_2X(S_2CNMe_2)]$ 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, $[Sn(S_2CNR_2)_2]$, 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 $[Sn(S_2CNMe_2)_4]$ the Sn atom is essentially six coordinate, with two of the dithiocarbamate ligands anisobidentate and two monodentate: The nonbonding Sn···S distances are 3.44 and 3.64 Å (94). In contrast, in $[Sn\{S_2CN(CH_2)_4\}_4]$ 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

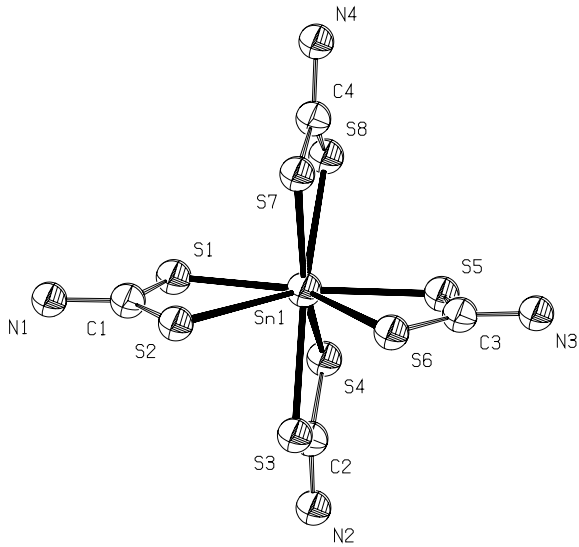

Figure 5. The ORTEP plot of $[Sn\{S_2CN(CH_2)_4\}_4]$, showing dodecahedral arrangement at tin. The N substituents omitted for clarity.

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), $[Pb(S_2CNR_2)_2]$, 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 Pb···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 $[Pb(S_2CNMe_2)_2]$ units stacked along the crystallographic *c* axis (96). Within the stack, each Pb atom has a long contact with two S atoms (Pb···S = 3.36 Å) of the unit directly above, giving a pseudo-six-coordinate metal center. The crystal structure of $[Pb\{S_2CN(Et)i\text{-}Pr\}_2]$ 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(pyrrolidinedithiocarbamate)lead (99), where all four S atoms form long-range interactions with a second $[Pb\{S_2CN(CH_2)_4\}_2]$ 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 Pb···Pb distance is 3.89 Å, 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 $Pb_2(S_2CNn\text{-}Pr_2)_4$ core, in which the two Pb atoms are bridged by S atoms from different

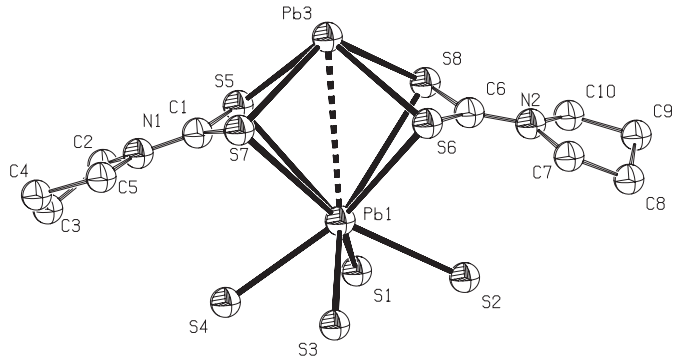

Figure 6. The ORTEP plot of $[Pb\{S_2CN(CH_2)_4\}_2]$, showing a section of the polymeric chain.

dithiocarbamate ligands. Two further [Pb(S_2CN*n*-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 [Pb(S_2CNR_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 [Pb(phen)(S_2C-NEt_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.

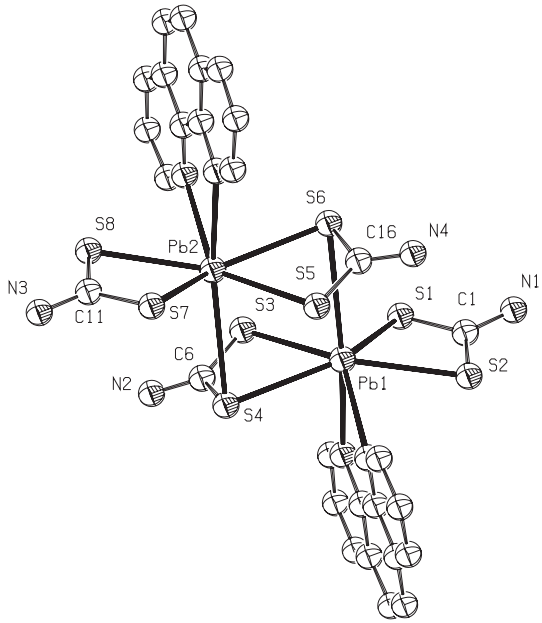

Figure 7. The ORTEP plot showing the dimeric structure of [Pb(phen)(S_2CNEt_2)]. The N substituents of the dithiocarbamates and atom labels of the phen ligands have been omitted for clarity.

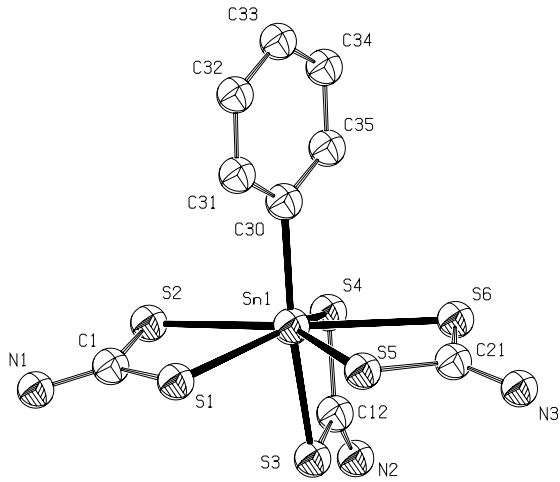

Figure 8. The ORTEP plot of $[SnR(S_2CN\textit{i}\text{-}Bu_2)_3]$ showing the distorted pentagonal bipyramidal coordination of tin in the complexes $[SnR(S_2CNR_2)_3]$ and $[SnX(S_2CNR_2)_3]$. The N substituents are omitted for clarity.

The majority of tin(IV) dithiocarbamate complexes are of the general type $[SnR_{4\text{-}n\,-\,m}X_n(S_2CNR_2)_m]$ (where R = alkyl or aryl; X = halide; $n = 0$, 1, 2, 3; $m = 1$, 2, or 3). In the tris(dithiocarbamate) complexes $[SnR(S_2CNR_2)_3]$ and $[SnX(S_2CNR_2)_3]$ (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 [Sn—S(ax) $\approx$ 2.48 Å; Sn—S(eq) $\approx$ 2.77 Å]; usually the two equatorial dithiocarbamates are also anisobidentate, but to a much lesser degree. The solution ^{119}Sn NMR chemical shift of $[SnPh(S_2CNEt_2)_3]$ 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 $[SnR_nX_{2\text{-}n}(S_2CNR_2)_2]$ (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 [$SnR_2(S_2CNR_2)_2$] complexes is highly variable (∼100–150°), 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 ∼89–96°, suggesting that the Lewis acidity of the metal center is an important factor.

Three crystalline modifications of [$SnMe_2(S_2CNEt_2)_2$] 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 [Sn*t*-$Bu_2(S_2CNMe_2)_2$] (150), [(Sn*t*-$Bu_2)_2$\{μ-$S_2CN(H)(CH_2)_2N(H)CS_2$\}] (124), and [Sn*t*-$Bu_2(S_2CNEt_2)_2$] (153) show some interesting structural differences. The molecular structure of [Sn*t*-$Bu_2(S_2CNEt_2)_2$] is very similar to that of the dimethyltin(IV) bis(dithiocarbamate) complexes, but in [Sn*t*-$Bu_2(S_2CNMe_2)_2$] 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, [Sn*t*-$Bu_2(S_2CNMe_2)_2$] is structurally more akin to the triorganotin(IV) dithiocarbamates. The Sn atoms in the centrosymmetric dimeric complex [(Sn*t*-$Bu_2)_2$ \{μ-$S_2CN(H)(CH_2)_2N(H)CS_2$\}$_2$] (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).

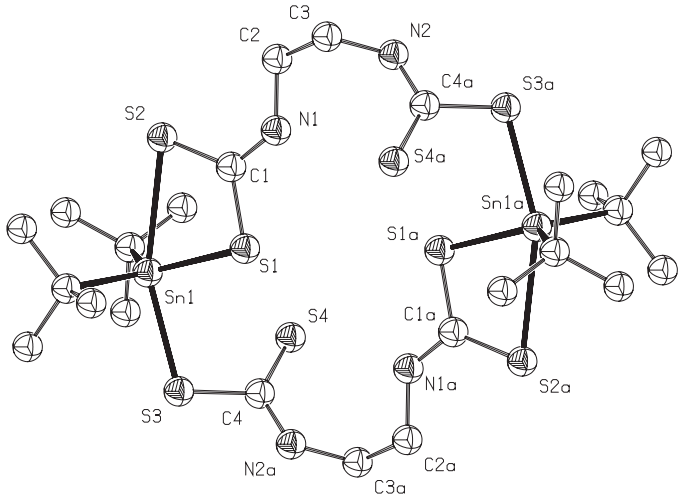

Figure 9. The ORTEP plot of [(Sn*t*-$Bu_2)_2$\{μ-$S_2CN(H)(CH_2)_2N(H)CS_2$\}].

The complex $[SnPh_2(S_2CNEt_2)_2]$ 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 [ΔSn—S = 0.10 Å (tetragonal) and 0.24 Å (monoclinic)].

The effects of the dithiocarbamate N substituents on the structures of the phenyl and vinyl complexes $[SnPh_2(S_2CNR_2)_2]$ and $[Sn(CHCH_2)_2(S_2CNR_2)_2]$ 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 $[SnRCl(S_2CNR'_2)_2]$ 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 [ΔSn—S(ave) $\approx$ 0.06 Å], 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, $[SnCl_2(S_2CNEt_2)_2]$ (157). The mechanism probably involves the initial formation of $[Sn(S_2CNEt_2)_2]$, 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 $[SnCl_2(S_2CNEt_2)_2]$, providing further evidence in support of the proposed mechanism. Interestingly, reaction of $[SnCl_2(S_2CNEt_2)_2]$ with 2-thiouracil in dimethyl sulfoxide (DMSO) yields the dithioester $CH_2(S_2CNEt_2)_2$ (167). The X-ray structure of $[SnCl_2(S_2CNEt_2)_2]$ 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 (ΔSn—S $\approx$ 0.06 Å). The two chloride ligands are cis

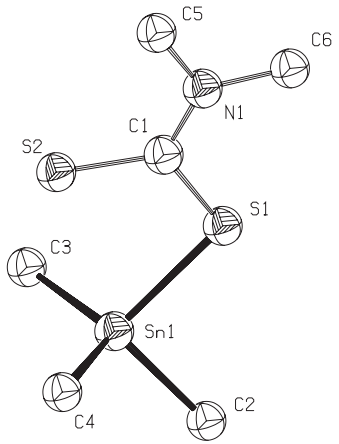

Figure 10. The ORTEP plot of $[SnMe_3(S_2CNMe_2)]$ showing the distorted tetrahedral coordination geometry of tin in the $[SnR_3(S_2CNR_2)]$ complexes.

(ClSnCl = 91.8°). The other dihalide complexes that have been characterized crystallographically are structurally analogous (133, 134, 140, 168).

The mono(dithiocarbamate) complexes $[SnR_{3-n}X_n(S_2CNR_2)]$ (R = alkyl or aryl; X = halide; $n = 0$, 1, 2, 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 Sn—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 [Sn—S(short) = 2.46 Å, Sn—S (long) = 2.71 Å], 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 Sn—S bond is axial. The reduction in the asymmetry of the Sn—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 $[SnPh_2R(S_2CNR'_2)]$ {R = 2-(2-pyridyl)ethyl, R′ = Me or Et; R = 2-(4-pyridyl)ethyl, R′ = Me; R = 2-(2-oxo-*N*-pyrrolidinyl)ethyl, R′ = Me}, and Das (176) reported the analogous complexes

$[SnMe_2R(S_2CNMe_2)]$ [R = 2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl or 3-(2-pyridyl)-2-thienyl] and $[Sn(p\text{-tolyl})_2R(S_2CNMe_2)]$ [R = 3-(2-pyridyl)-2-thienyl]. In the complexes of 2-(2-pyridyl)ethyl, 2-(4,4-dimethyl-2-oxazolinyl)-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*-pyrrolidinyl)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 $[SnPh_2R(S_2CNMe_2)]$ 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 $[SnX_{3-n}(ester)(S_2CNR_2)_n]$ and $[SnX_{2-n}(ester)_2(S_2CNR_2)_n]$ (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 (^{119}Sn and ^{1}H) indicate that the Sn atom in the monoester mono(dithiocarbamate) complexes $[Sn(CH_2CH_2COOR)(S_2CNMe_2)\{(XCH_2CH_2)_2Y\}]$ (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 $(XCH_2CH_2)_2Y$ ligand, which is always terdentate. X-ray structural data show clearly how the bonding of the dithiocarbamate ligand is influenced by the ancillary ligand, $(XCH_2CH_2)_2Y$; it is isobidentate in $[Sn(CH_2CH_2COOR)(S_2CNMe_2)(OCH_2CH_2)_2NMe]$ (i.e., X = O, Y = NMe), but highly anisobidentate, with one exceptionally long Sn—S contact (3.09 Å), in $[Sn(CH_2CH_2COOR)(S_2CNMe_2)(SCH_2CH_2)_2O]$ (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, $[SnCl(CH_2CH_2COOMe)_2(S_2CNMe_2)]$, with sodium sulfide (190) gives the known products $[Sn(CH_2CH_2COOMe_3)_2S]_3$ and $[Sn(CH_2CH_2COOMe)_2(S_2CNMe_2)_2]$. The corresponding reaction of the monoester tin dihalide complexes, $[SnCl_2\{CH_2CH_2COOMe\}(S_2CNMe_2)]$ and $[SnCl_2\{CH_2CH(COOMe)CH_2COOMe\}(S_2CNMe_2)]$ yields the pentacoordinate dimers, $[Sn(ester)(S_2CNMe_2)S]_2$,

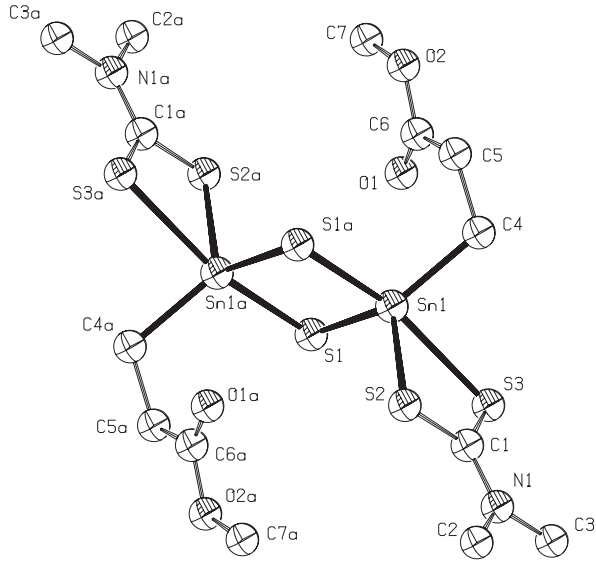

Figure 11. The ORTEP plot of $[Sn\{CH_2CH_2COOMe\}(S_2CNMe_2)S]_2$, showing the Sn_2S_2 ring found in the $[Sn(ester)(S_2CNMe_2)S]_2$ complexes.

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 $[\{Sn\{S_2CN(CH_2)_4CHMe\}\ S\}_2]$, which also possesses a Sn_2S_2 ring (194), as does $[Sn(S_2CNEt_2)_2S_2]$, which is the initial product of the decomposition of $[Sn(S_2CNEt_2)_4]$ (106). In all three cases, the dithiocarbamate ligands are bound in a bidentate fashion.

Reaction of $[\{SnPh(S_2CNEt_2)\}_2(CH_2)_3]$ with Na_2S gives $[\{SnPh(S_2CNEt_2)\}_2(CH_2)_3(\mu\text{-}S)]$, 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 $[SnBr_2(S_2CNEt_2)_2]$ is reported to initially give the expected product, $[SnBr(S_2CNEt_2)_2\{MeC(O)CHC(O)Me\}]$, although it has not been characterized fully. On prolonged standing in solution, orange, crystalline $[Sn(S_2CNEt_2)_2\{OC(Me)CSC(O)Me\}]$, which possesses a five-membered SnOC=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

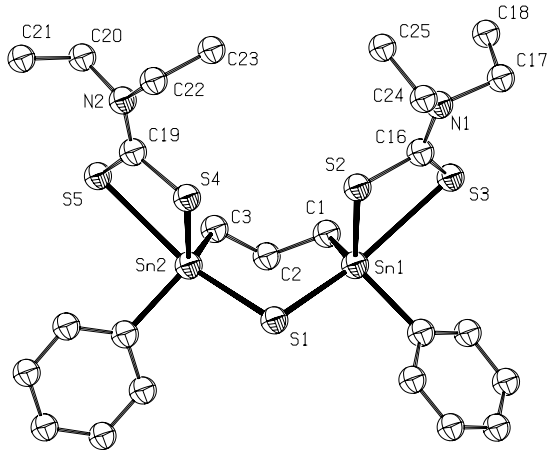

Figure 12. The ORTEP plot of $[\{SnPh(S_2CNEt_2)\}_2(CH_2)_3(\mu\text{-}S)]$. The phenyl C atom labels have been omitted for clarity.

tetraethylthiuram disulfide, which is known to be produced as a side product in the bromination of tin(II) dithiocarbamates (197); the starting material, $[SnBr_2(S_2CNEt_2)_2]$, was prepared by bromination of $[Sn(S_2CNEt_2)_2]$. The closely related catecholate complex, $[Sn(S_2CNEt_2)_2(o\text{-}C_6H_4O_2)]$, which possesses a five-membered SnOC=CO ring, is prepared by oxidative addition of tetraethylthiuram disulfide to $[Sn(o\text{-}C_6H_4O_2)]$ (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-oxathiastannolane (Fig. 13) and 2-*n*-butyl-2-(piperidyldithiocarbamate)-1,3,2-oxathiastannolane (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

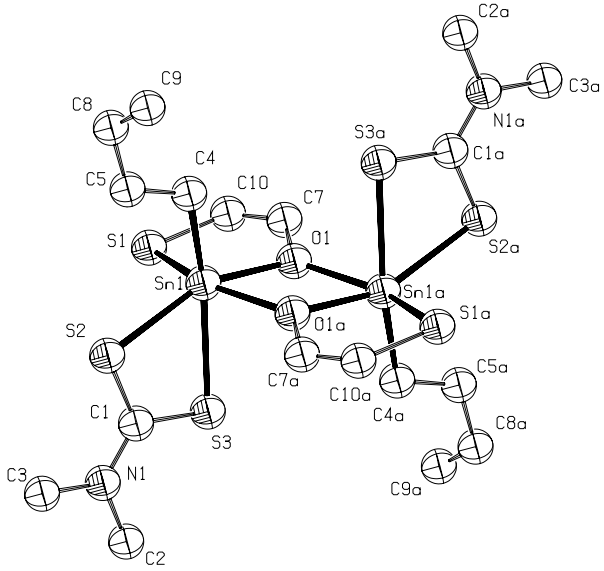

Figure 13. The ORTEP plot of 2-*n*-butyl-2-(dimethyldithiocarbamate)-1,3,2-oxathiastannolane.

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 $^{1}J_{SnC}$ and $^{2}J_{SnH}$ 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]	δ(^{119}Sn)	References
$[SnI_2(S_2CNEt_2)_2]$	−1861	134
$[SnBr_2(S_2CNEt_2)_2]$	−1092	134
$[SnPh(S_2CNEt_2)_3]$	−813	115
[Sn*n*-Bu{$S_2CN(Me)$*n*-Bu}$_3$]	−807	119
$[SnPh(S_2CNEt_2)_3]$	−807	117
$[Sn(MeO_2CCH_2CH_2)(S_2CNMe_2)_3]$	−804	189
[Sn{$S_2CN(Me)$*n*-Bu}$_4$]	−786	106
$[Sn(S_2CNEt_2)_4]$	−766	106
$[SnMe(S_2CNEt_2)_3]$	−752	115
$[Sn(S_2CNEt_2)_2S]_2]$	−736	106
[Sn{$S_2CN(CH_2)_5$}$_4$]	−729	95
$[SnPhBr(S_2CNEt_2)_2]$	−704	115
$[SnPh(S_2CNMe_2)_3]$	−695	111
$[SnPh\{S_2P(OEt_2)\}(S_2CNEt_2)_2]$	−689	115
$[Sn(PhS)_2(S_2CNEt_2)_2]$	−666	106
$[Sn(CF_3CH_2S)_2(S_2CNEt_2)_2]$	−661	106
[SnPh{$S_2CN(Me)$*n*-Bu}$_3$]	−655	119
$[SnPhCl(S_2CNEt_2)_2]$	−650	117
	−647	115
$[Sn(CyS)_2(S_2CNEt_2)_2]$	−649	106
$[Sn(o\text{-}C_6H_4O_2)(S_2CNEt_2)_2]$	−647	198
$[SnPh(S_2COEt)(S_2CNEt_2)_2]$	−645	115
[SnMe{$S_2CN(Me)$*n*-Bu)$_3$]	−605	119
$[SnCl(MeO_2CCH_2CH_2)(S_2CNMe_2)_2]$	−605	189
$[SnMeCl(S_2CNEt_2)_2]$	−598	115
$[SnCl_2(S_2CNEt_2)_2]$	−519	157
[$SnPh_2${$S_2CN(Me)$*n*-Bu}$_2$]	−505	119
$[SnPh_2(S_2CNEt_2)_2]$	−502	117
	−501	112
	−499	153
$[SnPhBr_2(S_2CNEt_2)]$	−472	115
$[SnMe_2L^1(S_2CNMe_2)]$	−466	147
$[SnMe_2L^1(S_2CNEt_2)]$	−463	147
$[Sn(MeO_2CCH_2CH_2)_2(S_2CNMe_2)_2]$	−439	190
$[SnPhBrCl(S_2CNEt_2)]$	−419	115
$[Sn(CH_2CH_2CO_2Me)\{(OCH_2CH_2)_2NMe\}(S_2CNMe_2)]$	−418	192
$[SnCl_2\{CH_2CH(CO_2Me)CH_2CO_2Me\}(S_2CNMe_2)]$	−405	191
$[SnCl_2(CH_2CH_2CO_2Me)(S_2CNMe_2)]$	−386	189
[SnPh{$S_2CN(CH_2)_4$}$_3$]	−378	121
[SnPhCl{$S_2CN(CH_2)_5$}$_2$]	−378	95
$[SnPhCl(S_2CNMe_2)_2]$	−361	111, 112, 147
$[SnPhCl_2(S_2CNEt_2)]$	−355	115
$[SnPhCl_2\{S_2CN(CH_2)_5\}]$	−354	181
[$SnMe_2${$S_2CN(Me)$*n*-Bu}$_2$]	−349	119
$[SnPhCl_2\{S_2CN(CH_2)_4NMe\}]$	−349	181
$[SnPhCl_2\{S_2CN(CH_2)_4O\}]$	−349	181
$[SnPh_2Br(S_2CNEt_2)]$	−343	153

TABLE III (*continued*)

Complex[a]	δ(^{119}Sn)	References
[Sn*n*-Bu_2{$S_2CN(Me)$*n*-Bu_2}]	−341	119
[$SnMe_2(S_2CNMe_2)_2$]	−338	112, 146, 147
[$SnMe_2${$S_2CN(CH_2)_4CHMe$}$_2$]	−336	143
[$SnMe_2(S_2CNEt_2)_2$]	−336	153
	−333	112, 146, 147
[Sn*n*-$Bu_2(S_2CNEt_2)_2$]	−336	153
[$SnMe_2${$S_2CN(CH_2)_5$}$_2$]	−335	143
[$SnMe_2${$S_2CN(CH_2)_4NMe$}$_2$]	−330	143
[$SnPh_2Cl(S_2CNEt_2)$]	−327	153
	−325; −340	117
[$SnPhCl_2${$S_2CN(CH_2)_4CHMe$}]	−326	181
[$SnMe_2${$S_2CN(CH_2)_4O$}$_2$]	−325	143
[Sn*n*-$BuCl_2${$S_2CN(CH_2)_4CHMe$}]	−299	181
[$SnMeCl_2(S_2CNEt_2)$]	−296	115
[Sn*n*-$BuCl_2${$S_2CN(CH_2)_5$}$_2$]	−293	181
[Sn*n*-$BuCl_2(S_2CNEt_2)$]	−285	131
[Sn*n*-$BuCl_2${$S_2CN(CH_2)_4NMe$}]	−283	181
[Sn*n*-$BuCl_2${$S_2CN(CH_2)_4O$}]	−273	181
[$SnMe_2${$S_2CN(CH_2)_4$}$_2$]	−267	121
[Sn*t*-$Bu_2(S_2CNEt_2)_2$]	−262	148
	−239	153
[$Sn(CH_2CH_2CO_2Me)_2Cl(S_2CNMe_2)$]	−259	190
[Sn*t*-$Bu_2(S_2CNMe_2)_2$]	−255	148
[{Sn*n*-$Bu(SCH_2CH_2O)(S_2CNMe_2)$}$_2$]	−251	199
[{Sn{$CH_2CH(CO_2Me)CH_2CO_2Me$}$(S_2CNMe_2)S$}$_2$]	−246	191
[{$Sn(CH_2CH_2CO_2Me)(S_2CNEt_2)S$}$_2$]	−233; −235	193
[{Sn*n*-$Bu(SCH_2CH_2O)${$S_2CN(CH_2)_5$}$_2$]	−231	199
[$Sn(CH_2CH_2CO_2Me)(S_2CNMe_2)S$}$_2$]	−230; −232	193
[Sn*t*-$Bu_2Cl(S_2CNEt_2)$]	−217	153
[Sn(*p*-tolyl)$_2(L^2)(S_2CNMe_2)$]	−211	176
[$SnPh_2L^3(S_2CNMe_2)$]	−202	116
[$SnMe_2Cl(S_2CNEt_2)$]	−201; −204	112, 153
[Sn*n*-$Bu_2Cl(S_2CNEt_2)$]	−200	153
[$SnPh_2L^4(S_2CNEt_2)$]	−198	116
[Sn{$CH_2CH_2CO_2Me$}{$(OCH_2CH_2)_2S$}(S_2CNMe_2)]	−196	192
[$SnPh_3(S_2CNEt_2)$]	−192	112, 117, 153
[$SnPh_3${$S_2CN(CH_2)_5$}]	−191	171
[$SnPh_3[S_2CN(CH_2)_2CHMe(CH_2)_2$]	−191	171
[$SnPh_3${$S_2CN(Me)$*n*-Bu}]	−190	119
[$SnPh_2L^3(S_2CNEt_2)$]	−183	116
[$SnPh_3${$S_2CN(CH_2)_2O(CH_2)_2$]	−182	171
[$Sn(CH_2CH_2CO_2Me){(SCH_2CH_2)_2O}(S_2CNMe_2)$]	−178	192
[$SnPh_3${$S_2CN(CH_2)_2NMe(CH_2)_2$}]	−176	171
[$SnMe_2(L^3)(S_2CNMe_2)$]	−174	176
[$SnCl_2${$S_2CN(CH_2)_4$}$_2$]	−140	121
[$SnMe_2(L^5)(S_2CNMe_2)$]	−139	176
[$SnPh_3${$S_2CN(CH_2)_4$}]	−131	121
[$SnPh_2L^6(S_2CNMe_2)$]	−128	116

TABLE III (*continued*)

Complex[a]	$\delta(^{119}Sn)$	References
$[SnMe_3\{S_2CN(CH_2)_2CHMe(CH_2)\}]$	17	171
$[SnMe_3\{S_2CN(CH_2)_5\}]$	20	171
$[SnMe_3(S_2CNEt_2)]$	21	153
$[Sn\textit{n}\text{-}Bu_3\{S_2CN(Me)\textit{n}\text{-}Bu\}]$	21	119
$[SnMe_3\{S_2CN(Me)\textit{n}\text{-}Bu\}]$	22	119
$[SnMe_3\{S_2CN(CH_2)_2NMe(CH_2)_2\}]$	23	171
$[SnMe_3(S_2CNMe_2)]$	25	112
$[SnMe_3\{S_2CN(CH_2)_2O(CH_2)_2\}]$	34	171

[a] Chemical shifts reported in ppm relative to $SnMe_4$ as an external standard. Data quoted at ambient temperature. L^1 = 1-(2-pyridylazo)-2-naphtholate. L^2 = 3-(2-pyridyl)-2-thienyl. L^3 = 2-(2-oxo-*N*-pyrrolidinyl)ethyl. L^4 = 2-ethylpyridine. L^5 = 2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl. L^6 = 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 $[N(SiMe_3)_2(S_2CNR_2)]$ (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_2CNEt_2)$_2$S}$_2$]	0.97	0.66	0.68	108
[SnPh{S_2CN(Me)*n*-Bu}$_3$]	1.11	1.81	1.63	121
[SnMe{S_2CN(Me)*n*-Bu}$_3$]	1.13	1.92	1.7	121
[Sn(*p*-tolyl)$_2$(L^1)(S_2CNMe_2)]	1.16	2.47	2.13	178
[SnPh$_2${$S_2CN(CH_2)_4$}$_2$]	1.2	1.7	1.42	91
[SnPh$_3${S_2CN(Me)*n*-Bu}]	1.23	1.79	1.46	121
[Sn*n*-Bu{S_2CN(Me)*n*-Bu}$_3$]	1.25	1.84	1.47	121
[SnPh$_2${S_2CN(Me)*n*-Bu}$_2$]	1.26	2.13	1.69	121
[SnPh$_2${2-(2-py)CH_2CH_2}(S_2CNEt_2)]	1.27	2.35	1.85	118
[SnPh$_2${2-(2-py)CH_2CH_2}(S_2CNMe_2)]	1.27	2.55	2.01	118
[SnPh$_2${2-(4-py)CH_2CH_2}(S_2CNMe_2)]	1.27	2.55	2.01	118
[SnMe$_3${S_2CN(Me)*n*-Bu}]	1.27	2.14	1.69	121
[SnMe$_2$(L^2)(S_2CNMe_2)]	1.27	2.59	2.04	178
[SnHex$_2$(S_2CNEt_2)$_2$]	1.29	3.02	2.34	147
[SnPh$_3${$S_2CN(CH_2)_4$}]	1.3	1.9	1.46	91
[SnPh$_2${2-(2-Oxo-*N*-pyr)CH_2CH_2}(S_2CNMe_2)]	1.3	2.18	1.68	118
[SnMe$_2$(L^1)(S_2CNMe_2)]	1.31	2.71	2.07	180
[Sn*n*-Bu$_3${S_2CN(Me)*n*-Bu}]	1.39	2.19	1.58	121
[SnMe$_2${S_2CN(Me)*n*-Bu}$_2$]	1.4	2.89	2.06	121
[SnHex$_2$(S_2CN*i*-Pr$_2$)$_2$]	1.4	2.83	2.02	147
[SnHex$_2${S_2CN(Me)Ph}$_2$]	1.42	2.89	2.04	147
[Sn*n*-Bu$_3${$S_2CN(CH_2)_4$}]	1.44	1.94	1.35	91
[SnMe$_2${$S_2CN(CH_2)_4$}$_2$]	1.44	2.84	1.97	91
[SnHex$_2$(S_2CNMe_2)$_2$]	1.45	2.96	2.04	147
[Sn*n*-Bu$_2$(S_2CNMe_2)$_2$]	1.49	2.93	1.97	147
[SnHex$_2${$S_2CN(CH_2)_2O(CH_2)_2$}$_2$]	1.51	2.89	1.91	147
[Sn*n*-Bu$_2${S_2CN(Me)*n*-Bu}$_2$]	1.52	2.89	1.9	121
[Sn*n*-Bu$_2${S_2CN(Me)Ph}$_2$]	1.55	2.68	1.73	147
[SnBz$_2${$S_2CN(CH_2)_4$}$_2$]	1.58	2.45	1.55	91
[SnOct$_2${$S_2CN(CH_2)_4$}$_2$]	1.58	2.92	1.85	91
[Sn*n*-Bu$_2$(S_2CNEt_2)$_2$]	1.59	2.71	1.7	147
[Sn*n*-Bu$_2${$S_2CN(CH_2)_4$}$_2$]	1.65	2.46	1.49	91
[SnEt$_2${$S_2CN(CH_2)_4$}$_2$]	1.65	2.83	1.72	89
[Sn*n*-Bu$_2$(S_2CN*i*-Pr$_2$)$_2$]	1.66	2.61	1.57	147
[Sn*n*-Bu$_2${$S_2CN(CH_2)_2O(CH_2)_2$}$_2$]	1.69	2.93	1.73	147
[Sn(S_2CNEt_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}. L^1 = 2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl. L^2 = 3-(2-pyridyl)-2-thienyl.

$N(SiMe_3)_2Br$ with the sodium salt of the appropriate dithiocarbamate, (2) reaction of $Na[N(SiMe_3)_2]$ with thiuram disulfides, and (3) reaction of $(SiMe_3)_2NMgBr$ with thiuram disulfides (202). The X-ray molecular structures show that the dithiocarbamates are essentially monodentate [N—S(short) ≈ 1.66 Å; N—S(long) ≈ 3.05 Å] with the amino nitrogen and dithiocarbamate coplanar (203). A variable temperature NMR study of the dimethyldithiocarbamate

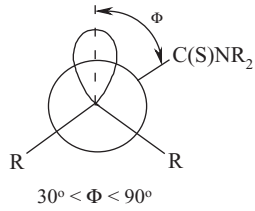

Figure 14. Newman projection showing the *gauche* arrangement of the P–S–C=S moiety in the complexes $[PR_2(S_2CNR'_2)]$.

complex indicates that the barrier to $(S_2)C-N(Me_2)$ 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 $[P(S_2CNMe_2)_3]$ (205), $[P(S_2CNEt_2)_3]$ (206), $[PPh(S_2CNEt_2)_2]$ (207, 208), and $[PPh_2(S_2CNEt_2)]$ (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 $[P(S_2CNMe_2)_3]$ 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 $[P(S)Ph_2(S_2CNEt_2)]$ adopts a similar structure to $[PPh_2(S_2CNEt_2)]$, 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, $[P(S)(OEt)_2(S_2CNR_2)]$ have been shown to display both antifungal and antiviral activity (210), although they are less active than classical organophosphorus reagents.

Bicyclic $P_4S_3I_2$ reacts with $[SnPh_3(S_2CNR_2)]$ or dithiocarbamic acids in the presence of dimethylamine to give $[P_4S_3I(S_2CNR_2)]$ or $[P_4S_3(S_2CNR_2)_2]$, depending on the stoichiometry (211). The dithiocarbamate ligands are bound in an essentially monodentate fashion, but variable temperature ^{31}P NMR

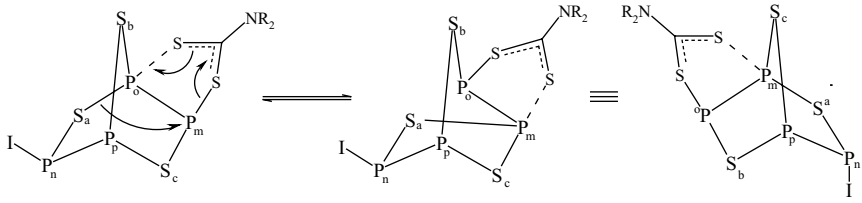

Figure 15. The skeletal rearrangement observed in $[P_4S_3I(S_2CNR_2)]$.

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, 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···Sb bridges, in the solid state. Thus, for example, while tris(diethanoldithiocarbamate)antimony(III) is monomeric (223), tris(diethydithiocarbamate)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···Sb = 3.47 Å (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

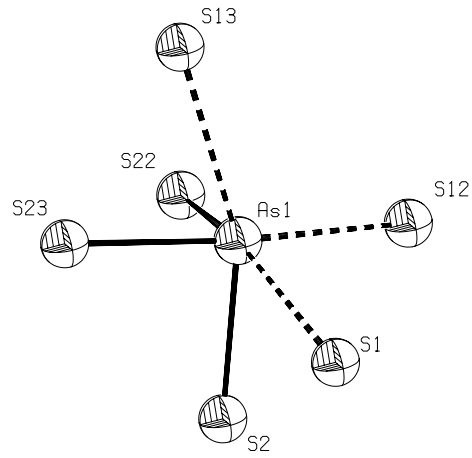

Figure 16. The ORTEP plot of the coordination sphere of As in the tris(dithiocarbamate) complexes $[As(S_2CNR_2)_3]$. The stereochemical active lone-pair caps the triangular face made by the three weakly bound S atoms, which are indicated by the dashed lines.

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 $[Sb(S_2CNMe_2)_2]^+$ and $[M(S_2CN\textit{n}\text{-}Bu_2)_2]^+$ (M = As or Sb) have also been prepared (246–248). The dithiocarbamate ligands are bond in an asymmetric fashion (ΔSb—S $\approx$ 0.16 Å). The metal is in a pyramidal coordination environment with the lone pair of electrons apical. In $[Sb(S_2CNMe_2)_2][CF_3SO_3]$, weak Sb$\cdots$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 $[Bi\{S_2CN(Me)CH_2CH_2OH\}_3]$ (224), $[Bi\{S_2CN(\textit{i}\text{-}Pr)CH_2CH_2OH\}_3]$ (225) and $[Bi\{S_2CN(Me)(Hex)\}_3]$ (240) are monomeric in the solid state, the tris(dithiocarbamate) complexes, $[Bi(S_2CNR_2)_3]$, 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 $[Bi_2\{S_2CN(CH_2CH_2OH)_2\}_6]$ 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 $[Bi_2\{S_2CN(Et)\textit{n}\text{-}Bu\}_6]$ (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.

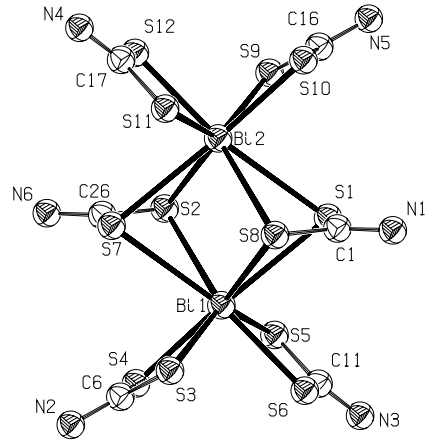

Figure 17. The ORTEP plots of $[Bi_2\{S_2CN(CH_2CH_2OH)_2\}_6]$. The N-substituents omitted for clarity.

The geometries at the two bismuth atoms in the pyrrolidinedithiocarbamate complex $[Bi_2\{S_2CN(CH_2)_4\}_6]$ are quite different (Fig. 18): One Bi atom is trigonal prismatic with a S atom capping one of the rectangular faces, while the other Bi atom lies approximately at the center of a pentagonal pyramid. The Bi···Bi distance is 4.264 Å (244).

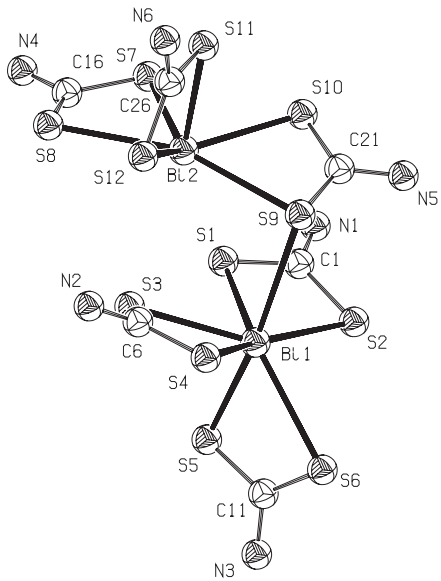

Figure 18. The ORTEP plot of $[Bi_2\{S_2CN(CH_2)_4\}_6]$ showing the two different Bi coordination environments. The N-substituents omitted for clarity.

The mixed tris(dithiocarbamate) complexes, $[Bi(S_2CNR_2)_2(S_2CNR'_2)]$ have been prepared by mixing $[Bi(S_2CNR_2)_3]$ and $[Bi(S_2CNR'_2)_3]$, although the rate of ligand scrambling is sufficiently slow to allow chromatographic separation of the complexes (220, 242). Ligand scrambling probably occurs via a dissociative route: The lability of the dithiocarbamate ligands is evidenced by mass spectrometry (219), in which the highest observable mass peaks in the tris(dithiocarbamate) complexes are due to the species $[M(S_2CNR_2)_2]^+$, and the ease by which the $[M(S_2CNR_2)_2]^+$ cation can be formed chemically (246–248). The same complexes can also be prepared by reaction of the halide complexes $[MX(S_2CNR_2)_2]$ with the appropriate dithiocarbamic acids or their salts (see below) (220, 249, 250).

Thermodynamic measurements on the tris(dithiocarbamate) complexes, $[M(S_2CNR_2)_3]$ (M = P, As, Sb, or Bi), show the M—S bond dissociation enthalpy decreases rapidly from P to As, then reduces more slowly down the group. The greater stability of the P—S bonds has been attributed to participation of $d(\pi)$–$d(\pi)$ bonding between phosphorus and sulfur (231–236). Thermal analytical studies (231, 232, 237–241) indicate that the complexes undergo thermal decomposition to yield various metal sulfides, such as M_2S_3, and the bismuth complexes have been used as single source precursors for the deposition of Bi_2S_3 (237–241). The tris(dithiocarbamate) complexes have also been shown to be useful lubricant additives, with excellent wear resistance properties even under extreme pressures (243). The complexation of dithiocarbamates to trivalent group 15 (V A) metal ions has been shown to be an effective method of preconcentration for the extraction and quantification of the metals in environmental samples (251, 252).

2. *Nonhomoleptic Bis(dithiocarbamate) Complexes*

Bis(dithiocarbamate) complexes of the type $[MR(S_2CNR_2)_2]$ and $[MX(S_2CNR_2)_2]$ (M = As, Sb, or Bi; R = alkyl, aryl, or organometallic group; X = halide) have also been studied extensively (212, 213, 219, 224, 241, 248, 253–270). The organyl complexes are prepared by reaction of the metal dihalides, RMX_2, with the appropriate dithiocarbamate salt (253, 254, 260–263, 266, 268). The As complexes are monomeric (263); the dithiocarbamate ligands are almost monodentate [As—S(short) $\approx$ 2.33 Å; As—S(long) $\approx$ 2.90 Å] and the metal center is thus best considered as possessing a pyramidal geometry, with the stereochemically active lone-pair apical.

The organoantimony and organobismuth bis(dithiocarbamate) complexes are structurally similar, forming dimers in the solid state via intermolecular M—S$\cdots$M bridges. The dimers are formed by the *side-on* docking of the $[MR(S_2CNR_2)_2]$ units (Fig. 19), such that the two metal and eight S atoms are essentially coplanar (255, 260, 261). The dithiocarbamate ligands are best

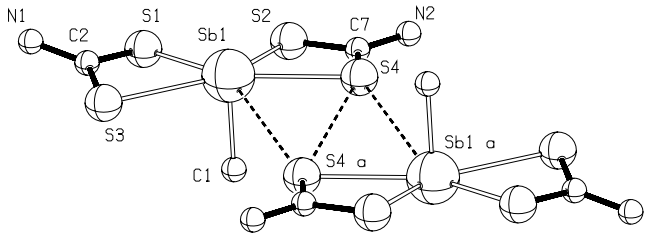

Figure 19. The PLUTON plot of $[SbMe(S_2CNEt_2)_2]$ showing the side-on docking of the molecular units found in the organyl complexes $[MR(S_2CNR_2)_2]$ (M = Sb or Bi). The dashed lines indicate intermolecular interactions. N substituents omitted for clarity.

considered as anisobidentate: The asymmetry in the M—S bonding decreases as the size of the metal increases. The overall geometry at the metal atom is pseudo-pentagonal bipyramidal, with the organyl group and the lone pair of electrons in axial positions.

Although monomeric, the Bi atom in $[BiR(S_2CNEt_2)_2]$ [{R = 2-(2′-pyridyl)-phenyl] is also pentagonal bipyramidal: The N atom of the pyridyl ring coordinates to the metal (Bi—N = 2.55 Å), completing the coordination sphere. The equatorial plane contains the four S atoms plus the nitrogen atom, with the C(phenyl) atom and stereochemically active lone pair in the axial positions (Fig. 20) (261).

The halide complexes $[MX(S_2CNR_2)_2]$ (M = Sb or Bi; X = Cl, Br, or I) have been prepared from both the trihalide, MX_3 (212, 213, 241), and the tris(dithiocarbamate) (219, 248) complexes. Several different structural motifs have been observed but, with the exception of $[SbCl\{S_2CN(CH_2)_4\}_2]$, which is monomeric

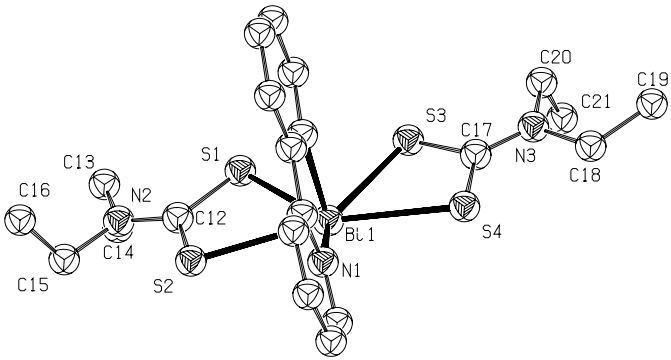

Figure 20. The ORTEP plot of $[BiL(S_2CNEt_2)_2]$; L = 2-(2′-pyridyl)phenyl. Atom labels for the ligand 2-(2′-pyridyl)phenyl omitted for clarity.

(265), all exhibit intermolecular interactions in the solid state. In all cases, the dithiocarbamate ligands are bound in an anisobidentate fashion: The degree of asymmetry is generally lower in the bismuth complexes. In solution, molecular mass measurements indicate the antimony species are monomeric, while the bismuth complexes retain a degree of association (213, 219): Both sets of complexes are non-electrolytes (213).

The iodide complexes, $[SbI(S_2CNEt_2)_2]$ (258), $[SbI\{S_2CN(CH_2)_4\}_2]$ (256) and $[BiI(S_2CNEt_2)_2]$ (257) form *zigzag* polymeric species in which metal moieties are linked by a single halide [Fig. 21(*a*)]. Although structurally similar,

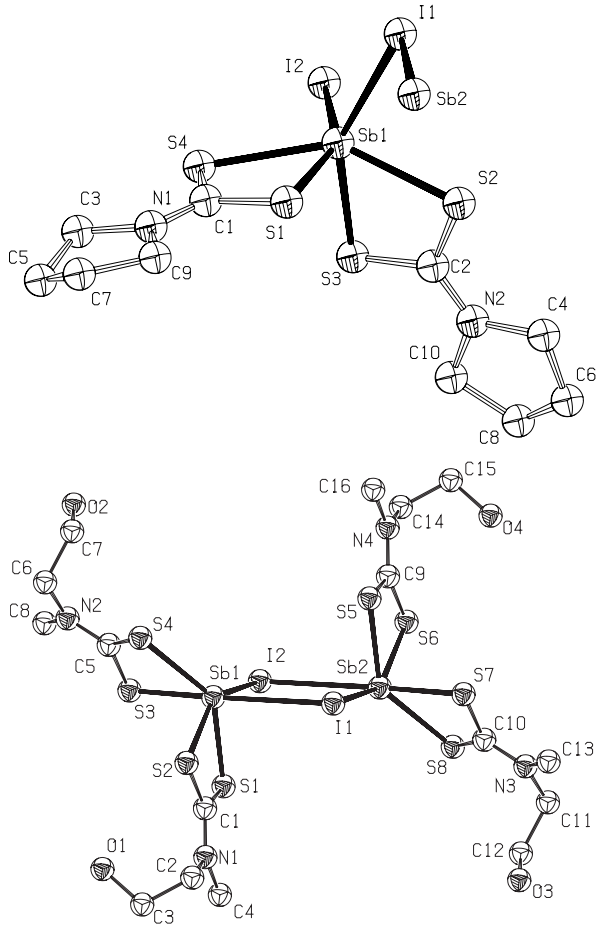

Figure 21. The two structural types observed in the iodide complexes $[MI(S_2CNR_2)_2]$ (M = Sb or Bi), exemplified by the ORTEP plots of (*a*) $[SbI\{S_2CN(CH_2)_4\}_2]$, showing part of the polymeric chain, and (*b*) $[SbI\{S_2CN(Me)CH_2CH_2OH\}_2]$.

there are a number of important differences between the antimony and bismuth diethydithiocarbamate complexes: In particular, the IMI bond angle is reduced from 135.8° in the antimony complex to just 89.7° in the Bi complex.

The complex $[SbI\{S_2CN(Me)CH_2CH_2OH\}_2]$ is structurally quite different (224). It is dinuclear in the solid state with the two $Sb(S_2CNR_2)_2$ units linked by a pair of iodides bridges [Fig. 21(*b*)]. In each of the above cases, the metal atom can be considered as being in a highly distorted octahedral coordination environment, with a stereochemically active lone-pair capping one of the faces.

The complex $[BiCl\{S_2CN(CH_2)_4\}_2]$ is also polymeric; however, both chloride and sulfur bridges are present, giving a pseudo-seven-coordinate metal center (241). The BiSBi and BiClBi bond angles are 90.9 and 97.1°, respectively. The two bridging Bi—S bonds are approximately equal (2.99 and 3.10 Å), as are the two Bi—Cl bonds (2.84 and 2.94 Å). The bromo compound $[BiBr(S_2CNEt_2)_2]$ is tetrameric in the solid state, with two distinctly different pairs of Br and Bi sites. One pair of the bromine atoms bridges two bismuth atoms, while the other bridges three atoms: Two of the Bi atoms are thus best described as being in a capped trigonal-prismatic environment, while the other two may be considered as being in a 5:2:1 pseudo-eight coordinate environment, including the stereochemically active lone pair (Fig. 22) (257). The dithiocarbamate ligands chelate to the metal centers in an asymmetric fashion.

Reaction of $BiCl_3$ with thiourea (tu) and ammonium pyrrolidinedithiocarbamate yields the dimeric Bi(III) complex, $[\{Bi(tu)S_2CN(CH_2)_4\}_2(\mu\text{-}Cl)_2]$ (244). The coordination environment at Bi is essentially pentagonal bipyramidal, with one Cl axial and the other equatorial. The Bi_2Cl_2 metallocycle is planar: The Bi···Bi distance is 4.603 Å.

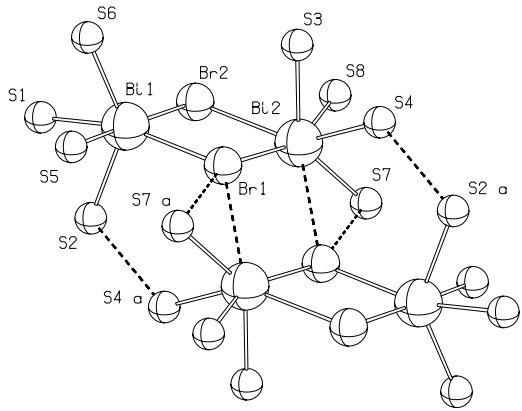

Figure 22. The PLUTON plot showing the different coordination spheres around the Bi atoms in the tetrameric complex $[BiBr(S_2CNEt_2)_2]$. Dashed lines indicate intermolecular interactions.

The halides are easily removed from the $[MX(S_2CNR_2)_2]$ complexes giving the homoleptic bis(dithiocarbamate) cations, $[M(S_2CNR_2)_2]^+$ (247, 248), and can be substituted for other ligands, such as a different dithiocarbamate, thiophosphates, xanthates, or β-diketonates, giving mixed-ligand complexes of the type $[M(S_2CNR_2)_2L]$, in which the metal atom is presumed to be hexacoordinate (220, 249, 250, 264, 270). The analogous mono(dithiocarbamate) complexes, $[M(S_2CNR_2)\{S_2P(OR')_2\}_2]$, can be prepared by reaction of $[MCl\{S_2P(OR)_2\}_2]$ with the appropriate dithiocarbamate salt (271, 272). Reaction of $[SbCl(S_2CNR_2)_2]$ with the sodium salts of either ethane-1,2-dithiolate or 4-methylbenzene-1,2-dithiolate (L) gives the dinuclear complexes $[\{Sb(S_2CNR_2)_2\}_2(\mu\text{-}L)]$ (269), analogous to the methylene bridged $[\{Sb(S_2CNR_2)_2\}_2(\mu\text{-}CH_2)]$ complexes (268). The antimony complexes $[SbCl(S_2CNR_2)_2]$ have also been shown to form stable 1:1 adducts with amines, revealing the metal center to be Lewis acidic (267).

3. Mono(dithiocarbamate) Complexes

A number of mono(dithiocarbamate) complexes of general formula $[MX_2(S_2CNR_2)]$ (M = As, Sb or Bi; X = Cl, Br, or I) have been reported (212, 273–279). The bismuth complexes have been the subject of particular interest because they exhibit interesting structural variations (274–279). The solid-state molecular structures adopted depend on the halogen and the conditions under which recrystallization is carried out. The complex $[BiI_2(S_2CNEt_2)]$ crystallizes by slow diffusion of *n*-butanol into a dimethylformamide (DMF) solution as an infinite polymeric array, $[BiI_2(S_2CNEt_2)]_\infty$, in which each pair of Bi atoms is bridged by two iodides and one S atom of the dithiocarbamate, which chelates in a slightly asymmetric fashion (274). Under identical conditions, the chloro- and bromo-analogues crystallize as the pentanuclear species $[Bi_5X_7(S_2CNEt_2)_8]$, in which one of the Bi atoms is bound to six chlorides, giving an octahedral $[BiX_6]^{3-}$ unit at the core of the array (276), but from acetonitrile (277) they crystallize as the polymeric $[BiX_2(S_2CNEt_2)]_\infty$ species, which are isomorphous with the iodo analogue, $[BiI_2(S_2CNEt_2)]_\infty$. Conversely, slow evaporation of a DMF/*n*-butanol solution of $[BiI_2(S_2CNEt_2)]$ gives $[Bi_5I_7(S_2CNEt_2)_8]$ (276).

Crystallization of $[BiI_2(S_2CNEt_2)]$ from DMF with a stoichiometric amount of tetraethylammonium iodide or bromide gives the isostructural complexes $[NEt_4]_2[\{BiI_2(S_2CNEt_2)\}_2(\mu\text{-}I)_2]$ and $[NEt_4]_2[BiI_2(S_2CNEt_2)(\mu\text{-}I)_2BiBrI(S_2CNEt_2)]$ (Fig. 23), respectively: The anions are centrosymmetric with Bi···Bi distances of 4.75 and 4.68 Å (275). Crystallization of $[BiX_2(S_2CNEt_2)]$ (X = Cl, Br, or I) from Py yields the monocular tris(pyridine) adducts, $[BiX_2(S_2CNEt_2)(py)_3]$ (278), while crystallization by slow evaporation of a Py/*n*-butanol solution, gives the tetranuclear $[Bi_4(S_2CNEt_2)_4Br_{10}]^{2-}$ anion as its pyridinium

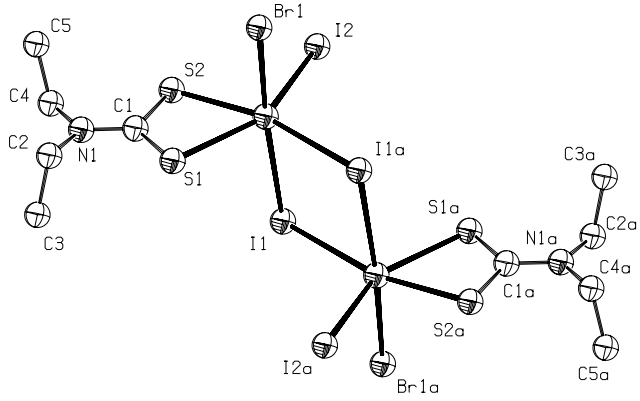

Figure 23. The ORTEP plot of $[NEt_4]_2[BiI_2(S_2CNEt_2)(\mu\text{-}I)_2BiBrI(S_2CNEt_2)]$. Cations omitted for clarity.

salt (276). The three Py adducts (X = Cl, Br, or I) are isomorphous. The Bi atom is in a distorted pentagonal bipyramidal coordination environment, with the two halides axial ($\angle$ XBiX $\approx$ 170–175°): there is no evidence of a stereochemically active lone pair. The pyridines are loosely bound, with the Bi—N distances (2.7–2.8 Å) slightly longer than the Bi—N(py) distance in $[BiL(S_2CNEt_2)_2]$ [L = 2-(2′-pyridyl)phenyl] (261). The 1:1 adducts of $[BiX_2(S_2CNEt_2)]$ with 2,2′-bipyridyl (bpy) and 2,2′:6′,2″-terpyridyl (terpy) have also been prepared (279). The terpy analogue (Fig. 24) is essentially isostructural with the tris(pyridine) adduct, while the bpy adduct crystallizes as the halide bridged dimer, $[\{Bi(S_2CNEt_2)(bpy)\}_2(\mu\text{-}X)_2]$. The geometry at the Bi atom in

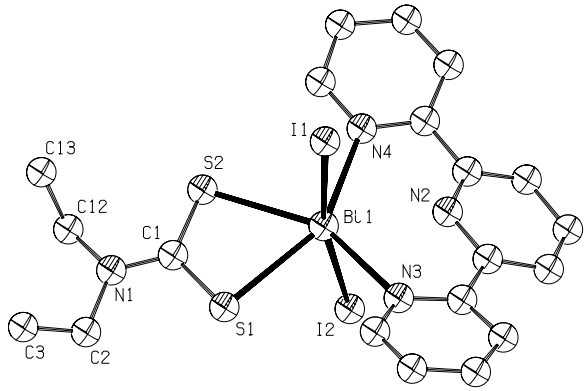

Figure 24. The ORTEP plot of $[BiI_2(S_2CNEt_2)(terpy)]$. Carbon atom labels on 2,2′:6′,2″-terpyridyl ligand have been omitted for clarity.

$[\{Bi(S_2CNEt_2)(bpy)\}_2(\mu\text{-}X)_2]$ is best described as pentagonal bipyramidal, the equatorial plane being defined by the two S atoms of the dithiocarbamate, one N donor of bpy and the two bridging halides. In all cases, the dithiocarbamate ligands are bound in an essentially symmetrical fashion.

Formal substitution of the two halides in the $[MX_2(S_2CNR_2)]$ (M = As or Sb) with a dithiolate ligand gives the mononuclear complexes $[M(S^{\frown}S)(S_2CNR_2)]$ ($S^{\frown}S$ = ethane-1,2-dithiolate, 4-oxaheptan-1,7-dithiolate, or 4-thiaheptan-1,7-dithiolate) (280–283) in which the dithiocarbamate is highly anisobidentate (281). The analogous phenoxyarsinyl complexes $[As\{(C_6H_4)_2O\}(S_2CNR_2)]$, prepared by reaction of $[AsCl\{(C_6H_4)_2O]$ with the sodium salt of the appropriate dithiocarbamic acid, have also been reported (284). The X-ray molecular structure of the pyrrolidinedithiocarbamate complex $[As\{(C_6H_4)_2O\}\{S_2CN(CH_2)_4\}]$ again shows the dithiocarbamate to be highly anisobidentate [As—S(short) = 2.28; As—S(long) = 3.18 Å]. If both S atoms are included in the arsenic coordination sphere, the arsenic atom can be considered as having a highly distorted trigonal-bipyramidal geometry: The equatorial plane is defined by one C atom, one S atom, and the stereochemically active lone pair. The dihedral angle between the arene rings of the phenoxyarsine moiety is 155.2°. Hydrogen-1 and ^{13}C solution NMR data show that the dithiocarbamate N substituents are inequivalent, consistent with the dithiocarbamate ligand being nonlabile on the NMR chemical shift time scale and with restricted rotation about the $(S_2)C—N$ bond.

Few mono(dithiocarbamate) complexes of the type $[MR_2(S_2CNR'_2)]$ and $[MRX(S_2CNR'_2)]$ (M = As or Sb; R = Me or Ph; X = Cl or Br) have been reported (262, 285, 286). The NMR and IR spectroscopy, as well as molecular mass data, are consistent with the species being monomeric in solution and the dithiocarbamate ligand bidentate: The complexes have therefore been assigned as possessing pentagonal-bipyramidal structures (assuming a stereochemically active lone pair) in solution (262, 286). However, ^{121}Sb Mössbauer spectroscopy indicates that the Sb atom is more likely to be pyramidal in the solid state, with the lone pair of electrons apical and the dithiocarbamate ligand essentially monodentate (214). Conductimetry measurements on the arsenic(III) diiodide complex $[AsI_2Me(S_2CNMe_2)]$, which is prepared by the reaction of tetramethylthiuram disulfide with AsI_2Me, show it is ionic in solution, although data are inconsistent with a simple 1:1 electrolyte (285). The X-ray structure reveals a two-dimensional (2D) network (Fig. 25), in which $I—As—I\cdots I_2\cdots I—As—I$ chains are $I\cdots As\cdots I$ cross-linked: The dithiocarbamate ligand is essentially isobidentate (As—S = 2.31–2.35 Å).

The As(III), Sb(III), and Bi(III) complexes $[ML_3XY]$, $[ML_2XY_2]$, and $[M_2LX_5Y_2]$ (L = $S_2CN(H)o\text{-}C_6H_4Me$; X and Y = neutral or anionic ligands) have been screened for their antifungal activities. Although a number of the complexes, and in particular those in which a chloride ligand is present, display some activity, it is, in all cases, limited (287).

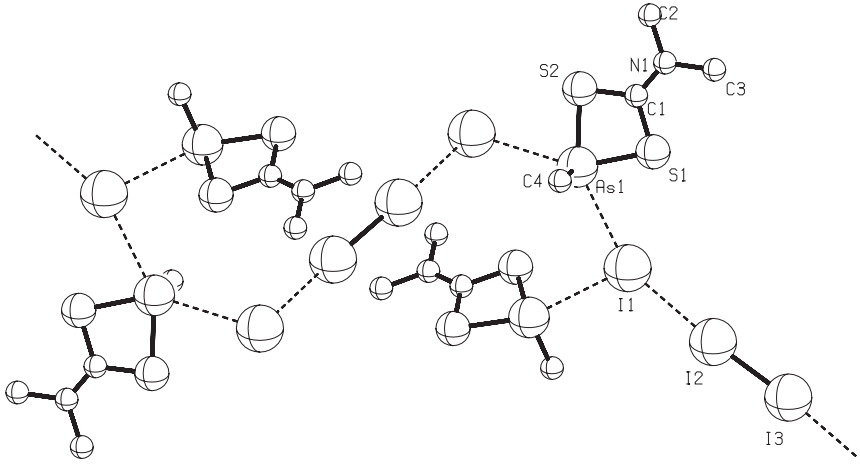

Figure 25. The PLUTON plot of $[AsI_2Me(S_2CNMe_2)]$ showing the 2D network of I···As···I cross-linked I–As–I···I_2···I–As–I chains. Intermolecular interactions are indicated by dashed lines.

4. Antimony(V) Complexes

The antimony(V) complexes $[SbMe_3(S_2CNR_2)_2]$ (288, 289), $[\{SbMe_3(S_2CNR_2)\}_2(\mu\text{-O})]$ (290), and $[SbAr_4(S_2CNR_2)]$ (Ar = phenyl or *p*-tolyl) (291, 292) have been prepared from the reaction of corresponding antimony halides (or dihalides) with the appropriate dithiocarbamate salts, although the reaction of $SbPh_3Cl_2$ with sodium diethyldithiocarbamate gave triphenylantimony(III), $SbPh_3$, and tetraethylthiuram disulfide (291). The dithiocarbamate ligands in $[SbMe_3(S_2CNMe_2)_2]$ are highly anisobidentate [Sb–S(short) = 2.61 (ave); Sb–S(long) = 3.30 Å (av)] (average = av) (289), whereas in $[SbPh_4(S_2CNMe_2)]$ (291) and $[SbAr_4(S_2CNEt_2)]$ (Ar = phenyl or *p*-tolyl) (292) there is little asymmetry. The geometry at Sb in $[SbMe_3(S_2CNMe_2)_2]$ is essentially trigonal bipyramidal, while in $[SbPh_4(S_2CNMe_2)]$ and $[SbAr_4(S_2CNEt_2)]$, it is octahedral.

5. Antimony-121 Mössbauer Spectroscopy

The ^{121}Sb Mössbauer spectra of a number of antimony dithiocarbamate complexes have been recorded (214, 246, 289): Data are reported in Table V. Data are difficult to interpret because subtle changes in the ligands can produce significant changes in the geometry at the metal atom, and examination of Table V does not reveal any clear correlation of the spectral parameters with the known structures.

TABLE V
Antimony-121 Mössbauer Data for Antimony Dithiocarbamate Complexes

Complex[a]	Geometry[b] at Sb	IS	QS	η	ρ	References
$[Sb(S_2CNn\text{-}Bu_2)_2][I_3]$	dtbp	−5.5	9.4	0.5	−1.7	214, 246
$[Sb(S_2CNn\text{-}Bu_2)_2]\cdot 0.5[Cd_2I_6]$	dtbp	−6.4	10.3	0.0	−1.6	214, 246
$[Sb(S_2CNEt_2)_3]$	ddh	−6.9	7.5	0.0	−1.1	214
		−6.8	7.8	0.0	−1.1	
$[Sb(S_2CNn\text{-}Bu_2)_3]$	ddh	−6.4	7.8	0.2	−1.2	214
$[SbCl(S_2CNEt_2)_2]$		−6.0	10.6	0.4	−1.8	214
$[SbBr(S_2CNEt_2)_2]$		−6.2	9.9	0.3	−1.6	214
$[SbI(S_2CNEt_2)_2]$	doh	−5.8	9.3	0.4	−1.6	214
$[SbCl_2(S_2CNEt_2)]$		−5.9	13.3	0.1	−2.3	214
$[SbBr_2(S_2CNEt_2)]$		−7.2	10.6	0.2	−1.5	214
$[SbI_2(S_2CNEt_2)]$		−7.2	8.1	0.0	−1.1	214
$[SbPh(S_2CNEt_2)_2]$	dpby	−4.1	22.2	0.2	−5.4	214
$[SbMe(S_2CNEt_2)_2]$	dpby	−4.0	25.1	0.2	−6.3	214
$[SbPh_2(S_2CNEt_2)]$		−2.5	20.0	1.0	−8.0	214
$[SbMe_3(S_2CNEt_2)_2]$	dtbp	2.7	−17.4	0.4	−6.4	214, 289
$[SbMe_4(S_2CNEt_2)]$	doh[c]	3.0	−2.1		−0.7	214

[a] IS = Isomer shift quoted in millimeters per second (mm s^{-1}) relative to InSb; QS = quadrupole splitting (in mm s^{-1}); η = asymmetry parameter; ρ = (QS/IS).
[b] From X-ray data where available. dtpy = distorted trigonal bipyramidal; ddh = distorted dodecahedral; dpby = distorted pentagonal bipyramidal; doh = distorted octahedral.
[c] Distorted octahedral geometry assumed on the basis that $[SbPh_4(S_2CNEt_2)]$ possesses a distorted octahedral geometry.

VI. GROUP 16 (VI A)

There are no oxygen dithiocarbamate complexes and, although dithiocarbamates do bond to sulfur, forming thiurams, these are considered as a separate class of compound and fall outside the scope of this chapter. While the dithiocarbamate complexes of selenium remain relatively few in number, those of tellurium have been studied more extensively, with particular attention being paid to the different possible coordination numbers and geometries displayed by the metal atom.

A. Homoleptic and Mixed Bidentate Ligand Complexes

Reaction of selenium(IV) dioxide with sodium dithiocarbamate salts yields the homoleptic selenium(II) bis(dithiocarbamate) complexes $[Se(S_2CNR_2)_2]$ (293–297). No selenium(IV) dithiocarbamate complexes appear to have been authenticated and dithiocarbamate ligands have been successfully employed as a method of separating selenites from selenates (298), as well as from other metal

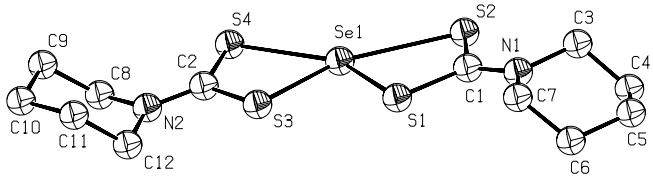

Figure 26. The ORTEP plot of $[Se\{S_2CN(CH_2)_5\}_2]$, showing the planar trapezoidal geometry at the metal center in the $[Se(S_2CNR_2)_2]$ complexes.

ions (299). The two dithiocarbamate ligands in the $[Se(S_2CNR_2)_2]$ complexes coordinate in an anisobidentate fashion [Se—S(av) = 2.31 (short) and 2.77 Å (long)]: The two S atoms with the short Se—S contacts are cis. The geometry at Se is planar trapezoidal (Fig. 26). Molecular mass measurements show that the complexes are monomeric in solution, and conductimetry and magnetic susceptibility measurements show them to be diamagnetic, non-electrolytes (293, 294).

Reaction of $[Se(S_2CNR_2)_2]$ with either bromine or iodine leads to the oxidative displacement of one of the dithiocarbamate ligands, yielding polymeric $[SeX(S_2CNR)]_\infty$, with the halide bridging and the dithiocarbamate bound in an essentially isobidentate fashion (ΔSe—S < 0.05 Å) (300, 301). The geometry at Se is, again, best described as planar trapezoidal (SSeS $\approx 77°$; XSeX $\approx 129°$). In solution, the complexes are only stable in the presence of the appropriate hydrohalic acid, HX (X = Br or I). The stability of the complexes increases as the size of the halogen increases; the corresponding chloro complex, $[SeCl(S_2CNR)]$, undergoes rapid decomposition via CS_2 elimination even in the presence of HCl (300).

Homoleptic dithiocarbamate complexes of both tellurium(II) (215, 293, 294, 296, 302–311) and tellurium(IV) (293, 294, 296, 302, 304–306, 309, 310, 312–315) are well known. The molecular structures of the bis(dithiocarbamate)tellurium(II) compounds, $[Te(S_2CNR_2)_2]$, are analogous to those of the corresponding Se compounds: The Te atom exhibits a planar trapezoidal coordination geometry, with the two dithiocarbamate ligands bound in an anisobidentate fashion [Te—S(ave) = 2.52 (short) and 2.83 Å (long)]. Tellurium(II) has a tendency for pentacoordination and, with the exception of $[Te(S_2CNCy_2)_2]$, which is monomeric (311), there is a short intermolecular Te···S contact (av 3.56 Å; cf. sum of van der Waals radii 3.86 Å) in the solid state, leading to the formation of weakly bound dimers. The geometry at Te atom in these complexes is thus described best as pentagonal bipyramidal with the five S atoms in the equatorial plane and the two, stereochemically active lone pairs axial. The mixed dithiocarbamate–xanthate complex, $[Te(S_2CNEt_2)(S_2COEt)]$ (316), is structurally analogous to the parent bis(dithiocarbamate) complex, $[Te(S_2CNEt_2)_2]$ (317). Like their Se analogues, all complexes are monomeric, diamagnetic, non-electrolytes in solution (293, 294).

The weak intermolecular Te···S interaction in the solid-state structures of the bis(dithiocarbamate)tellurium(II) complexes suggest that other ligands may be able to coordinate to the Te atom: This is indeed the case. The complexes $[Te(S_2CNEt_2)_2]$ and $[Te(S_2CN\textit{i}\text{-}Pr_2)_2]$ have been shown to form hemi-adducts with 4,4′-bipyridyl (4,4′-bpy) (318). The structure of $[\{Te(S_2CNEt_2)\}_2(\mu\text{-}4,4'\text{-bipy})]$ has been determined by X-ray crystallography. The geometry at each Te is pentagonal bipyramidal; the N and four S atoms lie in the equatorial plane and the two stereochemically active lone pairs are axial. The Te—N bonds are weak (2.70 Å) and the complexes are unstable with respect to loss of bpy.

With the exception of perchloric acid media, in which tris(dithiocarbamate)tellurium(IV) perchlorate species are formed (319), TeO_2 reacts with dithiocarbamate salts under acidic conditions to give the intensely colored homoleptic tetrakis(dithiocarbamate)tellurium(IV) complexes, $[Te(S_2CNR_2)_4]$. The intense coloration results form ligand-to-metal charge transfer (LMCT) bands in the visible region (293).

The $[Te(S_2CNR_2)_4]$ complexes are generally unstable. The complexes undergo facile decomposition to the corresponding bis(dithiocarbamate)tellurium(II) complex and thiuram disulfide. It has been suggested (320) that the mechanism of decomposition involves interligand S—S bond formation between the two spatially close S atoms, followed by cleavage of the corresponding Te—S bonds. This mechanism may be the dominant process, but the differences in the relative stabilities of the complexes do not correlate well with the (small) structural variations observed; other factors, such as the reducing ability of the ligand and intermolecular interactions, are also likely to play a role.

Despite their instability, several $[Te(S_2CNR_2)_4]$ complexes have been characterized crystallographically (312–315). In all cases, the Te atom possesses a slightly distorted dodecahedral geometry (Fig. 27), in which all eight S atoms are coordinated and the lone pair is stereochemically inert. A regular dodecahedron can be considered as being comprised of two interleaved, perpendicular trapezoids: The angles between the two planes in the dithiocarbamate complexes are 90° (*N*-2-hydroxyethyl-*N*-methyldithiocarbamate) (312), 86.5° (di-2-hydroxyethyldithiocarbamate) (313), 87.6° (diisopropyldithiocarbamate) (314) and 89.6° (diethyldithiocarbamate) (315). The trapezoidal planes are similar to those observed in the bis(dithiocarbamate)tellurium(II) complexes.

The attempted isolation of the cationic Te(IV) species $[Te(S_2CNEt_2)_3]^+$ by the substitution of the weakly coordinating perchlorate ligand in $[Te(S_2CNEt_2)_3][ClO_4]$ (319) with the hexafluorophosphate anion gave the mixed-valence species $[\{Te^{IV}(S_2CNEt_2)_3\}_2\{Te^{II}(S_2CNEt_2)_2\}][PF_6]_2$ (321), in which the $[Te(S_2CNEt_2)_2]$ moiety is sandwiched between the two $[Te(S_2CNEt_2)_3]^+$ units, held together by weak Te···Te (3.39 Å) and Te···S interactions (Fig. 28): the TeTeTe bond angle is 161.4°. The perchlorate complex, $[\{Te^{IV}(S_2CNEt_2)_3\}\{Te^{II}(S_2CNEt_2)_2\}][ClO_4]$ is also comprised of $[Te(S_2CNEt_2)_2]$ and

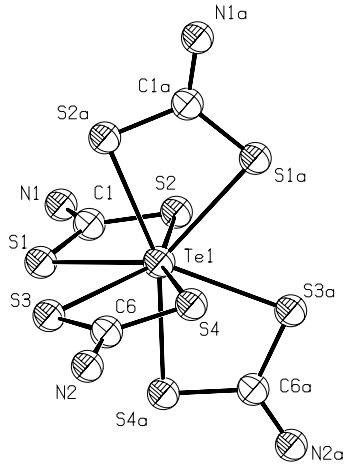

Figure 27. The ORTEP plot of $[Te(S_2CNEt_2)_4]$, showing the distorted dodecahedral geometry at Te in the tetrakis(dithiocarbamate) complexes $[Te(S_2CNR_2)_4]$. The N substituents omitted for clarity.

$[Te(S_2CNEt_2)_3]^+$ units, but in a 1:1 ratio, again held together by secondary Te···Te and Te···S contacts (321).

Dithiocarbamate ligands do not appear to complex tellurium(VI) and have been used successfully to separate aqueous mixtures of Te(IV) and Te(VI) (322).

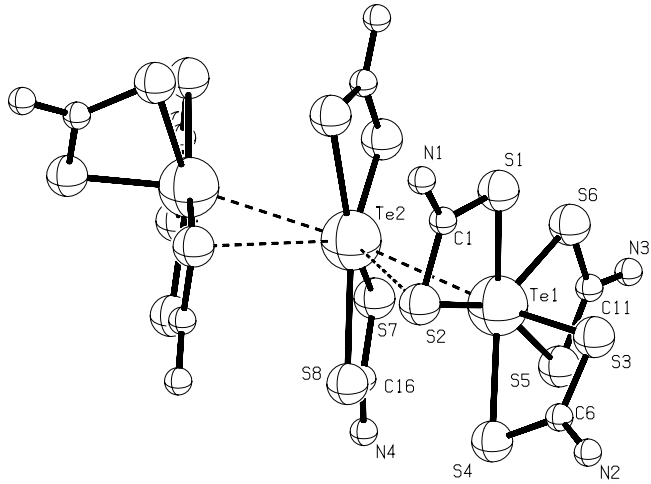

Figure 28. The PLUTON plot of $[\{Te^{IV}(S_2CNEt_2)_3\}_2\{Te^{II}(S_2CNEt_2)_2\}][PF_6]_2$. The PF_6 counterions omitted for clarity. Intermolecular interactions are indicated by dashed lines.

B. Nonhomoleptic Tellurium(II) Complexes

Formation of nonhomoleptic complexes by substitution of one of the dithiocarbamate ligands in the $[Te(S_2CNR_2)_2]$ complexes is generally difficult because of the strength of the Te—S bonds and is often only feasible when electron-withdrawing substituents, such as CH_2CH_2OH, are attached to the dithiocarbamate. However, improvements in synthetic methodologies have enabled organyl, halide and pseudo-halide substituted analogues to be prepared (309, 323–332).

The organic ligands in the $[TeR(S_2CNR'_2)]$ complexes [R = 2-phenylazophenyl, R′ = Me or Bz (323); R = 2-(2-quinolinyl)phenyl, R′ = Et (324); R = 2-(2-pyridyl)phenyl, R′ = Me (325); R = 8-(dimethylamino)-1-naphthyl, R′ = Et (331)] are C,N coordinated in the solid state, with the dithiocarbamate ligand highly anisobidentate: The Te—S distances are in the range 2.52–2.57 (short) and 3.23–3.67 Å (long). Two distinct geometries at Te are apparent (Fig. 29). In

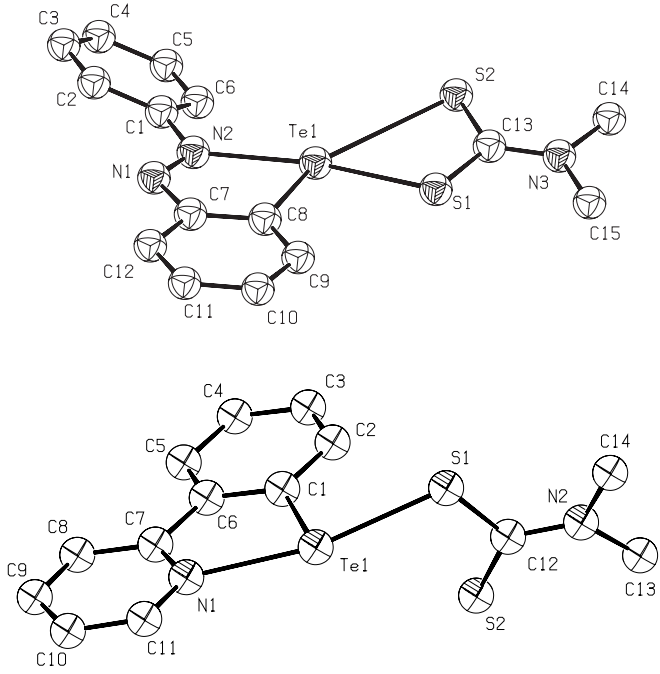

Figure 29. The ORTEP plots of (*a*) $[TeR(S_2CNMe_2)]$ (R = 2-phenylazophenyl) and (*b*) $[TeR(S_2CNMe_2)]$ [R = 2-(2-pyridyl)phenyl], showing the two types of coordination geometry exhibited by Te in the $[TeR(S_2CNR'_2)]$ complexes [R = 2-phenylazophenyl, 2-(2-quinolinyl)phenyl, 2-(2-pyridyl)phenyl or 8-(dimethylamino)-1-naphthyl].

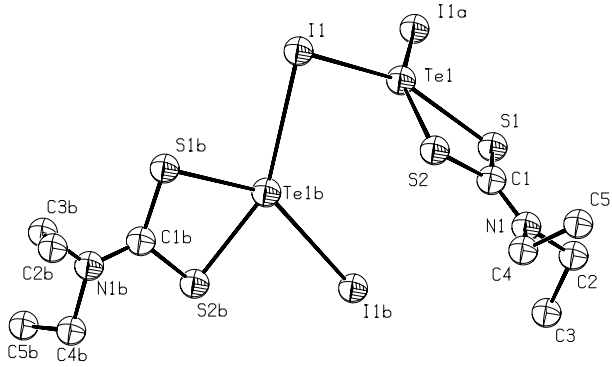

Figure 30. The ORTEP plot of $[TeI(S_2CNEt_2)_2]$, showing a section of the polymeric chain arrangement in the tellurium(II) complexes$[TeI(S_2CNR_2)]$.

the 2-phenylazophenyl and 8-(dimethylamino)-1-naphthyl complexes, the Te atom has a planar-trapezoidal geometry, with the two lone pairs above and below the plane, whereas in the 2-(2-quinolinyl)phenyl and 2-(2-pyridyl)phenyl complexes, in which the dithiocarbamate is essentially monodentate, the geometry is best considered as distorted trigonal planar.

The iodo-complex $[TeI(S_2CNEt_2)]$ can be prepared by reduction of $[TeI_2(S_2CNEt_2)_2]$ with elemental Te (327). The corresponding chloro and bromo complexes, $[TeX(S_2CNEt_2)]$, can be prepared by halide substitution, using AgX (X = Cl or Br) (329). In the solid state the halide bridges two Te atoms, forming a helical polymeric arrangement (Fig. 30). The TeI_2S_2 core is essentially planar, with the dithiocarbamate ligand coordinated in an anisobidentate fashion. There is an intermolecular Te $\cdots$ Te contact [distances vary from 3.88 (I) to 3.65 Å (Cl) (av = 3.76 Å)], indicating a weak bonding interaction (sum of van der Waals radii = 4.12 Å) and a long-range intermolecular Te $\cdots$ S interaction (average 3.74 Å).

The $[TeX(S_2CNEt_2)]$ compounds (X = Br or I) react with tetraethylammonium halide salts or phen, giving $[TeX_2(S_2CNEt_2)][NEt_4]$ and $[TeX_2(S_2CNEt_2)][H(phen)_2]$ (where X = Br or I), respectively; the corresponding chloro complexes are not formed (330). The Te atom in the $[TeX_2(S_2CNEt_2)]^-$ anion displays a planar trapezoidal coordination geometry as a consequence of the small bite angle of the dithiocarbamate ligand (av = 69.9°); the corresponding XTeX angle is (av) 126.7°. The almost isobidentate dithiocarbamate [ΔTe—S(av) = 0.04 Å] exerts a strong trans influence, weakening the Te—X bonds: Te—X(av) = 3.09 Å (I) and 2.95 Å (Br) [cf. sum of covalent radii: 2.70 Å (TeI); 2.43 Å (TeBr)].

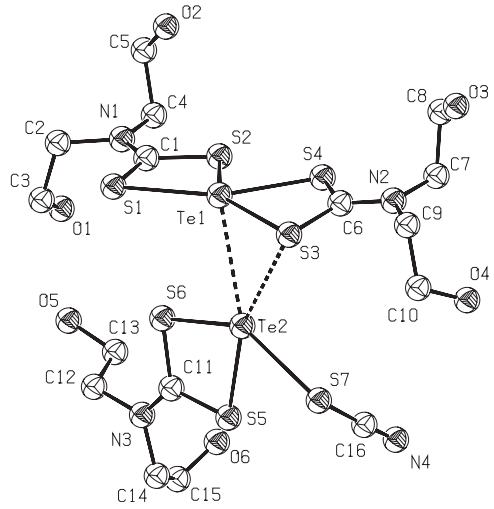

Figure 31. The ORTEP plot of $[Te_2(SCN)(S_2CNR_2)_3]$. Intermolecular contacts are indicated by dashed lines.

Reaction of $[Te\{S_2CN(CH_2CH_2OH)_2\}_2]$ with a large excess of KX (X = Br, I, or SCN) gives complexes of general formula $[Te_2X(S_2CNR_2)_3]$ (328). X-ray crystallography of the thiocyanato complex reveals a 1:1 adduct of $[Te\{S_2CN(CH_2CH_2OH)_2\}_2]$ and $[Te(SCN)\{S_2CN(CH_2CH_2OH)_2\}]$ held together by weak Te···Te (3.22 Å) and Te···S (3.48 Å) intermolecular interactions between the two moieties: Both Te atoms are thus pseudo-five coordinate (Fig. 31). The $[Te\{(S_2CN(CH_2CH_2OH)_2\}_2]$ moiety differs little chemically from that in the pure crystalline material (313). The dithiocarbamate ligand is bound in an isobidentate fashion in the $[Te(SCN)\{S_2CN(CH_2CH_2OH)_2\}]$ unit [Δ(Te–S) < 0.01 Å], which is also essentially planar: The dihedral angle between the TeS_4 and TeS_3 planes is 99.6°. The thiocyanato ligand is S bonded to Te.

Addition of sodium diethyldithiocarbamate or dimethyldithiocarbamate salts to the aryl complexes $[TeRL_2]Cl$ (R = 4-hydroxyphenyl, 4-methoxyphenyl, or 4-ethoxyphenyl; L = benzaldehyde or salicylaldehyde) leads to the displacement of both the chloride and the aldehyde ligand, yielding complexes of general formula $[TeR(S_2CNR'_2)][NaS_2CNR'_2]$ (R′ = Me or Et), in which it has been suggested the sodium dithiocarbamate is closely associated with the $[TeR(S_2CNR'_2)]$ moiety, presumably via an η^1 Te—S bonding mode (326). The structures of these complexes have yet to be confirmed by crystallography.

The complex $[Te_2I_3(S_2CN\textit{i}\text{-}Pr_2)_3]$ is a 1:1 adduct of the Te(IV) complex $[TeI_2(S_2CN\textit{i}\text{-}Pr_2)_2]$ and the Te(II) complex $[TeI(S_2CN\textit{i}\text{-}Pr_2)]$, in which the two Te units are bridged by an iodine atom (Fig. 32) (332). There is a weak Te···Te

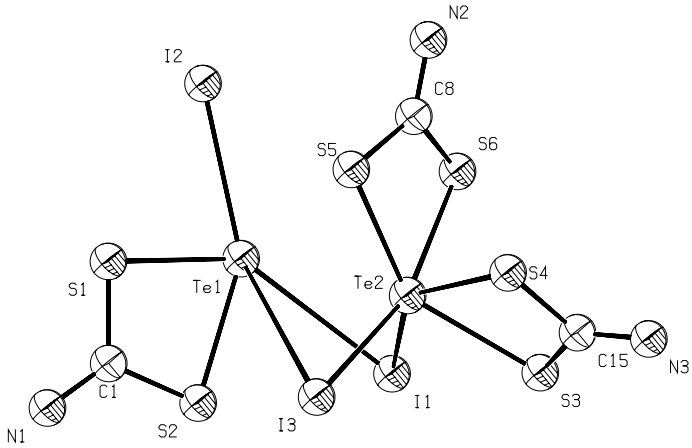

Figure 32. The ORTEP plot of $[Te_2I_3(S_2CN\textit{i}\text{-}Pr_2)_3]$, which is a 1:1 adduct of the tellurium(II) species $[TeI(S_2CN\textit{i}\text{-}Pr_2)]$ and the tellurium(IV) species $[TeI_2(S_2CN\textit{i}\text{-}Pr_2)_2]$. The N substituents omitted for clarity.

interaction (3.542 Å), so that the coordination geometries at both Te(II) and Te(IV) are best considered as distorted pentagonal bipyramidal: The stereochemically active lone pairs on Te(II) are axial. The Te—S bond lengths are 2.44 and 2.56 Å for Te(II) and for Te(IV), the Te—S bond lengths 2.48 and 2.55 (short), and 2.65 and 2.58 Å (long).

C. Nonhomoleptic Tellurium(IV) Complexes

1. Tris(dithiocarbamate) Complexes

Formal substitution of one of the dithiocarbamates in $[Te(S_2CNR_2)_4]$ by a uninegative ligand gives seven coordinate Te(IV) complexes of general formulas $[TeR(S_2CNR_2)_3]$ and $[TeX(S_2CNR_2)_3]$ (R = aryl; X = halide or pseudohalide) (293, 304, 309, 312, 319, 323, 333–342). In all cases the geometry at Te is distorted pentagonal bipyramidal, with the uninegative ligand (R or X) axial and one dithiocarbamate ligand spanning axial and equatorial positions. The bite angle of the dithiocarbamate ligand (mean STeS bond angle is 66.6°) is too small for the S atoms to be simultaneously in truly axial and equatorial positions and, consequently, two structural types can be distinguished (Fig. 33): (1) one of the S atoms is essentially axial (av $R/XTeS_{ax}$ angle = 171.5°) while the other is positioned below the equatorial plane and (2) one of the S atoms is in the equatorial plane, while the other is pulled away from a true axial position, reducing the $R/XTeS_{ax}$ bond angle to ∼144.3° (av). As the electronegativity of

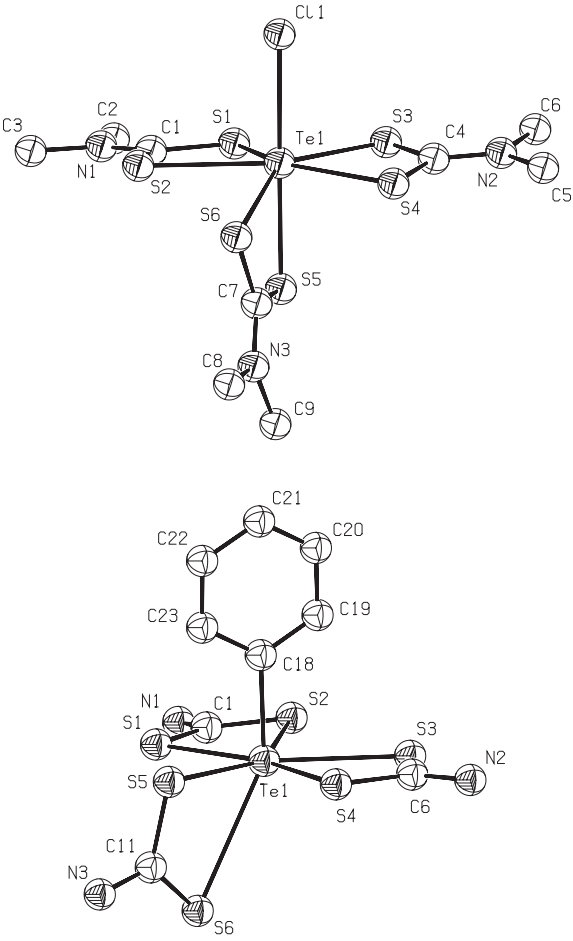

Figure 33. The ORTEP plots of (*a*) [$TeCl(S_2CNMe_2)_3$] and (*b*) [$TePh(S_2CNEt_2)_3$], showing the two structural types found in the [$TeR(S_2CNR_2)_3$] and [$TeX(S_2CNR_2)_3$] complexes (R = aryl; X = halide or pseudo-halide). The N substituents of [$TePh(S_2CNEt_2)_3$] omitted for clarity.

the tellurium substituent increases, so the structures tend toward the former type; thus halide and pseudo-halide complexes fall in category (1), while aryl complexes fall in category (2). In both cases, there is an approximate mirror plane perpendicular to the equatorial plane of the molecule. The unique axial–equatorial dithiocarbamate ligand is highly anisobidentate: The asymmetry in these Te—S bond lengths, which varies considerably (ΔTe—S = 0.15–0.69 Å), is smallest in the halide–pseudo-halide complexes; this is presumably because of the weaker trans influence of the halide–pseudo-halide and/or the increase in

Lewis acidity at the metal center. The long Te—S bond is equatorial in the halide and pseudo-halide complexes [type (1) structure] and axial in the aryl complexes [type (2) structure]. The two equatorial dithiocarbamate ligands, which are coordinated to the Te atom in a trapezoidal fashion, are also anisobidentate, although less so [ΔTe—S(av) $\approx$ 0.13 Å]. The lone pair of electrons on Te, which probably occupies a low-lying, ligand-centered antibonding orbital, is essentially stereochemically inert, although it does exert some influence on the precise geometry adopted at Te.

Tellurium dioxide reacts with sodium dithiocarbamate salts in the presence or perchloric acid to yield the perchlorate complexes $[Te(S_2CNR_2)_3(ClO_4)]$ or $[Te_3(S_2CNR_2)_9(ClO_4)(OH)_2]$, depending on the reaction conditions (319). The X-ray molecular structure of $[Te(S_2CNR_2)_3(ClO_4)]$ reveals that the perchlorate ligand is weakly bound to the metal center via two oxygen atoms (Te—O = 2.87 and 3.12 Å). The Te atom thus adopts a dodecahedral arrangement, formed by two interposing trapezoids. The dihedral angle between the two trapezoidal planes is 88.4°, comparable to that in the tetrakis(dithiocarbamate) complexes.

2. *Bis(dithiocarbamate) Complexes*

Several dihalogeno bis(dithiocarbamate) complexes, $[TeX_2(S_2CNR_2)_2]$ (X = Cl, Br, or I), have been reported (293, 309, 342–346). The complexes that have been analyzed crystallographically display one of two distinct structural types (Fig. 34): The $[TeBr_2(S_2CNEt_2)_2]$ (343) and $[TeI_2(S_2CN$*i*-$Pr_2)_2]$ (345) are monomeric in the solid state, with the halides essentially cis [XTeX(av) = 99.8°], whereas $[TeI_2(S_2CNEt_2)_2]$ (346) and $[TeI_2\{S_2CN(CH_2$-$CH_2OH)_2)_2]$ (344) are centrosymmetric halide-bridged dimers, with the halides essentially trans [XTeX(av) = 173.8°]. The dithiocarbamate ligands are unsymmetrically chelating in both cases, but the anisobidenticity is considerably greater in the dimeric species [ΔTe—S(av) = 0.04 and 0.22 Å, respectively]. The Te atom is thus six coordinate in the monomers and seven coordinate in the halide-bridged dimers. The halogen and three S atoms occupying the equatorial positions in the monomeric species have a trapezoidal arrangement, opening a space in the polyhedron, which may be occupied by the lone pair. It is difficult to determine unambiguously if the lone pair has a stereochemical role, but if it is considered active, then the geometry at Te would best be described as distorted pentagonal bipyramidal in both structural types.

Formal substitution of one of the halides with an alkyl or aryl group gives the complexes $[TeXR(S_2CNR'_2)_2]$ (347–352). The NMR data (347) indicate that the complexes are monomeric in solution, but secondary Te$\cdots$S or Te$\cdots$X interactions in the aryl complexes lead to the formation of centrosymmetric dimers in the solid state. The relative strengths of the secondary interactions are in the order Te$\cdots$I > Te$\cdots$Br > Te$\cdots$S > Te$\cdots$Cl, as expected for the soft Te

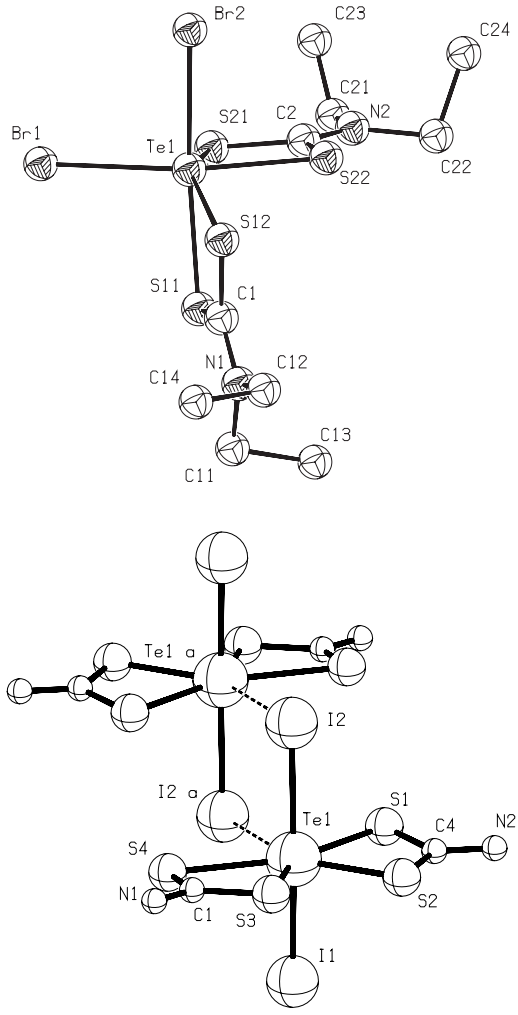

Figure 34. The two structural types exhibited by the $[TeX_2(S_2CNR_2)_2]$ complexes (X = Cl, Br, or I), exemplified by (*a*) the ORTEP plot of $[TeBr_2(S_2CNEt_2)_2]$ and (*b*) PLUTON plot of $[TeI_2(S_2CNEt_2)_2]$. Dashed lines indicate intermolecular contacts. The N substituents of $[TeI_2(S_2CNEt_2)_2]$ omitted for clarity.

atom; the type of secondary interaction appears to be governed by crystal packing effects (349). The halogen and four S atoms of the almost isobidentate dithiocarbamates comprise the equatorial plane, with the C(aryl) axial. The secondary interactions are directed toward the empty (axial) coordination site, indicating that the lone pair is essentially inert stereochemically. The alkyl

complex $[TeIMe(S_2CNEt_2)_2]$ is analogous to the aryl complexes, but there are no significant secondary interactions and it is monomeric both in the solid state and in solution (347).

In the perchlorate complex $[Te(p\text{-}C_6H_4OCH_3)(S_2CNMe_2)_2(ClO_4)]$ (353), an oxygen atom of the perchlorate coordinates to the Te in an equatorial position so that, with the exception that the dithiocarbamate ligands are anisobidentate (ΔTe—S = 0.29 Å), it is structurally similar to the $[TeXR(S_2CNR_2)_2]$ complexes.

The diorganyl complexes, $[TeR_2(S_2CNR_2)_2]$ (R = alkyl or aryl), which are prepared by the reaction of TeR_2Cl_2 with the appropriate sodium dithiocarbamate salt, are structurally very different from the $[TeXR(S_2CNR'_2)_2]$ complexes (152, 354–362). The dithiocarbamate ligands are highly anisobidentate, to the extent that they are often best considered as monodentate. The average Te—S(short) distance is 2.62 Å and varies little. The Te—S(long) bond lengths range between 3.05 and 3.33 Å (cf. sum of van der Waals radii = 4.05 Å); the corresponding normalized Pauling bond orders (360) vary between 0.38 and 0.20. If the dithiocarbamates are considered as monodentate, then the geometry at Te is trigonal bipyramidal; the stereochemically active lone pair and two organic groups are equatorial, and the two S atoms axial. There is some flexibility in the STeS angle, which varies between 162.2 and 179.0° (av = 170.9°), but there is no obvious trend in terms of either the dithiocarbamate or Te substituents.

Although the $[TeR_2(S_2CNR_2)_2]$ complexes undergo slow disproportionation to yield TeR_2 and the corresponding thiuram disulfide, they are sufficiently stable to allow detailed studies to be carried out. In solution, rapid intramolecular exchange occurs between η^1 and η^2 dithiocarbamate bonding modes (i.e., monodentate $\rightleftarrows$ bidentate), so that, on the NMR time scale, the Te atom has a 1:2:2:2 geometry, including the lone pair (355). Although it is slow on the NMR time scale, intermolecular ligand exchange also occurs readily in solution, allowing mixed-ligand complexes of the type $[TeR_2(S_2CNR'_2)L]$ (L = uninegative bidentate ligand) to be prepared (355, 357, 360, 362–365): the complexes are structurally analogous to the parent bis(dithiocarbamates).

3. *Mono(dithiocarbamate) Complexes*

With the exception of the $[TeX_2(aryl)(S_2CNEt_2)]$ complexes (X = Br or I; aryl = C_6H_5 or p-$MeOC_6H_4$) (370), the molecular structures of the mono (dithiocarbamate) species $[TeR_{3-n}X_n(S_2CNR_2)]$ (R = alkyl or aryl, X = Cl, Br or I, and n = 0, 1, 2, or 3) (323, 355, 358–360, 366–374) are all similar.

Although essentially monomeric in solution (366, 367), intermolecular Te$\cdots$S or Te$\cdots$X interactions in the $[TeR_{3-n}X_n(S_2CNR_2)]$ complexes (R = alkyl or aryl, X = Cl, Br, or I, and n = 0, 1, or 3) lead to the formation of dimers or

polymers in the solid state. The basic molecular structures can be considered as being derived from the formal substitution of one of the dithiocarbamate ligands in the bis(dithiocarbamate) complexes, $[TeR_{2-n}X_n(S_2CNR'_2)_2]$ ($n = 0$, 1, or 2), with an additional halide or organic group: Thus the Te atom is best considered as possessing a distorted-trigonal-bipyramidal geometry, with the stereochemically active lone-pair equatorial [Fig. 35(*a*)]. The dithiocarbamate ligands are anisobidentate; the asymmetry decreases essentially in line with increasing electronegativity of the Te substituents (i.e., with increasing Lewis acidity of the metal center). For dialkyl complexes the Te—S distances are in the range 2.43–2.55 Å (short) and 3.10–3.30 Å (long); the normalized Pauling bond order (360) of the latter is ~0.22 (av). The Te—S lengths are considerably longer in the triorganyl complexes [~3.10 (short) and 3.60 Å (long)] (368, 369), indicating a very weak interaction between the dithiocarbamate and the metal moiety. As would be expected, the Te—S bonds are much shorter (2.43 and 2.68 Å) in the triiodo complex, $[TeI_3(S_2CNEt_2)]$ (371).

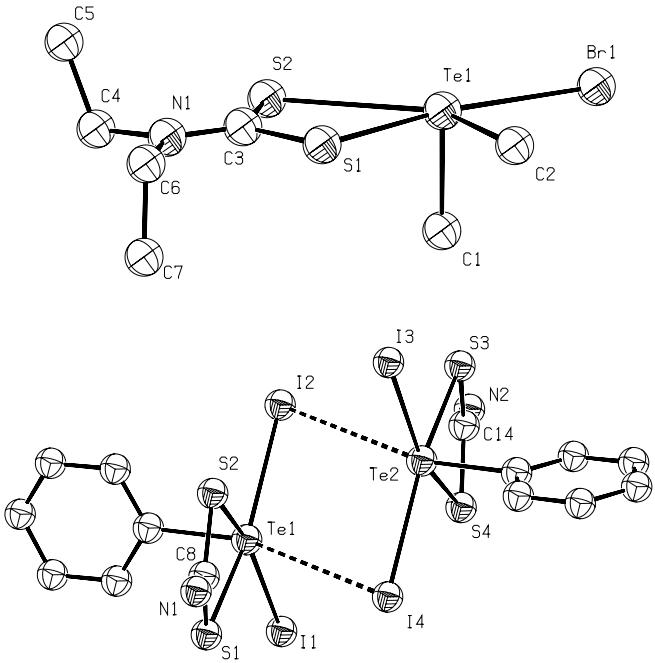

Figure 35. (*a*) The ORTEP plot of $[TeMe_2Br(S_2CNEt_2)]$ showing the basic molecular structure of the $[TeR_{3-n}X_n(S_2CNR_2)]$ complexes (R = alkyl or aryl, X = Cl, Br, or I, and $n = 0$, 1, or 3). (*b*) ORTEP plot of $[TePhI_2(S_2CNEt_2)]$, showing the dimeric solid-state structure of the [Te(aryl)$X_2(S_2CNEt_2)$] complexes (X = Br or I; aryl = C_6H_5 or *p*-$MeOC_6H_4$). The N substituents of $[TePhI_2(S_2CNEt_2)]$ and phenyl ring C atom labels omitted for clarity.

The geometry of the Te atom in the $[Te(aryl)X_2(S_2CNEt_2)]$ complexes (X = Br or I; aryl = C_6H_5 or *p*-$MeOC_6H_4$) (370), is octahedral: The two halogen atoms are cis (XTeX $\approx 110^\circ$) and the aryl group axial. The second axial position is occupied by a weakly bonding halogen atom of a neighboring molecule, giving a quasi-centrosymmetric dimmer [Fig. 35(*b*)]. The lone pair is essentially inert and the dithiocarbamate ligand almost isobidentate (ΔTe—S ≈ 0.02 Å).

The Te atom in the monomeric tetrahalo anions, $[TeX_4(S_2CNR_2)]^-$ (X = Br or I) (342, 375) is also octahedral, and the dithiocarbamate ligand is, again, essentially isobidentate.

The NMR spectra of the mono(dithiocarbamate) complexes are generally difficult to interpret due to ligand exchange reactions, metal-centered rearrangements and reductive elimination reactions occurring quite rapidly on the NMR time scale (358–360): The occurrence of these processes indicates that the dithiocarbamate is only weakly bound to Te. Furthermore, conductimetry measurements show the triphenyl complexes $[TePh_3(S_2CNR_2)]$ are close to 1:1 electrolytes, again indicative of the dithiocarbamate being only weakly associated with the metal moiety in solution (367, 369).

4. Tellurium-125 NMR and Mössbauer Spectroscopy

Tellurium-125 NMR spectroscopy has been applied extensively to the study of Te dithiocarbamate complexes (304, 306, 310, 323, 331, 347, 355, 357–360, 361, 363–366, 372, 374); data are reported in Table VI. Caution should be exercised in data interpretation because of the instability of many of the complexes in solution, and their ability to undergo facile intermolecular ligand-exchange reactions. The chemical-shift range for tellurium dithiocarbamate complexes appears to span just <2000 ppm (ca. -600 to 1240 ppm, relative to $TeMe_2$); the shifts of the Te(II) complexes occur at the high frequency end of the range. Data also reveal that the shifts generally move to higher frequency as the electronegativity of the Te substituents increases, consistent with the shifts being dominated by the contribution of valence orbital populations to the paramagnetic shielding term (304).

Tellurium NMR is particularly well suited to the study of ligand-exchange reactions. Although facile, the rate of exchange is generally comparable to, or slow on the NMR chemical shift time scale (304, 306, 347, 355, 357). Rates of exchange appear to be more rapid in Te(II) species than in Te(IV) (306). The ^{125}Te NMR spectrum of a mixture of $[Te(S_2CNEt_2)_2]$, $(Et_2NCS_2)_2$, and $(i\text{-}Pr_2NCS_2)_2$ displays five signals, assignable to $[Te(S_2CNEt_2)_4]$, $[Te(i\text{-}Pr_2NCS_2)(S_2CNEt_2)_3]$, $[Te(i\text{-}Pr_2NCS_2)_2(S_2CNEt_2)_2]$, $[Te(i\text{-}Pr_2NCS_2)_3(S_2CNEt_2)]$, and $[Te(i\text{-}Pr_2NCS_2)_4]$ (304). The generation of Te(IV) species from Te(II) and the thiuram disulfides shows clearly that the reductive elimination of thiuram disulfide from Te(IV) species is reversible.

TABLE VI
Tellurium-125 NMR[a] Data for Tellurium Dithiocarbamato Complexes

Complex	Solvent[b]	δ (^{125}Te)	References
$[Te(S_2CNEt_2)_4]$	C_6D_6	−600	306
	THF	−577	306
	$CDCl_3$	−561	304
$[Te(S_2CNEt_2)_3\{S_2CN(CH_2)_4O\}]$	THF	−570	306
$[Te(S_2CNEt_2)_2\{S_2CN(CH_2)_4O\}_2]$	THF	−564	306
$[Te(S_2CN\textit{n}\text{-}Pr_2)_4]$	$(CD_3)_2CO$	−561	304
$[Te(S_2CNEt_2)\{S_2CN(CH_2)_4O\}_3]$	THF	−559	306
$[Te\{S_2CN(CH_2)_4O\}_4]$	THF	−555	306
$[Te(S_2CN\textit{i}\text{-}Bu_2)_4]$	$(CD_3)_2CO$	−543	304
$[Te(S_2CN\textit{i}\text{-}Pr_2)_4]$	$(CD_3)_2CO$	−416	304
	$CDCl_3$	−403	304
$[Te(S_2CNBz_2)_4]$	$CDCl_3$	−299	304
$[TeI(S_2CNEt_2)_3]$	$CDCl_3$	−218	304
$[TeMeI(S_2CNEt_2)_2]$	CD_2Cl_2	−160	347
$[TeCl(S_2CNEt_2)_3]$	$CDCl_3$	−155	304
$[Te(SCN)(S_2CNEt_2)_3]$	$CDCl_3$	−129	304
$[TeMe(S_2CNEt_2)_2\{S_2P(OEt)_2\}]$	CD_2Cl_2	−36	347
$[TeMe(S_2CNEt_2)_2(S_2COEt)]$	CD_2Cl_2	10	347
$[TeMe(S_2CNEt_2)_3]$	CD_2Cl_2	59	347
$[TePhCl(S_2CNEt_2)_2]$	THF	110	347
$[TePh(S_2CNEt_2)_2\{S_2P(OEt)_2\}]$	CD_2Cl_2	169	347
$[TePh(S_2CNEt_2)_2(S_2COEt)]$	CD_2Cl_2	222	347
$[TePh(S_2CNEt_2)_3]$	THF	277	347
$[TeMe_2(S_2CNEt_2)_2]$	*c*	463	359
$[TeMe_2\{S_2CN(CH_2)_5\}_2]$	$CDCl_3$	465	360
$[TeMe_2\{S_2CN(CH_2)_4\}\{S_2CN(CH_2)_5\}]$	$CDCl_3$	469	360
$[TeMe_2(S_2CNEt_2)(S_2COMe)]$	$CDCl_3$	474	363
$[TeMe_2(S_2CNMe_2)_2]$	*c*	475	359
$[TeMe_2(S_2CNMe_2)(S_2COEt)]$	$CDCl_3$	488	363
$[TeMe_2(S_2CNMe_2)(S_2COMe)]$	$CDCl_3$	491	363
$[TeMe_2\{S_2CN(CH_2)_4\}_2]$	$CDCl_3$	500	360
$[TeMe_2I\{S_2CN(CH_2)_4\}]$	$CDCl_3$	500	360
$[TeMe_2I(S_2CNEt_2)]$	$CDCl_3$	501	372
$[TeMe_2I\{S_2CN(CH_2)_5\}]$	$CDCl_3$	501	360
$[TeMe_2I(S_2CNMe_2)]$	$CDCl_3$	507	372
$[TeMe_2Br(S_2CNEt_2)]$	$CDCl_3$	527	372
$[TeMe_2Br\{S_2CN(CH_2)_5\}]$	$CDCl_3$	529	360
$[TeMe_2Br\{S_2CN(CH_2)_4\}]$	$CDCl_3$	534	360
$[TeMe_2Br(S_2CNMe_2)]$	$CDCl_3$	536	372
$[TeMe_2Cl(S_2CNEt_2)]$	*c*	545	359
$[TeMe_2Cl\{S_2CN(CH_2)_5\}]$	$CDCl_3$	548	360
$[TeMe_2Cl\{S_2CN(CH_2)_4\}]$	$CDCl_3$	552	360
$[TeMe_2Cl(S_2CNMe_2)]$	*c*	554	359
$[Te(C_8H_8)(S_2CN\textit{i}\text{-}Pr_2)_2]$	CD_2Cl_2	590	355
$[Te(S_2CNEt_2)(S_2CN\textit{i}\text{-}Pr)]$	CD_2Cl_2	601	355
$[Te(C_8H_8)(S_2CNEt_2)_2]$	CD_2Cl_2	611	355

TABLE VI (*continued*)

Complex	Solvent[b]	δ (^{125}Te)	References
		627	362
[$TePhCl_2(S_2CNEt_2)$]	THF; 233 K	634	347
[$Te(C_8H_8)(S_2CNEt_2)(S_2COEt)$]	CD_2Cl_2	634	355
[$Te(C_8H_8)(S_2CN$*i*-$Pr_2)\{S_2P(OEt)_2\}$]	CD_2Cl_2	660	355
[$Te(C_8H_8)(S_2CN$*i*-$Pr_2)\{S_2P(O$*i*-$Pr)_2\}$]	$CDCl_3$	670	355
[$Te(C_8H_8)(S_2CNEt_2)\{S_2P(OEt)_2\}$]	CD_2Cl_2	672	355, 362
[$Te(C_8H_8)(S_2CNEt_2)\{S_2P(O$*i*-$Pr)_2\}$]	CD_2Cl_2	677	355
[$TePh_2(S_2CNEt_2)_2$]	CD_2Cl_2	692	357
[$TePh_2(S_2CN$*n*-$Pr_2)_2$]	*c*	703	358
[$TePh_2(S_2CN$*n*-$Bu_2)_2$]	*c*	704	358
[$Te($*p*-$MeOC_6H_4)(S_2CNEt_2)_2$]	*c*	711	359
[$Te($*p*-$MeOC_6H_4)(S_2CNMe_2)_2$]	*c*	724	359
[$Te(C_8H_8)\{S_2CN(CH_2)_5\}\{(SPPh_2)_2N\}$]	*c*	725	364, 365
[$Te(C_8H_8)I(S_2CNEt_2)$]	DMF; 233 K	726	366
	$CDCl_3$	773	374
[$Te(C_8H_8)(S_2CNEt_2)\{(SPPh_2)_2N\}$]	*c*	728	364, 365
[$TePh_2(S_2CNEt_2)(S_2COEt)$]	THF; 233 K	729	357
[$TePh_2(S_2CNEt_2)\{S_2P(OEt)_2\}$]	DMF; 233 K	736	357
[$Te(C_8H_8)\{S_2CN(CH_2)_4O\}\{(SPPh_2)_2N\}$]	*c*	736	364, 365
[$Te(C_8H_8)\{S_2CN(CH_2)_4S\}\{(SPPh_2)_2N\}$]	*c*	737	364, 365
[$Te(C_8H_8)Br(S_2CNEt_2)$]	DMF; 233 K	750	366
[$TePh_2Br(S_2CN$*i*-$Pr_2)$]	*c*	763	358
[$TePh_2Br(S_2CN$*n*-$Pr_2)$]	*c*	774	358
[$TePh_2Br(S_2CNEt_2)$]	*c*	774	358
[$Te(C_8H_8)I(S_2CNC_4H_6)$]	$CDCl_3$	775	374
[$TePh_2Br(S_2CN$*n*-$Bu_2)$]	*c*	775	358
[$TePh_2Br(S_2CNMe_2)$]	*c*	779	358
[$TePh_2Cl(S_2CN$*n*-$Bu_2)$]	*c*	779	358
[$Te(S_2CNEt_2)\{S_2CN(CH_2)_4O\}$]	CD_2Cl_2; 233 K	786	306
[$Te($*p*-$MeOC_6H_4)Cl(S_2CNEt_2)$]	*c*	788	359
[$TePh_2Cl(S_2CNEt_2)$]	DMF; 233 K	789	357
[$Te($*p*-$MeOC_6H_4)Cl(S_2CNMe_2)$]	*c*	794	359
[$Te(S_2CNEt_2)_2$]	CD_2Cl_2; 275 K	802	306
	$(CD_3)_2CO$	827	304
	$CDCl_3$	838	304
	$CDCl_3$	841	310[d]
[$Te(C_8H_8)(OAc)(S_2CNEt_2)$]	CD_2Cl_2	808	362
[$Te(S_2CN$*n*-$Pr_2)_2$]	$(CD_3)_2CO$	829	304
	$CDCl_3$	836	304
[$Te(S_2CN$*i*-$Pr_2)_2$]	$CDCl_3$	833	304
[$Te(S_2CN$*i*-$Bu_2)_2$]	$(CD_3)_2CO$	845	304
[$Te(S_2CNEt_2)(S_2CNBz_2)$]	$CDCl_3$	852	310[d]
[$Te(C_8H_8)Cl(S_2CNEt_2)$]	DMF; 233 K	863	366
[$Te(S_2CNBz_2)_2$]	$CDCl_3$	865	304
	$CDCl_3$	868	310[d]
[$Te\{S_2CN(CH_2)_4O\}_2$]	CD_2Cl_2	879	306
[$Te\{S_2CN(CH_2)_4\}_2$]	$CDCl_3$	1117	304

TABLE VI (*continued*)

Complex	Solvent[b]	δ (^{125}Te)	References
$TeL^1(S_2CNEt_2)]$	$CDCl_3$	1124	331
$[Te(C_6H_4N_2Ph)(S_2CNMe_2)]$	$CDCl_3$	1229	323
$[Te(C_6H_4N_2Ph)(S_2CNEt_2)]$	$CDCl_3$	1239	323

[a] Chemical shifts reported relative to Me_2Te as an external standard (corrections from other references applied where necessary). L^1 = 8-(dimethylamino)-1-naphthyl.
[b] Data at ambient temperature, unless otherwise stated. THF = tetrahydrofuran. DMF = dimethylformamide.
[c] Solvent not specified.
[d] Incorrectly reported as the tetrakis(dithiocarbamato)tellurium(IV) complex.

Tellurium-125 Mössbauer spectroscopy has not be employed widely in the study of tellurium dithiocarbamate complexes, probably because isomer shifts are subject to substantial errors and are generally quite insensitive to the environment at Te. Generally, however, isomer shifts and quadrupole splittings are expected to be more positive for Te(II) complexes than for Te(IV) (323). The ^{125}Te NMR and Mössbauer spectra of the organotellurium dithiocarbamate complexes $[Te(C_6H_4N_2Ph)(S_2CNMe_2)]$ and $[Te(C_6H_4N_2Ph)(S_2CNMe_2)_3]$ have been reported by McWhinnie and co-workers (323). While NMR data for the two complexes are almost identical, suggesting that the Te(IV) complex has undergone reductive elimination of tetramethylthiuram disulfide in solution, the quadrupole splittings are significantly different, ruling out the possibility that the tris(dithiocarbamate) Te(IV) complex is simply a mixture of $[Te(C_6H_4N_2Ph)(S_2CNMe_2)]$ and $(Me_2NCS_2)_2$ in the solid state: Data tend to suggest a loose charge-transfer complex between the mono(dithiocarbamate) complex and the disulfide.

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ABBREVIATIONS

av	Average
ax	Axial
2D	Two dimensional
Bpy	2,2′-Bipyridyl ($C_{10}H_8N_2$)
Bz	Benzyl ($CH_2C_6H_5$)

Cp	Cyclopentadienyl anion ($C_5H_5^-$)
Cy	Cyclohexyl (C_6H_{11})
ddh	Distorted dodecahedral
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
doh	Distorted octahedral
dpby	Distorted pentagonal bipyramidal
dtpy	Distorted trigonal bipyramidal
Et	Ethyl (CH_2CH_3)
eq.	equitorial
^{1}H NMR	Proton NMR
Hex	Hexyl ($CH_2CH_2CH_2CH_2CH_2CH_3$)
i-Bu	isobutyl (CH_2CHMe_2)
i-Pr	isopropyl ($CHMe_2$)
IR	Infrared
IS	Isomer shift
L	Any unspecified ligand
Me	Methyl (CH_3)
MLCT	Metal-to-ligand charge transfer
n-Bu	Normal-Butyl ($CH_2CH_2CH_2CH_3$)
NMR	Nuclear magnetic resonance
n-Pr	Normal-Propyl ($CH_2CH_2CH_3$)
NQR	Nuclear quadruple resonance
phen	1,10-Phenanthroline ($C_{12}H_8N_2$)
py	Pyridine (ligand)
Py	Pyridine (solvent) (C_5H_5N)
QS	Quadrupole splitting
R	Any unspecified alkyl or aryl group
ρ	QS/IS ratio
terpy	4,4′:6′,2″-Terpyridine
thf	Tetrahydrofuran (ligand)
THF	Tetrahydrofuran (solvent)
tu	Tetramethylthiourea
VBS	Valence bond sum
X	Any unspecified halide or pseudohalide

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