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Main group metal complexes of semicarbazones and thiosemicarbazones. A structural review

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Abstract

The structural aspects of the complexes formed by thiosemicarbazones (TSCs) and semicarbazones (SCs) with the metallic elements of Groups 12, 13, 14 and 15 are surveyed up to 1998. Descriptions of 71 structures containing neutral or deprotonated TSCs and ten with SCs include information on the metal-to-ligand bonds and the coordination behaviour of the ligand. The survey shows that TSCs are very versatile coordination agents with these acceptors.

Keywords: Main group metal complexes; Thiosemicarbazonates; Semicarbazonates; Zn, Cd and Hg complexes; Al, Ga, In and Tl complexes; Sn and Pb complexes; Bi complexes

Nomenclature

H_4AABMeTSC	2,4-pentanedione bis(N^1-methylthiosemicarbazone)
H_2AcPhTSC	Acetophenone N^1-phenylthiosemicarbazone
HAPEtTSC	2-Acetylpyridine N^1-ethylthiosemicarbazone
HAPHTSC	2-Acetylpyridine N^1-azepanylthiosemicarbazone
HAPhTSC	Acetone N^1-phenylthiosemicarbazone
H_2AP^iprTSC	2-Acetylpyridine N^1-isopropylthiosemicarbazone
HAPMeTSC	2-Acetylpyridine N^1-methylthiosemicarbazone
H_2APPhTSC	2-Acetylpyridine N^1-phenylthiosemicarbazone

HAPTSC	2-Acetylpyridine thiosemicarbazone
H_2APT	Bis(2-acetylpyridine) thiocarbohydrazone
HATSC	Acetone thiosemicarbazone
H_2BCy	Cyclohexane-1,2-dione bis(thiosemicarbazone)
HBrBTSC	Bromobenzaldehyde thiosemicarbazone
HBTSC	Benzaldehyde thiosemicarbazone
H_2CHDSC	Cyclohexane-1,2-dione bis(semicarbazone)
HClBTSC	Chlorobenzaldehyde thiosemicarbazone
HCPTSC	Cyclopentanone thiosemicarbazone
HDAPMTSC	2,6-Diacetylpyridine monothiosemicarbazone
H_2DAPSC	2,6-Diacetylpyridine bis(semicarbazone)
H_2DAPTSC	2,6-Diacetylpyridine bis(thiosemicarbazone)
HDIPSC	Di-2-pyridylketone semicarbazone
H_3DAPSCH	2,6-Diacetylpyridine semicarbazone 2-(semicarbazono)propionyl hydrazone
HEPT	Ethylpyruvic acid thiosemicarbazone
HFMeTSC	Furan-2-carbaldehyde N^1-methylthiosemicarbazone
H_2KTSC	3-Ethoxy-2-oxobutyraldehyde bis(thiosemicarbazone)
HMBTSC	4-Methoxybenzaldehyde thiosemicarbazone
H_2MeOSTSC	*o*-Vanillin thiosemicarbazone
H_2MeSTSC	2-Hydroxyacetophenone thiosemicarbazone
HPATSC	2-Acetylpyridine N^1-(3-methyl pentamethylene)thiosemicarbazone
H*p*-ATSC	*p*-Anisaldehyde thiosemicarbazone
H_2PHENSC	2,9-Diformyl-1,10-phenanthroline bis(semicarbazone)
H_3P^iprTSC	Pyrrole-2-carbaldehyde N^1-isopropyl thiosemicarbazone
H_2PT	Pyruvic acid thiosemicarbazone
HPTSC	Pyrrole-2-carbaldehyde thiosemicarbazone
H_2PxTSC	Pyridoxal thiosemicarbazone
HPyTSC	Pyridine-2-carbaldehyde thiosemicarbazone
HSITSC	Salicylaldehyde *S*-ethyl isothiosemicarbazone
H_2SPITSC	Salicylaldehyde N^1-[2-diacetylethen-1-yl]-*S*-propyl-isothiosemicarbazone
H_2SSC	Salicylaldehyde semicarbazone
H_2STSC	Salicylaldehyde thiosemicarbazone
HTFHTSC	2-Acetylthiophene N^1-azepanylthiosemicarbazone
H_2TFPhTSC	Thiophene-2-carbaldehyde N^1-phenylthiosemicarbazone

1. Introduction

According to the IUPAC recommendations for the nomenclature of organic compounds [1], derivatives of semicarbazide of the types

$$\text{R-CH=N–NH–CX–NH}_2 \text{ and } \text{R}^1\text{R}^2\text{C=N–NH–CX–NH}_2$$

which are usually obtained by condensation of semicarbazide with suitable aldehydes and ketones, may be named by adding the class name ‘semicarbazone’

($X = O$) or 'thiosemicarbazone' ($X = S$) after the name of the condensed aldehyde RCHO or ketone RR′C=O. It is usual also to include in this class derivatives with substituents on the amide or thioamide nitrogen,

$R^1R^2C{=}N{-}NH{-}CX{-}NR^3R^4$

on the X atom,

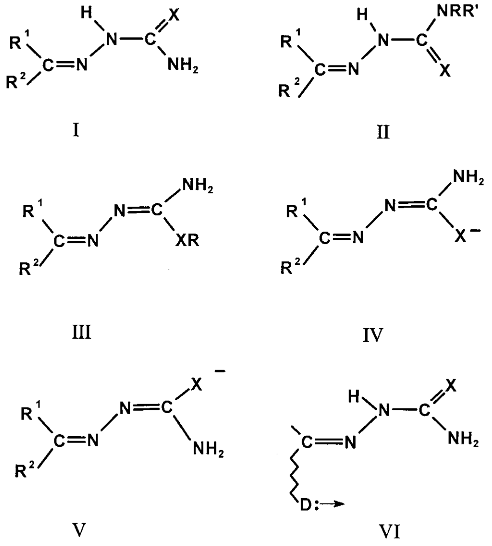
$R^1R^2C{=}N{-}N{=}CXR^3{-}NH_2$

or on the 'hydrazinic' nitrogen.

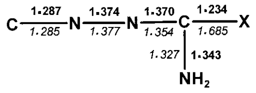
$R^1R^2C{=}N{-}NR^3{-}CX{-}NH_2$

These classes of compounds usually react with metallic cations giving complexes in which the semicarbazones (SCs) and thiosemicarbazones (TSCs) behave as chelating ligands. Research on the coordination chemistry [2], analytical applications [3] and biological activities [4] of these complexes has increased steadily for many years: a search of the Cambridge Structural Database (CSD [5]) found more than a thousand relevant papers published in the last decade.

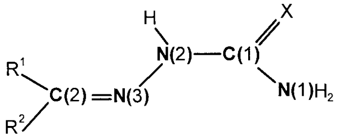
A review of ca. 70 SC and ca. 90 TSC structures included in the CSD shows that in free unsubstituted SCs and TSCs in solid state the $C{=}N{-}NH{-}CX{-}NH_2$ backbone



Scheme 1.



Scheme 2.



Scheme 3.

is usually almost planar, with the X (O, S) atom *trans* to the azomethine N (configuration E; see Scheme 1, **I**). Few SCs are exceptions to this rule. Although there are several electronic and steric factors that may contribute to the adoption of this arrangement, the most important is probably that the *trans* arrangement places the amine and azomethine nitrogen atoms in relative positions suitable for intramolecular hydrogen bonding [6]. In fact, TSCs in which the amine group is fully substituted crystallize with the S atom *cis* to the azomethine N (Z-configuration; Scheme 1, **II**). Substitution of the hydrazinic H seems not to change the usual E-configuration of unsubstituted TSCs. Curiously, however, S-substituted TSCs adopt the Z form (Scheme 1, **III**; $X = S$, $R =$ alkyl).

In Scheme 1, conventional single and double bonds are represented. However, as was pointed out by Palenik et al. [7] on the basis of their pioneering work in the field, TSCs are extensively delocalized systems, especially when aromatic radicals are bound to the azomethine carbon atom. Scheme 2 indicates the mean bond lengths of the SCs (bold) and S-unsubstituted TSCs (italics) found in the CSD. The C=O distance is equal to the average for amides [8], and the C=S distance is close to the average for thioureas [8]. Replacing O by S, hardly affects the lengths of the N–N and azomethine bonds, but significantly alters the bond lengths in the $-NH-CX-NH_2$ moiety, the lesser electronegativity of the sulphur atom allowing increased involvement of the two C–N bonds in π-charge delocalization.

SCs and TSCs are versatile ligands in both neutral and anionic forms. Although the proton lost by the anions formally belongs to the hidrazinic –NH group, the anion is usually represented in the canonical thiol form (Scheme 1, **IV** and **V**) and usually in Z-configuration. This convention will be followed in this review, but it should nevertheless be borne in mind that, as in the neutral molecules, the π-charge is actually delocalized.

The coordination possibilities deriving from the many potential donor atoms in the SC or TSC backbone are increased if substituents R^1 and/or R^2 include additional donor atoms (Scheme 1, **VI**), and can also be modified by placing substituents on backbone donor atoms (e.g. by the formation of S-alkyl derivatives; Scheme 1, **III**).

This review surveys the structural aspects of the SC and TSC derivatives containing main group metal cations that have been described in the literature up to the end of 1998. It is arranged in four main sections, each devoted to one group of the Periodic Table. Since no semicarbazonates or thiosemicarbazonates in which SC or TSC is bound to a Group 1 or Group 2 metal have been found, the first group considered is Group 12. Within each group, complexes are described in order of increasing atomic number of the acceptor; for each acceptor in order of increasing coordination number; and for each coordination number in order of increasing kernel heterogeneity, i.e. complexes with kernels containing more atoms of the same element are described before those with more heterogeneous kernels. When two kernels are equally homogeneous, the one with the lighter donor atoms is described first. Tables 1–4 list all the compounds described. In the column listing M–L bond lengths, bonds involving the SC or TSC backbone are indicated by bold type. When the ligand is a bis-SC or bis-TSC, the two SC or TSC moieties are distinguished by writing A or B in parentheses, since they usually have slightly different bond lengths. If two SC or TSC molecules are involved, they are distinguished, when necessary, by Roman numerals (I and II).

The IUPAC semicarbazide numbering scheme [1] is not very appropriate for describing the structural data of SCs and TSCs because the numbering of C and N atoms on the SC or TSC chain does not run on into the numbering of R^1 and R^2 groups. This is probably why a variety of different numbering schemes have been used in the literature. In this review we adopt the scheme shown in Scheme 3, which gives priority to the SC or TSC backbone and assigns larger consecutive numbers to the R^1 and R^2 atoms.

2. Group 12

Structural data for complexes with Group 12 metals are listed in Table 1.

2.1. Zn

Two structures have been reported for zinc complexes containing SCs, and 16 for complexes with TSCs.

2.1.1. Coordination number 4

The reaction of the bis(thiosemicarbazone) $H_2DAPTSC$ with zinc dichloride in methanol affords the complex $[Zn_2(DAPTSC)_2]\cdot MeOH\cdot H_2O$ [9] (Fig. 1). The two zinc atoms of this dinuclear compound have different coordination environments.

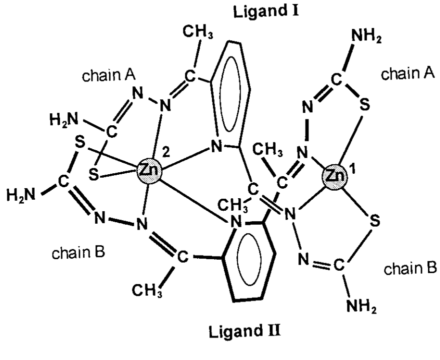


Fig. 1. Adapted from Ref. [9].

Table 1
Complexes of semicarbazones and thiosemicarbazones with Group 12 metals (Zn, Cd and Hg)

Semicarbazone complexes

Compound	CN[kernel]	d(M–L) (Å)	$d(C^2–N^3)$ (Å)	$d(N^2–N^3)$ (Å)	$d(N^2–C^1)$ (Å)	$d(C^1–N^1)$ (Å)	$d(C^1–O)$ (Å)	Reference
$[Zn(H_3DAPSCH)(H_2O)_2]$-$(ClO_4)_2·1.5H_2O$	$7[ZnN_3O_4]$	N 2.181(7)						[20]
		2.207(7)						
		2.227(8)	1.28(1)	1.35(1)	1.39(1)	1.35(1)	1.28(1)	
		O 2.087(7)						
		2.113(6)						
		2.219(7)						
		2.281(6)						
$[ZnCl(H_2DAPSC)(H_2O)]$-$Cl_2·H_2O$	$7[ZnClN_3O_3]$	Cl 2.433(3)						[21]
		N **2.222(10)**(A)	1.267(17)	1.367(15)	1.389(17)	1.331(17)	1.224(16)	
		2.229(8)						
		2.247(10)(B)	1.294(18)	1.358(17)	1.381(18)	1.331(18)	1.239(16)	
		O 2.121(9)						
		2.184(9)(B)						
		2.207(9)(A)						

Thiosemicarbazone complexes

Compound	CN[kernel]	d(M–L) (Å)	$d(C^2–N^3)$ (Å)	$d(N^2–N^3)$ (Å)	$d(N^2–C^1)$ (Å)	$d(C^1–N^1)$ (Å)	$d(C^1–S)$ (Å)	Reference
$[Zn_2(DAPTSC)_2]$ $·MeOH·H_2O$	$4[ZnN_2S_2]$	N **2.07(1)**(A,II)	1.298 [a]	1.399 [a]	1.308 [a]	1.351 [a]	1.756 [a]	[9]
		2.07(1)(B,I)	1.276 [a]	1.422 [a]	1.323 [a]	1.360 [a]	1.726 [a]	
Two independent Zn atoms with two different kernels, $[ZnN_2S_2]$ and $[ZnN_4S_2]$		S **2.317(3)**(B,I)						
		2.327(4) (A,II)						
$[ZnCl_2(HAPhTSC)_2]$	$4[ZnCl_2S_2]$	Cl 2.218(1)						
		2.287(1)						
		S **2.362(1)**	1.280(4)	1.387(4)	1.336(4)	1.333(4)	1.710(4)	
		2.367(1)	1.274(5)	1.394(4)	1.349(4)	1.313(4)	1.723(3)	[10]

Table 1 (*Continued*)

Thiosemicarbazome complexes

Compound	CN[kernel]	d(M–L) (Å)	d(C^2–N^3) (Å)	d(N^2–N^3) (Å)	d(N^2–C^1) (Å)	d(C^1–N^1) (Å)	d(C^1–O) (Å)	Reference
[ZnCl$_2$(HBTSC)$_2$]	4[ZnCl$_2$S$_2$]	Cl 2.264(1)						
		2.276(1)						
		S **2.341(1)**	1.268(6)	1.380(5)	1.334(6)	1.320(6)	1.699(5)	
		2.355(1)	1.270(5)	1.376(5)	1.328(5)	1.309(6)	1.708(4)	[11]
[ZnCl$_2$(HATSC)]	4[ZnCl$_2$NS]	Cl 2.203(2)	1.292(7)	1.302(7)	1.332(7)	1.313(8)	1.712(6)	[12]
		2.262(2)						
		N **2.116(4)**						
		S **2.303(2)**						
[Zn$_2$(SITSC)(OAc)$_3$]	5[ZnO$_5$]	O 1.961(6)						[13]
Two Zn atoms with two different		1.973(6)						
kernels, [ZnO$_5$] and [ZnN$_2$O$_3$]		2.034(6)						
		2.056(6)						
		2.387(6)						
[Zn(SPITSC)(Py)]	5[ZnN$_3$O$_2$]	N **2.079(6)**	1.265(8)	1.412(8)	1.295(9)	1.410(9)	1.747(7)	[14]
		2.081(6)						
		2.089(5)						
		O 1.942(5)						
		2.049(5)						
[Zn$_2$(SITSC)(OAc)$_3$]	5[ZnN$_2$O$_3$]	N **2.032(7)**	1.28(1)	1.39(1)	1.36(1)	1.26(1)	1.75(9)	[13]
Two Zn atoms with two different		**2.096(7)**						
kernels, [ZnO$_5$] and [ZnN$_2$O$_3$]		O 1.954(6)						
		1.995(6)						
		2.111(6)						
[Zn(MeOSTSC)	5[ZnNO$_3$S]	N **2.150(7)**	1.306 ^{a}	1.363 ^{a}	1.289 ^{a}	1.425 ^{a}	1.664 ^{a}	[15]
(DMF)]$_2$		O 2.020(1)						
		2.045(5)						
		2.064(7)						
		S **2.299(4)**						

Table 1 (*Continued*)

Thiosemicarbazone complexes

Compound	CN[kernel]	d(M–L) (Å)	d(C^2–N^3) (Å)	d(N^2–N^3) (Å)	d(N^2–C^1) (Å)	d(C^1–N^1) (Å)	d(C^1–O) (Å)	Reference
[Zn(APEtTSC)(OAc)]$_2$ Two different Zn atoms with two different kernels, [ZnN$_2$O$_2$S] and [ZnN$_2$O$_3$S]	5[ZnN$_2$O$_2$S]	N **2.13(2)** 2.21(2) O 1.963(11) 2.027(11) S **2.410(6)**	1.317 [a]	1.360 [a]	1.344 [a]	1.338 [a]	1.743 [a]	[16]
[Zn(KTSC)(H$_2$O)]	5[ZnN$_2$OS$_2$]	N **2.125** (A) **2.148** (B) O 2.091 S **2.357** (B) **2.361** (A)	1.262 1.281	1.365 1.374	1.372 1.326	1.353 1.346	1.733 1.735	[17]
[Zn(BCy)(H$_2$O)]·DMF	5[ZnN$_2$OS$_2$]	N **2.118(4)**(A) **2.120(4)**(B) O 2.052(8) S **2.333(2)**(B) **2.352(2)**(A)	1.283(6) 1.289(6)	1.384(6) 1.373(6)	1.316(6) 1.315(6)	1.339(8) 1.350(8)	1.737(5) 1.738(5)	[18]
[ZnCl(H$_2$BCy)]Cl·2H$_2$O	5[ZnClN$_2$S$_2$]	Cl 2.292(2) N **2.117(6)**(A) **2.179(6)**(B) S **2.282(2)**(B) **2.371(2)**(A)	1.275(9) 1.255(9)	1.343(8) 1.319(8)	1.345(9) 1.315(9)	1.314(9) 1.295(10)	1.637(7) 1.694(7)	[18]
[{ZnCl(HPxTSC)}$_2$]·2H$_2$O	5[ZnCl$_2$NOS]	Cl 2.328(1) 2.698(1) N **2.110(2)** O 1.955(2) S **2.286(1)**	1.294(4)	1.363(4)	1.338(4)	1.329(4)	1.746(3)	[19]
[ZnCl$_2$(HEPT)]	5[ZnCl$_2$NOS]	Cl 2.230(2) 2.252(2) N **2.139(4)** O 2.295(4) S **2.432(2)**	1.274(7)	1.355(5)	1.359(7)	1.316(6)	1.689(5)	[19]

Table 1 (*Continued*)

Thiosemicarbazone complexes

Compound	CN[kernel]	*d*(M–L) (Å)	*d*(C^2–N^3) (Å)	*d*(N^2–N^3) (Å)	*d*(N^2–C^1) (Å)	*d*(C^1–N^1) (Å)	*d*(C^1–O) (Å)	Reference
[Zn$_2$(DAPTSC)$_2$]·MeOH·H$_2$O	6[ZnN$_4$S$_2$]	N **2.10(1)**(B,II)	1.306 [a]	1.374 [a]	1.327 [a]	1.351 [a]	1.726 [a]	[9]
Two independent Zn atoms with two different kernels, [ZnN$_2$S$_2$] and [ZnN$_4$S$_2$]		**2.12(1)**(A,I)	1.306 [a]	1.380 [a]	1.309 [a]	1.389 [a]	1.729 [a]	
		2.266(9)(II)						
		2.46(1)(I)						
		S **2.405(4)**(A,I)						
		2.436(4)(B,II)						
[Zn$_2$(DAPTSC)$_2$]·2DMF	6[ZnN$_4$S$_2$]	N **2.095(4)**(A,I)	1.292 [a]	1.378 [a]	1.315 [a]	1.370 [a]	1.737 [a]	[9]
		2.102(4)(B,II)						
		2.571(4)(I)						
		2.705(5)(II)						
		S **2.345(2)**(A,II)						
		2.370(2)(B,I)	1.280 [a]	1.385 [a]	1.322 [a]	1.363 [a]	1.721 [a]	
[Zn(APEtTSC)(OAc)]$_2$	6[ZnN$_2$O$_3$S]	N **2.09(2)**	1.267 [a]	1.378 [a]	1.332 [a]	1.347 [a]	1.737 [a]	[16]
Two different Zn atoms with two different kernels [ZnN$_2$O$_2$S] and [ZnN$_2$O$_3$S]		2.155(14)						
		O 2.042(13)						
		2.150(10)						
		2.681(14)						
		S **2.368(5)**						
[Zn(HPT)$_2$]	6[N$_2$O$_2$S$_2$]	N **2.120(4)**	1.261(9)	1.385(6)	1.336(9)	1.337(7)	1.684(5)	[19]
		O 2.167(6)						
		S **2.474(2)**						
[Zn(H$_2$DAPTSC)(H$_2$O)$_2$](NO$_3$)$_2$	7[N$_3$O$_2$S$_2$]	N 2.213(7)						[9]
		2.344(9)(A)	1.297 [a]	1.370 [a]	1.407 [a]	1.308 [a]	1.698 [a]	
		2.348(9)(B)	1.306 [a]	1.357 [a]	1.375 [a]	1.348 [a]	1.686 [a]	
		O 2.128(9)						
		2.13(1)						
		S **2.573(3)**(A)						
		2.586(3)(B)						

Table 1 (*Continued*)

Thiosemicarbazone complexes

Compound	CN[kernel]	d(M–L) (Å)	d(C^{2}–N^{3}) (Å)	d(N^{2}–N^{3}) (Å)	d(N^{2}–C^{1}) (Å)	d(C^{1}–N^{1}) (Å)	d(C^{1}–O) (Å)	Reference
[CdBr$_2$(HClBTSC)$_2$]	4[CdBr$_2$S$_2$]	Br 2.583(2)						[22]
		2.599(2)						
		S **2.526(2)**	1.292(6)	1.350(6)	1.322(6)	1.346(4)	1.699(6)	
		2.541(3)	1.294(5)	1.350(7)	1.323(5)	1.346(5)	1.687(6)	
[CdI$_2$(HATSC)]·H$_2$O	4[CdI$_2$S$_2$]	I 2.730(1)	1.290(1)	1.390(1)	1.340(1)	1.300(1)	1.705(9)	[23]
		2.743(1)						
		S **2.575(3)**						
[CdI$_2$(HBrBTSC)$_2$]	5[CdI$_3$S$_2$]	I 2.738(1)						[24]
		2.770(1)						
		4.105(6)						
		S **2.541(3)**				1.328(5)	1.698(5)	
		2.621(2)		1.359(6)	1.330(6)	1.297(4)	1.726(5)	
[CdI$_2$(HClBTSC)$_2$]	5[CdI$_3$S$_2$]	I 2.748(1)						[22]
		2.780(1)						
		4.120(8)						
		S **2.548(3)**	1.306(6)	1.387(7)	1.344(6)	1.328(5)	1.708(6)	
		2.634(2)	1.262(6)	1.393(6)	1.353(6)	1.298(5)	1.729(5)	
[CdCl$_2$(HPyTSC)]·H$_2$O	5[CdCl$_2$N$_2$S]	Cl 2.451(1)	1.282(4)	1.355(4)	1.356(4)	1.323(5)	1.687(4)	[25]
		2.4777(9)						
		N **2.359(3)**						
		2.374(3)						
		S **2.593(1)**						
[Cd(PyTSC)$_2$]	6[CdN$_4$S$_2$]	N **2.347(8)**(I)	1.28(1)	1.36(1)	1.33(1)	1.36(1)	1.74(1)	[25]
		2.358(9)(II)	1.29(1)	1.36(1)	1.33(1)	1.37(2)	1.71(1)	
		2.423(9)(I)						
		2.427(9)(II)						
		S **2.575(3)**(II)						
		2.579(3)(I)						

Table 1 (*Continued*)

Thiosemicarbazone complexes

Compound	CN[kernel]	*d*(M–L) (Å)	*d*(C^2–N^3) (Å)	*d*(N^2–N^3) (Å)	*d*(N^2–C^1) (Å)	*d*(C^1–N^1) (Å)	*d*(C^1–O) (Å)	Reference
[Cd$_3$(HMeOSTSC)$_4$](OAc)$_2$ ·0.5DMSO·2H$_2$O Trinuclear with two different types of kernel, [CdN$_2$O$_2$S$_2$] and [CdO$_8$]	6[CdN$_2$O$_2$S$_2$]	2.2–2.6	No data available					[26]
[CdCl$_2$(HDAPMTSC)(H$_2$O)]·H$_2$O	7[CdCl$_2$N$_2$O$_2$S]	Cl 2.563(2) 2.686(2) N 2.437(7) **2.527(7)** O 2.346(7) 2.488(6) S **2.617(2)**	1.28(1)	1.377(9)	1.35(1)	1.32(1)	1.681(9)	[27]
[Cd$_3$(HMeOSTSC)$_4$](OAc)$_2$ ·0.5DMSO·2H$_2$O Trinuclear, with two different types of kernel, [CdN$_2$O$_2$S$_2$] and [CdO$_8$]	8[CdO$_8$]	O 2.248 2.297 2.474 2.567	No data available					[26]
[HgMe(CPTSC)]	3[HgCNS]	C 2.09(1) N **2.537(8)** S **2.380(3)**	1.26(1)	1.39(1)	1.30(1)	1.35(1)	1.75(1)	[28]
[HgPh(CPTSC)]	4[HgCN$_2$S]	C 2.063(7) N **2.489(6)** **3.001(6)** S **2.382(2)**	1.264(9)	1.403(8)	1.302(9)	1.348(9)	1.751(7)	[29]
[Hg(PyPh)(HSTSC)]	4[HgCN$_2$S]	C 2.083(7) N 2.576(6) **3.126(6)** S **2.357(2)**	1.274(9)	1.387(7)	1.288(9)	1.352(8)	1.782(7)	[30]

Table 1 (*Continued*)

Thiosemicarbazone complexes

Compound	CN[kernel]	*d*(M–L) (Å)	*d*(C^2–N^3) (Å)	*d*(N^2–N^3) (Å)	*d*(N^2–C^1) (Å)	*d*(C^1–N^1) (Å)	*d*(C^1–O) (Å)	Reference
[HgPh(MBTSC)]	4[$HgCNS_2$]	C 2.069(10) N **2.611(7)** S **2.357(3)** **3.518(3)**	1.292(11)	1.384(10)	1.296(11)	1.339(11)	1.781(9)	[29]
[HgPh(PTSC)]	4[$HgCNS_2$]	C 2.049(11) N **2.492(9)** S **2.377(3)** **3.528(3)**	1.28(2)	1.400(12)	1.30(2)	1.36(2)	1.742(11)	[29]

[a] Data from CSD [5].

Table 2
Complexes of semicarbazones and thiosemicarbazones with Group 13 metals (Al, Ga, In and Tl)

Thiosemicarbazone complexes

Compound	CN[kernel]	d(M–L) (Å)	d(C^2–N^3) (Å)	d(N^2–N^3) (Å)	d(N^2–C^1) (Å)	d(C^1–N^1) (Å)	d(C^1–O) (Å)	Reference
[In(H_2DAPSC)(H_2O)$_2$](OH)(NO_3)$_2$	7[InN_3O_4]	N **2.257**(A) 2.272 **2.310**(B) O 2.135 **2.151**(A) 2.154 **2.216**(B)	No data available					[38]

Thiosemicarbazone complexes

Compound	CN[kernel]	d(M–L) (Å)^b	d(C^2–N^3) (Å)	d(N^2–N^3) (Å)	d(N^2–C^1) (Å)	d(C^1–N^1) (Å)	d(C^1–S) (Å)	Reference
[(AlMe)(AlMe$_2$)$_2$(AABMeTSC)] Trinuclear with two types of kernel, [AlC_2N_2] and [$AlCN_2S_2$]	4[AlC_2N_2]	C 1.936(5) 1.944(5) N **1.897(4)** **2.001(3)**	1.287(5)	1.394(4)	1.364(5)	1.307(5)	1.720(4)	[32]
[(AlMe$_2$)$_2$(AP^{i}prTSC)] Two independent molecules, each with two kernels: [AlC_2N_2] (Al_2 and Al_4) and [AlC_2N_2S] (Al_1 and Al_3)	4[AlC_2N_2]	Al_2 C 1.939(7) 1.953(7) N **1.915(5)** **1.946(5)**	1.320(7)	1.362(6)	1.380(7)	1.318(7)	1.691(6)	[33]
		Al_4 C 1.928(8) 1.946(8) N **1.913(5)** **1.953(5)**	1.299(6)	1.349(6)	1.380(7)	1.309(7)	1.709(5)	

Table 2 (*Continued*)

Thiosemicarbazone complexes

Compound	CN[kernel]	d(M–L) (Å)	d(C^2–N^3) (Å)	d(N^2–N^3) (Å)	d(N^2–C^1) (Å)	d(C^1–N^1) (Å)	d(C^1–O) (Å)	Reference
[(AlMe)(AlMe$_2$)(P^{i}prTSC)]$_2$ Tetranuclear with two different kernels, [AlC$_2$N$_2$] and [AlCN$_2$S]	4[AlC$_2$N$_2$]	C 1.946(7) 1.957(7) N **1.910(4)** **1.955(4)**	1.307(6)	1.416(6)	1.362(6)	1.305(6)	1.755(5)	[34]
[(AlMe)(AlMe$_2$)(P^{i}prTSC)]$_2$ Tetranuclear, with two different kernels, [AlC$_2$N$_2$] and [AlCN$_2$S]	4[AlCN$_2$S]	C 1.944(6) N **1.885(4)** **1.902(4)** S **2.326(2)**	1.307(6)	1.416(6)	1.362(6)	1.305(6)	1.755(5)	[34]
[(AlMe)(AlMe$_2$)$_2$(AABMeTSC)] Trinuclear, with two types of kernel [AlC$_2$N$_2$] and [AlCN$_2$S$_2$]	5[AlCN$_2$S$_2$]	C 1.936(6) N **1.967(3)** S **2.414(1)**	1.287(5)	1.394(4)	1.364(5)	1.307(5)	1.720(4)	[32]
[(AlMe$_2$)$_2$(AP^{i}prTSC)] Two independent molecules, each with two different kernels: [AlC$_2$N$_2$] (Al$_2$ and Al$_4$) and [AlC$_2$N$_2$S] (Al$_1$ and Al$_3$)	5[AlC$_2$N$_2$S]	Al$_1$ C 1.947(7) 1.962(7) N **2.040(5)** **2.076(5)** S **2.491(3)** Al$_3$ C 1.951(7) 1.977(7) N **2.057(5)** **2.088(5)** S **2.487(2)**	1.320(7) 1.299(6)	1.362(6) 1.349(6)	1.380(7) 1.380(7)	1.318(7) 1.309(7)	1.691(6) 1.709(5)	[33]
[(GaMe$_2$)$_2$(AcPhTSC)] Two Ga atoms, with kernels [GaC$_2$N$_2$] and [GaC$_2$NS], coordinated to the same thiosemicarbazone ligand	4[GaC$_2$N$_2$]	C 1.940(6) 1.965(6) N **1.996(4)** **2.070(3)**	1.281(6)	1.401(5)	1.363(6)	1.318(5)	1.747(5)	[33]

Table 2 (*Continued*)

Thiosemicarbazone complexes

Compound	CN[kernel]	*d*(M–L) (Å)	*d*(C^2–N^3) (Å)	*d*(N^2–N^3) (Å)	*d*(N^2–C^1) (Å)	*d*(C^1–N^1) (Å)	*d*(C^1–O) (Å)	Reference
[(GaMe$_2$)$_2$(AcPhTSC)] Two Ga atoms, with kernels [GaC$_2$N$_2$] and [GaC$_2$NS], coordinated to the same thiosemicarbazone ligand	4[GaC$_2$NS]	C 1.953(6) 1.961(7) N **2.033(3)** S **2.378(1)**	1.281(6)	1.401(5)	1.363(6)	1.318(5)	1.747(5)	[33]
[(GaMe$_2$)$_2$(TFPhTSC)] Two different Ga atoms, with kernels [GaC$_2$NS] and [GaC$_2$N$_2$S], coordinated to the same ligand	4[GaC$_2$NS]	C 1.936(5) 1.950(4) N **2.056(3)** S **2.407(1)**	1.302(4)	1.384(4)	1.358(4)		1.727(4)	[34]
[(GaMe$_2$)$_2$(TFPhTSC)] Two different Ga atoms, with kernels [GaC$_2$NS] and [GaC$_2$N$_2$S], coordinated to the same ligand	5[GaC$_2$N$_2$S]	C 1.956(5) 1.959(4) N **1.968(3)** **2.109(3)** S **3.30**	1.302(4)	1.384(4)	1.358(4)		1.727(4)	[34]
[GaCl$_2$(PATSC)]	5[GaCl$_2$N$_2$S]	Cl 2.195(4) 2.213(4) N **2.047(9)** S **2.344(4)**	No data available					[35]
[GaMe$_2$(FMeTSC)]	5[GaC$_2$NOS]	C 1.93(1) 1.96(1) N **2.089(7)** O 2.88 S **2.328(3)**	1.29(1)	1.40(1)	1.31(1)	1.35(1)	1.74(1)	[34]

Table 2 (*Continued*)

Thiosemicarbazone complexes

Compound	CN[kernel]	*d*(M–L) (Å)	*d*(C^2–N^3) (Å)	*d*(N^2–N^3) (Å)	*d*(N^2–C^1) (Å)	*d*(C^1–N^1) (Å)	*d*(C^1–O) (Å)	Reference
[(InMe)(InMe$_2$)$_2$(APPhTSC)$_2$]·THF	5[InC$_2$N$_3$]	C 2.143(7)	1.296(6)	1.370(5)	1.389(6)	1.291(7)	1.746(5)	[36]
Trinuclear with two types of In		2.151(7)						
kernel, [InC$_2$N$_3$] and [InCN$_2$S$_2$]		N **2.298(4)**						
		2.317(4)						
		2.418(4)						
[(InMe)(InMe$_2$)$_2$(AABMeTSC)(THF)$_2$]	5[InCN$_3$S]	C 2.17(4)						[36]
Trinuclear, with three types of In		N **2.16(1)**	1.28(1)	1.38(1)	1.36(2)	1.31(2)	1.77(1)	
kernel, [InCN$_3$S], [InC$_2$N$_2$O] and		**2.271(9)**	1.29(1)	1.36(1)	1.36(1)	1.329 [a]	1.75(1)	
[InC$_2$NOS]		**2.30(1)**						
		S **2.550(4)**						
[(InMe)(InMe$_2$)$_2$(AABMeTSC)(THF)$_2$]	5[InC$_2$N$_2$O]	C 2.13(1)	1.29(1)	1.36(1)	1.36(1)	1.329 [a]	1.75(1)	[36]
Trinuclear, with three types of In		2.13(2)						
kernel, [InCN$_3$S],[InC$_2$N$_2$O] and		N **2.19(1)**						
[InC$_2$NOS]		**2.358(9)**						
		O 2.572(8)						
[(InMe)(InMe$_2$)$_2$(APPhTSC)$_2$]·THF	5[InCN$_2$S$_2$]	C 2.10(1)	1.296(6)	1.370(5)	1.389(6)	1.291(7)	1.746(5)	[36]
Trinuclear with two types of In		N **2.394(4)**						
kernel, [InC$_2$N$_3$] and [InC$_2$NS$_2$]		S **2.491(2)**						
[(InMe)(InMe$_2$)$_2$(AABMeTSC)(THF)$_2$]	5[InC$_2$NOS]	C 2.13(4)	1.28(1)	1.38(1)	1.36(2)	1.31(2)	1.77(1)	[36]
Trinuclear with three types of In		2.18(2)						
kernel, [InCN$_3$S], [InC$_2$N$_2$O] and		N **2.33(1)**						
[InC$_2$NOS]		O 2.57(1)						
		S **2.561(4)**						

Table 2 (*Continued*)

Thiosemicarbazone complexes

Compound	CN[kernel]	d(M–L) (Å)	d(C^2–N^3) (Å)	d(N^2–N^3) (Å)	d(N^2–C^1) (Å)	d(C^1–N^1) (Å)	d(C^1–O) (Å)	Reference
[In(APTSC)$_2$]PF$_6$	6[InN$_4$S$_2$]	N **2.230(4)**(I)	1.294(6)	1.381(5)	1.313(6)	1.337 [a]	1.745(5)	[37]
		2.250(4)(II)	1.294(6)	1.369(5)	1.312(6)	1.343 [a]	1.749(5)	
		2.283(4)(I)						
		2.297(4)(II)						
		S **2.505(1)**(II)						
		2.519(1)(I)						
(H$_2$APTSC)[InCl(APTSC)(mnt)]	6[InClN$_2$S$_3$]	Cl 2.751(2)						[37]
·0.5H$_2$O								
		N **2.286(5)**	1.301(8)	1.367(7)	1.328(8)	1.350 [a]	1.729(6)	
		2.308(5)						
		S 2.510(2)						
		2.529(2)						
		2.561(2)						
[InCl(APTSC)(Et$_2$dtc)]	6[InClN$_2$S$_3$]	Cl 2.50	No data available					[37]
		N **2.24**						
		2.32						
		S **2.50**						
		2.51						
		2.68						
[InCl$_2$(APTSC)(MeOH)]	6[InCl$_2$N$_2$OS]	Cl 2.412(2)						[37]
		2.465(3)						
		N 2.233(7)						
		2.269(6)	1.30(1)	1.375(9)	1.33(1)	1.337 [a]	1.744(7)	
		O 2.363(6)						
		S **2.483(3)**						

Table 2 (*Continued*)

Thiosemicarbazone complexes

Compound	CN[kernel]	*d*(M–L) (Å)	*d*(C^2–N^3) (Å)	*d*(N^2–N^3) (Å)	*d*(N^2–C^1) (Å)	*d*(C^1–N^1) (Å)	*d*(C^1–O) (Å)	Reference
{O[In(HDAPTSC)(OH)]$_2$}·5MeOH	7[$InN_3O_2S_2$]	N 2.92(7)						[37]
		2.357(8)(A)	1.298 [a]	1.38(1)	1.33(1)	1.352 [a]	1.71(1)	
		2.391(8)(B)	1.32(1)	1.34(1)	1.34(1)	1.344 [a]	1.64(1)	
		O 2.0750(9)						
		2.170(7)						
		S **2.558(3)**(A)						
		2.595(3)(B)						
[InCl$_2$(HDAPTSC)]·2DMSO	7[$InCl_2N_3S_2$]	Cl 2.497(2)						[37]
		2.535(2)						
		N 2.330(5)						
		2.335(5)(A)	1.280(8)	1.377 [a]	1.322(8)	1.335 [a]	1.743(6)	
		2.458(5)(B)	1.281(8)	1.376(7)	1.361(8)	1.318 [a]	1.680(6)	
		S **2.572(2)**(A)						
		2.670(2)(B)						
[TlMe$_2$(CPTSC)(HCPTSC)]	5[TlC_2NS_2]	C 2.07(3)	1.30(2)	1.39(2)	1.31(2)	1.36(2)	1.78(2)	[39]
		2.13(3)						
		N **2.55(1)**						
		S **2.627(5)**						
		3.249(5)						
[TlMe$_2$(*p*-ATSC)]	5[TlC_2NS_2]	C 2.14(2)	1.30(2)	1.37(2)	1.31(2)	1.39(2)	1.73(2)	[40]
		2.15(2)						
		N 2.56(1)						
		S 2.991(4)						
		3.304(4)						

Table 2 (*Continued*)

Thiosemicarbazone complexes								
Compound	CN[kernel]	d(M–L) (Å)	d(C^2–N^3) (Å)	d(N^2–N^3) (Å)	d(N^2–C^1) (Å)	d(C^1–N^1) (Å)	d(C^1–O) (Å)	Reference
[TlMe$_2$(PyTSC)] Two independent Tl atoms, Tl(1) and Tl(2), with slightly different kernels	6[$TlC_2N_2S_2$]	**Tl(1)** C 2.115(8) 2.12(1) N **2.557(5)** 2.686(8) S **2.848(3)** **3.671(2)**	1.259(8)	1.378(8)	1.30(1)	1.368(9)	1.738(8)	[41]
		Tl(2) C 2.125(9) 2.13(1) N 2.700(6) **2.712(5)** S **2.803(2)** **3.207(3)**	1.267(8)	1.363(8)	1.331(9)	1.351(9)	1.719(7)	
[TlMe$_2$(HPxTSC)(H$_2$O)]$_2$	6[$TlC_2O_2S_2$]	C 2.134(8) 2.136(8) O 2.630(4) 3.124(4) S **2.832(1)** **3.190(1)**	1.303(7)	1.343(6)	1.338(7)	1.333(7)	1.742(6)	[42]

Table 2 (*Continued*)

Thiosemicarbazone complexes									
Compound	CN[kernel]	d(M–L) (Å)		$d(C^2–N^3)$ (Å)	$d(N^2–N^3)$ (Å)	$d(N^2–C^1)$ (Å)	$d(C^1–N^1)$ (Å)	$d(C^1–O)$ (Å)	Reference
$[TlMe_2(DAPMTSC)]_2$	$7[TlC_2N_2O_2S]$	C	2.128(9)	1.289(10)	1.364(8)	1.300(11)	1.376(10)	1.696(10)	[43]
			2.133(9)						
		N	**2.590(6)**						
			2.686(2)						
		O	2.883(6)						
			3.050(6)						
		S	**2.872(2)**						
$[TlPh_2(DAPMTSC)]_2·2CHCl_3$	$7[TlC_2N_2O_2S]$	C	2.13(2)	1.27(2)	1.35(2)	1.29(2)	1.34(2)	1.71(2)	[43]
			2.16(2)						
		N	**2.56(2)**						
			2.579(14)						
		O	2.86(1)						
			3.42(1)						
		S	**2.791(6)**						

[a] Data from CSD [5].

Table 3
Complexes of semicarbazones and thiosemicarbazones with Group 14 metals (Sn and Pb)

Semicarbazone complexes

Compound	CN[kernel]	d(M–L) (Å)		d(C^2–N^3) (Å)	d(N^2–N^3) (Å)	d(N^2–C^1) (Å)	d(C^1–N^1) (Å)	d(C^1–O) (Å)	Reference
[SnBu$_2$(SSC)]	5[SnC$_2$NO$_2$]	C	2.142(21)						[45]
			2.176(15)						
		N	**2.149(8)**	1.289 [a]	1.403 [a]	1.305 [a]	1.325 [a]	1.279 [a]	
		O	2.089(10)						
			2.137(9)						
[SnCl$_2$(H$_2$DAPSC)]Cl$_2$·2H$_2$O	7[SnCl$_2$N$_3$O$_2$]	Cl	2.3544(24)						[53]
			2.3681(24)						
		N	**2.259(6)**(A)	1.297(11)	1.336(10)	1.367(12)	1.322(12)	1.267(10)	
			2.260(7)						
			2.272(7)(B)	1.277(12)	1.371(9)	1.360(12)	1.304(11)	1.282(10)	
		O	**2.123(6)**(A)						
			2.127(5)(B)						
[SnMeCl(H$_2$DAPSC)]Cl$_2$·2H$_2$O	7[SnCClN$_3$O$_2$]	C	2.122(9)						[54]
		Cl	2.386(2)						
		N	**2.252(7)**(A)	1.295 [a]	1.355 [a]	1.378 [a]	1.329 [a]	1.266 [a]	
			2.262(2)						
			2.284(7)(B)	1.293 [a]	1.377 [a]	1.360 [a]	1.333 [a]	1.266 [a]	
		O	**2.177(6)**(B)						
			2.180(6)(A)						
[PbCl(H$_2$DAPSC)]NO$_3$	6[PbClN$_3$O$_2$]	Cl	2.707(4)	No data available					[57]
		N	2.523(8)						
			2.556(8)(A)						
			2.668(7)(B)						
		O	**2.607(6)**(A)						
			2.872(7)(B)						
[Pb(NO$_3$)$_2$(HDIPSC)]	7[PbN$_2$O$_5$]	N	**2.547(4)**	1.291(6)	1.347(7)	1.372(6)	1.327(8)	1.249(6)	[58]
			2.598(4)						

Table 3 (*Continued*)

Semicarbazone complexes

Compound	CN[kernel]	d(M–L) (Å)	d(C^{2}–N^{3}) (Å)	d(N^{2}–N^{3}) (Å)	d(N^{2}–C^{1}) (Å)	d(C^{1}–N^{1}) (Å)	d(C^{1}–O) (Å)	Reference
		O **2.548(4)** 2.651(5) 2.676(6) 2.755(4) 2.801(5)						
[PbCl$_2$(H$_2$CHDSC)(DMF)]	7[PbCl$_2$N$_2$O$_3$]	Cl 2.870(3) N **2.585(6)** O **2.577(6)** 2.805(17)	1.29(1)	1.362(8)	1.37(1)	1.347(9)	1.228(9)	[58]
[Pb(NO$_3$)$_2$(H$_2$PHENSC)]	10[PbN$_4$O$_6$]	N **2.727** 2.731 **O** 2.735 **2.739** 2.823	1.271 [a]	1.361 [a]	1.388 [a]	1.337 [a]	1.231 [a]	[60]

Thiosemicarbazone complexes

Compound	CN[kernel]	d(M–L) (Å)[b]	d(C^{2}–N^{3}) (Å)	d(N^{2}–N^{3}) (Å)	d(N^{2}–C^{1}) (Å)	d(C^{1}–N^{1}) (Å)	d(C^{1}–S)(Å)	Reference
[SnPh$_3$(HMeSTSC)]	4[SnC$_3$S]	C 2.113(4) 2.115(5) 2.150(4) S **2.440(2)**	1.283 [a]	1.411 [a]	1.289 [a]	1.343 [a]	1.741 [a]	[44]
[SnBu$_2$(STSC)]	5[SnC$_2$NOS]	C 2.096(11) 2.132(10) N **2.227(4)** O 2.103(6) S **2.537(2)**	1.293 [a]	1.378 [a]	1.310	1.331 [a]	1.712 [a]	[45]

Table 3 (*Continued*)

Thiosemicarbazone complexes

Compound	CN[kernel]	*d*(M–L) (Å)	*d*(C^2–N^3) (Å)	*d*(N^2–N^3) (Å)	*d*(N^2–C^1) (Å)	*d*(C^1–N^1) (Å)	*d*(C^1–O) (Å)	Reference
[SnMe$_2$(STSC)]	5[SnC$_2$NOS]	C 2.103(3) 2.125(3) N **2.199(2)** O 2.111(2) S **2.5425(8)**	1.300(3)	1.384(3)	1.312(3)	1.337(3)	1.724(3)	[46]
[SnPh$_2$(STSC)]	5[SnC$_2$NOS]	C 2.127(5) 2.128(5) N **2.196(4)** O 2.072(3) S **2.546(1)**	1.295(6)	1.396(6)	1.300(6)	1.358(7)	1.733(5)	[46]
[SnMe$_2$(PyTSC)Cl]·0.5H$_2$O	5[SnC$_2$ClNS]	C 2.105(7) 2.108(7) Cl 2.672(1) N **2.359(4)** S **2.478(2)**	1.290(6)	1.377(5)	1.318(6)	1.329(6)	1.726(5)	[47]
[SnCl(HPT)]$_2$	5[SnClNO$_2$S]	Cl 2.489 N **2.491** O 2.268 2.822 S **2.862**	1.288 [a]	1.364 [a]	1.362 [a]	1.315 [a]	1.681 [a]	[48]
[SnCl$_3$(PyTSC)]	6[SnCl$_3$N$_2$S]	Cl 2.360(1) 2.415(1) 2.433(1) N **2.194(2)** 2.225(3) S **2.463(1)**	1.275(4)	1.368(3)	1.324(4)	1.326 [a]	1.753(3)	[49]
[SnPh$_2$Cl$_2$(HATSC)$_2$]	6[SnC$_2$Cl$_2$S$_2$]	C 2.142(3) Cl 2.589(1) S **2.712(1)**	1.278(3)	1.396(3)	1.327(2)	1.313(3)	1.724(2)	[50]

Table 3 (*Continued*)

Thiosemicarbazone complexes

Compound	CN[kernel]	d(M–L) (Å)	d(C^2–N^3) (Å)	d(N^2–N^3) (Å)	d(N^2–C^1) (Å)	d(C^1–N^1) (Å)	d(C^1–O) (Å)	Reference
[SnMe$_2$(PyTSC)(OAc)]·HOAc	6[SnC$_2$N$_2$OS]	C 2.096(6)	1.286(6)	1.359(6)	1.318(7)	1.326(7)	1.733(5)	[51]
		2.104(5)						
		N **2.431(4)**						
		2.561(4)						
		O 2.220(3)						
		S **2.509(1)**						
[SnPh$_2$(HAPT)Cl]·H$_2$O	6[SnC$_2$N$_2$ClS]	C 2.130(6)	1.300(10)	1.379(8)	1.304(9)	1.369(9)	1.748(6)	[52]
		2.135(9)						
		N **2.331(5)**						
		2.509(8)						
		Cl 2.601(2)						
		S **2.505(2)**						
[SnPh$_2$(DAPTSC)]·2DMF	7[SnC$_2$N$_3$S$_2$]	C 2.178(4)						[55]
		2.179(4)						
		N 2.368(3)						
		2.421(4)(A)	1.306(7)	1.381(5)	1.333(6)	1.338(6)	1.729(5)	
		2.427(4)(B)	1.307(6)	1.365(5)	1.331(7)	1.341(6)	1.731(5)	
		S **2.593(1)**(B)						
		2.603(1)(A)						
[SnPh$_2$(HDAPTSC)]Cl	7[SnC$_2$N$_3$S$_2$]	C 2.163(4)						[56]
		2.170(4)						
		N 2.348(4)						
		2.353(4)(A)	1.290(6)	1.371(5)	1.322(6)	1.351(6)	1.731(5)	
		2.491(4)(B)	1.290(6)	1.377(6)	1.347(7)	1.327(7)	1.694(6)	
		S **2.592(1)**(A)						
		2.703(1)(B)						
[SnMeCl(HDAPTSC)]Cl·MeOH	7[SnCClN$_3$S$_2$]	C 2.166(8)						[54]
		Cl 2.476(2)						
		N 2.238(6)						
		2.288(6)(A)	1.259 [a]	1.364 [a]	1.303 [a]	1.344 [a]	1.738 [a]	
		2.430(6)(B)	1.283 [a]	1.373 [a]	1.359 [a]	1.309 [a]	1.682 [a]	
		S **2.527(2)**(A)						
		2.633(2)(B)						

Table 3 (*Continued*)

Thiosemicarbazone complexes								
Compound	CN[kernel]	d(M–L) (Å)	d(C^2–N^3) (Å)	d(N^2–N^3) (Å)	d(N^2–C^1) (Å)	d(C^1–N^1) (Å)	d(C^1–O) (Å)	Reference
[SnBu$_2$(APTS)(Oac)]	7[SnC$_2$N$_2$O$_2$S]	**Sn(1)**						
Two independent Sn atoms, Sn(1) and Sn(2), with slightly different kernels		C 2.130(6)	1.301(6)	1.382(5)	1.327	1.346(7)	1.725(5)	[52]
		2.149(5)						
		N **2.370(4)**						
		2.445(4)						
		O 2.337(3)						
		2.545(4)						
		S **2.582(2)**						
		Sn(2)						
		C 2.140(8)	1.300(7)	1.370(7)	1.317(7)	1.341(7)	1.737(5)	
		2.144(7)						
		N **2.367(4)**						
		2.383(5)						
		O 2.404(4)						
		2.436(4)						
		S **2.641(2)**						
[Pb(APMeTSC)(OAc)]	7[PbN$_3$O$_3$S]	N **2.482(7)**	1.291 [a]	1.391 [a]	1.340 [a]	1.338 [a]	1.742 [a]	[59]
		2.546(8)						
		3.039(8)						
		O 2.352(7)						
		2.996(7)						
		3.244(8)						
		S **2.730(3)**						
[Pb(HPT)$_2$]$_2$	7[PbN$_2$O$_3$S$_2$]	N **2.731**(I)	1.30(3)	1.39(2)	1.36(3)	1.30(3)	1.70(2)	[48]
		2.765(II)	1.28(3)	1.36(3)	1.37(3)	1.31(2)	1.69(2)	
		O 2.427						
		2.807[a]						
		2.942						
		S **2.876**(II)						
		3.059(I)[a]						

[a] Data from CSD [5].

Table 4
Complexes of thiosemicarbazones with Group 15 metals (Bi)

Compound	CN[kernel]	d(M–L) (Å)[b]	d(C^2–N^3) (Å)	d(N^2–N^3) (Å)	d(N^2–C^1) (Å)	d(C^1–N^1) (Å)	d(C^1–S) (Å)	Reference
[Bi(TFHTSC)$_2$(NO$_3$)]·MeOH	5[BiN$_2$OS$_2$]	N **2.438(10)**(I)	No data					[61]
		2.445(11)(II)						
		O 2.889(11)						
		S **2.561(3)**(II)						
		2.565(4)(I)						
[BiCl$_2$(TFHTSC)(HTFHTSC)]	5[BiCl$_2$NS$_2$]	Cl 2.605(4)	No data					[61]
		2.630(4)						
		N **2.518(8)**(I)						
		S **2.527(3)**(I)						
		2.992(3)(II)						
[Bi(N$_3$)(DAPTSC)]·0.5DMSO	6[BiN$_4$S$_2$]	N 2.25(2)						[62]
		2.44(2)						
		2.46(2)(A)	1.24(3)	1.41(3)	1.31(3)	1.36(3)	1.71(2)	
		2.58(2)(B)	1.24(3)	1.39(3)	1.36(3)	1.28(3)	1.80(3)	
		S **2.685(7)**(A)						
		2.717(8)(B)						
[BiCl$_2$(APHTSC)]$_2$	6[BiCl$_3$N$_2$S]	Cl 2.583(3)	No data					[61]
		2.791(3)						
		3.162						
		N 2.501(8)						
		2.355(8)						
		S **2.583(3)**						
[Bi(APHTSC)$_2$(NO$_3$)]	7[BiN$_4$OS$_2$]	N **2.471(8)**(I)	No data					[61]
		2.581(8)(II)						
		2.649(9)(II)						
		2.711(10)(I)						
		O 2.731(11)						
		S **2.584(4)**(I)						
		2.654(4)(II)						

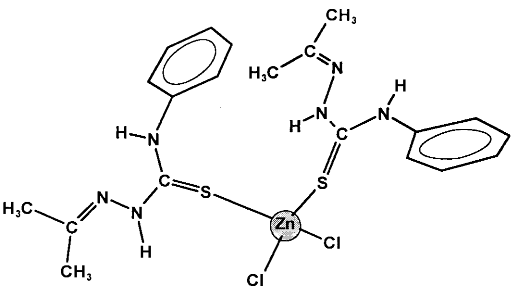


Fig. 2. Adapted from Ref. [10].

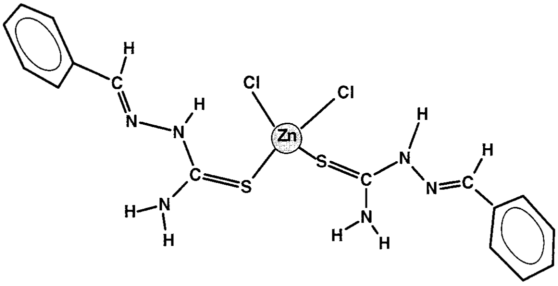


Fig. 3. Adapted from Ref. [11].

Zn(1) has a distorted tetrahedral geometry created by *N*(3),*S*-chelation by one TSC chain of each of two DAPTSC^{2-} anions. Both TSC chains which in the free ligand have *E*-configuration (Scheme 1, **I**) achieve the *Z*-configuration required for *N*(3),*S*-chelation (Scheme 1, **IV**) by rotating 180° around the N(2)–C(1) bond; this is the commonest arrangement found among TSC complexes. Zn(2), which is *N*(3),*S*-chelated by the other TSC chains of the two DAPTSC^{2-} anions, also interacts with the two pyridine N atoms, giving rise to a distorted octahedral coordination geometry.

Acetone *N*^{1}-phenylthiosemicarbazone and zinc dichloride form the adduct [ZnCl$_2$(HAPhTSC)$_2$] (Fig. 2). In this case, each of the two undeprotonated TSC ligands coordinates to the metal only through its sulphur atom, retaining the usual *E*-configuration of the free, unsusbtituted, undeprotonated ligand around the N(2)–C(1) bond. The metal centre is surrounded by the two chloride ligands and the two sulphur atoms in a distorted tetrahedral arrangement [10]. An intramolecular hydrogen bond between one of the Cl ligands and the –N(2)H group of a neighbouring molecule lengthens the corresponding Zn–Cl bond.

Like [ZnCl$_2$(HAPhTSC)$_2$], [ZnCl$_2$(HBTSC)$_2$] (Fig. 3) contains two neutral TSC ligands in *E*-configuration that are both *S*-bound to the zinc atom. In this case, both Cl ligands are involved in both intra and intermolecular hydrogen bonds [11], which may be why the two Zn–Cl distances are more equal and the Zn–S bonds a little shorter than in the HAPhTSC adduct.

Surprisingly, acetone thiosemicarbazone (HATSC) [that is, HAPhTSC without the phenyl group on N(1)] forms a 1:1 adduct with $ZnCl_2$ in ethanol [12]: the colourless needles obtained recrystallizing from hot ethanol the solid first isolated consist of molecules of [$ZnCl_2$(HATSC)] in which the metal coordinates to an *N*,*S*-chelating TSC ligand and to two Cl ligands in a severely distorted tetrahedral coordination sphere (Fig. 4). As usual in *N*(3),*S*-chelating TSC (Scheme 1, **II**), the ligand adopts the *Z*-configuration with respect to the N(2)–C(1) bond. Hydrogen bonds link the [$ZnCl_2$(HATSC)] molecules in centro-symmetric dimer-like units.

2.1.2. Coordination number 5

Yampol'skaya et al. [13] prepared new thiosemicarbazonates of Zn(II) by reacting the acetate of the metal with several *S*-alkyl derivatives of salicylaldehyde thiosemicarbazone. The crystal structure of the *S*-ethyl derivative was solved by X-ray diffraction. Its basic structural unit is the dinuclear complex [Zn_2(SITSC)-$(OAc)_3$] (Fig. 5) in which the isothiosemicarbazone ligand has a deprotonated phenol group and adopts the imino form of the N(1)–C(1) bond, with a short N(1)–C(1) distance and N(1) and N(2) with one hydrogen atom each. The deprotonated hydroxyl group forms a one-atom bridge between the two zinc centres, as does one of the acetato ligands, while another acetato forms a three-atom bridge.

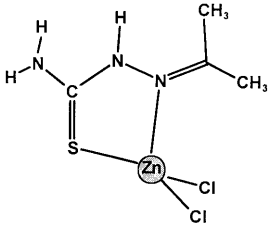


Fig. 4. Adapted from Ref. [12].

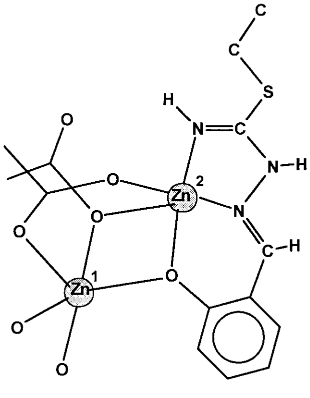


Fig. 5. Adapted from Ref. [13].

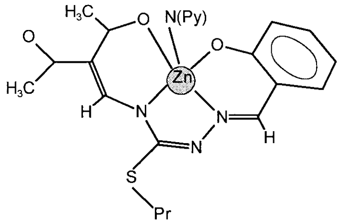


Fig. 6. Adapted from Ref. [14].

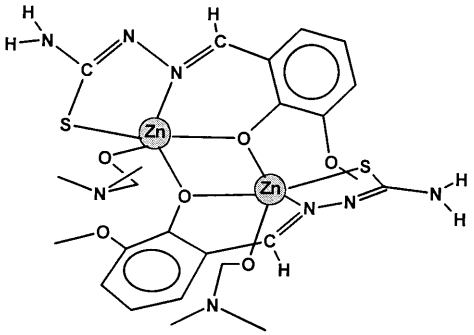


Fig. 7. Adapted from Ref. [15].

Both the zinc centres are five-coordinated: in one case the remaining two bonds are with the O atoms of the third acetato, and in the other with the N(1) and N(3) atoms of the isothiosemicarbazone chain, which accordingly adopts the *E*-configuration.

H_2SPITSC, an *S*-alkyl derivative of salicylaldehyde thiosemicarbazone that is also mono-substituted at N(1), reacts with zinc(II) acetate in methanol giving [Zn-(SPITSC)(MeOH)], which upon recrystallization from acetonitrile in the presence of pyridine affords [Zn(SPITSC)(Py)] [14] (Fig. 6). In this compound the metal ion is coordinated to a tetradentate SPITSC^{2-} ligand and to the N atom of the heterocycle. The coordination polyhedron can be described as a distorted tetragonal pyramid, the base of which comprises the four coordinated atoms of the SPITSC^{2-} anion which as in [Zn_2(SITSC)$(OAc)_3$] adopts the *E*-configuration allowing *N*(1),*N*(3)-chelation.

In the dimer [Zn(MeOSTSC)(DMF)]$_2$ (DMF = dimethylformamide), each dideprotonated *o*-vanillin thiosemicarbazone ligand adopts *Z*-configuration, coordinating through its N(3) and S atoms to one zinc ion and through its deprotonated hydroxyl O atom to both [15] (Fig. 7). The coordination number of each zinc is made up to 5 by a Zn–O bond coordinating it to a DMF molecule. The coordination polyhedron around each Zn(II) can be described as a distorted trigonal bipyramid.

Another dimer, [Zn(APEtTSC)(OAc)]$_2$, is afforded by deprotonation of 2-acetylpyridine N^1-ethylthiosemicarbazone (HAPEtTSC) with powdered sodium in

THF and subsequent reaction with zinc(II) acetate [16] (Fig. 8). In this case the metallic centres are bridged by two acetato ligands, one of which also chelates one of the metal ions in anisobidentate fashion. There are thus two different chromophores in the dimer; one [Zn(1)N_2O_2S] has trigonal bypyramidal coordination geometry, and the other, [Zn(2)N_2O_3S], pseudooctahedral geometry.

The structures of certain metal complexes of 3-ethoxy-2-oxobutyraldehyde bis(thiosemicarbazone) (H_2KTSC) have been determined in search of structure-activity relationships given their anti-tumour activity. In the complex [Zn(KTSC)(H_2O)] the Zn(II) ion is coordinated to a tetradentade $KTSC^{2-}$ anion and to a molecule of water [17] (Fig. 9). The coordination polyhedron is rather irregular lying

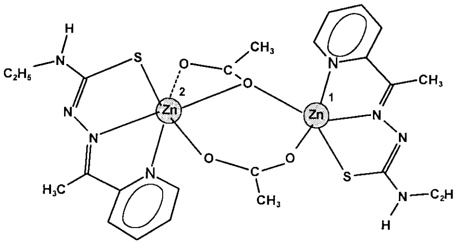


Fig. 8. Adapted from Ref. [16].

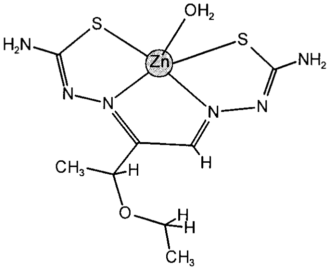


Fig. 9. Adapted from Ref. [17].

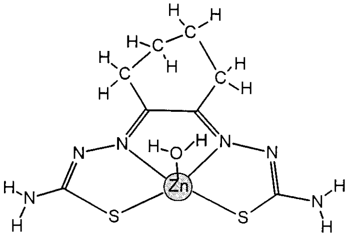


Fig. 10. Adapted from Ref. [18].

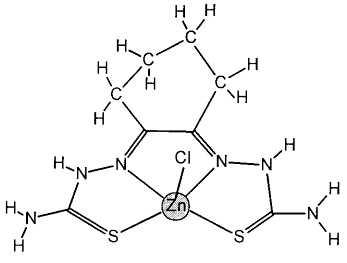


Fig. 11. Adapted from Ref. [18].

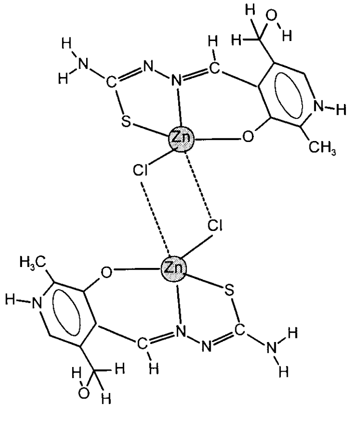


Fig. 12. Adapted from Ref. [19].

between a square pyramid and a trigonal bipyramid. Each arm of the bis(thiosemicarbazone) chelates the zinc ion via its S and N(3) atoms. Although the majority of the atoms of the chelate rings are coplanar, one thioamide group lies outside this plane.

A recent study of complexes of cyclohexane-1,2-dione bis(thiosemicarbazone) (H_2BCy) with zinc(II) ion [18] found that [Zn(BCy)]·EtOH (obtained reacting $Zn(OAc)_2$ with the TSC in ethanol) gave [Zn(BCy)(H_2O)]·DMF (Fig. 10) upon recrystallization from DMF, and that [Zn(H_2BCy)Cl_2]·EtOH (prepared mixing equimolar solutions of $ZnCl_2$ and the TSC in ethanol) gave [ZnCl(H_2BCy)]Cl·2H_2O (Fig. 11) upon recrystallization from methanol. Both contain five-coordinated metal ions in a distorted square-pyramidal arrangement in which the donor atoms of the two *N*(3),*S*-bidentate TSC arms form the base of the pyramid and an H_2O or Cl ligand occupies the apical position. As in other bis(thiosemicarbazonates), the metal–ligand bond lengths are not exactly the same for the two TSC arms; Table 1 includes values for both arms (A and B). The Zn–O distance in [Zn(BCy)(H_2O)]·DMF is unexceptional, but the Zn–Cl distance in the cationic complex $[ZnCl(H_2BCy)]^+$ is among the longest known values for non-bridging Zn–Cl bonds, possibly because the Cl is involved in three hydrogen bonds.

In [{ZnCl(HPxTSC)}$_2$]·2H_2O, centrosymmetric dimers are formed by asymmetric chloride bridges [19] (Fig. 12). The monodeprotonated ligands are coordinated to the zinc ion via the S and N(3) atoms of a TSC moiety in *Z*-configuration and the oxygen atom of the deprotonated phenolic hydroxyl group. The N(2) proton is also lost, but the ring N atom is protonated. The Zn(II) has coordination number five, and the coordination polyhedron is a distorted trigonal bipyramid with N(3) and the most distant Cl in the axial positions and the closest Cl, the sulphur and the phenolic oxygen in the equatorial positions.

In the monomer [$ZnCl_2$(HEPT)] [19] (Fig. 13), the zinc ion is bound to the TSC sulphur, N(3) and non-esterified carboxyl O atoms, and to two chloride ions. Although S and N(3) are well positioned for chelation, the Zn–S distance is rather long and the Zn–O distance (2.295 Å) is significantly longer than in [{ZnCl(HPxTSC)}$_2$]·2H_2O (1.955 Å), presumably because the ligand is neutral in [$ZnCl_2$(HEPT)].

2.1.3. Coordination number 6

The reaction of zinc dichloride and H_2DAPTSC in DMF gives a complex with stoichiometry [Zn_2(DAPTSC)$_2$]·2DMF. In spite of the similarity of this formula with

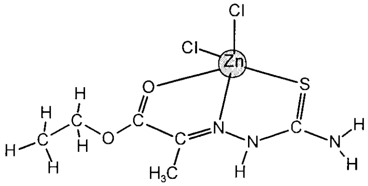


Fig. 13. Adapted from Ref. [19].

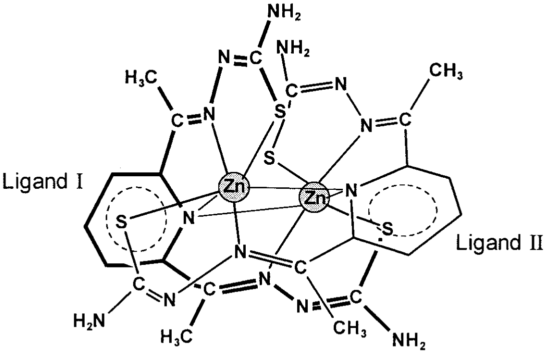


Fig. 14. Adapted from Ref. [9].

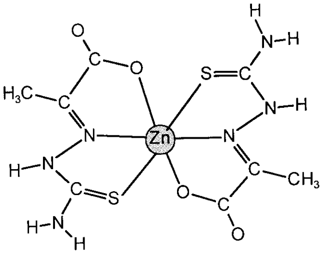


Fig. 15. Adapted from Ref. [19].

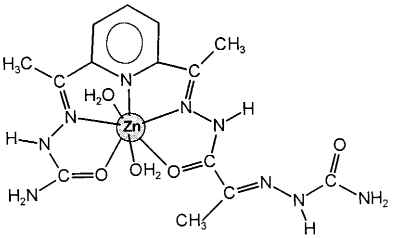


Fig. 16. Adapted from Ref. [20].

that of the compound formed in methanol (vide supra, coordination number 4), there are some significant structural differences between the two. Thus the complex isolated from DMF (Fig. 14) is a structural isomer of the other [9]. Both are dinuclear, but the former has a C_2 symmetry and the two pyridine nitrogens coordinated to both metal ions instead of just one. As a result, both the Zn(II) ions have coordination number 6, although the Zn–N(Py) distances [identified in Table 1 by (I) and (II)] are rather long and may be considered as indicating weak interactions.

Hydrolysis of methyl pyruvate TSC in the presence of zinc dichloride affords a complex of pyruvic acid TSC, $[Zn(HPT)_2]$ [19] (Fig. 15). In the *S*,*N*(3),*O*-tridentate ligands the carboxyl group is deprotonated but not the N(2)–H group, so the C(1)–S bond has the same length as in the free ligand (1.684 Å [19]) and the Zn–S distance is very long, suggesting a weak interaction. By contrast, the Zn–O distance is shorter than in $[ZnCl_2(HEPT)]$, in which the carboxyl group is uncharged. The metal ion is six-coordinated in a distorted octahedral geometry.

2.1.4. Coordination number 7

The two zinc(II) semicarbazone derivatives that have been studied by X-ray diffractometry, $[Zn(H_3DAPSCH)(H_2O)_2](ClO_4)_2 \cdot 1.5H_2O$ [20] and $[ZnCl(H_2DAPSC)(H_2O)]Cl \cdot 2H_2O$ [21], have closely related heptacoordinate structures. In the former (Fig. 16), the donor atoms of an almost planar pentadentate neutral ligand form the equatorial plane of a pentagonal bipyramidal coordination polyhedron having aquo ligands in its axial positions. An extensive network of hydrogen bonds involving the cationic complex, the perchlorate anions and the water of crystallization runs throughout the lattice. Note that since the donor atoms of the long arm of the ligand do not belong to the SC chain (in spite of being part of a very similar moiety), their bond lengths are not shown in bold type in Table 1.

The second zinc semicarbazone derivative (Fig. 17) has basically the same coordination pattern as the first, except that a chlorine ligand replaces an aquo ligand in one of the apical positions of the coordination polyhedron. In this complex the Zn–O distances are shorter and two of the Zn–N distances (one involving the pyridine nitrogen) are longer than in the other semicarbazonate.

The only TSC complex with coordination number seven has a multidentate ligand similar to those of the semicarbazonates. If zinc(II) acetate is used instead of zinc(II) chloride in the reaction with H_2DAPTSC in MeOH, subsequent acidification with nitric acid leads to the cationic complex [Zn(H_2DAPTSC)($H_2O)_2$]($NO_3)_2$ [9]. The five donor atoms of the bis-TSC form the equatorial plane of a pentagonal bipyramidal coordination polyhedron with the aquo ligands in the apical positions (Fig. 18). Although the TSC arms are not deprotonated, they coordinate through the N(3) and S atoms, creating typical five-membered chelate rings.

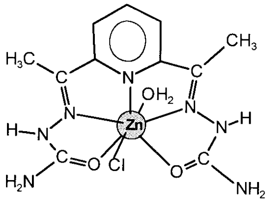


Fig. 17. Adapted from Ref. [21].

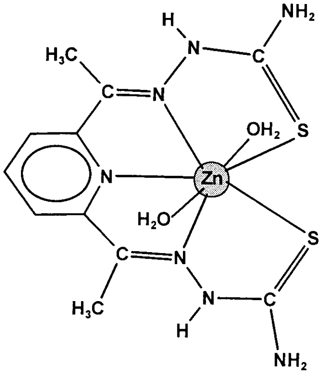


Fig. 18. Adapted from Ref. [9].

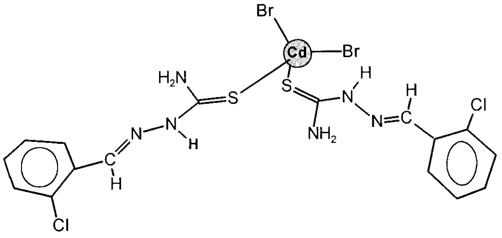


Fig. 19. Adapted from Ref. [22].

2.2. Cd

Eight complexes of Cd(II) containing TSC ligands have been studied by X-ray diffractometry. Only two include thiosemicarbazonato anions, the other six being adducts of cadmium dihalides. It seems that no SC complexes have had their crystal structures identified.

2.2.1. Coordination number 4

$[CdBr_2(HClBTSC)_2]$ consists of individual molecules in which two neutral TSC ligands in *E*-configuration are *S*-bound to the metal [22] (Fig. 19). Together with the two cadmium–bromide bonds, the two S–Cd bonds give the metal a distorted tetrahedral coordination geometry.

Direct reaction of CdI_2 and thiosemicarbazide in a mixture of acetone and H_2O affords $[CdI_2(HATSC)_2]\cdot H_2O$ where HATSC is neutral acetone thiosemicarbazone formed in situ [23]. The crystals of this complex consist of individual molecules similar to those of $[CdBr_2(HClBTSC)_2]$ (Fig. 19) with I ligands instead of Br ligands.

2.2.2. Coordination number 5

In all the remaining TSC adducts of cadmium(II) the metal is five-coordinated. $[CdI_2(HBrBTSC)_2]$ and $[CdI_2(HClBTSC)_2]$ have a larger coordination number than $[CdBr_2(HClBTSC)_2]$ and $[CdI_2(HATSC)_2]\cdot H_2O$ due to weak intermolecular Cd···I interactions that create discrete centrosymmetric dimers and give the metal ion a distorted trigonal bipyramidal environment [22,24].

In the complex $[CdCl_2(HPyTSC)]\cdot H_2O$ [25] the metal coordinates to the S,N(3) and pyridine N atoms of an *N*,*N*,*S*-tridentate pyridine-2-carbaldehyde thiosemicarbazone ligand and to the two chloro ligands in a very distorted trigonal bipyramidal structure in which the S and pyridine N atoms occupy the axial positions (Fig. 20). The main geometric distortion is due to the narrow bite of the ligand, which makes the S–Cd–N angle 141.5° instead of the theoretical 180°.

2.2.3. Coordination number 6

The first Cd(II) complex with a deprotonated TSC to be studied by X-ray diffractometry was $[Cd(PyTSC)_2]$, which was prepared by reacting HPyTSC with $Cd(OAc)_2$ in methanol [25]. The two *N*,*N*,*S*-coordinated ligands give the metal ion a highly distorted octahedral coordination polyhedron (Fig. 21). Although the configuration of the ligand is the same as in $[CdCl_2(HPyTSC)]\cdot H_2O$ and the Cd–N(3) distances in the two complexes are also similar, the Cd–S bonds seem stronger and Cd–N(Py) bonds weaker in $[Cd(PyTSC)_2]$. Also, in this compound the modifications of the structural parameters associated with the thiocarbamide group suggest evolution towards the thiol form.

Recrystallization from DMSO of the solid isolated when *o*-vanillin TSC reacts with cadmium(II) acetate in ethanol gives the polynuclear complex $[Cd_3(HMeOSTSC)_4](OAc)_2\cdot 0.5DMSO\cdot 2H_2O$ [26] (Fig. 22; for clarity, only one TSC anion is represented). The three Cd ions are bridged by the oxygen atoms of the deprotonated phenolic hydroxy groups belonging to the four TSC ligands, placing

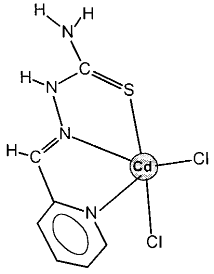


Fig. 20. Adapted from Ref. [25].

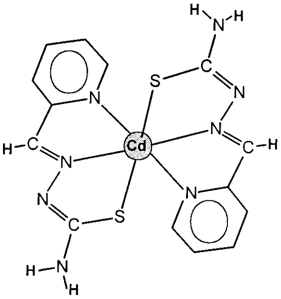


Fig. 21. Adapted from Ref. [25].

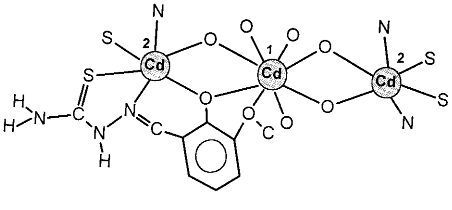


Fig. 22. Adapted from Ref. [26].

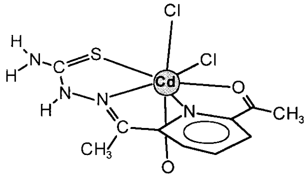


Fig. 23. Adapted from Ref. [27].

consecutive metal centres 3.607 Å apart. Each type 2 (terminal) Cd(II) is additionally coordinated to the N(3) and S atoms of two TSC ligands in *Z*-configuration, giving a $[CdN_2O_2S_2]$ kernel with distorted octahedral geometry, while the type 1 (central) Cd(II) attains a coordination number of eight through additional bonding to the four methoxy groups, giving a triangular dodecahedral coordination geometry.

2.2.4. Coordination number 7

A study of the interaction between cadmium dichloride and 2,6-diacetylpyridine bis(thiosemicarbazone), serendipitously led to isolation of the adduct $[CdCl_2(HDAPMTSC)(H_2O)]\cdot H_2O$, in which the monothiosemicarbazone ligand chelates the metal through its S, N(3), N(Py) and O(carbonyl) atoms [27] (Fig. 23). Together with one Cl ligand, these atoms form the equatorial plane of a distorted pentagonal bipyramid, the apical positions of which are occupied by the other chloride and the aquo ligand. The Cd–S, Cd–N(3) and Cd–N(Py) distances are longer than the equivalent bonds in $[CdCl_2(HPyTSC)]\cdot H_2O$, probably due to the increase in the coordination number from 5 to 7. The Cd–O(carbonyl) distance is rather long (see Table 1), while the Cd–O_w distance is within the usual range for coordinated water in cadmium(II) compounds.

2.2.5. Coordination number 8

See coordination number 6 (Ref. [26], Fig. 22).

2.3. Hg

The five TSC complexes of mercury that have been studied by X-ray diffractometry all contain organomercuric moieties. As usual in mercury(II) coordination chemistry, their coordination numbers are small and their kernels contain two strong linear bonds and one or more weak (secondary) bonds.

2.3.1. Coordination number 3

The only HgTSC complex with coordination number 3, [HgMe(CPTSC)], is a typical methylmercury(II) coordination compound. Prepared by reacting MeHgCl with the sodium salt of cyclopentanone thiosemicarbazone, its crystal is composed of isolated molecules containing three-coordinated mercury(II) [28] (Fig. 24). The deprotonated TSC ligand coordinates to the metal in the usual *Z*-configuration through a strong Hg–S bond and a weak Hg–N(3) bond, which together with the Hg–C bond give the metal T-shaped coordination scheme. The existence of the Hg–N(3) bond is supported by the non-linearity of the S–Hg–C bond angle (167.7°), which suggests a change in the sp hybridization of the metal atom to accommodate the additional bond with N(3).

2.3.2. Coordination number 4

The reactions of phenylmercury(II) acetate with several TSCs in ethanol recently led to the isolation and structural characterization of the complexes [HgPh(CPTSC)], [HgPh(MBTSC)] and [HgPh(PTSC)] [29]. In all these compounds the coordination scheme is similar to that of [HgMe(CPTSC)] (Fig. 24), but in the phenylmercury(II) derivatives the T-shaped molecules are associated in pairs as centrosymmetric dimers via secondary N(2)···Hg bonds (in the CPTSC$^-$ compound) or weak S···Hg bonds (in the other two complexes), increasing the coordination number to four.

The complexes formed when TSCs react in ethanol with [2-(pyridin-2′-yl)phenyl]mercury(II) acetate also contain the deprotonated thiosemicarbazonato ligand [30]. One of these compounds, [Hg(PyPh)(HSTSC)], recrystallizes from a CH_2Cl_2–$CHCl_3$–CH_3OH mixture as pale yellow crystals that consist of discrete molecular [Hg(PyPh)(HSTSC)] units in which the metal forms almost colinear primary bonds with a phenyl carbon and the TSC S atom (C–Hg–S = 177.7°) and a substantial secondary bond with the pyridine N atom (Hg···N = 2.576 Å), as well as interacting rather weakly with the TSC N(3) atom [Hg···N(3) = 3.126 Å] (Fig. 25). If the secondary interaction with N(3) is ignored, then the coordination geometry can be described as T-shaped, as in the preceeding compounds. If, on the

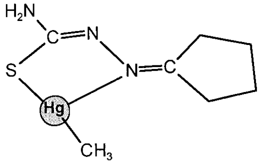


Fig. 24. Adapted from Ref. [28].

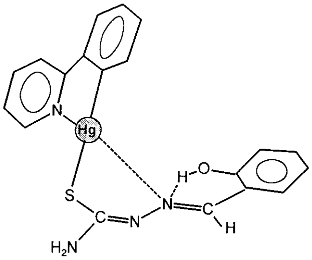


Fig. 25. Adapted from Ref. [30].

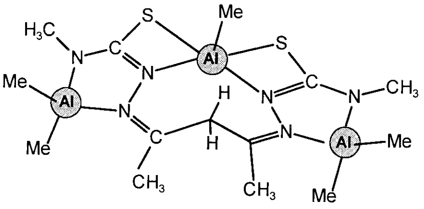


Fig. 26. Adapted from Ref. [32].

other hand, the value 2.0 Å is a good estimate of the van der Waals radius of mercury [31], then the N(3)···Hg distance is clearly less than the sum of the van der Waals radii of the two atoms (3.55 Å), and the coordination number is therefore four.

3. Group 13

Structural data for thiosemicarbazone complexes of Group 13 metals are listed in Table 2.

3.1. Al

No aluminium semicarbazone complexes have been described so far. All the compounds described below are organoaluminium complexes with N^1-substituted thiosemicarbazones.

3.1.1. Coordination number 4

Reaction of $AlMe_3$ in toluene with H_4AABMeTSC [2,4-pentanedione bis(N^1-methylthiosemicarbazone)] affords, after 2 h heating and stirring, the trinuclear complex [(AlMe)$(AlMe_2)_2$(AABMeTSC)] (Fig. 26), releasing methane in the process [32]. This polynuclear complex contains two $AlMe_2^+$ units with coordination number four and one $AlMe^{2+}$ unit with coordination number five. The metals of both $AlMe_2^+$ units have identical tetrahedral environments, the aluminium atom coordinating to two C atoms and two N atoms [(N(1) and N(3)]. The $AlMe^{2+}$ unit coordinates to both thiosemicarbazone chains through their S and N(2) atoms, giving rise to a square pyramidal coordination polyhedron with the C atom apical. This coordination mode forces the ligand to retain *E* conformation with respect to C(1)–N(2). All the potential donor atoms of the tetradeprotonated thiosemicarbazone ligand are involved in coordination to the aluminium atoms. The bond lengths in the thiocarbamide group indicate evolution to the thiol form together with a redistribution of π-charge along the chain.

The dinuclear complex [$(AlMe_2)_2$(AP^{i}prTSC)] was prepared similarly to [(AlMe)$(AlMe_2)_2$(AABMeTSC)] by reaction of $AlMe_3$ with 2-acetylpyridine N^1-isopropyl thiosemicarbazone in 2:1 mole ratio [33]. The asymmetric unit of this compound contains two molecules with slightly different bond lengths and angles; Fig. 27 shows one of them. Again, all the potential donor atoms of the thiosemicarbazone ligand coordinate to one or other of the two Al atoms, acting as a bideprotonated ligand: N(1) and N(2), coordinate to one of the $AlMe_2^+$ units in which the Al atom has coordination number 4 in a tetrahedral environment, while S, N(3) and N(Py) all coordinate to the other $AlMe_2^+$ unit, in which the Al atom is pentacoordinated in an environment described by the authors as a distorted trigonal bipyramid. The simultaneous coordination of S, N(3) and N(Py) to the same metallic centre forces the ligand to adopt a *Z*-conformation.

The tetranuclear complex $[(AlMe)(AlMe_2)(P^i prTSC)]_2$ is prepared by reacting $AlMe_3$ and pyrrolecarbaldehyde N^1-isopropylthiosemicarbazone in 2:1 mole ratio [34] under conditions similar to those used for the organoaluminium complexes described above. Unlike $H_2AP^i prTSC$, $H_3P^i prTSC$ can act as a trideprotonated ligand, and in this complex it coordinates to two types of organoaluminium units: one $AlMe_2^+$ unit [through N(1) and N(3)] and two $AlMe^{2+}$ units [one through N(pyrrole) and N(2) and the other through S] (Fig. 28). The presence of two $AlMe^{2+}$ units, both coordinating to both TSC ligands, gives rise to a centrosymmetric dimer. Both kinds of Al atom have a tetrahedral environment. Coordination of N(1) and N(3) to the same metallic atom necessitates that the ligands adopt an *E*-conformation; there is also considerable evolution towards the thiol form.

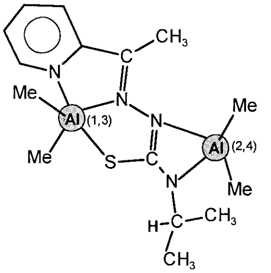


Fig. 27. Adapted from Ref. [33].

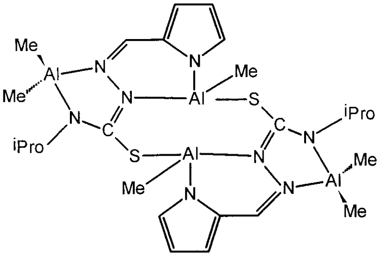


Fig. 28. Adapted from Ref. [34].

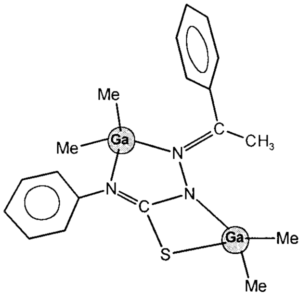


Fig. 29. Adapted from Ref. [33].

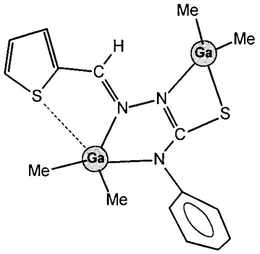


Fig. 30. Adapted from Ref. [34].

3.1.2. Coordination number 5

See coordination number 4 (Refs. [32,33], Figs. 26 and 27).

3.2. Ga

No complexes of Ga with SC ligands have been described and, as in the case of Al, its only know TSC complexes have coordination number 4 or 5; three of these four compounds are organometallic derivatives.

3.2.1. Coordination number 4

Reactions paralleling those of $AlMe_3$ with TSCs allow synthesis of the complexes $[(GaMe_2)_2(AcPhTSC)]$ [33] (Fig. 29) and $[(GaMe_2)_2(TFPhTSC)]$ [34] (Fig. 30). In $[(GaMe_2)_2(AcPhTSC)]$ there are two distorted tetrahedral kernels, $[GaC_2N_2]$ and $[GaC_2NS]$. The dideprotonated and bis-bidentate TSC ligand, adopts an *E*-conformation, coordinating to one $GaMe_2^+$ unit via N(1) and N(3) and to the other via N(2) and S. The structure of $[(GaMe_2)_2(TFPhTSC)]$ is similar, except that the Ga coordinated to N(1) and N(3) has an additional weak interaction with the thiophene S atom. If this weak interaction is taken into account, this Ga atom has a distorted trigonal bipyramidal coordination polyhedron with a $[GaC_2N_2S]$ kernel.

3.2.2. Coordination number 5

Like one of the Ga atoms in [$(GaMe_2)_2$(TFPhTSC)] (vide supra, coordination number 4; Fig. 30), those of the complexes [$GaCl_2$(PATSC)] [35] and [$GaMe_2$(FMeTSC)] [34] have coordination number 5. [$GaCl_2$(PATSC)] has been prepared by reaction of $GaCl_3$ and the TSC ligand in 1:1 mole ratio in absolute ethanol [35]. The monodeprotonated TSC ligand, in Z-conformation, coordinates to the $GaCl_2^+$ unit via S, N(3) and N(Py), although the Ga–N(py) distance is not available and is not listed in Table 2 (Fig. 31). The geometry around the metal is described as a square pyramid with the almost planar thiosemicabazone anion and one Cl in the basal plane and the second Cl at the apex.

The mononuclear organogallium(III) complex [$GaMe_2$(FMeTSC)] [34] has been obtained by reaction of furan-2-carbaldehyde N^1-methythiosemicarbazone and $GaMe_3$ in about 1:1.5 mole ratio in toluene. The Ga atom is strongly coodinated to two Me C atoms, N(3) and S, and more weakly to the furan oxygen, making the coordination number five and the coordination polyhedron a distorted trigonal bipyramid (Fig. 32). The monodeprotonated TSC ligand is tridentate and adopts the Z-conformation.

3.3. In

Crystal structures described for In complexes comprise organometallic and non-organometallic derivatives with coordination numbers ranging from 5 to 7.

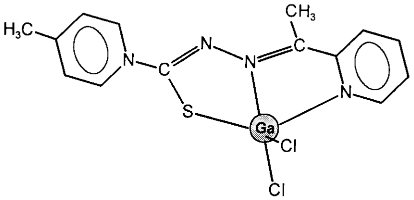


Fig. 31. Adapted from Ref. [35].

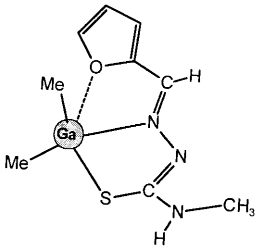


Fig. 32. Adapted from Ref. [34].

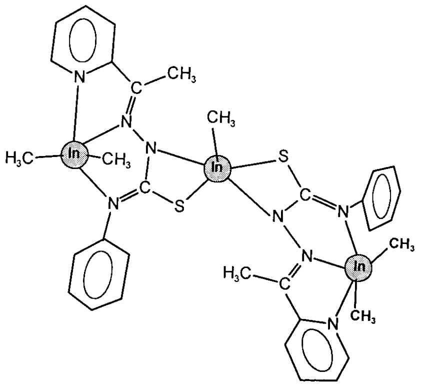


Fig. 33. Adapted from Ref. [36].

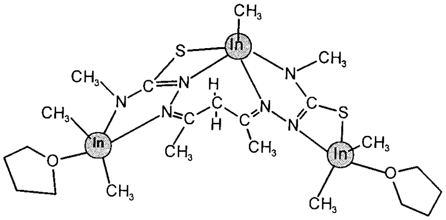


Fig. 34. Adapted from Ref. [36].

3.3.1. Coordination number 5

Only two organoindium(III) compounds have been described with coordination number 5 $[(InMe)(InMe_2)_2(APPhTSC)_2]\cdot THF$ and $[(InMe)(InMe_2)_2(AABMeTSC)(THF)_2]$ [36]. Both are trinuclear and were obtained in reactions similar to those described for organoaluminium and organogallium compounds.

$[(InMe)(InMe_2)_2(APPhTSC)_2]\cdot THF$ contains two identical $InMe_2^+$ units with $[InC_2N_3]$ kernels and one $InMe^{2+}$ unit with a $[InCN_2S_2]$ kernel [36] (Fig. 33). In both types of kernel the indium atoms has a distorted square-based pyramidal environment. Each $InMe_2^+$ moiety coordinates to the N(1), N(3) and N(Py) atoms of one of the completely deprotonated ligands, the S and N(2) atoms of which are coordinated to $InMe^{2+}$. This coordination pattern requires the ligands to adopt an *E* configuration.

In the crystal structure of $[(InMe)(InMe_2)_2(AABMeTSC)(THF)_2]$ [36]] (Fig. 34) there are three distinct types of In atom: two, with $[InC_2N_2O]$ and $[InC_2NOS]$ kernels, included in $InMe_2^+$ fragments, and the other, with an $[InCN_3S]$ kernel, in an $InMe^{2+}$ unit. All three are coordinated to a tetradeprotonated bisthiosemicarbazone ligand (both the TSC chains of which have *E*-configuration), and the two $InMe_2^+$ indiums are also each coordinated to a THF molecule. The $[InCN_3S]$ and

[InC_2NOS] indiums have distorted square pyramidal environments and the [InC_2N_2O] indium a distorted trigonal bypiramidal environment.

3.3.2. Coordination number 6

Crystals of [$In(APTSC)_2$]PF_6 have been obtained by reaction of $In(NO_3)_3 \cdot 5H_2O$, HAPTSC and NH_4PF_6 in methanol [37]. They are composed of discrete [$In(APTSC)_2$]$^+$ cations and PF_6^- anions. In the cation (Fig. 35), two almost planar thiosemicarbazonato anions in Z conformation coordinate to the metal via their S, N(3) and N(Py) atoms. Both C(1)–S bond lengths suggest evolution towards the thiol form.

When the same ligand, HAPTSC, reacts with $InCl_3$ in methanol, yellow crystals of the complex [$InCl_2$(APTSC)(MeOH)] can be obtained [37]. Subsequent reaction of this complex with Na_2mnt or Na(Et_2dtc) results in the replacement of a Cl^- ligand by mnt^{2-} (1,2-dicyanoethene-1,2-dithiolate) or Et_2dtc^- (diethyldithiocarbamate), giving crystals of (H_2APTSC)[InCl(APTSC)(mnt)]$\cdot 0.5H_2O$ and [InCl(APTSC)(Et_2dtc)], respectively [37]. In (H_2APTSC)[InCl(APTSC)(mnt)] a tridentate thiosemicarbazonato anion in Z-configuration coordinates to the metal via S, N(3) and N(Py) (Fig. 36). The relatively short C(1)–N(2) distance and relatively long C(1)–S distance (Table 2) suggest an extended π-system along the TSC chain. Together with the three APTSC donors atoms, two mnt^{2-} S atoms and a Cl^- make the coordination number of the metal up to six. In [In-

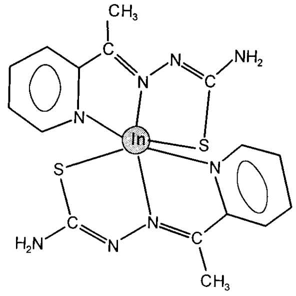


Fig. 35. Adapted from Ref. [37].

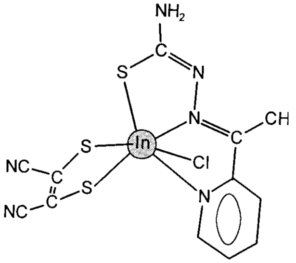


Fig. 36. Adapted from Ref. [37].

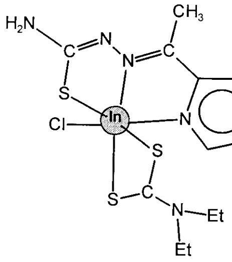


Fig. 37. Adapted from Ref. [37].

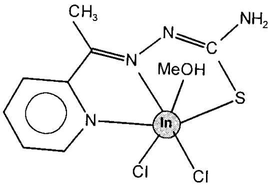


Fig. 38. Adapted from Ref. [37].

Cl(APTSC)(Et_2dtc)] the In atom has a very similar coordination environment and the TSC ligand is likewise (*N*(Py),*N*(3),S)-tridentate [37] (Fig. 37).

(*N*(Py),*N*(3),*S*)-tridentate acetylpyridine thiosemicarbazonate in *Z*-configuration also appears in the complex [$InCl_2$(APTSC)(MeOH)] [37] (Fig. 38). Together with two Cl atoms and an MeOH oxygen the three TSC donor atoms give rise to an octahedral environment around the In atom, with the O atom and one of the Cl ligands in axial positions.

3.3.3. Coordination number 7

Coordination number 7 is reached in In complexes containing bis(semicarbazone) or bis(thiosemicarbazone) ligands.

[In(H_2DAPSC)(H_2O)$_2$](OH)(NO_3)$_2$, obtained by reacting hydrated indium nitrate and 2,6-diacetylpyridine bis(semicarbazone) (H_2DAPSC) in water–ethanol, contains the cation [In(H_2DAPSC)(H_2O)$_2$]$^{3+}$, in which the In ion has a pentagonal bipyramidal coordination polyhedron [38] (Fig. 39). The bis(semicarbazone) ligand is practically planar and both semicarbazone chains are undeprotonated and adopt *Z*-configuration, which allows pentadentate coordination via the N(Py) atom and the N(3) and O atoms of both semicarbazone chains.

Abram et al. [37] have prepared two 2,6-diacetylpyridine bis(thiosemicarbazone) indium derivatives, {O[In(HDAPTSC)(OH)]$_2$}·5MeOH and [$InCl_2$-(HDAPTSC)]·2DMSO, by reacting H_2DAPTSC with In(NO_3)$_3$·5H_2O and $InCl_3$, respectively. In {O[In(HDAPTSC)(OH)]$_2$}·5MeOH (Fig. 40) there are two μ-oxo-bridged [In(HDAPTSC)(OH)] units each comprise an In ion coordinated to monodeprotonated bis(thiosemicarbazonato) ligand in a *Z*-configuration and to a terminal hydroxo ligands. The bond lengths in the thiosemicarbazone chains (Table 2) are in keeping with one being monodeprotonated and the other undeprotonated. The coordination polyhedron around the metal may be described as a distorted pentagonal bipyramid with O atoms in apical positions and the pentadentate bis(thiosemicarbazonato) ligand in the equatorial plane.

Like the previous compound, the mononuclear complex $[InCl_2-(HDAPTSC)]\cdot 2DMSO$ contains monodeprotonated bis(thiosemicarbazone) ligands pentacoordinated to In atoms [37] (Fig. 41). Two Cl atoms in apical positions complete a distorted pentagonal bipyramid around the metal atom.

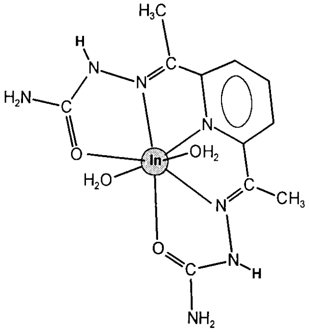


Fig. 39. Adapted from Ref. [38].

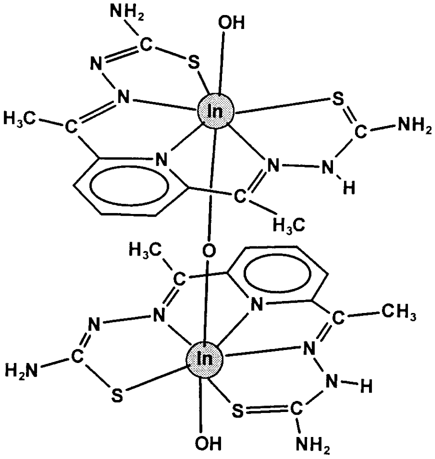


Fig. 40. Adapted from Ref. [37].

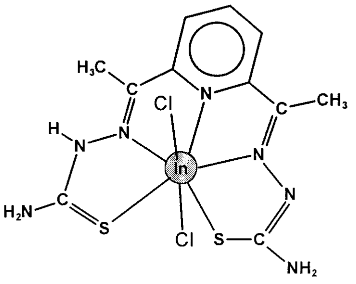


Fig. 41. Adapted from Ref. [37].

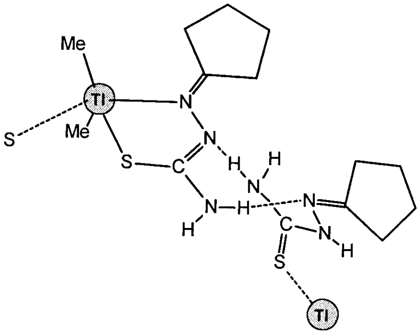


Fig. 42. Adapted from Ref. [39].

3.4. Tl

No semicarbazonates of diorganothallium(III) have been described, only thiosemicarbazonates, most of which contain $TlMe_2^+$ units.

3.4.1. Coordination number 5

Fig. 42 shows the crystal structure of the dimethylthallium complex [$TlMe_2$(CPTSC)(HCPTSC)], obtained by reaction of cyclopentanone thiosemicarbazone and $TlMe_2OH$ in 1:1 mole ratio in methanol–water [39]. This compound contains both, deprotonated and undeprotonated ligands. An almost planar deprotonated ligand in *Z*-configuration coordinates strongly to the $TlMe_2^+$ unit through N(3) and the thiolic S. An undeprotonated ligand in *E*-configuration coordinates very weakly via its S atom. If the weak Tl–S interaction is taken into account, the coordination polyhedron of the thallium atom may be described as a deformed octahedron with one vacant position.

In *p*-anisaldehyde thiosemicarbazonato dimethylthallium(III), [$TlMe_2$(*p*-ATSC)], unusual coordination to the thallium atom via S and N(2) allows the deprotonated ligand to retain the *E*-configuration [40] (Fig. 43). A weak intermolecular Tl···S interaction makes the coordination number of the metal up to five.

3.4.2. Coordination number 6

[$TlMe_2$(PyTSC)], obtained by reacting $TlMe_2OH$ and HPyTSC in hot ethanol, contains two independent molecules in each asymmetric unit. They have similar coordination schemes, but differ slightly in bond lengths and angles [41]; one is shown in Fig. 44. In both molecules a monodeprotonated tridentate (*N*(Py), *N*(3), *S*)-ligand is coordinated in *Z*-configuration to the thallium atom, which also has a weak intermolecular interaction with the S atom of a neighbouring ligand (although in one case the Tl···S(1) distance, 3.671 Å, is close to the sum of the van der Waals radii [31]).

Also an unusual coordination mode for a thiosemicarbazonato anion is found in the dimethylthallium compound [$TlMe_2$(HPxTSC)(H_2O)]$_2$ [42] (Fig. 45). In this

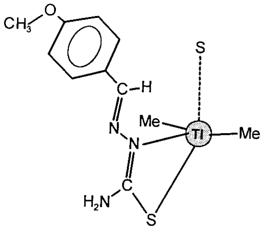


Fig. 43. Adapted from Ref. [40].

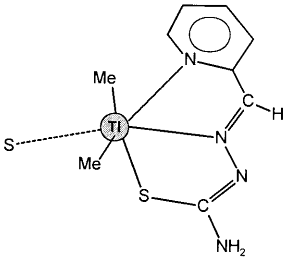


Fig. 44. Adapted from Ref. [41].

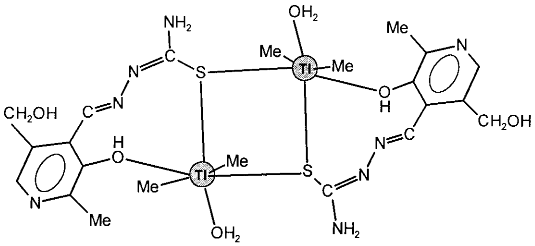


Fig. 45. Adapted from Ref. [42].

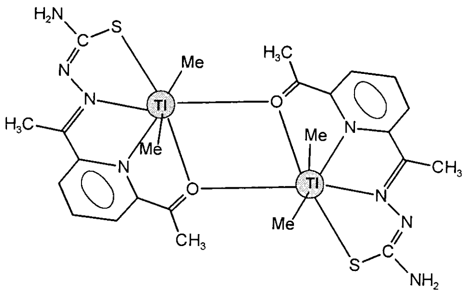


Fig. 46. Adapted from Ref. [43].

compound the pyridoxal thiosemicarbazonato anion in its thiol form coordinates to the thallium atom through its phenolic hydroxyl oxygen and through its S atom, which is also weakly bound to the thallium atom of a neigbouring molecule, giving rise to a weakly bonded dimer. The $TlMe_2^+$ unit is also coordinated strongly to a water molecule. If all these bonds are taken into account, the metal atom has a distorted octahedral coordination polyhedron with the methyl groups in the apical positions.

3.4.3. Coordination number 7

Dimethyl (2,6-diacetylpyridine monothiosemicarbazonato) thallium(III), $[TlMe_2(DAPMTSC)]_2$ (Fig. 46) and diphenyl-(2,6-diacetylpyridine monothiosemicarbazonato) thallium(III) chloroform solvate, $[TlPh_2(DAPMTSC)]_2 \cdot 2CHCl_3$, were prepared by reacting the corresponding diorganothallium(III) hydroxides with HDAPMTSC [43]. Both complexes consist of molecules in which the deprotonated ligand in the *Z*-conformation is *S*,*N*(3),*N*(Py),*O*-bound to the thallium atom. A weak intermolecular Tl···O interaction between neighbouring molecules gives rise to weakly bonded dimers in which the thallium atoms have a distorted pentagonal bipyramidal environment, with the Me or Ph groups in the apical positions.

4. Group 14

Table 3 list the structural data for SC and TSC complexes of tin and lead.

4.1. Tin

There are only three reported structures for tin complexes of SCs, as against fourteen for TSCs. The majority of the latter contain organotin units.

4.1.1. Coordination number 4

Only one structure for a tin complex with coordination number 4 has been reported, that of $[SnPh_3(HMeSTSC)]$, a compound obtained by slow evaporation of a solution of triphenyltin hydroxide and the thiosemicarbazone in 1:1 mole ratio in ethanol [44]. In this compound the *S*-coordinated TSC retains the *E*-configuration it has in the hemihydrate of the free ligand, although the thiosemicarbazonato fragment is twisted rather than planar. Together with three C atoms of the phenyl groups, the TSC S atom defines a distorted tetrahedral coordination polyhedron for the tin atom (Fig. 47).

4.1.2. Coordination number 5

Ng et al. [45] have prepared the dibutyltin salicylaldehyde semicarbazonate [$SnBu_2$(SSC)] and the dibutyltin salicylaldehyde thiosemicarbazonate [$SnBu_2$(STSC)] by melting together equimolar amounts of dibutyltin oxide and the appropriate ligand. The structures of these two compounds are almost identical, with an (*O*,*N*,*O*)- or (*S*,*N*,*O*)-tridentate ligand in *Z*-configuration and a *cis*-trigonal bipyramidal coordination polyhedron with the phenolic hydroxyl O in one axial positions and the semicarbazonate O or thiosemicarbazonate S in the other (Fig. 48).

Similar structures have been reported [46] for [$SnMe_2$(STSC)] and [$SnPh_2$(STSC)], the slight differences being due to the different organotin units. Both these compounds were obtained by refluxing SnR_2(O) and salicylaldehyde thiosemicarbazone in benzene and removing the resulting azeotropic benzene–water mixture by distillation in a Dean-Stark apparatus.

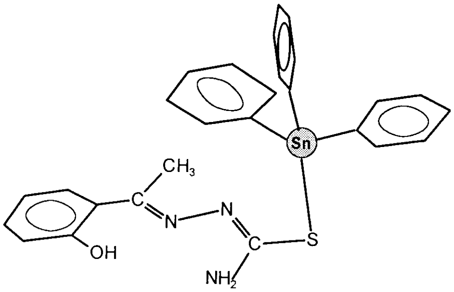


Fig. 47. Adapted from Ref. [44].

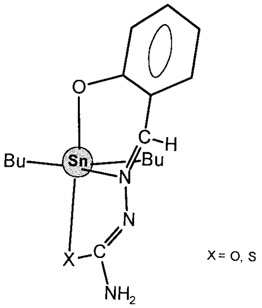


Fig. 48. Adapted from Ref. [45].

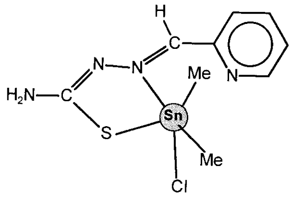


Fig. 49. Adapted from Ref. [47].

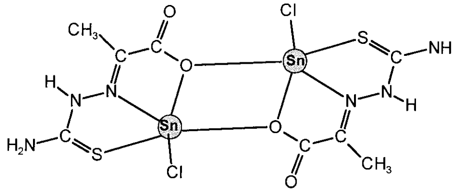


Fig. 50. Adapted from Ref. [48].

The potentially tridentate ligand pyridine-2-carbaldehyde thiosemicarbazone is only (*S*,*N*(3))-bidentate in $[SnMe_2(PyTSC)Cl]\cdot0.5\ H_2O$ [47] (Fig. 49). The authors argue that the coordination of the pyridine N atom is prevented by a severe distortion together with steric hindrance by the two methyl groups. The ligand has *Z*-configuration and is deprotonated. The tin atom is five-coordinated in a severely distorted trigonal bipyramidal arrangement with N(3) and Cl occupying the axial positions.

By mixing warm solutions of $SnCl_2\cdot2H_2O$ and pyruvic acid thiosemicarbazone in methanol Burshtein et al. obtained $[SnCl(HPT)]_2$ [48], the only tin(II) compound included in this review. In this complex the ligand has *Z*-configuration and is tridentate, coordinating via its S and N(3) atoms and through one of the carboxyl O atoms (Fig. 50). A bridging O atom belonging to a neighbouring molecule leads to the formation of dimers, and together with the Cl atom makes the coordination number of the tin atom up to five.

4.1.3. Coordination number 6

In $[SnCl_3(PyTSC)]$ the ligand is (*N*,*N*,*S*)-tridentate, through its N(3), S and pyridine N atoms [49] (Fig. 51). The distorted octahedral coordination polyhedron of the tin atom is completed by three Cl atoms. The difference in coordination mode with respect to $[SnMe_2(PyTSC)Cl]\cdot0.5H_2O$ in which the same ligand, with very similar geometry, is bidentate, is attributable to the replacement of two Me groups by Cl atoms on the tin atom, which eliminates steric hindrance and increases the acceptor strength of the tin atom, shortening the Sn–N(3) and Sn–S bond lengths and allowing coordination to the pyridine N atom.

By reacting a solution of $SnPh_2Cl_2$ in ethanol with a solution of thiosemicarbazide in a mixture of ethanol and acetone, Teoh et al. [50] obtained

$[SnPh_2Cl_2(HATSC)_2]$, acetone thiosemicarbazone (HATSC) having been derived in situ from thiosemicarbazide and acetone. In this compound, which has interesting biological activity, the ligand has the *E*-configuration usual in free TSCs, and is monodentate, coordinating to the tin via its S atom (Fig. 52). The C–S bond is longer than in the free ligand. The coordination polyhedron is a distorted all-*trans* octahedron.

Refluxing a mixture of HPyTSC and $SnMe_2(OAc)_2$ in dry methylene chloride affords $[SnMe_2(PyTSC)(OAc)]\cdot HOAc$ [51]. In this compound the PyTSC ligand adopts *Z*-configuration and is planar and (*N*,*N*,*S*)-tridentate (Fig. 53). Although the acetate anion is monodentate (the distance of the tin atom from the other acetate O atom, 2.740 Å is not in the range considered as allowing bonding), the non-coordinated O atom probably plays an important role in determining the geometry of the coordination polyhedron around the tin atom, which may be described as a distorted pentagonal bipyramid with the methyl groups axial and one of the equatorial positions ‘partially’ occupied.

In $[SnPh_2Cl(HAPT)]\cdot H_2O$ [52] (Fig. 54) the monodeprotonated bis(2-acetylpyridine) thiocarbonohydrazone ligand is (*N*,*N*,*S*)-tridentate through its N(3), thiocarbamide S and one of the pyridine N atoms. The coordination sphere of the metal is completed by a chloro atom and the two C atoms belonging to the phenyl

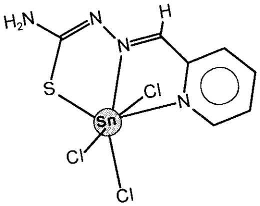


Fig. 51. Adapted from Ref. [49].

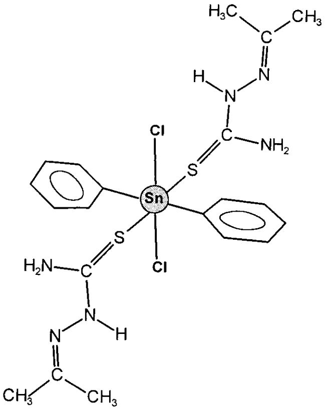


Fig. 52. Adapted from Ref. [50].

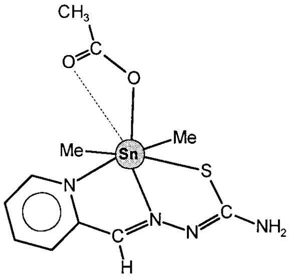


Fig. 53. Adapted from Ref. [51].

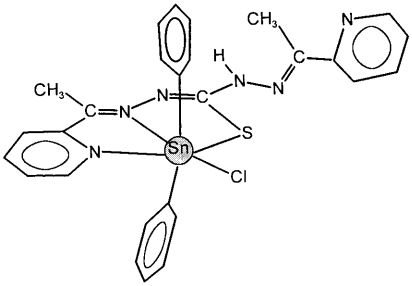


Fig. 54. Adapted from Ref. [52].

groups. Coordination polyhedron can be described as highly distorted octahedral with the phenyl groups in *trans*-positions [52]. As usually, the main distortion from the regular octahedral geometry comes from the stereochemical constrains imposed by the bite of the ligand. The changes in the bond distances of the thiocarbamide group in $HAPT^-$ relative to free H_2APT indicate that metallation induce thione-to-thiol evolution. The water molecule is involved in an intermolecular O···Cl hydrogen bond.

4.1.4. Coordination number 7

Tin has attained coordination number 7 with only two Sc or TSC ligands, both of them derivatives of diacetylpyridine: 2,6-diacetylpyridine bis(semicarbazone) (H_2DAPSC) and its thio analogue, 2,6-diacetylpyridine bis(thiosemicarbazone) ($H_2DAPTSC$). Two tin complexes of H_2DAPSC have been characterized structurally, and three tin complexes of $H_2DAPTSC$.

By reacting $(CH_4N)_3[Pt(SnCl_3)_5]$ with H_2DAPSC, Sommerer and Palenik unexpectedly obtained $[SnCl_2(H_2DAPSC)]Cl_2\cdot 2H_2O$ [53]. In the $[SnCl_2(H_2DAPSC)]^{2+}$ cation, the planar H_2DAPSC moiety is (*N*,*N*,*N*,*O*,*O*)-pentadentate, defining around the tin the equatorial plane of a slightly distorted pentagonal bipyramid in which the two Cl atoms are axial (Fig. 55).

A similar structure is possessed by the cation $[SnMeCl(H_2DAPSC)]^{2+}$, which is found in $[SnMeCl(H_2DAPSC)]Cl_2\cdot 2H_2O$ [54]. Replacement of a Cl by an Me group does not significantly change the Sn–N bond lengths, and just slightly lengthens the Sn–O distances (Table 3).

By reacting H_2DAPTSC with diphenyltin(IV) oxide in DMF, Casas et al. [55] obtained [$SnPh_2$(DAPTSC)]·2DMF, in which the bis(thiosemicarbazone) ligand is dideprotonated and pentadentate (Fig. 56). This ligand occupies the equatorial positions of a distorted pentagonal bipyramid around the tin atom; the two phenyl groups are axial.

N(2) is protonated in one of the arms of the bis(thiosemicarbazone) in [$SnPh_2$(HDAPTSC)]Cl which has been obtained by refluxing H_2DAPTSC·HCl and $SnPh_2Cl_2$ in methanol [56]. This does not significantly modify bond lengths in either the thiosemicarbazone arms or the coordination polyhedron (Table 3), and angles undergo only small changes. Furthermore, the geometrical differences between the two arms are of the same order as in bis(semicarbazones) in which neither or both arms are protonated [53,54].

A similar situation is found in the cation [SnMeCl(HDAPTSC)$]^+$ in [SnMeCl(HDAPTSC)]Cl·MeOH [54], although the differences between the two arms do not affect the same bonds as in [$SnPh_2$(HDAPTSC)]Cl.

[Sn^nBu_2(APTSC)(OAc)], obtained by reacting $Sn^nBu_2(OAc)_2$ with 2-acetylpyridine thiosemicarbazone in refluxing ethanol, contains two crystallograph-

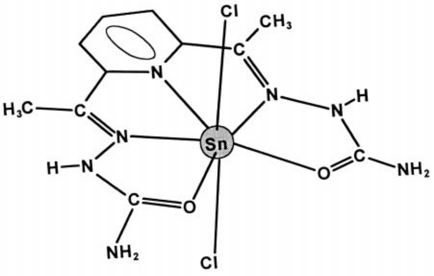


Fig. 55. Adapted from Ref. [53].

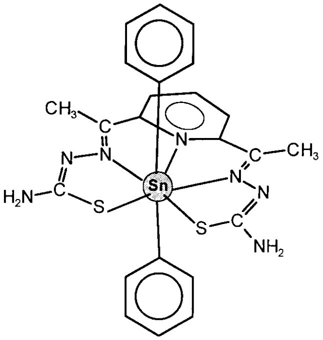


Fig. 56. Adapted from Ref. [55].

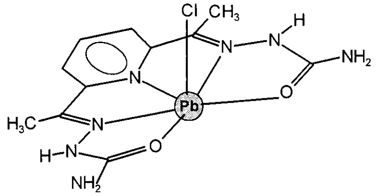


Fig. 57. Adapted from Ref. [57].

ical independent molecules in the unit-cell A and B [52]. As in the similar complex $[SnMe_2(PyTSC)(OAc)]\cdot HOAc$ (vide supra, Fig. 53), the thiosemicarbazonato ligand is (*N*,*N*,*S*)-terdentate, but the acetato ligand is (*O*,*O*)-bidentate instead monodentate giving a coordination number 7 and a coordination polyhedron around the tin atom which may be described as a distorted pentagonal bipyramide with the butyl groups axial and the equatorial positions occupied by $APTSC^-$ and AcO^- donor atoms. The Sn–S distances are larger and the Sn–N distances mostly shorter in the A and B molecules than in $[SnMe_2(PyTSC)(OAc)]\cdot HOAc$, while the C–Sn–C fragments are more lineal. Besides the small differences in bond distances and angles, A and B differ as regards of the coordination mode of the acetato group which is more anisobidentate in A [Sn–O 2.337(3), 2.545(4) Å] than in B [Sn–O 2.404(4), 2.436(4) Å].

4.2. Lead

4.2.1. Coordination number 6

H_2DAPSC is also planar and (*N*,*N*,*N*,*O*,*O*)-pentadentate in $[PbCl(H_2DAPSC)]NO_3$ [57] (Fig. 57). Pentagonal pyramidal geometry around the Pb is completed by a Cl ligand at a short distance. The nitrate ion is located on the other side of the H_2DAPSC plane from the Cl ligand; the long Pb–O distances, 2.973 and 3.095 Å, are attributed by the authors to the lone pair of electrons on the Pb(II) ion.

4.2.2. Coordination number 7

By refluxing di-2-pyridylketone semicarbazone (HDIPSC) with $Pb(NO_3)_2$ in methanol, Battaglia et al. [58] obtained $[Pb(NO_3)_2(HDIPSC)]$, the structure of which is shown in Fig. 58. The HDIPSC ligand is coordinated to the Pb atom via the semicarbazone N(3) and O atoms and the N atom of one of the pyridine rings. The Pb atom achieves heptacoordination by binding two asymmetric bidentate nitrate groups. The resulting irregular coordination polyhedron exhibits a large unoccupied solid angle suggesting the influence of a lone pair.

Fig. 59 shows the structure of $[PbCl_2(H_2CHDSC)(DMF)]$, which was obtained by heating a mixture of $PbCl_2$ and cyclohexane-1,2-dione bis(semicarbazone) in DMF [58]. The bis(semicarbazone) ligand is simetrically coordinated and the coordination polyhedron is a very distorted pentagonal bipyramid in which the two Cl atoms are axial and the equatorial plane is defined by the planar (*N*,*N*,*O*,*O*)-tetradentate H_2CHDSC ligand and the O atom of a statistically distributed DMF molecule.

Another example of heptacoordination involving Pb(II) is [Pb(APMeTSC)(OAc)], which has been obtained by stirring a mixture of lead acetate trihydrate, a small quantity of sodium powder and HAPMeTSC in THF [59] (Fig. 60). The APMeTSC ligand is the only N(1)–Me ligand with which a Group 14 metal has formed a complex characterized by X-ray diffractometry. In [Pb(APMeTSC)(OAc)] it has a *Z*-configuration and is (*N*,*N*,*S*)-tridentate. A bidentate

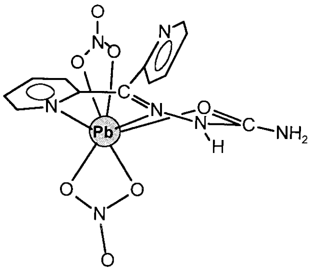
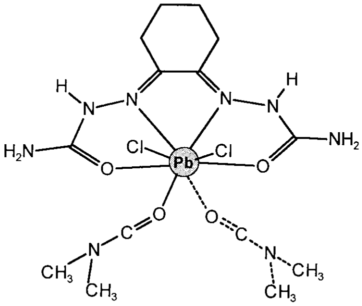


Fig. 58. Adapted from Ref. [58].



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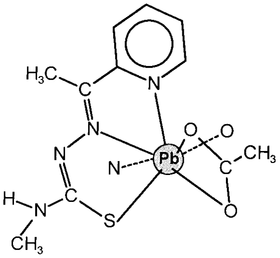


Fig. 60. Adapted from Ref. [59].

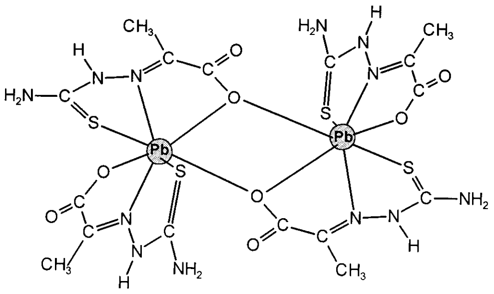


Fig. 61. Adapted from Ref. [48].

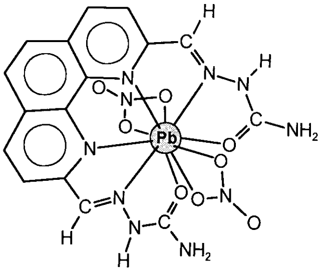


Fig. 62. Adapted from Ref. [60].

acetate group raises the coordination number of the metal to five, and additional interactions with acetate O and N(2) atoms of neighbouring molecules lead to a polymeric structure in which Pb is heptacoordinated in an extremely irregular coordination polyhedron.

The last example of heptacoordination by Pb(II) is $[Pb(HPT)_2]_2$, in which both the ligands have *Z*-configuration and are essentially planar and (*S*,*N*,*O*)-tridentate [48] (Fig. 61). The coordinated O-atom of one of the ligands bridges to a neighbouring molecule, leading to the formation of dimers and giving the Pb atom a distorted heptacoordinate environment.

4.2.3. Coordination number 10

In $[Pb(NO_3)_2(H_2PHENSC)]$ a two-fold axis of symmetry passes through the Pb atom and the $H_2PHENSC$ ligand [60] (Fig. 62). The Pb atom has the highest coordination number in this review, binding to four N and two O atoms of the hexadentate ligand and to two O atoms of each two nitrate groups. The coordination geometry is described as a 2-6-2 polyhedron, with the two capping nitrate groups rotated 60° relative to each other and no evidence that the lone pair of Pb(II) is stereochemically active.

5. Group 15

5.1. Bi

The reported complexes of bismuth include TSC and bis(TSC) derivatives with coordination numbers ranging from 5 to 7. The main structural data for these compounds are listed in Table 4.

5.1.1. Coordination number 5

Reaction of bismuth(III) nitrate pentahydrate and bismuth(III) chloride with HTFHTSC affords [Bi(TFHTSC)$_2$(NO$_3$)]·MeOH and [BiCl$_2$(TFHTSC)-(HTFHTSC)], respectively [61]. In the former (Fig. 63) two deprotonated bidentate ligands coordinate to the Bi atom through S and N(3), and a weak Bi···O interaction with a nitrate oxygen makes the coordination number of the Bi atom up to five in a coordination environment described by the authors as a distorted trigonal antiprism, in which one position is occupied by the Bi lone pair.

[BiCl$_2$(TFHTSC)(HTFHTSC)] contains one deprotonated and one protonated ligand [61] (Fig. 64). The deprotonated ligand coordinates strongly to the metal atom in *Z*-conformation via its thiolic S and N(3) atoms, while the protonated TSC is monodentate, coordinating weakly via the thioketo S. The authors describe the coordination polyhedron as a square bipyramid with the lone pair of the metal in one site of the square face.

5.1.2. Coordination number 6

Reaction of the bis(thiosemicarbazone) H$_2$DAPTSC with BiCl$_3$ in 1:1 mole ratio, followed by addition of an excess of NaN$_3$, affords dark red crystals of the complex [Bi(N$_3$)(DAPTSC)]·0.5DMSO [62] (Fig. 65). The ligand coordinates to the metal

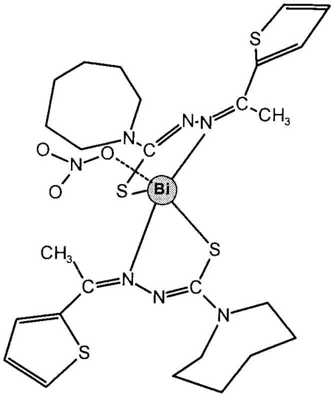


Fig. 63. Adapted from Ref. [61].

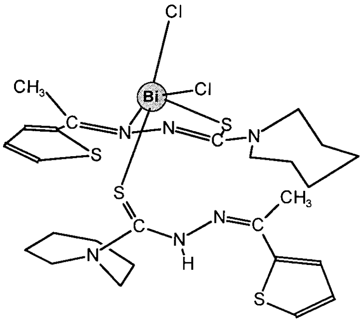


Fig. 64. Adapted from Ref. [61].

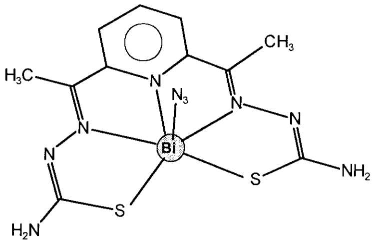


Fig. 65. Adapted from Ref. [62].

atom asymmetrically via N(Py) and the two S and two N(3) atoms (Table 4). Both thiosemicarbazone side chains are deprotonated and adopt *Z*-conformation. The coordination polyhedron is described as a pentagonal pyramid with the N_3^- ligand at the apex.

$[BiCl_2(APHTSC)]_2$, obtained by reacting $BiCl_3$ and HAPHTSC in HCl solution, crystallizes as a dimeric complex with two chlorine atoms bridging between the two Bi atoms [61] (Fig. 66). The deprotonated thiosemicarbazone ligands coordinate to the Bi atom via N(Py), N(3) and S. These three atoms together with the three Cl atoms give the Bi atom coordination number 6.

5.1.3. Coordination number 7

When $Bi(NO_3)_3$ reacts with HAPHTSC in 1:2 mole ratio the complex $[Bi(APHTSC)_2(NO_3)]$ is obtained. In this compound the metal is heptacoordinated in an environment described as a distorted trigonal dodecahedron with the lone pair in one position [61] (Fig. 67). The unusual conformation of free HAPHTSC [63] remains in the complex allowing coordination through N(Py), N(3) and thiolic S atoms. The nitrate ion is bound via one of its oxygen atoms.

6. Conclusions

This review describes 71 structures containing neutral or deprotonated TSCs or bis-TSCs coordinated to the metallic elements of Groups 12, 13, 14 and 15 of the Periodic Table. Almost half of these structures (29) concern the Group 12 metals Zn, Cd and Hg, and more than a quarter (18) compounds of the lightest of these metals, zinc. However, only ten SC derivatives have been found in the literature, most of them involving Group 14 metals (three tin and four lead).

The coordination behaviour exhibited by TSCs is considerably more varied than the simple monodentate coordination allowed by the configuration of the free ligands or the *N*(3),*S*-chelation which becomes possible when the *Z*-configuration is adopted with respect to the N(2)–C(1) bond. The coordination modes that have been described are summarized in Scheme 4 as regards the ligand–metal bonds involving the thiosemicarbazide chain (the extra possibilities that arise when the ligand possesses additional donor atoms (Scheme 1,**V**) as is often the case, are ignored). The elements of Group 12 form complexes in which the ligand adopts coordination modes **I** to **IV**. The two first modes occurs in adducts with metal halides, while *N*(1),*N*(3)-coordination (mode **IV**) occurs in *S*-alkylated ligands. The

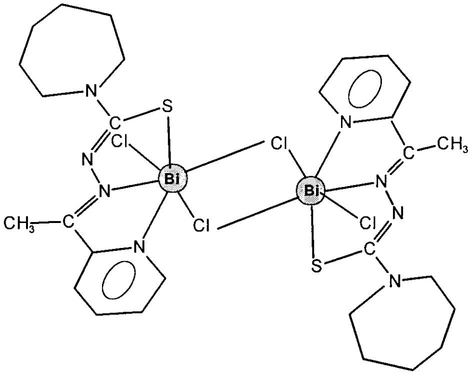


Fig. 66. Adapted from Ref. [61].

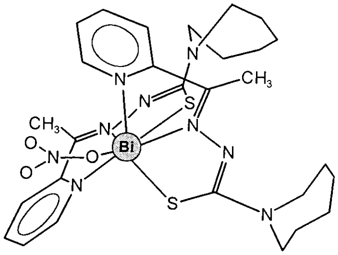
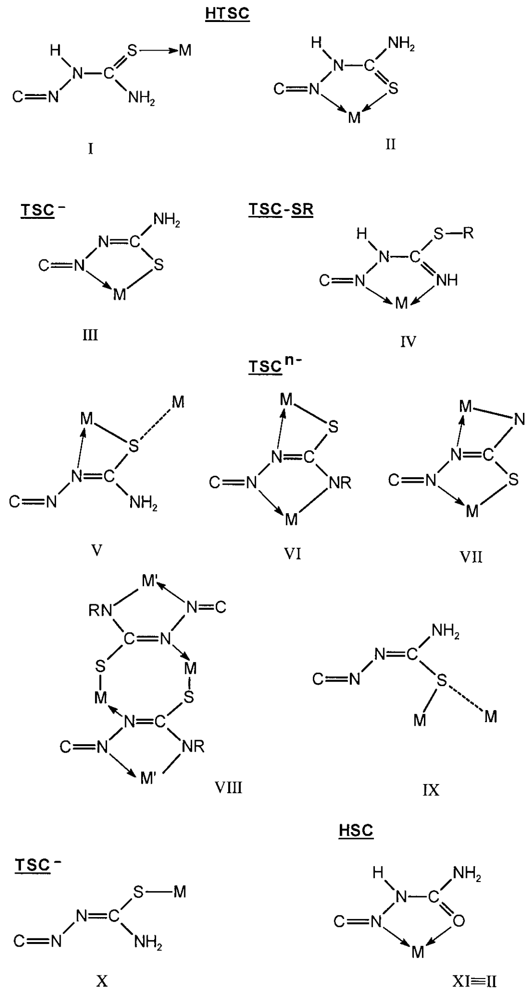


Fig. 67. Adapted from Ref. [61].



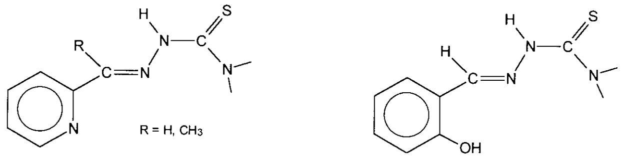
Scheme 4.

commonplace N(3),*S*-coordination of the thiosemicarbazonate anion in *Z*-configuration (mode **III**) is illustrated by several examples.

The structures of Group 13 metal thiosemicarbazonates, which have been explored only recently, are especially interesting because they exhibit several previously undescribed coordination modes. It seems that the metallic and organometallic ions of this group are able to use simultaneously all the potential donors of both *E* and *Z*-TSC chains. Coordination modes **V** to **IX** of Scheme 4 are particularly associated with the complexes of this group, although some of the preceding modes also occur. Mode **V**, in which there is four-membered metallacycle, was first described in a dimethylthallium(III) compound [40], but has since been found in the complexes of the other Group 13 metals. Coordination modes **VI** and **VII** use all the donor atoms of the deprotonated TSC chain, while mode **VIII** is an interesting example of bridging in Scheme 4 which a ligand in *E*-configuration binds to three metallic centres, again using all its potential donor atoms. Finally, mode **IX** consists in rather unusual monodentate bridging behaviour; it has been found only in a complex of the $TlMe_2^+$ cation with pyridoxal thiosemicarbazone (Fig. 45) in which the expected coordination via N(3) may be blocked by a strong hydrogen bond between N(3) and the pyridoxal phenolic hydroxyl group. Group 14 adds another mode (**X**), monodentate coordination by a deprotonated TSC; in this mode, found in the complex of triphenyltin(IV) with salicylaldehyde thiosemicarbazone [44], there is no bridging by the S atom, possibly because of steric hindrance by the bulky phenyl groups.

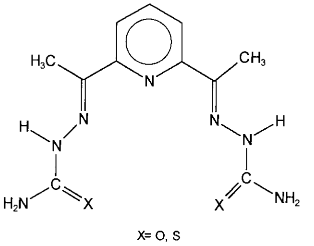
In the few SC complexes characterized by X-ray diffractometry the ligands show simpler coordination behaviour than TSCs. All adopt the chelating mode **XI**, which is equivalent to TSC mode **II**, and becomes possible when the *E*-conformation of the free ligand changes to *Z*-conformation. All these semicarbazonates contain non-deprotonated SCs, so the coordination bonds indicated in Scheme 4 (**XI**) involve the lone pairs of the N(3) and O atoms.

Of the 36 different TSCs and 6 SCs that are included in the complexes listed in Tables 1–4, some appear much more frequently than others. Scheme 5 shows most widely used families, which have also been extensively studied as regards their coordination transition metals [2]. All include a supplementary donor atom in addition to the thiosemicarbazide donors; as a result the mono-TSCs usually behave as tridentate ligands while the bis-SC and bis-TSC normally bind to the metal centre through the two X atoms, the two N(3) atoms and the pyridine N.



Formyl and acetylpyridine thiosemicarbazones

Salicylaldehyde thiosemicarbazones



Diacetylpyridine semicarbazone and thiosemicarbazone

Scheme 5.

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