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Structural aspects of the coordination chemistry of organothallium(III) and organomercury(II) derivatives

J.S. Casas *, M.S. García-Tasende, J. Sordo

Departamento de Química Inorgánica, Facultade de Farmacia, Universidade de Santiago de Compostela, 15706 Santiago de Compostela, Spain

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* Corresponding author. Tel.: +34-981-594636; fax: +34-981-594912.
E-mail address: qiscasas@usc.es (J.S. Casas)

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Abstract

This review surveys the main structural aspects of the coordination chemistry of mono-, di- and triorganothallium(III) and mono- and diorganomercury(II) complexes. It covers all organothallium(III) derivatives reported up to the end of 1997 and the organomercury compounds reported between 1993 and 1997. Structures are classified primarily by coordination number and secondarily by kernel complexity.

Keywords: Metal complexes; Organothallium(III) complexes; Organomercury(II) complexes; X-ray structure; Crystal structure

Nomenclature

$(NO_2)_3C_6H_2O$	2,4,6-trinitrophenolate
$(SPPh)_2N$	tetraphenyldithioimidodiphosphinate
acac	acetylacetonate
AcFPhEt	(E)-1-acetoxy-1-(4-fluorophenyl)-2-phenylethen-2-yl and (E)-1-acetoxy-2-(4-fluorophenyl)-1-phenylethen-2-yl
AMMeT	4-amino-5-mercapto-3-methyl-1,2,4-triazolate
AMTFMT	4-amino-5-mercapto-3-trifluoromethyl-1,2,4-triazolate
aza–aza	azaindolyl–azaindolyl
$B_{10}H_{12}$	η^4-decaborate (dianion)
bismuthiol I	1,3,4-thiodiazole-2,5-dithiolate
bpy	bipyridine
BTAPy	2,6-bis[1-methyl-2-(2-thiolophenyl)-2-azaethene]pyridine
C_3H_5	cyclopropyl
$C_4H_3NSi(CHMe_2)_3$	*N*-[tri(isopropyl)silyl)]pyrrol-3-yl
$C_4H_7O_2$	isobutyrate
$C_5H_6O_2$	diacetylmethylene
$C_5H_7O_2$	diacetylmethyl
C_6F_4	perfluorophenylene
C_6H_{11}	cyclohexyl

C_6H_2O	picrate
$C_6H_4CH(Me)NMe_2$	[(dimethylamino)ethyl]phenyl
$C_6H_4CH_2$-NMe_2	2-dimethylaminomethylphenyl
$C_6H_4N{=}NPh$	2-phenylazophenyl
$C_6H_8O_3$	ethylacetoacetate (dianion)
$C_7H_5O_2$	salicylaldehydate
$C_8H_8O_3$	ethyl-3-oxo-butanoate
$C_9H_{11}N_2O_5$	2-deoxyuridin-5-yl
$CBrCl_2$	bromodichloromethyl
CPTSC	cyclopentanone thiosemicarbazonate
DABRd	*p*-dimethylaminobenzylidenerhodaninate
DAPMTSC	2,6-diacetylpyridinemonothiosemicarbazonate
DB18C6	dibenzo-18-crown-6
DCH18C6	dicyclohexano-18-crown-6
DDC18C6	didecalino-18-crown-6
dimeU	1,3-dimethyluracil-5-yl
DL-TRP	DL-tryptophanate
dmphen	2,9-dimethyl-1,10-phenanthroline
dpa	2,2′-dipyridylamide ion
DPP	$[o\text{-}(Ph_2PCH_2)C_6H_4]^-$
dpphen	2,9-diphenyl-1,10-phenanthroline
dppm	$Ph_2PCH_2PPh_2$
DTDA	1,3,2,4-dithiodiazolyl
Et	ethyl
Et_2dtc	diethyldithiocarbamate
Et_2F	diethylformamide
Et_3terpy	triethylterpyridyl
EtOH	ethanol
FcN	2-(dimethylaminomethyl)ferrocenyl
Ferrocenylimine-Et	[(4-chlorophenylimino)ethyl]ferrocene
Ferrocenylimine-Me	[(4-methoxyphenylimino)methyl]ferrocene
Ferrocenylimine-Ph	[(phenylimino)phenylmethyl]ferrocene
fth	2-furanthiocarboxyhydrazidate
H_2tot	2-thioorotate
HDz	dithizonate (dithizone = 3-mercapto-1,5-diphenylformazan)
Htuc	2-thiouracilate (monoanion)
^{i}Pr	isopropyl
L-PHE	L-phenylalaninate
Me	methyl
MeA	9-methyladeninate
MeC	1-methylcytosinate (dianion)
mes	mesityl
mop	methyleneoxydiphenyl phosphinate
mtp	methylenethiodiphenyl phosphinate
N_3	azide ion

N-AcPyr	*N*-acetylpyrrol-2-yl
N^{n}BuPh	3-nitro-6-*n*-butoxyphenyl
NOR	norbornenyl
np3	$N(CH_2CH_2PPh_2)_3$
^{n}Pr$_2$dtc	di-*n*-propyldithiocarbamate
OAc	acetate
OC_6H_4Cl-*o*	*o*-chlorophenoxy
OOCpFPh	pentafluorobenzoate
OPh	phenoxy
OPy2S	1-oxido-pyridinium-2-thiolate
OTMIPh	*o*-(1-oxyl-2,2,5,5-tetramethyl-Δ^3-4-imidazolinyl)phenyl
p-ATSC	*p*-anisaldehyde thiosemicarbazonate
pFPh	pentafluorophenyl
Ph	phenyl
Phen	1,10-phenanthroline
PhPy	2-(pyridin-2-yl)phenyl
P$_i$NR	1-hydroxy-2,2,6,6-tetramethyl-3-piperidinomethyl-Δ^4-dehydropiperidyl
PMBP	1-phenyl-3-methyl-4-benzoyl-5-pyrazolonate
prop	propynoate
PSTHFC	poly(spirotetrahydrofuranyl)cyclohexyl
PxTSC	pyridoxal thiosemicarbazonate
Py	pyridine
PyEt	4-pyridylethynyl
Pyqx	2-(2′-pyridyl)quinoxaline
PyRd	5-(2-pyridinylmethylene)rhodaninate
PySeSePy	2,2-dipyridyldiselenide
PyTd	5-(2-pyridinylmethylene)-2-thiohydantoinate
PyTSC	pyridine-2-carbaldehyde thiosemicarbazonate
pzTp	tetrakis(pyrazol-1-yl)borate
Rd	rhodaninate
S_2COEt	*o*-ethyldithiocarbonato-κS
S_2PEt_2	diethyldithiophosphinate
S_2PPh_2	diphenyldithiophosphinate
$SC_6H_4NO_2$-*o*	*o*-nitrobenzenethiolate
SPh	thiophenoxy
SPy	pyridine-2-thiolate
TbSMe	2-S-methylthiobarbiturate (dianion)
TDC18C6	tridecalino-18-crown-6
terpy	2,2′:6′,2″-terpyridyl
tFPh	tetrafluorophenyl
THF	tetrahydrofuran
TMPh	tetramethylphenyl biradical
Tol	*p*-tolyl
TPP	5,10,15,20-tetraphenylporphinate

Tpsi	$(Ph_2MeSi)_3C$
$trenMe_6$	tris(2-dimethylaminoethyl)amine
trop	tropolonate
tuc	2-thiouracilate (dianion)
X18C5	1,3-xylylen-2-yl-18-crown-5

1. Organothallium(III) compounds

1.1. Introduction

The first synthesis of an organothallium compound was achieved by Hansen [1] in 1870, 9 years after the discovery of the element by Sir William Crookes [2]. After trying unsuccessfully to react diethylzinc with thallium monochloride or metallic thallium, he finally observed a reaction when thallium(III) chloride was prepared in situ by chlorination of TlCl in anhydrous ether; subsequent addition of dilute hydrochloric acid to the reaction mixture converted the product (probably triethylthallium) to diethylthallium chloride, which was obtained in pure form by recrystallization. The sulphate and nitrate salts of $TlEt_2^+$ were also prepared in this pioneering work [1].

Although Hansen's was the first chemical synthesis of a diorganothallium compound, it is now known that biosynthesis of dimethylthallium(III) cation from thallium(I) acetate can be achieved by anaerobic bacteria under laboratory conditions [3]. Thus although no evidence for biomethylation of thallium in the wild has been found, it is possible that methylated species of the metal have existed in the environment ever since anaerobic bacteria evolved.

Studies of the structures of organothallium compounds began very early, elucidation of the crystal structure of dimethylthallium chloride by X-ray diffraction first having been carried out in 1934 [4] (more modern calculations were performed in 1974 [5]) and the first X-ray studies of thallium coordination compounds in 1967 [6,7]. However, in spite of these precedents and the stability of diorganothallium(III) compounds in water, organothallium chemistry did not attract much attention until about 1960, when a rapid advance began in connection with the increasing application of thallium intermediates in organic synthesis [8].

The coordination chemistry of organothallium compounds is limited by their being weaker Lewis acids than analogous organic derivatives of aluminium, gallium or indium [8] (of course, the acidity of TlR_nX_{3-n} increases as the electronegativity

of the R groups increases or n decreases). However, it is precisely the medium-weak acceptor character of diorganothallium species, together with their stability against moisture and molecular oxygen and their ready crystallization, that may make their coordination behaviour worthy of greater interest than it has received hitherto (only about 70 structures of diorganothallium complexes were reported prior to 1998). The coordination chemistry of monoorganothallium compounds has been even less thoroughly explored (only about ten structures have been elucidated), possibly because they are believed to be prone to symmetrization (although monoalkenyl- and monoarylthallium(III) compounds are reasonably stable), and only three structures containing TlR_3 have been reported.

This review surveys the coordination chemistry of the mono-, di- and triorganothallium(III) compounds reported up to the end of 1997 (some published in 1998 are also included). It thus aims to fill a gap that has been growing for some time, i.e. since Kurosawa's [9a] important contribution to Volume 1 of *Comprehensive Organometallic Chemistry*, (although a list of organothallium papers reporting structures obtained by diffraction methods up to 1994 was compiled by Bruce [9b]). Furthermore, although Kurosawa [9a] covered the pre-1980 literature in detail, our approach differs from his in being based on both primary and secondary bonds (vide infra), and we therefore include the structures published before 1980. Specifically, we review all structural studies of $TlRL_2$ and TlR_2L compounds, which can be considered as complexes of the cations TlR^{2+} and TlR_2^+, and all TlR_3 compounds with at least one further Tl···L interaction (even when L is a simple organic radical). We have not included compounds with Tl–C bonds where the carbon belongs to an inorganic group such as carborane or cyanide.

Sections 1.2, 1.3 and 1.4 below are respectively devoted to mono-, di- and triorganothallium compounds. Within each section the compounds are ordered by increasing coordination number, and for each coordination number compounds with more homogeneous kernels, i.e. with a greater number of equal atoms, are described before those with more heterogeneous kernels. When two kernels are equally homogeneous, the one with the lighter atoms is described first. Tables 1–3 list all the compounds described.

Following the usual procedure in organomercury complexes, the kernel of each complex has been determined on the basis of Grdenic's *effective coordination number* (CN) [10,11]. Thus all atoms closer to thallium than the sum of the van der Waals radii are included in the coordination sphere. The conservative value taken for the van der Waals radius of thallium, 2.0 Å [12], is a little longer than Bondi's original estimate (1.96 Å) [13] but is shorter than that proposed in the more recent work of Batsanov, 2.2–2.3 Å [14]. The use of Grdenic's coordination number means that we have taken into account both strong (primary) bonds with distances close to the sum of the covalent radii and weak (secondary) bonds with distances closer to, but less than, the sum of the van der Waals radii. This approach is almost inevitable because, as will be seen, the borderline between primary and secondary bonds

is rather diffuse for organothallium complexes. However, only secondary interactions noted by the authors of the original structural study are included in the review, except for a few cases in which mention of obvious secondary bonds had

Table 1
Structural data of monoorganothallium(III) compounds

Compound	CN [kernel]	d(Tl–C) (Å)	d(Tl–L)(Å)	Ref.
$[Tl(mes)_2]\cdot[TlCl_3(mes)]$ polymeric chain	4[$TlCCl_3$]	2.149(10)	Cl 2.464(3) 2.482(3) 2.536(3)	[16]
[TlMeTPP]	5[$TlCN_4$]	2.147(12)	N 2.287(9) 2.290(9) 2.290(10) 2.298(10)	[17]
[Tl(NOR)TPP]	5[$TlCN_4$]	2.09	N 2.24 2.26 2.32 2.33	[18]
$[Tl(tol)(Et_2dtc)_2]$	5[$TlCS_4$]	2.15(1)	S 2.546(4) 2.591(2) 2.728(3) 2.795(3)	[19]
$[TlPh\{S_2P(C_6H_{11})_2\}_2]$	5[$TlCS_4$]	2.13(2)	S 2.547(4) 2.547(4) 2.863(3) 2.879(3)	[20]
$[NMe_4][Tl(C_6H_4N{=}NPh)Cl_3]$	5[$TlCNCl_3$]	2.138(10)	N 2.786(8) Cl 2.427(3) 2.500(4) 2.575(3)	[21]
$[Tl(C_6H_4CH_2NMe_2)Cl_2]$	5[$TlCNCl_3$]	2.127(10)	N 2.513(8) Cl 2.392(3) 2.530(4) 2.937(3)	[21]
[TlMe(BTAPy)]	6[$TlCN_3S_2$]	2.073	N 2.673 2.673 2.794 S 2.587 2.683	[22]
$[Tl(C_3H_5)(C_4H_7O_2)_2]$	7[$TlCO_6$]	2.160(33)	O 2.125(19) 2.495(12) 2.497(12) 2.568(12) 2.669(12) 2.718(19)	[23]
$[Tl(P^iNR)(C_4H_7O_2)_2]^{\bullet}$ (radical)	7[$TlCNO_5$]	2.09(2)	N 2.64(2) O 2.12(2) 2.43(1) 2.47(2) 2.58(2) 2.67(2)	[24,25]

somehow been omitted. In these cases, the suspected interaction was included after being confirmed by consultation of the CSD (Cambridge Structural Database) [15].

1.2. Monoorganothallium(III) compounds

Structural data for monoorganothallium compounds are listed in Table 1.

1.2.1. Coordination number 4

The compound $[Tl(mes)_2][TlCl_3(mes)]$ (Fig. 1) [16] basically consists of isolated $[Tl(mes)_2]^+$ cations (vide infra) and $[TlCl_3(mes)]^-$ anions. Tl···Cl–Tl bridges between the two ions give rise to polymeric chains, but the Tl···Cl interaction must be mainly electrostatic. In the $[TlCl_3(mes)]^-$ anions the thallium atom has coordination number four in a rather distorted tetrahedral environment.

1.2.2. Coordination number 5

The porphinate derivative [TlMeTPP] [17] has been obtained by reacting tetraphenylporphyrin (H_2TPP) with diacetatomethylthallium(III) in chloroform. The metal coordinates to the four porphinate N atoms and the methyl carbon in a square pyramidal configuration in which the thallium atom lies 1.11 Å from the plane of the macrocycle. The Tl–C bond (2.147(12) Å) makes an angle of 1.2° with the normal to this plane, and the Tl–N bond lengths range from 2.287(9) to 2.298(10) Å, so there is little deviation from C_{4v} symmetry.

Another monoalkylthallium(III) complex with the same porphinate ligand is formed when H_2TPP is reacted with diacetato{2-*exo*-bicyclo[2.2.1]hept-*exo*-3-acetato-5-enyl}thallium(III) $[Tl(NOR)(OAc)_2]$ instead of $TlMe(OAc)_2$ [18]. In [Tl(NOR)TPP] the norbornenyl group, unlike the methyl group in [TlMeTPP], deviates significantly from the normal to the N_4 plane, by an average of 20°. This structural difference is attributed to non-bonding interactions between the porphyrin ring and one of the oxygen atoms belonging to the acetate substituent on the norbornenyl bicycle, O(1). Although the reported Tl···O(1) distance, 2.97 Å, is considerably shorter than the sum of the van der Waals radii, it is considered to be imposed by the configuration of the norbornenyl group.

In crystals of *p*-tolylbis(diethyldithiocarbamato)thallium(III) $[Tl(tol)(Et_2dtc)_2]$ [19], the *p*-tolylthallium(III) moiety is bound to two slightly different anisobidentate dithiocarbamate ligands, for one of which the Tl–S distances are 2.591(2) and 2.728(3) Å and for the other 2.546(4) and 2.795(3) Å. According to the author [19], the coordination polyhedron can be described as a trigonal bipyramid in which the equatorial plane is formed by the C atom and the two S atoms closest to the metal. The S–Tl–S angle defined by the more weakly bound apical S atoms is 144.3(1)°.

Treatment of diphenylthallium(III) compounds with dicyclohexyldithiophosphinic acid can bring about protodemetallation (the loss of one phenyl group) and the formation of $[TlPh\{S_2P(C_6H_{11})_2\}_2]$ [20], the crystals of which are formed by discrete molecules in which the thallium atom is coordinated to the phenyl carbon and to the four sulphur atoms of two anisobidentate dicyclohexyldithiophosphinate

Table 2
Structural data of diorganothallium(III) compounds

Compound	CN [kernel]	d(Tl–C) (Å)	d(Tl–L) (Å)	C–Tl–C (°)	Ref.
$[TlMe_2(OPh)]$, dimer, two independent Tl atoms, average values are given	4[TlC_2O_2]	2.20(7)	O 2.36(10) 2.37(9)	173(3)	[26]
$[TlMe_2(OC_6H_4Cl\text{-}o)]$, dimer, two independent Tl atoms, average values are given	4[TlC_2O_2]	2.14(2)	O 2.40(1) 2.43(1)	166.2(10)	[26]
$[TlPh_2\{(SPPh_2)_2N\}]$, two independent Tl atoms	4[TlC_2S_2]	Tl(1) 2.099(8) 2.175(6)	S 2.736(3) 2.788(2)	151.0(3)	[27]
		Tl(2) 2.145(7) 2.204(8)	2.740(2) 2.766(2)	148.1(4)	
$[Tl(Me_3SiCH_2)_2Cl]$, dimer	4[TlC_2Cl_2]	2.17(3) 2.21(4)	Cl 2.76(1) 2.99(1)	168(1)	[28]
$[Tl(mes)_2][TlCl_3(mes)]$, polymeric chain	4[TlC_2Cl_2]	2.121(11) 2.131(10)	Cl 3.046(3) 3.119(3)	173.1(4)	[16]
$[Tl(pFPh)_2OH]$, polymer	5[TlC_2O_3]	2.12(3)	O 2.23(2) 2.51(2) 2.69(2)	138.5(5)	[29]
$[TlPh_2(trop)]$, dimer	5[TlC_2O_3]	2.129(6) 2.131(6)	O 2.421(9) 2.422(10) 2.612(9)	162.6(3)	[30]
$[TlMe_2(prop)]$, polymer	5[TlC_2O_3]	2.16(4)	O 2.39(2) 2.65(2) 2.76(2)	174.(1)	[31]
$[TlMe_2(SPh)]$, dimer	5[TlC_2S_3]	2.10(3) 2.11(3)	S 2.748(8) 2.991(8) 3.40	163.5(9)	[25]
$[TlPh_2(Et_2dtc)]$, polymer	5[TlC_2S_3]	2.158(32) 2.160(29)	S 2.717(16) 2.722(16) 3.413	148.4(1.6)	[30]

Table 2 (continued)

$[TlMe_2(S_2PEt_2)]$, polymer	$5[TlC_2S_3]$	2.128(11)	S 2.981(3) 2.991(4) 3.334(3)	169.7(6)	[32]
$[Tl(tFPh)_2Br]$, polymeric chain formed by dimers with two independent Tl atoms	$5[TlC_2Br_3]$	Tl(1) 2.11(1) 2.13(1)	Br 2.734(2) 3.016(2) 3.214(1)	149.9(5)	[33]
		Tl(2) 2.12(1) 2.14(1)	Br 2.728(2) 3.073(2) 3.172(1)	144.2(4)	
$[TlMe_2(DL\text{-}TRP)(H_2O)]$, dimer	$5[TlC_2NO_2]$	2.106(14) 2.120(13)	N 2.659(8) O 2.468(6) 2.593(8)	165.7(4)	[34]
$[Tl(Me_3SiCH_2)_2\{N(SO_2Me)_2\}]$, polymer	$5[TlC_2NO_2]$	2.122(5) 2.129(6)	N 2.609(3) O 2.799(3) 2.813(3)	175.9(2)	[35]
$[Tl(FcN)_2Cl]$	$5[TlC_2N_2Cl]$	2.128(8)	N 2.660(9) Cl 2.581(3)	145.2(5)	[36]
$[TlMe_2(PyTd)]$, two different coordination entities: $[TlC_2N_2S]$ and $[TlC_2NOS_2]$, polymer	$5[TlC_2N_2S]$	2.15(2) 2.17(2)	N 2.33(1) 2.61(1) S 3.406(4)	157.7(7)	[37]
$[TlMe_2(Rd)]$, polymer	$5[TlC_2O_2S]$	2.1435(8)	O 2.659(7) 2.723(7) S 2.949(3)	171.4(6)	[38]
$[Tl(pFPh)_2Cl\{Au(pFPh)_3(PPh_2CH_2PPh_2(O))\}_2]$, monomer	$5[TlC_2O_2Cl]$	2.115(13) 2.18(2)	O 2.550(7) 2.559(7) Cl 2.469(7)	142.3(5)	[39]
$[TlMe_2(AMTFMT)]$, polymeric chain formed by dimers	$5[TlC_2NS_2]$	2.11(3) 2.13(3)	N 2.61(2) S 2.85(1) 3.18(3)	173(2)	[40]
$[TlMe_2(CPTSC)(HCPTSC)]$, polymer	$5[TlC_2NS_2]$	2.07(3) 2.13(3)	N 2.55(1) S 2.627(5) 3.249(5)	150(1)	[41]

Table 2 (continued)

$[TlMe_2(SPy)]$, polymer	5$[TlC_2NS_2]$	2.159(8) 2.199(8)	N 2.494(7) S 2.870(2) 3.160(3)	158.0(4)	[42]
$[TlMe_2(p\text{-}ATSC)]$, polymer	5 $[TlC_2NS_2]$	2.14(2) 2.15(2)	N 2.56(1) S 2.991(4) 3.304(4)	169.7(7)	[43]
$[Tl(tFPh)_2Cl(OPPh_3)]$, dimer	5$[TlC_2OCl_2]$	2.144(12) 2.147(14)	O 2.391(9) Cl 2.541(3) 2.936(3)	140.6(5)	[44]
$[TlPh_2(HDz)(EtOH)]$	5$[TlC_2NOS]$	2.12(1) 2.14(1)	N 2.62(1) O 2.64(1) S 2.648(4)	152.7(5)	[45]
$[TlMe_2(Htuc)]$, polymer	5$[TlC_2NOS]$	2.16(5) 2.18(4)	N 2.55(2) O 2.72(3) S 2.869(8)	106(1)	[46]
$[PMePh_3]$ $[TlMe_2(B_{10}H_{12})]$, monomeric anion	6$[TlC_2B_4]$	2.21(3) 2.23(2)	B 2.51(2) 2.61(2) 2.76(2) 2.77(2)	134.1(8)	[47]
$[TlMe_2(N_3)]$, polymer	6$[TlC_2N_4]$	2.07(5)	N 2.76(3)	180	[48]
$[TlMe_2(NCS)]$(monoclinic), two independent Tl atoms with two different kernels: $[TlC_2N_4]$ and $[TlC_2S_4]$	6$[TlC_2N_4]$	2.17(9) 2.18(12)	N 2.77(4)	180	[48]
$[TlMe_2\{C(CN)_3\}]$, polymer	6$[TlC_2N_4]$	2.13(3)	N 2.67(3) 2.91(1)	178.7	[49]
$[TlMe_2\{N(CN)_2\}]$, polymer	6$[TlC_2N_4]$	2.08(4) 2.15(5)	N 2.60(4) 2.79(4) 2.81(4) 2.90(3)	176.0	[49]
$[Tl(pFPh)_2(dpa)]$, dimer with two independent Tl atoms	6$[TlC_2N_4]$	2.16(4) 2.12(4)	N 2.27(3) 2.46(3) 2.57(4) 3.18(3)–3.32(3)	127(1)	[50]

Table 2 (continued)

$[TlEt_2(C_7H_5O_2)]$, polymer	$6[TlC_2O_4]$	2.12(4) 2.23(4)	O 2.46(2) 2.61(2) 2.65(2) 3.15(2)	172(1)	[7]
$[TlMe_2(OAc)]$, linear polymer	$6[TlC_2O_4]$	2.05(4)	O 2.61(2) 2.67(2)	171.8(16)	[51]
$[TlMe_2(trop)]$, linear polymer	$6[TlC_2O_4]$	2.13(2)	O 2.47(1) 2.74(1)	166.9(9)	[51]
$[TlMe_2(acac)]$, linear polymer	$6[TlC_2O_4]$	2.12(5)	O 2.45(2) 2.95(2)	170.0(20)	[51]
$[Tl(pFPh)_2(OOCpFPh)(OPPh_3)]$, dimer	$6[TlC_2O_4]$	2.099(12) 2.111(14)	O 2.375(6) 2.389(7) 2.531(6) 2.761(6)	151.6(5)	[52]
$[Tl(pFPh)_2(acac)\{(O)Ph_2PCH_2PPh_2(O)\}]$, polymeric chains	$6[TlC_2O_4]$	2.129(8) 2.141(7)	O 2.310(5) 2.338(5) 2.531(5) 2.761(5)	156.4(2)	[53]
$[TlMe_2][AlMe_3NCS]$	$6[TlC_4S_2]$	2.15(2)	C 3.15 S 3.13(1)	177(2)	[54]
$[TlMe_2(NCS)]$ (monoclinic), two independent Tl atoms with two different kernels: $[TlC_2N_4]$ and $[TlC_2S_4]$	$6[TlC_2S_4]$	2.18(12) 2.17(9)	S 3.12(1)	180	[48]
$[TlMe_2(^nPr_2dtc)]$, polymer	$6[TlC_2S_4]$	2.09(3) 2.26(4)	S 2.695(5) 2.802(6) 3.469(6) 3.704(5)	153(1)	[55]
$[TlMe_2(S_2PPh_2)]$, polymer with two independent Tl atoms	$6[TlC_2S_4]$	Tl(1) 2.15(1) 2.16(2)	S 2.964(4) 2.993(5) 3.147(4) 3.364(4)	165.1(6)	[56]
		Tl(2) 2.13(2) 2.17(2)	S 2.976(4) 3.003(4) 3.101(4) 3.360(4)	171.6(6)	

Table 2 (continued)

$[Et_4N][TlMe_2(S_2PPh_2)_2]$	$6[TlC_2S_4]$	2.124(8) 2.126(8)	S 2.908(2) 3.064(2) 3.125(2) 3.290(2)	171.2(3)	[56]
$[TlPh_2\{S_2P(C_6H_{11})_2\}]$, polymer	$6[TlC_2S_4]$	2.107(9) 2.117(9)	S 2.789(3) 2.816(3) 3.563(3) 3.614(3)	160.6(4)	[20]
$[Et_4N][TlPh_2(S_2PPh_2)_2]$, two independent molecules	$6[TlC_2S_4]$	Tl(1) 2.143(6) 2.149(6)	S 2.809(2) 2.846(2) 3.316(2) 3.459(2)	159.2(2)	[57]
		Tl(2) 2.139(7) 2.140(7)	2.790(2) 2.790(2) 3.370(2) 3.442(2)	154.9(2)	
$[TlPh_2(S_2PEt_2)]$, polymer	$6[TlC_2S_4]$	2.14(1)	S 2.854(5) 2.933(4) 3.321(4) 3.729(5)	165.6(5)	[32]
$[TlMe_2Cl]$, polymer	$6[TlC_2Cl_4]$	2.139(5)	Cl 3.029(0)	180	[4],[5]
$[TlMe_2$(L-PHE)], two independent polymeric chains	$6[TlC_2NO_3]$	Tl(a) 2.060(19) 2.152(19)	N 2.527(13) O 2.629(12) 2.655(15) 3.130	165.6(8)	[58]
		Tl(b) 2.098(20) 2.176(18)	N 2.534(13) O 2.539(12) 2.665(15) 3.056	163.7(8)	
$[Tl(Me_3SiCH_2)_2\{N(SO_2Me)_2\}(OH_2)]$, polymer	$6[TlC_2NO_3]$	2.133(3)	N 2.723(3) O 2.512(2) 2.775(2) 2.881(3)	172.3(1)	[35]

Table 2 (continued)

$[(TlMe_2)_2$(bismuthiol I)], polymer with two independent Tl atoms	$6[TlC_2NS_3]$	Tl(1) 2.19(4) 2.35(5)	N 2.70(4) S 3.05(2) 3.21(1) 3.45(2)	162(1)	[59]
		Tl(2) 2.14(7) 2.30(7)	N 2.70(4) S 3.08(1) 3.39(2) 3.46(1)	165(1)	
$[TlMe_2$(Phen)$](ClO_4)$, polymer	$6[TlC_2N_2O_2]$	2.12 (3)	N 2.570(27) O 2.88(3)	168(1)	[6]
$[TlMe_2$(NCO)] (orthorhombic)	$6[TlC_2N_2O_2]$	2.01(17) 2.03(15)	N 2.66(4) O 2.85(3)	166.(5)	[48]
$[TlMe_2$(NCO)] (trigonal)	$6[TlC_2N_2O_2]$	2.10(7) 2.15(7)	N 2.58(3) O 2.85(4)	166.(2)	[48]
$[Tl(OTMIPh)_2(CF_3COO)]^{\bullet}$ (radical), dimer with two independent molecules. Average values are given	$6[TlC_2N_2O_2]$	2.13 2.14	N 2.54 2.56 O 2.50 2.62	173	[60]
$[Tl\{CH_2C(O)Me\}_2(\mu\text{-}CF_3SO_3)$(bpy)], dimer	$6[TlC_2N_2O_2]$	2.161(8) 2.171(7)	N 2.456(5) 2.500(4) O 2.739(6) 2.806(4)	160.8	[61]
$[TlMe_2$(NCS)] (orthorhombic)	$6[TlC_2N_2S_2]$	2.08(11) 2.17(11)	N 2.80(6) S 3.11(2)	177(3)	[48]
$[TlMe_2$(fth)], two independent Tl atoms with different kernels, $[TlC_2N_2S_2]$ and $[TlC_2N_2O_2S]$, polymer	$6[TlC_2N_2S_2]$	Tl(1) 2.16(1) 2.18(2)	N 2.586(7) 3.210(8) S 2.862(2) 3.367(2)	163.0(4)	[62]
$[TlMe_2$(PyTSC)], two independent molecules, dimers	$6[TlC_2N_2S_2]$	Tl(1) 2.115(8) 2.12(1)	N 2.557(5) 2.686(8) S 2.848(3) 3.671(2)	165.7(3)	[63]

Table 2 (continued)

		Tl(2) 2.125(9) 2.13(1)	N 2.700(6) 2.712(5) S 2.803(2) 3.207(3)	166.5(4)	
$[TlMe_2(OPy2S)]$, polymer	$6[TlC_2O_2S_2]$	2.143(9) 2.148(8)	O 2.577(6) 2.849(13) S 2.889(2) 3.284(6)	168.5(4)	[64]
$[TlMe_2\{S(O)PPh_2\}]$, polymer	$6[TlC_2O_2S_2]$	2.14(1) 2.17(1)	O 2.509(7) 3.143(7) S 2.919(3) 3.402(3)	166.9(5)	[65]
$[TlMe_2(PxTSC)(H_2O)]$, dimer	$6[TlC_2O_2S_2]$	2.134(8) 2.136(8)	O 2.630(4) 3.124(4) S 2.832(1) 3.190(1)	164.7(3)	[66]
$[TlMe_2(DABRd)]$, polymer	$6[TlC_2\ NOS_2]$	2.078(9) 2.128(9)	N 2.660(6) O 2.613(5) S 3.051(2) 3.266(2)	166.2(4)	[67]
$[TlMe_2(PyTd)]$, two different coordination entities: $[TlC_2N_2S]$ and $[TlC_2NOS_2]$, polymer	$6[TlC_2\ NOS_2]$	2.15(2) 2.16(2)	N 2.807(9) O 2.681(9) S 2.986(4) 3.038(4)	169.7(6)	[37]
$[TlMe_2(PyRd)]$, polymer	$6[TlC_2\ NOS_2]$	2.138(7) 2.149(7)	N 2.540(5) O 2.594(4) S 3.200(3) 3.530(2)	172.8(3)	[37]
$[TlMe_2(H_2Tot)(H_2O)]$, polymer	$7[TlC_2O_4S]$	2.15(2)	O 2.668(9) 2.770(9) 2.81(2) 2.86(1) S 3.220(4)	178.2(6)	[68]

Table 2 (continued)

$[TlMe_2(S_2COCH_3)]$, polymer	7[TlC_2OS_4]	2.07(11) 2.10(8)	O 3.13 S 2.96(3) 2.98(2) 3.19 3.35	170.9	[69]
$[(TlMe_2)_3(Et_3terpy)_2(NO_3)_3]$, two independent Tl atoms with different kernels: [$TlC_2N_3O_2$] and [TlC_2O_6], trimer	7[$TlC_2N_3O_2$]	Tl(1) 2.04(4) 2.09(4)	N 2.61(3 2.62(3) 2.66(3) O 2.99(3) 3.11(3)	166(1)	[70]
$[TlMe_2(terpy)(H_2O)(NO_3)]$	7[$TlC_2N_3O_2$]	2.116(14) 2.131(15)	N 2.620(10) 2.631(10) 2.650(9) O 2.932(12) 3.250(19)	169.6(6)	[70]
$[TlMe_2\{(Py)_2CH_2\}(NO_3)]$, dimer	7[$TlC_2N_2O_3$]	2.108(13) 2.139(13)	N 2.658(9) 2.666(9) O 2.770(9) 2.847(12) 2.915(10)	171.7(5)	[70]
$[TlMe_2(fth)]$, two independent Tl atoms with different kernels, [$TlC_2N_2S_2$] and [$TlC_2N_2O_2S$], polymer	7[$TlC_2N_2O_2S$]	Tl(2) 2.156(9) 2.22(1)	N 2.734(7) 2.908 O 2.994(6) 3.279(7) S 2.831(2)	164.9(4)	[62]
$[TlMe_2(DAPMTSC)]$, dimer	7[$TlC_2N_2O_2S$]	2.128(9) 2.133(9)	N 2.590(6) 2.686(2) O 2.883(6) 3.050(6) S 2.872(2)	164.3(4)	[71]
$[TlPh_2(DAPMTSC)] \cdot CHCl_3$, dimer	7$TlC_2N_2O_2S$]	2.13(2) 2.16(2)	N 2.56(2) 2.579(14) O 2.86(1) 3.42(1) S 2.791(6)	169.2(6)	[71]

Table 2 (continued)

$[TlMe_2(S_2CPPh_2)(THF)]$, polymer	7[TlC_2OPS_3]	2.15(3) 2.18(4)	O 2.80(3) P 3.545(9) S 2.98(1) 3.04(1) 3.21(1)	168(1)	[72]
$[TlMe_2(DB18C6)][(NO_2)_3C_6H_2O]$	8[TlC_2O_6]	2.110(18) 2.180(17)	O 2.694(10) 2.698(9) 2.769(8) 2.770(11) 2.791(8) 2.818(11)	178(1)	[73], [74]
$[TlMe_2(DCH18C6)][(NO_2)_3C_6H_2O]$, two isomers (A and B)	8[TlC_2O_6]	(A)2.097(9) 2.115(8)	O 2.677(5) 2.737(5) 2.782(5) 2.795(5) 2.805(5) 2.979(5)	177.5(4)	[75], [76]
		(B) 2.113(9)	O 2.736(5) 2.762(5) 2.867(5)	180	
$[(TlMe_2)_3(Et_3terpy)_2(NO_3)_3]$, two independent Tl atoms with different kernels, $[TlC_2N_3O_2]$ and $[TlC_2O_6]$	8[TlC_2O_6]	Tl(2) 1.97(4)	O 2.72(2) 2.81(2) 2.85(3)	180	[70]
$[TlMe_2(DDC18C6)]ClO_4$	8[TlC_2O_6]	2.150(28) 2.170(42)	O 2.608(17) 2.677(18) 2.818(17) 2.842(14) 2.890(18) 2.939(17)	179(2)	[77]
$[TlMe_2(TDC18C6)]ClO_4$	8[TlC_2O_6]	2.099(18)	O 2.801(7)	180	[78]

Table 3
Structural data of triorganothallium(III) compounds

Compound	CN [kernel]	d(Tl–C) (Å)	d(Tl–L) (Å)	C–Tl–C (°)	Ref.
$[Tl(FcN)_3]$	4[TlC_3N]	2.176(6) 2.181(6) 2.202(5)	N 2.523(5)	114.0(2) 118.5(2) 125.9(2)	[79]
$[TlMe_3]$	5[TlC_5]	2.22 2.30 2.34	C 3.16 3.31	110(3) 118(3) 131(3)	[80]
$[Tl(DPP)_3]\cdot C_7H_8$	5[TlC_3P_2]	2.210(4) 2.214(4) 2.226(3)	P 2.795(1) 3.558(2)	108.1(1) 122.5(1) 124.2(1)	[81]

ligands. As in the preceding dithiocarbamate compound, the bond angles suggest a coordination polyhedron closer to a trigonal bipyramid than a square pyramid, even though the angle formed by Tl and the apical S atoms, 158.7(1)°, again differs widely from 180°.

Monoorganothallium(III) derivatives of 2-(phenylazo)phenyl and 2-(dimethylaminomethyl)phenyl radicals have been prepared by reacting $[NMe_4]_2[TlCl_5]$ with the corresponding diorganomercury(II) compounds [21]. Crystals of $[NMe_4][Tl(C_6H_4N{=}NPh)Cl_3]$ contain discrete anions that, if a weak intramolecular Tl···N interaction is recognized (Tl···N = 2.786(8) Å), exhibit distorted trigonal bipyramidal geometry with the coordinated N and a Cl atom apical and the C and the other two Cl atoms equatorial (Fig. 2).

The neutral compound $[Tl(C_6H_4CH_2NMe_2)Cl_2]$ [21] consists of dimers with asymmetric chlorine bridges (Fig. 3). The Tl–N bond is shorter (2.513(8) Å) than in the above anionic compound. The coordination polyhedron is again a distorted trigonal bipyramid, with the N and a bridging chloride apical.

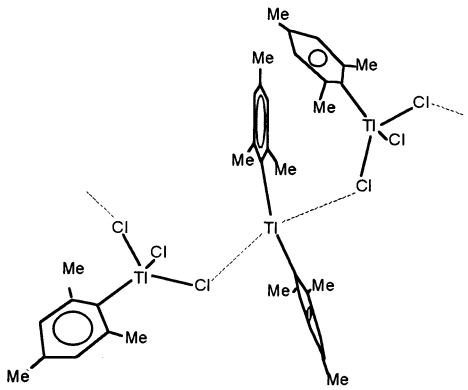

Fig. 1. Adapted from Ref. [16].

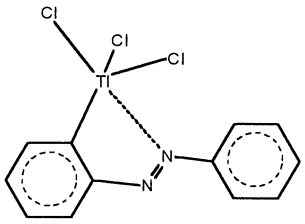

Fig. 2. Adapted from Ref. [21].

1.2.3. Coordination number 6

The reaction of 2,6-bis(2-methyl-2-benzothiazolinyl)pyridine with diacetatomethylthallium(III) in chloroform leads via deprotonation and ring opening to [TlMe(BTAPy)] (Fig. 4), which is isolated as orange crystals [22]. The $BTAPy^{2-}$ dianion coordinates to the metal as a quinquedentate ligand through its N and S atoms, the Tl–N distances (2.673 Å for the azaethene nitrogens and 2.794 Å for the pyridine nitrogen) all being well below the sum of the van der Waals radii, 3.55 Å. Together with the Me carbon (axial position), the $BTAPy^{2-}$ donor atoms define a highly distorted pentagonal pyramid, the main source of distortion being the non-planarity of the ligand.

1.2.4. Coordination number 7

The exchange reaction between dicyclopropylisobutyratothallium(III) and bis(isobutyrato)mercury(II) gives cyclopropylbis(isobutyrato)thallium(III) as colourless crystals which consist of $[Tl(C_3H_5)(C_4H_7O_2)_2]$ units linked in linear chains by oxygen bridges involving one of the isobutyrato groups [23]. This bridging isobutyrato ligand is practically isobidentate, with Tl–O distances of 2.495(12) and 2.497(12) Å, while the other is strongly anisobidentate (2.125(19) and 2.718(19) Å). If the intermolecular Tl–O distances (2.568(12) and 2.669(12) Å) are considered as evidence of coordination, the polyhedron around the thallium atom can be described as a distorted pentagonal bipyramid in which the apical positions are occupied by the C atom and the O atom belonging to the anisobidentate isobu-

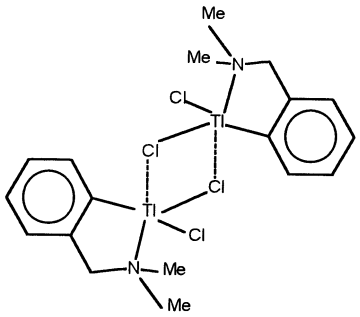

Fig. 3. Adapted from Ref. [21].

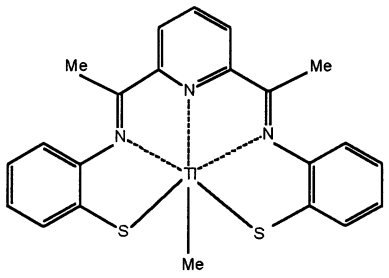

Fig. 4. Adapted from Ref. [22].

tyrato ligand (the one with the shortest Tl–O bond). It is the bite of this ligand, which also contributes an equatorial donor atom, that imposes the main distortion.

In a search for stable nitroxyl radicals, the monoorganothallium derivative $[Tl(P_iNR)(C_4H_7O_2)_2]^{\bullet}$ was prepared [24,25]. According to the structural information given by the authors, which does not include atomic coordinates, this radical crystallizes as centrosymmetric dimers in which bonds between each Tl and one of the Tl-bound carboxylate oxygen atoms of the other monomer create a planar Tl_2O_2 ring with Tl–O distances of 2.43(1) and 2.58(2) Å (Fig. 5). The coordination sphere of each metal is completed by the carbon atom of the nitrosyl ring, the nitrogen atom of the piperidinomethyl radical and the other three diisobutyrate oxygen atoms (for one of which the Tl–O distance quoted 2.12(2) Å [24], seems to be anomalously short).

1.3. Diorganothallium(III) compounds

Structural data for diorganothallium complexes are given in Table 2.

1.3.1. Coordination number 4

Diorganothallium(III) complexes with anions that can be good bridging groups usually crystallize as dimers. This is the case of dimethylthallium(III) phenoxide, $[TlMe_2(OPh)]$ (Fig. 6), and dimethylthallium(III) *ortho*-chlorophenoxide, $[TlMe_2(OC_6H_4Cl\text{-}o)]$ [26]. Both molecules form dimeric structures in which the

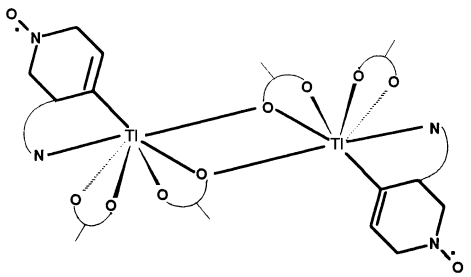

Fig. 5. Adapted from Ref. [24].

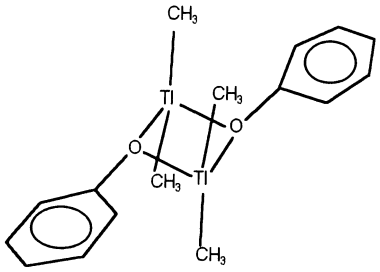

Fig. 6. Adapted from Ref. [26].

thallium atoms are tetracoordinated to two C and two O atoms. No close contacts with other molecules are reported. The coordination polyhedron around the metal is best described as a distorted trigonal bipyramid with axial methyl groups and a vacant equatorial coordination site.

Reacting potassium tetraphenyldithioimidodiphosphinate, $[K(SPPh_2)_2N]$, with diphenylthallium (III) bromide in methanol yields the compound $[TlPh_2\{(SPPh_2)_2N\}]$ [27]. An X-ray diffraction study has shown its unit cell to contain two independent molecules with small structural differences. In both molecules, the thallium atom is coordinated to two phenyl carbons and to two sulphurs belonging to a roughly isobidentate chelating ligand. The diphenylthallium(III) moiety bends back from the bite of the ligand (the average C–Tl–C bond angle for the two molecules is 149.5°) giving, together with the narrow S–Tl–S angle (average value for the two molecules 97.7°), a thallium environment which can be described as intermediate between tetrahedral and ψ-trigonal bipyramidal[1].

The diorganothallium(III) derivative $[Tl(Me_3SiCH_2)_2Cl]$ [28] is also dimeric, with two bridging chlorine atoms coordinating to both thallium atoms. The coordination polyhedron around the thallium atom is described as a distorted trigonal bipyramid with one equatorial position vacant.

In $[Tl(mes)_2][TlCl_3(mes)]$ [16] the $[Tl(mes)_2]^+$ cations, which are almost linear (C–Tl–C = 173(4)°), are very weakly bound to the $[TlCl_3(mes)]^-$ anions through Tl···Cl interactions (see Fig. 1). If these weak interactions are taken into account, the coordination number of the thallium atom in the cations is four.

1.3.2. Coordination number 5

In $[Tl(pFPh)_2(OH)]$ [29] the thallium atom is strongly coordinated to two carbon atoms and one oxygen atom, and weakly to two other oxygens; and each OH ligand bridges among three $Tl(pFPh)_2^+$ units (Fig. 7). The polyhedron around the metal is described as a very distorted trigonal bipyramid with the C atoms in equatorial position and a C–Tl–C angle that accordingly differs widely from 180°.

The tropolone derivative $[TlPh_2(trop)]$ [30] is dimeric, with bridging O atoms. The coordination polyhedron around the metal is described as a slightly distorted

[1] ψ-Polyhedron: a polyhedron with at least one vacant site.

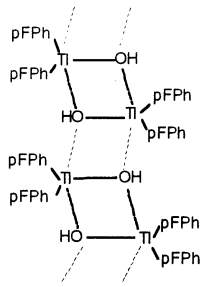

Fig. 7. Adapted from Ref. [29].

pentagonal bipyramid with two vacant equatorial sites and the phenyl groups in the axial positions.

Dimethylthallium(III) propynoate, $[TlMe_2(prop)]$ [31] (Fig. 8) is a polymer in which each propynoate anion is coordinated to three dimethylthallium units and each dimethylthallium unit to three anions. The thallium has square pyramidal geometry with the C atoms in basal positions. The C–Tl–C unit is almost linear and the Tl–C distances are within the usual range.

The crystal structure of $[TlMe_2(SPh)]$ [26] is very similar to those of $[TlMe_2(OPh)]$ and $[TlMe_2(OC_6H_5Cl\text{-}o)]$ [26]. A weak intermolecular Tl···S contact with no equivalent in the other two compounds is not considered to involve coordination by the original authors but is recognized here because the Tl···S distance is less than the sum of the van der Waals radii.

$[TlPh_2(Et_2dtc)]$ (Fig. 9) is described by its authors [30] as a discrete monomer with a highly distorted tetrahedral coordination polyhedron in which Tl has coordination number four. However, since there is also a weak intermolecular Tl···S interaction the structure must be considered as polymeric and Tl as having coordination number five according to the criteria of this review. The Tl–C distances are unremarkable and the C–Tl–C angle bends slightly away from the bite of the ligand.

$[TlMe_2(S_2PEt_2)]$ (Fig. 10) has been synthesized by reaction of the corresponding diorganothallium hydroxide with $NaS_2PEt_2 \cdot 2H_2O$, and characterized by X-ray crystallography [32]. The thallium atom is coordinated to the two sulphur atoms of

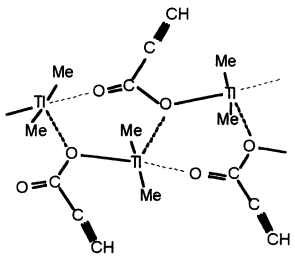

Fig. 8. Adapted from Ref. [31].

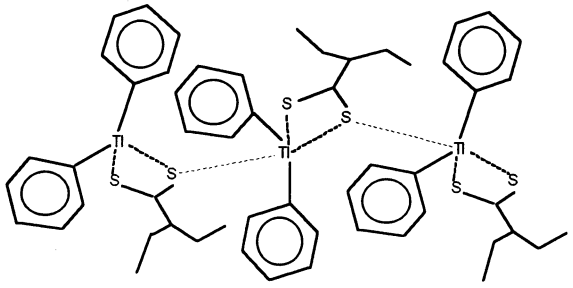

Fig. 9. Adapted from Ref. [30].

the diethyldithiophosphinato ligand and to two carbon atoms. The TlS_2P chelate ring lies in a crystallographic plane of symmetry. A weak intermolecular interaction with one of the sulphur atoms of a neighbouring molecule makes the coordination number of the thallium atom up to five. The polyhedron around the metal is described as a distorted square pyramid with an S atom in the apical position.

The crystal of $[Tl(tFPh)_2Br]$ [33] (Fig. 11) contains two crystallographically distinct molecules linked in a dimer by two asymmetric bromide bridges. Weak Tl···Br contacts between dimers give rise to a polymeric chain. The coordination polyhedron around the metal, very similar to that of $[Tl(pFPh)_2OH]$ [29], is described as a distorted trigonal bipyramid with the tFPh groups in equatorial positions.

$[TlMe_2(DL\text{-}TRP)] \cdot H_2O$ [34] (Fig. 12) forms centrosymmetric dimers in which each of the two amino acids is coordinated to one thallium via its NH_2 group and to both thallium atoms via its carboxyl group, which acts as a monodentate bridging group. The coordination around the thallium is described as a distorted octahedron with one vacant coordination site. A weak intermolecular Tl···N interaction between dimers is also described. The Tl–C distances and C–Tl–C angle are in the normal ranges.

In $[Tl(Me_3SiCH_2)_2\{N(SO_2Me)_2\}]$ [35] two thallium atoms are linked by two (NSO) bridges belonging to different $(MeSO_2)_2N^-$ ligands, originating eight-membered $[TlNSO]_2$ rings. These rings are connected by Tl–O bonds. The coordination polyhedron around the thallium atom, a distorted trigonal bipyramid, is defined by

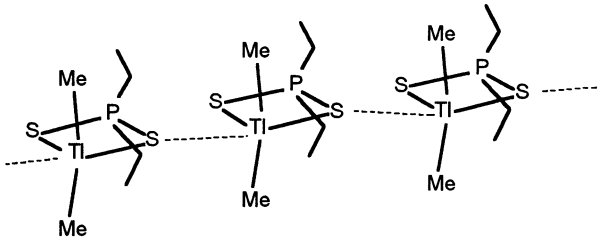

Fig. 10. Adapted from Ref. [32].

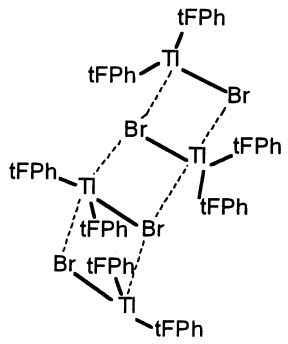

Fig. 11. Adapted from Ref. [33].

two C atoms in axial positions and one N and two oxygens in the equatorial plane (Fig. 13).

$[Tl(FcN)_2Cl]$ (Fig. 14) [36] was prepared by reacting $Tl(FcN)_3$ with $VOCl_3$. Each ferrocenyl acts as a C,N bidentate ligand chelating the thallium atom in a five-membered ring. One donor of each of these ligands occupies an axial position of a trigonal bipyramid, and the other an equatorial position; the third equatorial position is occupied by the Cl atom.

5-(2-Pyridinylmethylene)-2-thiohydantoin reacts with dimethylthallium(III) hydroxide to form $[TlMe_2(PyTd)]$ [37]. In the crystals of this compounds there are two PyTd desmotropes and two different coordination kernels linked by weak Tl···S···Tl interactions (Fig. 15). In one, $[TlC_2N_2S]$, the dimethylthalliun unit is coordinated to the deprotonated thiohydantoin N(1) atom, the pyridine nitrogen and the S atom; while in the other, $[TlC_2NOS_2]$, it is coordinated to this same S atom, to the S and deprotonated thiohydantoin N(3) atoms of a second ligand, and to the oxygen of a third (likewise of the N(3)-deprotonated type). These Tl···O interactions link the two asymmetric units, giving rise to centrosymmetric dimers comprising four Tl atoms and four ligands.

$[TlMe_2(Rd)]$ [38] crystallizes forming a polymeric chain (Fig. 16). The thallium atom is coordinated to two oxygen atoms and a sulphur atom, all belonging to different rhodanine ligands, as well as to the carbon atoms of the methyl groups. The coordination geometry around the metal is described as pseudo-octahedral,

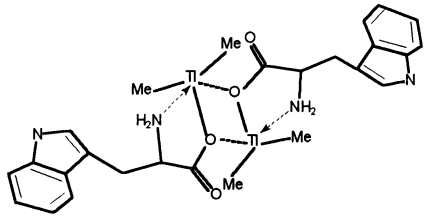

Fig. 12. Adapted from Ref. [34].

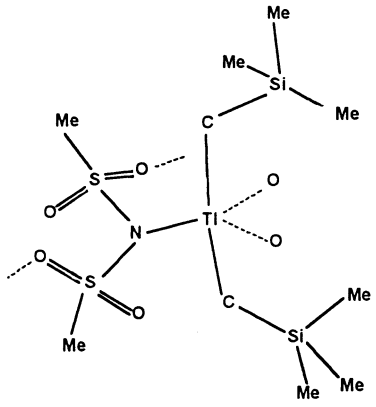

Fig. 13. Adapted from Ref. [35].

with one site of the octahedron vacant. Another thallium atom lies approximately in the direction of the empty site at a distance virtually equal to the sum of the van der Waals radii. The Tl–C distances and the C–Tl–C angle are unexceptional.

The trinuclear complex $[Tl(pFPh)_2Cl\{Au(pFPh)_3(PPh_2CH_2PPh_2(O))\}_2]$ has been studied by X-ray diffraction [39], but due to disorder problems affecting the diorganothallium unit the data must be interpreted with caution. The oxygen atoms of the two phosphine oxide ligands, the Cl atom and two pFPh C atoms define an irregular trigonal bipyramid around the thallium atom, the axial positions being occupied by the O atoms (the O–Tl–O angle is 165.89(5)°). The Tl–C distances are unremarkable and the C–Tl–C angle deviates from linearity by about 40°.

Fig. 17 shows the environment of the thallium atom in $[TlMe_2(AMTFMT)]$ [40]. The metal is coordinated to two carbon atoms and to the sulphur atom of one ligand molecule and an N atom of another, and is involved in a weak Tl···S interaction with a third ligand. The coordination polyhedron may be described as a very distorted octahedron with a vacant equatorial position. The C–Tl–C unit is almost linear and the Tl–C distances are in the normal range.

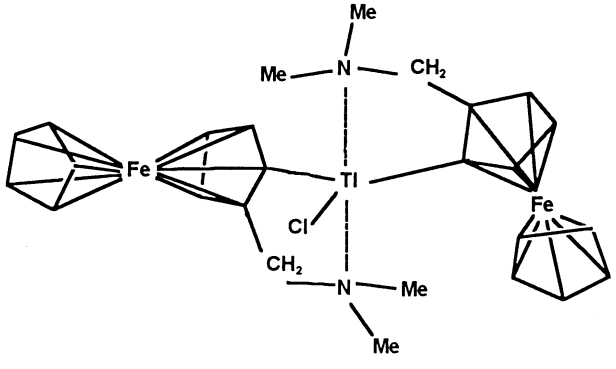

Fig. 14. Adapted from Ref. [36].

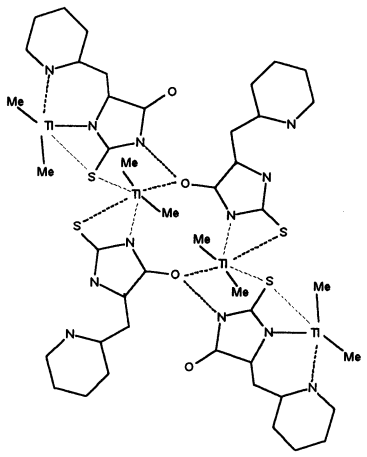

Fig. 15. Adapted from Ref. [37].

The dimethylthallium complex of cyclopentanone thiosemicarbazone, [$TlMe_2$(CPTSC)(HCPTSC)] [41] (Fig. 18), contains deprotonated and protonated ligands linked by hydrogen bonds. If the weak Tl···S interaction is included, the coordination polyhedron may be described as a deformed octahedron with one vacant position. The Tl–C distances are quite normal and the C–Tl–C angle is 150°.

In the complex [$TlMe_2$(SPy)] [42] the $TlMe_2^+$ units are coordinated to one SPy ligand via N (strongly) and S (weakly) and to another via S (strongly). If the weak Tl···S interaction is included, the coordination number of Tl is five and the

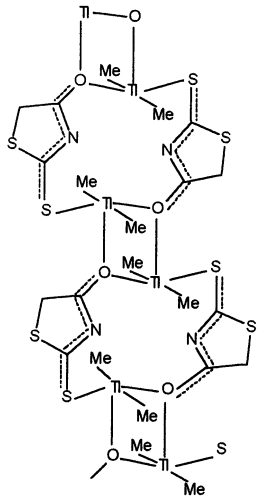

Fig. 16. Adapted from Ref. [38].

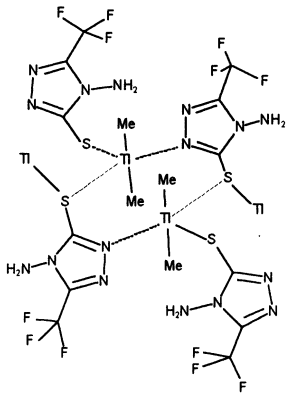

Fig. 17. Adapted from Ref. [40].

coordination polyhedron is a deformed octahedron with one vacant position. The C–Tl–C unit bends to make an angle of 158°.

In [$TlMe_2$(p-ATSC)] [43] (Fig. 19) the ligand retains the typical structure of a free thiosemicarbazone and coordinates to the metal via its N(2) and S atoms, a rather unusual coordination mode for this type of ligand. Weak intermolecular interactions with a second S atom belonging to another ligand molecule give rise to a polymer. The Tl–C distances are unremarkable and the C–Tl–C unit is bent slightly back from the bite of the ligand.

[$Tl(tFPh)_2Cl(OPPh_3)$] [44] forms dimers with asymmetric chlorine bridges. The thallium has trigonal bipyramidal stereochemistry defined by two C atoms and one Cl in equatorial positions and one O and one Cl in axial positions (O–Tl–Cl = 168.7(3)°). The C–Tl–C angle deviates markedly from linearity.

[$TlPh_2$(HDz)(EtOH)] [45] is a monomeric complex of the dithizone ligand with a distorted trigonal bipyramidal coordination polyhedron in which the thallium atom is coordinated to two C atoms and one S in equatorial positions and to one O and one N in axial positions (N–Tl–O = 157.5(3)°). The C–Tl–C angle deviates by about 27° from linearity.

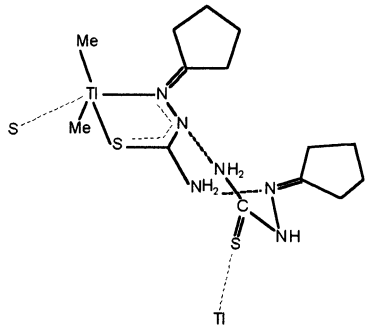

Fig. 18. Adapted from Ref. [41].

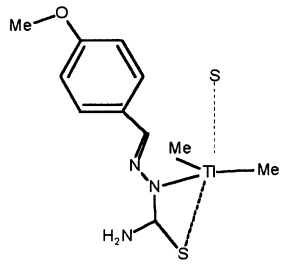

Fig. 19. Adapted from Ref. [43].

An X-ray diffraction study of $[TlMe_2(Htuc)]$ [46] (Fig. 20) has shown that the C–Tl–C angle is 106°, much more acute than in any other $TlMe_2^+$ compound studied so far, although the Tl–C bond lengths are quite normal. The thallium atom is coordinated to the two methyl carbons, to the sulphur and one of the nitrogen atoms of one thiouracilate group, and to the oxygen of another. The coordination polyhedron may be described as a rather distorted square pyramid with S, N, $C(Me_1)$ and O as its base, and $C(Me_2)$ as its apex.

1.3.3. Coordination number 6

$[PMePh_3][TlMe_2(B_{10}H_{12})]$ [47] contains the monomeric anion $[TlMe_2(B_{10}H_{12})]^-$, in which the dimethylthallium unit coordinates to an η^4-decaborate ligand (Fig. 21). Metal–ligand coordination is considered to occur via two three-centre two-electron bonds between Tl and the formally bidentate *nido*-$[B_{10}H_{12}]^{2-}$ anion. The C–Tl–C angle, 134°, is the narrowest of those found in compounds in which Tl has coordination number six (in which the carbons are usually in the axial positions of a distorted octahedron), and the Tl–C bond lengths (average 2.22(3) Å) are at the upper limit for $TlMe_2^+$ units.

The crystal structures of dimethylthallium azide, thiocyanate and cyanide (this last not included in Table 2) have been studied by Chow et al. [48]. No crystals of $[TlMe_2(CN)]$ suitable for single crystal X-ray diffraction studies were obtained, but powder diffractometry showed a sodium chloride structure (with the unit Me–Tl–Me occupying the cationic sites) in which the C–Tl–C angle is 180° and the Tl···N(C) (or Tl···C(N)) distance is 2.82 Å. $[TlMe_2(N_3)]$ also has a (distorted) NaCl structure; the environment around the metal atom may be described as tetragonal bipyramidal, but the interaction between the $TlMe_2^+$ cations and N_3^- anions is

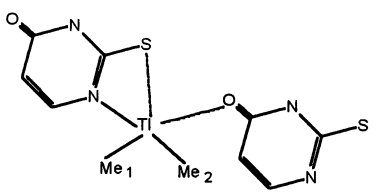

Fig. 20. Adapted from Ref. [46].

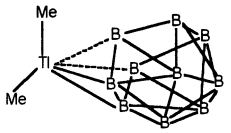

Fig. 21. Adapted from Ref. [47].

essentially ionic. $[TlMe_2(NCS)]$ crystallizes as both monoclinic and orthorhombic crystals. The monoclinic form has a distorted NaCl structure in which the thallium atoms occur in two different kernels, $[TlC_2N_4]$ and $[TlC_2S_4]$, in both of which the C–Tl–C angle is linear and the interaction between $TlMe_2^+$ and NCS^- is mainly ionic. In the orthorhombic form the thallium atoms all lie in a $[TlC_2N_2S_2]$ kernel and are all equivalent; the dimethylthallium group is practically linear and the Tl···S and Tl···N interactions are best described as ionic.

In dimethylthallium tricyanomethide, $[TlMe_2\{N(CN)_3\}]$, and dimethylthallium dicyanamide, $[TlMe_2\{N(CN)_2\}]$ [49], the almost linear $TlMe_2^+$ unit is coordinated in the equatorial plane to four N atoms. In both cases the Tl–N interactions may be considered as mainly ionic.

$[Tl(pFPh)_2(dpa)]$ (Fig. 22) [50] is considered as an asymmetric dimer, the geometries of the two monomers whose Tl atoms are linked by the two tridentate dpa ligands being identical to within measurement error except for the weak Tl···N bond, the length of which is 3.18(3) Å in one monomer and 3.32(3) Å in the other. The polyhedron around each Tl atom (weak Tl···N interaction apart) is described as a very distorted trigonal bipyramid with the C atoms in equatorial positions and a C–Tl–C angle that accordingly differs widely from 180°.

$[TlEt_2(C_7H_5O_2)]$ [7] crystallizes forming a polymeric chain of four-membered TlO_2Tl rings in which one phenolic oxygen and one aldehyde oxygen of the salicilaldehydato ligand bridge between the two Tl atoms. Each metal is hexacoordinated to two ethyl groups, the two bridging atoms and the two oxygens of a chelating ligand.

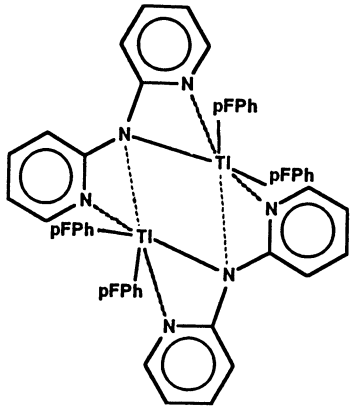

Fig. 22. Adapted from Ref. [50].

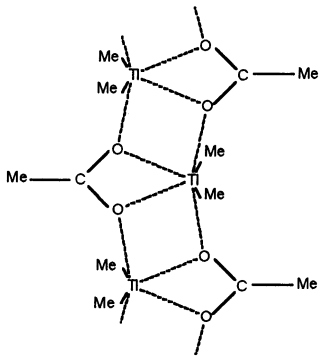

Fig. 23. Adapted from Ref. [51].

$[TlMe_2(OAc)]$ (Fig. 23), $[TlMe_2(trop)]$ and $[TlMe_2(acac)]$ [51] all form infinite linear polymers in which the thallium atom is coordinated to two methyl groups and to four oxygens in a very distorted octahedral environment. In all three compounds each ligand chelates one thallium atom, and through its two oxygens bridges between the neighbouring thalliums on either side.

Because the presence of the triphenylphosphine oxide blocks polymerization, $[Tl(pFPh)_2(OOCpFPh)(OPPh_3)]$ [52] (Fig. 24), unlike other diorganothallium carboxylates, crystallizes as a dimer, with one of the carboxyl O atoms bridging asymmetrically between the two thallium atoms. The latter have an irregular environment consisting of two pFPh carbon atoms and four oxygen atoms, two of them belonging to a chelating carboxylate ligand, one to the other monomeric unit in the dimer, and the fourth to the $OPPh_3$ ligand. If because of its small bite the carboxylate ligand is considered as occupying only one coordination position, the coordination polyhedron may be regarded as a distorted trigonal bipyramid with two carbon atoms and the carboxylate group in the equatorial plane.

An X-ray study of $[Tl(pFPh)_2(acac)\{(O)Ph_2PCH_2PPh_2(O)\}]$ [53] shows irregular geometry around the thallium atom. The Tl–C bond lengths are normal, the C–Tl–C angle is 156.4°. The environment of the metal is completed by two

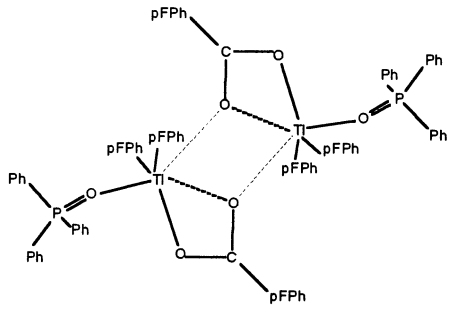

Fig. 24. Adapted from Ref. [52].

oxygens belonging to acetylacetonate ligands and two belonging to diphosphine dioxide ligands (one in each asymmetric unit). Polymeric chains result from each diphosphine dioxide ligand bridging between two Tl atoms.

Dimethylthallium isothiocyanatotrimethylaluminate, $[TlMe_2][AlMe_3NCS]$, has been prepared by reacting thallium(I) thiocyanate and trimethylaluminium in a sealed tube [54]. The dimethylthallium cation in this compound is almost linear. The authors of its synthesis describe the environment of the thallium atom as essentially octahedral, involving the two dimethylthallium C atoms, two isothiocyanato S atoms and two $AlMe_3$, even though the Tl···S interactions are described as mainly electrostatic and the $AlMe_3$ carbons as non-bonded.

Several dithiocarbamates of dimethylthallium(III) have been prepared [55], but only $[TlMe_2(^nPr_2dtc)]$ has been studied by X-ray diffraction. The thallium atom is strongly coordinated to the two sulphur atoms of a slightly anisobidentate dithiocarbamate ligand and to the two methyl groups, which together form a highly distorted tetrahedral environment, but additional weak intermolecular interactions with neighbouring ligands give rise to a spatial arrangement similar to that of $[TlMe_2(OAc)]$ (Fig. 25). Note that the weak intermolecular interactions differ from those in $[TlPh_2(Et_2dtc)]$ [30], in which the coordination number of the metal is only five.

Dimethyl(diphenyldithiophosphinato)thallium(III), $[TlMe_2(S_2PPh_2)]$ [56], crystallizes with two independent molecules per asymmetric unit, in both of which the metal is coordinated to two methyl groups, to the two sulphur atoms of one bidentate dithiophosphinate ligand and, weakly, to two sulphur atoms belonging to neighbouring molecules. The coordination polyhedron around the thallium atom is described as a highly deformed octahedron.

In $[Et_4N][TlMe_2(S_2PPh_2)_2]$ [56] the thallium atom is coordinated to two methyl groups and to two anisobidentate dithiophosphinate ligands. No intermolecular interactions are described. The coordination geometry of the thallium atom is similar to that observed in $[TlMe_2(S_2PPh_2)]$, but since the second anion replaces the intermolecular secondary bonds of the latter the polymerization process observed in $[TlMe_2(S_2PPh_2)]$ is blocked.

In $[TlPh_2\{S_2P(C_6H_{11})_2\}]$ [20] the thallium atom is coordinated to two phenyl carbons and to the two sulphur atoms of a practically isobidentate dithiophosphi-

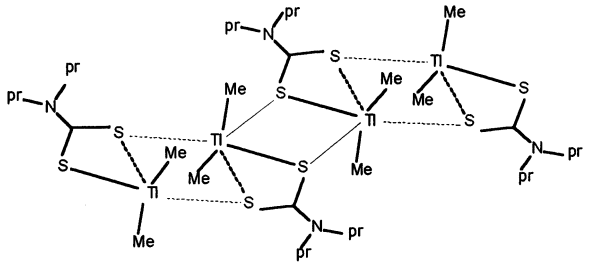

Fig. 25. Adapted from Ref. [55].

nate ligand, and two weak Tl–S interactions with neighbouring molecules give rise to infinite ribbons. If all of these interactions are taken into account, each thallium atom has a very distorted octahedral coordination polyhedron with the phenyl carbon atoms apical and the sulphur atoms equatorial.

The asymmetric unit of the crystal of $[Et_4N][TlPh_2(S_2PPh_2)_2]$ [57] contains two independent molecules which differ slightly in both bond lengths and angles. In each molecule the thallium atom is coordinated to two carbon atoms and to four sulphur atoms belonging to two strongly anisobidentate dithiophosphinate ligands. If all these interactions are included, the polyhedron around the thallium atom can be described as a very deformed octahedron with the carbon atoms apical and the sulphur atoms equatorial. This arrangement is similar to that found in $[Et_4N][TlMe_2(S_2PPh_2)_2]$ [56], but the steric and/or electronic influence of the organometallic phenyls causes the weak Tl···S bonds to be longer, the strong Tl–S bonds shorter and the C–Tl–C angle narrower in the diphenylthallium(III) derivative.

In $[TlPh_2(S_2PEt_2)]$ [32] the thallium is coordinated to one carbon atom of each phenyl group and the two sulphur atoms of the dithiophosphinato ligand. Two weak intermolecular Tl···S interactions (one linking the molecules in chains and the other connecting neighbouring chains) complete the coordination sphere of the metal. Note that the structure differs from that of $[TlMe_2(S_2PEt_2)]$ [32], in which the thallium is only pentacoordinated.

$[TlMe_2Cl]$ [5] is a fundamentally ionic compound in which $TlMe_2^+$ cations and Cl^- anions form an NaCl-type structure. The coordination geometry around the thallium atom is tetragonal bipyramidal, with the methyl groups in axial positions and four Cl^- anions in equatorial positions at 3.029 Å from the Tl atom.

As part of their study of interactions between the dimethylthallium cation and amino acids, Henrick et al. characterized the complex $[TlMe_2(L\text{-PHE})]$ [58] by X-ray diffraction (Fig. 26). The unit cell contains two independent molecules, each linked in independent polymeric chains by O-bridges to like molecules. Each thallium atom is hexacoordinated to two methyl groups, to the nitrogen and one oxygen of its 'own' L-PHE ligand, to an oxygen of the neigbouring molecule in its own chain, and to an oxygen of a molecule belonging to the other independent chain. The polyhedron around the thallium is described as a distorted octahedron.

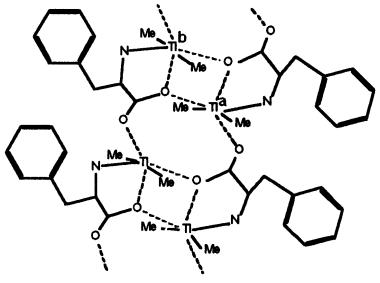

Fig. 26. Adapted from Ref. [58].

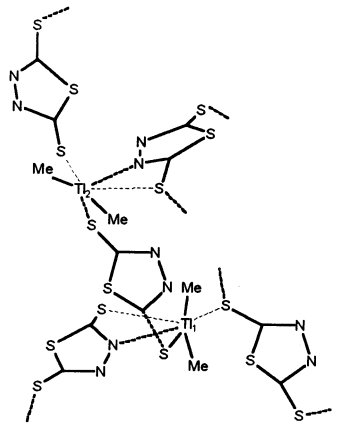

Fig. 27. Adapted from Ref. [59].

The $N(SO_2Me)_2$ ligand of $[Tl(Me_3SiCH_2)_2\{N(SO_2Me)_2\}(OH_2)]$, unlike that of $[Tl(Me_3SiCH_2)_2\{N(SO_2Me)_2\}]$ [35], coordinates through its N atom and one O atom to the same thallium. Two carbons, an oxygen belonging to a neighbouring $N(SO_2Me)_2$ ligand and the oxygen of the water molecule make the coordination number up to six, creating a very irregular environment that could be described as a pentagonal bipyramid with one vacant site.

$[(TlMe)_2$(bismuthiol I)] [59] (Fig. 27) contains two independent quasi-octahedral Tl atoms in each asymmetric unit. Both are bound axially to two methyl groups, equatorially to three sulphurs, each belonging to a different ligand, and to a nitrogen belonging to one of these ligands. All the equatorial interactions are weak and probably have a large ionic component.

$[TlMe_2(phen)](ClO_4)$ was one of the first dimethylthallium derivatives to be studied by X-ray diffraction [6]. Its coordination polyhedron is a distorted octahedron with the two methyl groups apical and an equator composed of two phenanthroline nitrogens and two oxygens belonging to two different perchlorate ligands. Each of the perchlorate ligands coordinates to two thallium atoms, giving rise to a helicoidal structure.

$[TlMe_2(NCO)]$ [48] has two different crystallographic forms, one orthorhombic and the other trigonal; both have the same $[TlC_2N_2O_2]$ kernel and distorted octahedral geometry around the thallium atom. The C–Tl–C angle is about 166° in the trigonal form and may be about the same in the orthorhombic form. The orthorhombic cyanate is described as containing infinite Tl–N–Tl–N chains bound together in layers by Tl–O interactions. The trigonal cyanate is described as made up of Tl_2N_2 dimers likewise bound together by Tl–O interactions. For both forms there is some uncertainty about the orientation of the cyanate group (NCO or OCN).

The asymmetric unit of the radical $[Tl(OTMIPh)_2(CF_3COO)]^{\bullet}$ [60] contains two independent molecules forming two independent dimers in which the trifluoroac-

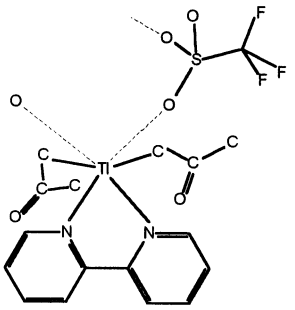

Fig. 28. Adapted from Ref. [61].

etate ligands bridge between the two Tl atoms. The environment of the thallium is described as a distorted octahedron with two phenyl C atoms axial and an equatorial plane defined by two imidazoline nitrogens and two trifluoroacetate oxygens.

Thallation of acetone in the presence of CF_3SO_3H affords $[Tl\{CH_2C(O)Me\}_2(CF_3SO_3)]$, which reacts with bpy to form $[Tl\{CH_2C(O)Me\}_2(\mu\text{-}CF_3SO_3)(bpy)]_2$ [61] (Fig. 28). An X-ray study of this latter compound has shown distorted octahedral geometry around the thallium atom, with two acetonyl carbons in apical positions and an equator defined by the two bipyridine nitrogens and two weakly bound oxygens belonging to two different triflate anions. The triflate ligands bridge between Tl atoms to form centrosymmetric dimers.

The asymmetric unit of the dimethylthallium derivative of 2-furanthiocarboxyhydrazide $[TlMe_2(fth)]$ [62] (Fig. 29) contains two different kernels: $[TlC_2N_2S_2]$ centred on Tl(1) and $[TlC_2N_2O_2S]$ centred on Tl(2). Tl(1) is bound to the methyl groups in an unexceptional dimethylthallium unit and to the S and terminal N atoms of a chelating ligand, and also has additional weak interactions with an N and an S belonging to two further ligands. If these secondary interactions are included, Tl(1) has a rather distorted octahedral environment. Tl(2) is bound

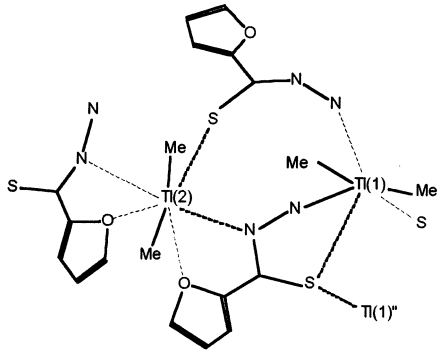

Fig. 29. Adapted from Ref. [62].

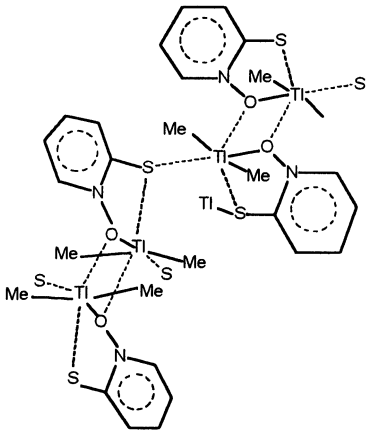

Fig. 30. Adapted from Ref. [64].

strongly to its methyl groups, to the non-terminal N of the ligand chelating Tl(1) and to an S belonging to a different asymmetric unit; additional weak interactions with the O of the ligand chelating Tl(1) and with the O and non-terminal N atoms of another ligand complete the coordination sphere, which can be described as a distorted pentagonal bipyramid.

The dimethylthallium thiosemicarbazonate [$TlMe_2$(PyTSC)] was prepared by reacting dimethylthallium hydroxide and pyridine-2-carbaldehyde thiosemicarbazone [63]. The unit cell has two independent molecules in each asymmetric unit; both contain an *N*,*N*,*S*-tridentate ligand and both have nearly linear C–Tl–C units and unremarkable Tl–C distances, but otherwise there are significant differences in bond lengths and angles. A weak interaction with the S atom of a neighbouring ligand results in the molecules centred on Tl(2) forming weakly bonded dimers.

In [$TlMe_2$(OPy2S)] [64] (Fig. 30) the ligand is bound to Tl through its oxygen and sulphur atoms. The coordination number of the thallium is increased by bridging oxygen and sulphur atoms belonging to neigbouring asymmetric units. Due to these weak interactions the metal has a very deformed octahedral environment with the two methyl groups in apical positions.

In the monomeric unit of [$TlMe_2${S(O)PPh_2}] [65] the dimethylthallium(III) unit is coordinated strongly to the S atom and weakly to the O atom of a chelating ligand. Strong Tl–O interactions and weak Tl···S contacts with neighbouring molecules give rise to a polymeric ribbon formed by supramolecular association of four-membered TlSOP chelate rings. Taking all the interactions into account, the thallium atom has severely distorted octahedral geometry.

In dimethylthallium(III) pyridoxalthiosemicarbazonate monohydrate, [$TlMe_2$-(PxTSC)(H_2O)] [66], the thiosemicarbazonate anion is coordinated to the metal via its S atom in an unusual mode, a weak interaction with the Tl atom of a neighbouring molecule creating an asymmetric sulphur bridge and weakly bonded dimers. The thallium atom also coordinates to the O atom of a water molecule and

the O atom of the phenolic hydroxyl group. If all the interactions are considered, the metal has a distorted octahedral coordination polyhedron with the methyl groups occupying the apical positions.

An X-ray study of $[TlMe_2(DABRd)]$ [67] (Fig. 31) has shown the thallium atom to be coordinated to two deprotonated ligand molecules through the carbonyl oxygen of one and the endocyclic nitrogen of the other, the exocyclic sulphur of which has a weaker interaction with the same thallium atom and forms a sulphur bridge to another metal atom. A weak Tl···S interaction with a third deprotonated ligand makes the coordination number up to six. If both strong and weak interactions are taken into account, the metal atom has very distorted octahedral coordination, while if only the short bonds are considered it has a very distorted tetrahedral environment.

The crystal of $[TlMe_2(PyRd)]$ [37] contains $[TlMe_2(PyRd)]_2$ dimers interconnected by weak Tl···S bridges. The dimethylthallium cation is coordinated to the O atom of one pyridinylmethylene rhodanine ligand and chelated by one N and one S atom of a second ligand. A distorted octahedron is defined around the metal atom by these bonds, the Tl–C bonds and the weakly coordinated S atom of a neighbouring dimer. The C–Tl–C unit is almost linear and the Tl–C distances are unremarkable.

1.3.4. Coordination number 7

Reacting dimethylthallium(III) hydroxide with 2-thioorotic acid (H_3Tot) yields the compound $[TlMe_2(H_2Tot)(H_2O)]$ [68] (Fig. 32). The thallium atom is bound to the methyl carbons and to one of the carboxylate oxygens of a ligand molecule, and

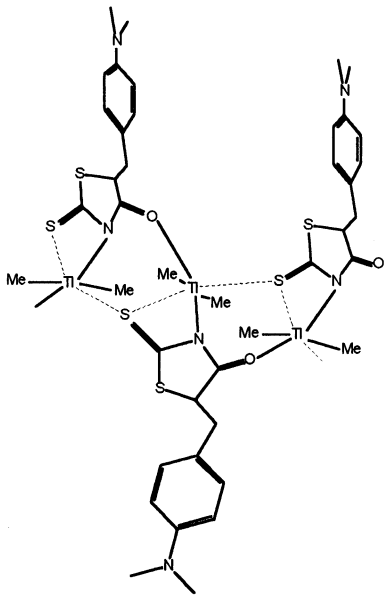

Fig. 31. Adapted from Ref. [67].

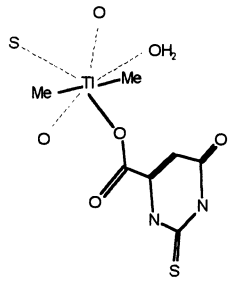

Fig. 32. Adapted from Ref. [68].

forms further weak bonds with a carbonyl oxygen, a carboxyl oxygen and a thiocarbonyl sulphur of three other ligands, and with the oxygen of a water molecule. The coordination polyhedron about the thallium atom is a deformed pentagonal bipyramid with the methyl groups in the axial positions. The C–Tl–C unit is almost linear, with unexceptional Tl–C distances.

In dimethylthallium methylxanthogenate, $[TlMe_2(S_2COCH_3)]$ [69], the thallium atom is bonded to two methyl groups and to the two ligand sulphur atoms. Three weak intermolecular interactions with two neighbouring molecules (one Tl···O and two Tl···S) make the coordination number up to seven.

Structural studies of the dimethylthallium(III) nitrate derivatives $[(TlMe_2)_3(Et_3terpy)_2(NO_3)_3]$ (Fig. 33), $[TlMe_2(terpy)(H_2O)(NO_3)]$ and $[TlMe_2\{(Py)_2CH_2\}(NO_3)]$ [70] have revealed a high coordination number for the thallium atom in all three cases. In the trinuclear complex $[(TlMe_2)_3(Et_3terpy)_2(NO_3)_3]$, two Tl atoms coordinated to Et_3terpy ligands via their three N atoms are linked by a $TlMe_2(NO_3)_3$ unit. In the former, the $TlMe_2^+$ units bend slightly away from the Tl–N interactions. In the $TlMe_2(NO_3)_3$ unit the thallium atom reaches a coordination number of eight, its coordination polyhedron being formed by six O atoms (two from each of the three bidentate nitrate ligands) and by the two methyl carbon atoms, which occupy apical positions. In $[TlMe_2(terpy)(H_2O)(NO_3)]$ the C–Tl–C unit also bends slightly away from the tridentate terpy ligand; in addition to its

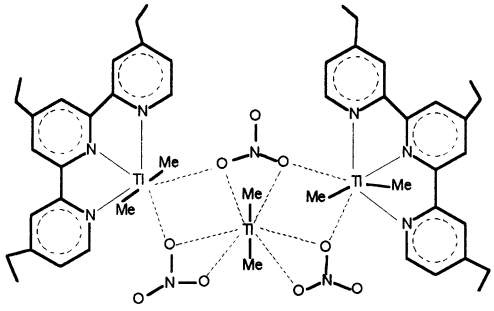

Fig. 33. Adapted from Ref. [70].

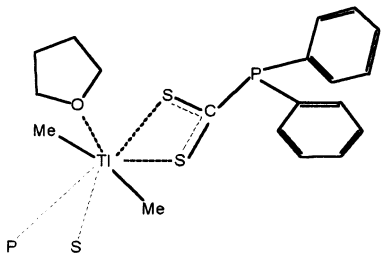

Fig. 34. Adapted from Ref. [72].

Tl–C and Tl–N bonds the Tl atom has weak interactions with two oxygen atoms from water molecules [Tl···O = 2.932(12)Å] and with a nitrate anion [Tl···O = 3.250(19) Å, probably an electrostatic interaction]. $[TlMe_2\{(Py)_2CH_2\}(NO_3)]$ is a dimer with two NO_3^- anions bridging between the two thallium atoms.

Two diorganothallium(III) complexes of 2,6-diacetylpyridinemonothiosemicarbazone, have been characterized structurally, $[TlMe_2(DAPMTSC)]$ and $[TlPh_2(DAPMTSC)]\cdot CHCl_3$ [71]. In both the deprotonated ligand is *S*,*N*(3),*N*(4),*O*–bonded to the thallium atom. A weak intermolecular Tl···O interaction gives rise to weakly bonded dimers. The coordination sphere may be described as a distorted pentagonal bipyramid with the carbon atoms in apical positions.

Several diorganophosphinodithioformato-*S*,*S*′ complexes of dimethylthallium(III) have been prepared [72], and one of them, $[TlMe_2(S_2CPPh_2)(THF)]$ (Fig. 34), has been studied by X-ray diffraction. In this compound the thallium atom is coordinated to two methyl groups, the two sulphur atoms of the phosphinodithioformato ligand and the oxygen atom of the THF molecule. A weak intermolecular Tl···S interaction is also described, and an additional even weaker intermolecular interaction with a P atom may also exist (Tl···P is shorter than, although close to, the sum of the van der Waals radii).

1.3.5. Coordination number 8

Five structures with this high coordination number have been reported, all of them with a $[TlC_2O_6]$ kernel. Four of these structures are complexes of $TlMe_2^+$ with crown ether ligands.

Matthews et al. reported the first crystal structure of a complex of this type, that of $[TlMe_2(DB18C6)][(NO_2)_3C_6H_2O]$ [73,74]. The thallium atom is located in the O_6 plane, with Tl–O distances ranging between 2.694 and 2.818 Å, and the almost linear TlC_2 unit is perpendicular to this plane. The *syn* conformation of the ligand probably makes the Tl–C distances slightly different.

Hughes and Truter [75,76] have reported the crystal structures of complexes of dimethylthallium(III) picrate with two isomers of dicyclohexano-18-crown-6 (DCH18C6), *cis-syn-cis* (A) and *cis-anti-cis* (B). Both compounds contain the cationic complex $[TlMe_2(DCH18C6)]^+$ (Fig. 35) and picrate anions $[(NO_2)_3C_6H_6O]^-$. In both isomers the cyclohexane rings are in the chair form. In

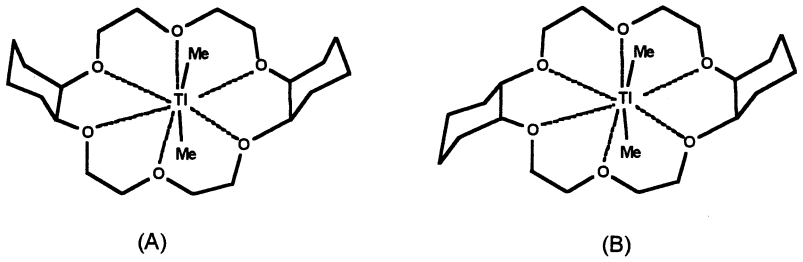

Fig. 35. Adapted from Ref. [75].

isomer B the C–Tl–C unit is linear, with equal Tl–C distances; in isomer A C–Tl–C is slightly bent and the Tl–C distances are different. In both compounds the thallium atom is coordinated to the two methyl carbons and to six nearly coplanar oxygens belonging to the crown.

The Tl atom also lies in the O_6 plane of $[TlMe_2(DDC18C6)]ClO_4$ [77]. The C–Tl–C unit is perpendicular to this plane and practically linear. The Tl–O distances are all different (ranging from 2.608 to 2.939 Å) as also are the two Tl–C distances. To obtain further information about the embedding effect of decalin moieties, Kobiro et al. also synthesized, and studied by X-ray diffraction, the complex of $TlMe_2^+$ with the crown ether tridecalino-18-crown-6 (TDC18C6), $[TlMe_2(TDC18C6)]ClO_4$ [78]. The structural study revealed D3 symmetry, with the thallium atom in the O_6 plane, all six Tl–O distances equivalent and a symmetric, linear C–Tl–C unit.

As already noted (vide supra, coordination number 7), one of the metal atoms in the complex $[(TlMe_2)_3(Et_3terpy)_2(NO_3)_3]$ [70] has coordination number eight (see Fig. 33).

1.4. Triorganothallium(III) compounds

Structural data of triorganothallium compounds are given in Table 3.

1.4.1. Coordination number 4

The compound $[Tl(FcN)_3]$ was the first 2-(dimethylaminoethyl)ferrocenyl compound featuring both the coordination modes of this ligand [79]. The thallium atom is bound to each ferrocenyl ligand via a cyclopentadienyl C atom, and also to the N atom of a dimethylaminoethyl group. The lengthening of the Tl–C bond in the *C,N*-coordinated FcN ligand, in which its length is 2.202(5) Å as against 2.176(6) and 2.181(6) Å in the other ligands, introduces severe distortion in a tetrahedral coordination polyhedron.

1.4.2. Coordination number 5

The crystal structure of $TlMe_3$ was determined by Sheldrick and Sheldrick in the early seventies [80]. The crystals could be described as formed by planar $TlMe_3$

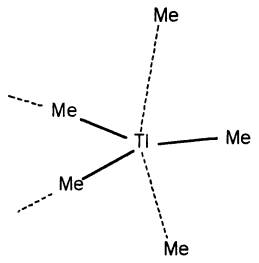

Fig. 36. Adapted from Ref. [80].

molecules connected by asymmetric linear Tl–Me..Tl bridges in a polymeric three-dimensional network. Each molecule has two bridging methyl groups (with Tl–C bond lengths of 2.30 and 2.34 Å) and one non-bridging group (Tl–C 2.22 Å). The coordination number is made up to five by two additional weak intermolecular Tl···Me interactions (Tl–C 3.16 and 3.31 Å) with Me groups occupying the apical positions of a distorted trigonal bipyramidal coordination polyhedron (Fig. 36).

The anionic phosphine ligand $[o\text{-}(Ph_2PCH_2)C_6H_4]^-$ (DPP) forms with Tl(III) the compound $[Tl(DPP)_3]$ [81], in which the metal is coordinated to one P atom (Tl–P distance 2.795(1) Å) and to three C atoms belonging to the C_6H_4 rings. The C,P-chelating ligand forms a five-membered ring with the metal, but chelation by the other two ligands appears to be prevented by mismatch between the span of the ligand and the large size of the thallium atom. The low coordination number can nevertheless be considered as made up to five by a weak interaction with another P atom 3.558(2) Å from the metal, a distance within the sum of the van der Waals radii (3.85 Å). The resulting coordination polyhedron is a distorted trigonal bipyramid with the P atoms apical (the C–Tl–C angles in the equatorial plane sum to 354.8°).

1.5. Conclusions

The structures of more than eighty organothallium(III) compounds have been analysed, most of them diorganothallium derivatives.

Among monoorgano derivatives (ten structures), Tl–C bonds range in length from 2.07 to 2.16 Å, Tl–N bonds from 2.24 to 2.79 Å, Tl–O bonds from 2.12 to 2.72 Å, Tl–S bonds from 2.55 to 2.88 Å, and Tl–Cl bonds from 2.43 to 2.94 Å. The coordination numbers of these compounds range from four to seven if both strong and weak interactions are considered, with tetrahedral geometry for CN four, trigonal bipyramidal or square pyramidal geometry for CN five, pentagonal pyramidal geometry for CN six and pentagonal bipyramidal geometry for CN seven.

Diorganothallium compounds (73 structures) are formally isoelectronic with HgR_2 derivatives, although the former may be expected to be better Lewis acids because of their extra charge. Most Tl–C distances lie between 2.10 and 2.20 Å, but some are shorter (e.g. in the azide, cyanide and isocyanate of dimethylthallium, and the complexes $[TlMe_2(L\text{-PHE})]$, $[TlMe_2(DABRd)]$ and $[(TlMe_2)_3(Et_3terpy)_2(NO_3)_3]$)

and some longer (e.g. in $[TlMe_2(fth)]$, $[TlMe_2(B_{10}H_{12})]^-$ and $[TlEt_2(C_7H_5O_2)]$). According to a CSD histogram [15], values between 2.13 and 2.15 Å are nevertheless the most usual. The two Tl–C bonds often differ significantly in length e.g. by about 0.17 Å in $[TlMe_2(^nPr_2dtc)]$ [55], and this disparity possibly contributes to there not being any clear relationship between Tl–C distances and C–Tl–C angles. The latter range from 180° to 106(1)°, and there are about twenty structures with values less than 160°. Tl–N, Tl–O, Tl–S and Tl–Cl distances lie in the ranges 2.27–3.43, 2.23–3.42, 2.63–3.70 and 2.47–3.03 Å, respectively. These ranges, and that of Tl–C distances, lie above the corresponding ranges for mono-organoderivatives because of the smaller acceptor capacity of TlR_2^+ cations. Coordination numbers range from four to eight if secondary interactions are considered; the most usual value is six, and the most usual coordination polyhedron is a deformed octahedron (even some pentacoordinate thallium complexes adopt this octahedral stereochemistry, leaving one position vacant in the coordination sphere). The other coordination polyhedra described are square pyramids and trigonal, tetragonal, pentagonal and hexagonal bipyramids. Probably as a consequence of the medium-weak acceptor character of diorganothallium cations and their undemanding stereochemistry, two or more different isomers can often be obtained from their reactions with ligands with several different coordination modes. This property, their tendency to form supramolecular materials, and the ready crystallization and stability of diorganothallium(III) complexes, suggest that these compounds deserve more attention than has hitherto been afforded to them.

As was noted above, structural data for TlR_3 compounds are scarce, but the data of Table 3 nevertheless suggest a brief comment on the Tl–C bond length. Just as the value of this parameter is greater in di- than in mono-organothallium(III) compounds, so it seems to be greater still in TlR_3 compounds, probably because of the inductive effect of the additional R group.

2. Organomercury(II) compounds

2.1. Introduction

Far more attention has been given to the structures of organomercury compounds than to those of organothallium compounds. After the pioneering work of Grdenic [10], the importance of secondary bonds for the coordination chemistry of mercury (and possibly for its toxicology [82]) was progressively established, and their involvement in its metalorganic compounds was confirmed as soon as structural data were gathered. The contribution of Kuz'mina to this field [83] is very significant, and the literature up to 1981 is covered by her review [83]. Almost at the same time, Wardell [84a] gave a detailed description of the structures of organomercury compounds published up to 1980. Although Bruce [9b] listed organomercury papers reporting structures obtained by diffraction methods up to 1994, and Davies and Wardell [84b] gave some structural information in their review of the chemistry of organomercury compounds, the most recent paper to concentrate on the

structure of these species is Holloway and Melník's [85] comprehensive survey of the literature published prior to the end of 1992. The present review extends coverage up to the end of 1997.

As in Section 1 on organothallium compounds, the complexes, listed in Tables 4 and 5, are ordered firstly by the number of tightly bound organic radicals, secondly by effective coordination number [10], and thirdly by kernel homogeneity. As in the case of thallium, there is some controversy concerning the van der Waals radius of mercury. As Canty and Deacon noted [86], the accepted value of 1.55 Å, estimated from the critical volume of the metal [12], is probably too short. They suggest 1.73 Å, but accept that a value as high as 2.00 Å may be possible. Batsanov even suggests 2.1–2.2 Å [14]. In this review, the existence of secondary bonds was established using the upper limit mentioned by Canty and Deacon, 2.0 Å. As in the previous section, secondary bonds not mentioned by the original authors were not sought systematically but were included, following confirmation using CSD data [15], if obvious in the original paper.

2.2. Monoorganomercury(II) compounds

Structural data for monoorganomercury compounds are listed in Table 4.

2.2.1. Coordination number 2

The tendency of Hg to be involved in inter- or intramolecular secondary interactions results in there being only a small number of Hg complexes with coordination number two.

Reaction of equimolar amounts of $Ph_3P{=}C(Me)H$ and $Hg[N(SiMe_3)_2]_2$ in toluene has given crystals of $[Hg\{Ph_3P{=}C(Me)\}\{N(SiMe_3)_2\}]$, which decompose immediately on exposure to air [87]. X-ray study of this compound showed that the coordination kernel of the Hg atom is almost linear, with a rather short Hg–C bond length and an Hg–N distance within the range expected for Hg–N bonds. No additional inter- or intramolecular interactions of the Hg atom have been described.

Treatment of 1,1,1-tris(mercaptomethyl)ethane with methyl mercury iodide (HgMeI) allows isolation of the trinuclear compound $[(HgMe)_3\{MeC(CH_2S)_3\}]$ [88]. This compound crystallizes with two independent molecules in the asymmetric unit, A and B, each containing three independent Hg atoms. Three of these six metallic atoms have an [HgCS] kernel and the other three have an additional Hg···S interaction giving an $[HgCS_2]$ kernel. The C–Hg–S angle ranges from 168.2(9) to 176.1(9)°, and the Hg–C bond lengths (av. 2.106(5) Å) are similar to those found in other methylmercury compounds. The Hg–S primary bond lengths are rather short, ranging from 2.351(6) to 2.371(7) Å.

Slow evaporation of a 0.1 M NaCl solution containing 5-chloro-mercurio-2′-deoxyuridine, $[Hg(C_9H_{11}N_2O_5)Cl]$ [89], an intermediate in the synthesis of C5-substituted pyrimidine nucleoside derivatives, has afforded colourless needles suitable for X-ray study. No secondary Hg interactions were found, in keeping with which the C–Hg–Cl fragment is almost linear and the Hg–C and Hg–Cl bond lengths are within the expected ranges. The compound $[Rh(C{\equiv}CCH_2OMe)(HgPh)Cl(P^iPr_3)_2]$

Table 4
Structural data of monoorganomercury(II) compounds

Compound	CN [kernel]	d(Hg–C) (Å)	d(Hg–L_{trans}) (Å)	C–Hg–L_{trans} (°)	d(Hg–L) (Å)	Ref.
[Hg{Ph_3P=CMe}{$N(SiMe_3)_2$}], monomer	2[HgCN]	2.027(2)	N 2.068(6)	175.4(3)		[87]
[$(HgMe)_3${$MeC(CH_2S)_3$}], two independent molecules: A, with one [HgCS] and two [$HgCS_2$] kernels; and B, with two [HgCS] and one [$HgCS_2$] kernel	2[HgCS]	(A)				[88]
		Hg(3) 2.09(3)	S 2.351(6)	176.1(8)		
		(B)				
		Hg(5) 2.10(3)	S 2.371(7)	170.1(8)		
		Hg(6) 2.13(3)	S 2.353(6)	176.1(9)		
[$Hg(C_9H_{11}N_2O_5)Cl$], polymer (hydrogen bonds)	2[HgCCl]	2.06(2)	Cl 2.298(4)	179.0(4)		[89]
[$Rh(C{\equiv}CCH_2OMe)(HgPh)Cl(P^iPr_3)_2$], monomer	2[HgCRh]	2.082(5)	Rh 2.5008(4)	175.5(1)		[90]
[Hg{(5-Me)Thien-2-yl}(pzTp)], monomer	3[$HgCN_2$]	1.98(2)	N 2.09(1)	174.8(5)	N 2.62(1)	[91]
[HgPh(PMBP)], monomer	3[$HgCO_2$]	2.040(11)	O 2.087(7)	168.6(3)	O 2.585(9)	[92]
[$(HgMe)_3${$MeC(CH_2S)_3$}], two independent molecules: A, with one [HgCS] and two [$HgCS_2$] kernels; and B, with two [HgCS] and one [$HgCS_2$] kernel	3[$HgCS_2$]	(A)				[88]
		Hg(1) 2.10(3)	S 2.363(6)	175.6(10)	S 3.22	
		Hg(2) 2.11(2)	S 2.358(6)	168.3(7)	S 3.21	
		(B)				
		Hg(4) 2.11(3)	S 2.357(7)	168.2(9)	S 3.21	
[HgPh(S_2COEt)], monomer	3[$HgCS_2$]	2.06(1)	S 2.342(3)	176.1(4)	S 3.209(4)	[93]
[Hg(Tpsi)Cl], dimer, two independent Hg atoms	3[$HgCCl_2$]	Hg(1) 2.105(9)	Cl 2.328(3)	171.0(3)	Cl 3.194(3)	[94]
		Hg(2) 2.092(9)	Cl 2.320(3)	171.3(3)	Cl 3.392(3)	
[$(HgPh)_2$TbSMe], two independent molecules (1 and 2), with two independent Hg atoms (Hg(1) and Hg(2) in molecule 1 and Hg(3) and Hg(4) in molecule 2, with [Hg(1)CNO], [Hg(2)CNO_2S], [Hg(3)CNO_2] and [Hg(4)CNO_2] kernels), polymer	3[HgCNO]	Hg(1) 2.029(14)	N 2.117(10)	172.9(6)	O 2.627(10)	[95]
[Hg(dimeU)(MeA)(H_2O)]NO_3	3[HgCNO]	2.04(1)	N 2.06(1)	174.6(4)	O 2.769(9)	[96]
[Hg(ferrocenylimine-Me)Cl], monomer	3[HgCNCl]	2.016(3)	Cl 2.2959(9)	176.84(8)	N 2.897(2)	[97]

Table 4 (continued)

$[Hg_2(C_6H_8O_3)Cl_2(0.5\ CH_3CN)]$, dimer with three different kernels distributed as follows: [Hg(1)CNOCl] and [Hg(2)COCl] in one monomer and [Hg(3)COCl] and [Hg(4)CO_2Cl] in the other	3[HgCOCl]	Hg(2) 2.13(1) Hg(3) 2.08(1)	Cl 2.351(4) Cl 2.319(4)	172.1(4) 176.1(5)	O 2.80(1) O 2.91(1)	[98]
$[PPh_4][HgPh(\eta^3\text{-}B_6H_6)]$, monomer	4[$HgCB_3$]	2.0682(11)			B 2.4072(14) 2.4085(14) 2.4268(11)	[99]
$[\{(Hg_2TMPh)_2(OOCCF_3)_2\}_2(Et_2F)_3]$, four independent Hg atoms. Hg–C and Hg–O bond distances and C–Hg–O angles in the almost linear C–Hg–O fragment were obtained from [15]	4[$HgCO_3$]	Hg(1) 2.012	O 2.095	176.263	O 2.64(2) 2.81(2)	[15,100]
		Hg(2) 2.089	O 2.023	176.509	O 2.82(2) 3.00(2)	
		Hg(3) 2.079	O 2.104	175.298	O 2.74(2) 2.94(2)	
		Hg(4) 2.054	O 2.086	174.600	O 2.78(2) 2.81(2)	
$[C(HgSO_4)_2(HgOH_2)_2]$, two independent Hg atoms with an [$HgCO_3$] kernel for Hg(1) and an [$HgCO_5$] kernel for Hg(2)	4[$HgCO_3$]	Hg(1) 2.065(12)	O 2.104(9)	171.3(3)	O 2.760(11) 2.991(9) 2.991(9)	[101]
$[HgMe(np_3)][CF_3SO_3]$.toluene, monomer	4[$HgCP_3$]	2.18(3)			P 2.600(9) 2.615(9) 2.808(7)	[102]
$[HgPh(S_2PEt_2)]$, polymer	4[$HgCS_3$]	2.07(2)	S 2.375(3)	177.0(3)	S 3.182(3) 3.183(3)	[103]
$[Ph_3PCHCOPh.HgCl_2].CH_3OH$, dimer	4[$HgCCl_3$]	2.208(8)			Cl 2.417(3) 2.624(2) 2.710(2)	[104]
[Hg(AcFPhEt)Cl], polymer	4[$HgCCl_3$]	2.06(1)	Cl 2.320(3)	176.2(3)	Cl 3.201 3.288	[15,105]
$[Hg\{C_4H_3NSi(CHMe_2)_3\}Cl]$, polymer	4[$HgCCl_3$]	2.007	Cl 2.324	177.9	Cl 3.206 3.268	[106]
$[Ph_3PCHCOPh.HgI_2]$, dimer	4[$HgCI_3$]	2.312(13)			I 2.705(1) 2.812(1) 3.010(1)	[104]
$[CH_3CH\{Hg(bpy)\}COOH]\ NO_3$, polymer	4[$HgCN_2O$]	2.11(1)	N 2.226(9)	153.5(4)	N 2.423(7) O 2.802(9)	[107]

Table 4 (continued)

[$(HgPh)_2$TbSMe], two independent molecules (1 and 2), each with two independent Hg atoms (Hg(1) and Hg(2) in molecule 1 and Hg(3) and Hg(4) in molecule 2, with [Hg(1)CNO], [Hg(2)CNO_2S], [Hg(3)CNO_2] and [Hg(4)CNO_2] kernels), polymer	4[$HgCNO_2$]	Hg(3) 2.043(14) Hg(4) 2.04(2)	N 2.091(11) O 2.088(10)	175.6(5) 171.4(5)	O 2.797(10) 2.86(6) N 2.707(11) O 2.617(9)	[95]
[HgPh(aza-aza)(CH_3OH)], polymer	4[$HgCN_2O$]	2.052(10)	N 2.071(8)	177.5(3)	N 2.831(8) O 3.173(8)	[108]
[HgMe(aza-aza)(CH_3OH)], polymer	4[$HgCNO_2$]	2.068(9)	N 2.058(6)	174.0(3)	O 2.831(6) 3.007(6)	[108]
[HgMe(AMMeT)], polymer	4[$HgCN_2S$]	2.071(9)	S 2.391(2)	167.5(3)	N 2.717(6) 3.216(5)	[109]
[Hg($C_5H_7O_2$)Cl], dimer	4[$HgCO_2Cl$]	2.11(1)	Cl 2.329(3)	161.1(3)	O 2.57(1) 2.69(1)	[110]
[Hg_2($C_6H_8O_3$)Cl_2(0.5 CH_3CN)], dimer with three different kernels distributed as follows: [Hg(1)CNOCl] and [Hg(2)COCl] in one monomer and [Hg(3)COCl] and [Hg(4)CO_2Cl] in the other	4[$HgCO_2Cl$]	Hg(4) 2.11(2)	Cl 2.305(4)	176.9(5)	O 2.84(1) 2.90(1)	[98]
[Hg(PSTHFC)Cl], two diastereomeric forms, A and B, both with two independent Hg atoms with different kernels: [Hg(1)CO_2Cl] and [Hg(2)CO_2Cl_2] in A, and [Hg(1)$COCl_2$] and [Hg(2)CO_2Cl_2] in B	4[$HgCO_2Cl$]	(B) Hg(1) 2.087	Cl 2.334	176.117	O 3.172 3.175	[15,111]
[Hg(dpphen)Cl], dimers. There are two distinct structural units in the crystal	4[$HgCNCl_2$]	2.11(3)	Cl 2.317(8)	173.2(8)	N 2.80(3) Cl 3.240(8)	[112]
[Hg(ferrocenylimine-Et)Cl]	4[$HgCNCl_2$]	2.037(9)	Cl 2.390(3)	179.1(3)	N 2.766 Cl 3.489	[15,113]
[Hg(ferrocenylimine-Ph)Cl]	4[$HgCNCl_2$]	2.03(1)	Cl 2.306(3)	177.3(2)	N 2.870 Cl 3.539	[15,114]

Table 4 (continued)

[Hg{$C_6H_4CH(Me)NMe_2$}Cl], polymer	4[$HgCNCl_2$]	2.04(1)	Cl 2.323(3)	174.2(3)	N 2.65(1) Cl 3.1	[115]
[Hg(*N*-AcPyr)Cl], dimer	4[$HgCOCl_2$]	2.042(16)	Cl 2.292(4)	178.6(4)	O 2.78(2) Cl 3.281	[15,116]
[Hg(PSTHFC)Cl], two diastereomeric forms, A and B, both with two independent Hg atoms with different kernels: [Hg(1)CO_2Cl] and [Hg(2)CO_2Cl_2] in A, and [Hg(1)$COCl_2$] and [Hg(2)CO_2Cl_2] in B	4[$HgCOCl_2$]	(B) Hg(1) 2.097	Cl 2.317	177.198	O 2.865 Cl 3.222	[15,111]
[Hg{$C_6H_4CH(Me)NMe_2$}Br], polymer	4[$HgCNBr_2$]	2.07(1)	Br 2.451(2)	173.8(4)	N 2.64(2) Br 3.4	[115]
[Hg{$C_6H_4CH(Me)NMe_2$}I], polymer	4[$HgCNI_2$]	2. 02(1)	I 2.622(1)	174.0(3)	N 2.63(1) I 3.8	[115]
[PtCl(HgMe)(dmphen){$MeO_2CCH{=}CHCO_2Me$}]	4[$HgCO_2Pt$]	2.06(2)	Pt 2.558(1)	173.9(8)	O 2.79(2) 2.90(2)	[117]
[$Hg_3O(dimeU)_3$]$NO_3 \cdot 2H_2O$, two different molecules I and II, each containing three independent Hg atoms (Hg(1) to Hg(3) in molecule I and Hg(4) to Hg(6) in molecule II), with a [$HgCOHg_2$] kernel for Hg(3)-Hg(5) and an [$HgCOHg_3$] for Hg(1), Hg(2) and Hg(6). Only average values are given	4[$HgCOHg_2$]	Hg(3) Hg(4) 2.05 Hg(5)	O 2.05	175.9	Hg 3.4705(9)–3.5859(5)	[118]
[$Hg_2(C_6H_8O_3)Cl_2(0.5CH_3CN)$], dimer with three different kernels distributed as follows: [Hg(1)CNOCl] and [Hg(2)COCl] in one monomer and [Hg(3)COCl] and [Hg(4)CO_2Cl] in the other	4[HgCNOCl]	Hg(1) 2.10(1)	Cl 2.333(4)	177.1(5)	N 3.00(3) O 2.89(1)	[98]
[$Hg_2(C_5H_6O_2)Cl_2$].CH_3CN, polymer, two independent Hg atoms	4[HgCNOCl]	Hg(1) 2.11(1)	Cl 2.326(3)	174.5(3)	N 3.07(2) O 2.88(1)	[119]
		Hg(2) 2.11(1)	Cl 2.306(4)	172.5(3)	N 3.12(2) O 2.844(9)	
[$(OC)_3${$(MeO)_3Si$}Fe(μ-dppm)Hg(C_6Cl_5)]	4[HgCOPFe]	2.117(7)	Fe 2.528(3)	172.1(2)	P 3.170(3) O 3.079(8)	[120]

Table 4 (continued)

$[HgPh(trenMe_6)][CF_3SO_3]$	5[$HgCN_4$]	2.09(3)	N 2.27(2)	179.5(9)	N 2.68(3) 2.70(3) 2.74(3)	[121]
$[C(HgNO_3)_4(H_2O)]$, four independent Hg atoms with two types of kernel, [$HgCO_4$] for Hg(1) and [$HgCO_5$] for Hg(2), Hg(3) and Hg(4)	5[$HgCO_4$]	Hg(1) 2.09(3)	O 2.10(3)	176.8(9)	O 2.75(2) 2.78(4) 2.84(3)	[101]
[Hg(dimeU)(OAc)]	5[$HgCO_4$]	2.07(3)	O 2.11(2)	177.6(18)	O 2.75(2) 2.88(3) 2.91(2)	[122]
$[\{Pt(CH_3NH_2)_2(MeC)_2Hg_3(OH)(NO_3)\}_2](NO_3)_4 \cdot 4H_2O$, dimer with two slightly different organometallic mercury atoms, Hg(5) and Hg(5′)	5[$HgCO_4$]	Hg(5') 2.05(2)	O 2.09(1)	175.0(6)	O 2.678 2.935 3.073	[15,123]
$[\{Hg(PhPy)\}_2(tuc)]$, dimer. Two independent Hg atoms with different kernels, [$Hg(1)CN_2OS$] and [$Hg(2)CN_3S$]	5[$HgCN_3S$]	Hg(2) 2.10(2)	S 2.350(5)	173.3(5)	N 2.69(2) 2.99(1) 3.11(2)	[124]
$[HgMe(SC_6H_4NO_2\text{-}o)]$, polymer, two independent Hg atoms	5[$HgCOS_3$]	Hg(1) 2.08(2)	S 2.379(4)	176.4(5)	O 3.48(2) S 3.322(4) 3.539(4)	[125]
		Hg(2) 2.04(2)	S 2.366(4)	177.0(5)	O 3.61(3) S 3.257(4) 3.647(5)	
[Hg(X18C5)Br], monomer	5[$HgCO_3Br$]	2.057(9)	Br 2.430(1)	175.0(2)	O 2.754(6) 2.855(6) 3.060(6)	[126]
$[Hg_3O(dimeU)_3]NO_3 \cdot 2H_2O$, two different molecules, I and II, each containing three independent Hg atoms (Hg(1) to Hg(3) in molecule I and Hg(4) to Hg(6) in molecule II), with a [$HgCOHg_2$] kernel for Hg(3)-Hg(5) and an [$HgCOHg_3$] kernel for Hg(1), Hg(2) and Hg(6), only average values are given	5[$HgCOHg_3$]	Hg(1) Hg(2) 2.05 Hg(6)	O 2.05	175.9	Hg 3.4552–3.6728	[118]

Table 4 (continued)

$[Hg(CH_2COCH_3)(ClO_4)(Pyqx)]$, dimer	5[$HgCN_2O_2$]	2.104(11)	N 2.175(8)	175.3(3)	N 2.560(5) O 2.875(12) 3.015(7)	[127]
$[HgMe\{S(O)PPh_2\}]$, polymer	5[$HgCO_2S_2$]	2.073(6)	S 2.391(2)	177.3(2)	O 2.831(4) 2.897(4) S 3.516(2)	[128]
[Hg(PSTHFC)Cl], two diastereomeric forms, A and B, both with two independent Hg atoms with different kernels: [Hg(1)CO_2Cl] and [Hg(2)CO_2Cl_2] in A, and [Hg(1)$COCl_2$] and [Hg(2)CO_2Cl_2] in B	5[$HgCO_2Cl_2$]	(A) Hg(2) 2.095	Cl 2.335	170.281	O 3.094 3.220 Cl 3.273	[15,111]
		(B) Hg(2) 2.072	Cl 2.343	176.884	O 3.128 3.200 Cl 3.305	
$(NBu_4)_2[(C_6F_5)_3Pt(\mu\text{-}OH)(\mu\text{-}HgC_6F_5)Pt(C_6F_5)_3]$	5[$HgCF_2Pt_2$]	2.09(2)			F 2.985(8) Pt 2.718(1)	[129]
$[\{Hg(PhPy)\}_2(tuc)]$, dimer, two independent Hg atoms with different kernels: [Hg(1)CN_2OS] and [Hg(2)CN_3S]	5[$HgCN_2OS$]	Hg(1) 2.07(1)	N 2.12(1)	174.8(6)	N 2.61(2) O 3.09(1) S 3.158(5)	[124]
$[(HgPh)_2TbSMe]$, two independent molecules (1 and 2), each with two independent Hg atoms (Hg(1) and Hg(2) in molecule 1 and Hg(3) and Hg(4) in molecule 2, with [Hg(1)CNO], [Hg(2)CNO_2S], [Hg(3)CNO_2] and [Hg(4)CNO_2] kernels), polymer	5[$HgCNO_2S$]	Hg(2) 2.054(3)	N 2.105(10)	176.6(5)	O 2.829(10) 2.833(10) S 3.270(4)	[95]
$[C(HgNO_3)_4(H_2O)]$, four independent Hg atoms with two types of kernels, [$HgCO_4$] for Hg(1) and [$HgCO_5$] for Hg(2), Hg(3) and Hg(4)	6[$HgCO_5$]	Hg(2) 2.06(2)	O 2.08(2)	174.0(9)	O 2.77(2) 2.88(3) 2.94(3) 3.05(3)	[101]
		Hg(3) 1.99(2)	O 2.12(2)	176.2(10)	O 2.88(3) 2.91(2) 2.96(3) 3.05(2)	

Table 4 (continued)

		Hg(4) 2.09(2)	O 2.14(2)	171.7(9)	O 2.87(3) 2.89(3) 2.93(3) 3.02(2)	
$[C(HgSO_4)_2(HgOH)_2]$, two independent Hg atoms with an $[HgCO_3]$ kernel for Hg(1) and an $[HgCO_5]$ kernel for Hg(2)	6$[HgCO_5]$	Hg(2) 2.064(11)	O 2.131(11)	173.6(3)	O 2.747(8) 2.893(12) 2.991(10) 3.001(12)	[101]
[Hg(PhPy)(OAc)], polymer	6$[HgC_2NO_3]$	1.99(1)	O 2.005(7)	176.1(4)	C 3.36(1) N 2.727(9) O 2.870(7) 2.925(8)	[130]
$[\{Pt(CH_3NH_2)_2(MeC)_2Hg_3(OH)(NO_3)\}_2](NO_3)_4 \cdot 4H_2O$, dimer with two slightly different organometallic mercury atoms, Hg(5) and Hg(5′)	7$[HgCO_6]$	Hg(5) 2.04(2)	O 2.06(1)	178.6	O 2.746 2.927 3.040 3.083 3.432	[15,123]

Table 5
Structural parameters of diorganomercury(II) compounds

Compound	CN[kernel]	(Hg-C) (Å)	d(Hg–L)(Å)	C–Hg–C (°)	Ref.
$[Hg(PyEt)_2]$, polymer	3[HgC_2N]	2.02(3)	N 2.64(3)	172(1)	[131]
$[HgPh(CBrCl_2)]$, dimer with two independent molecules	3[HgC_2X] (X = Cl, Br)	Hg(1) 2.048(15) 2.136(15)	X 3.468(3)	178.3(6)	[132]
		Hg(2) 2.046(14) 2.12(2)	3.516(4)	179.5(6)	
$[HgBr(mop)_2Li(H_2O)(THF)]$, dimer	3[HgC_2Br]	2.105(6) 2.110(6)	Br 3.127(1)	176.9(3)	[133]
$[Hg_2(mtp)_4Pt](PF_6)_2 \cdot 0.5(CH_2)_2Cl_2$, two independent Hg atoms, dimer	3[HgC_2Pt]	2.08(1)–2.11(1)	Pt 3.138(1)	173.0(4)	[134]
$[Hg_2(mtp)_4Pt](BPh_4)_2 \cdot CH_2Cl_2$	3[HgC_2Pt]	2.093 2.112	Pt 3.021	176.66	[15,134]
$[Hg(PhPy)_2]$	4[HgC_2N_2]	2.098(8)	N 2.798(7)	180.0	[135]
$[Hg(N\text{-}AcPyr)_2]$	4[HgC_2O_2]	2.068(9)	O 2.87(1)	180.0	[116]
$[Hg(N^nBuPh)_2]$	4[HgC_2O_2]	2.068(3)	O 3.015(2)	180.0	[136]
$[Hg(dimeU)_2]$	4[HgC_2O_2]	2.05(1)	O 2.901(8) 3.180(8)	179.2(8)	[137]
$[(Me_2N)_3S][(CF_3)_2HgF]$, dimer	4[HgC_2F_2]	2.086(14)	F 2.395(7) 2.418(7)	162.1(5)	[138]

Table 5 (continued)

$[PPh_4]_2[\{HgC(CF_3)_2\}_5Cl_2]$, pentamer with five independent Hg atoms	$4[HgC_2Cl_2]$	2.051–2.133	Cl 3.089–3.388	172.1–176.1	[139]
$[^nBu_4N][\{HgC_6F_4\}_3(SCN)]$, polymeric chain. Three independent mercury atoms.	$4[HgC_2S_2]$	2.005–2.083	S 3.06(1)–3.87(1)	171.3–176.7	[15,141]
$[PPh_4]_2[S_2WS_2Hg(CH{=}CH_2)_2] \cdot 0.5Me_2CO$	$4[HgC_2S_2]$	2.04(2)	S 2.743(6) 2.724(6)	143(1)	[142]
$[PPh_4]_2[S_2WS_2Hg(C{\equiv}CH)_2] \cdot 0.5MeCHO$	$4[HgC_2S_2]$	2.00(3) 2.05(3)	S 2.728(8) 2.738(9)	147(2)	[142]
$[Hg(pFPh)_2(PySeSePy)]$	$4[HgC_2Se_2]$	2.066(4)	Se 3.4780(6)	180.0	[143]
$[PPh_4]_2[\{HgC(CF_3)\}_5Br_2]$, pentamer with five independent Hg atoms	$4[HgC_2Br_2]$	2.04–2.20	Br 3.229–3.453	170.2–174.5	[140]
$[Hg(X18C5)_2]$	$6[HgC_2O_4]$	2.070(4)	O 2.984(3) 3.064(3)	180	[126]
$[Hg(DTDA)_2][AsF_6]$	$6[HgC_2F_4]$	2.074(12)	F 2.814(9) 2.916(11)	180	[144]
$[Hg\{o\text{-}C_6H_4[InCl_2(THF)_2]\}_2]$	$6[HgC_2O_2Cl_2]$	2.086(6) 2.090(6)	O 3.302 3.405 Cl 3.729 3.914	178.7(3)	[145]
$[Hg(CHCl_2)_2]$	$8[HgC_2Cl_6]$	2.068(13) 2.098(13)	Cl 3.307 3.342 3.431 3.505 3.557 3.624	179.4(5)	[15,146]

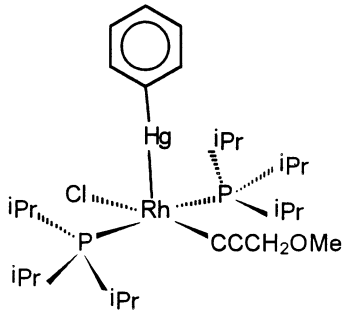

Fig. 37. Adapted from Ref. [90].

(Fig. 37), obtained by reacting *trans*-[RhCl{=C=C($SnPh_3$)CH_2OMe}(P^iPr_3)$_2$] and HgPhCl in toluene [90], was the first monomeric dimetallic Rh–Hg complex studied by X-ray diffraction. The HgPh fragment occupies the apical position of a square pyramid defined around the Rh atom. The short Hg–Rh bond length is the most striking feature of this compound. The authors argue that this distance, which is shorter than the sum of the covalent radii, is consistent with the existence of a dπ–pπ bond.

2.2.2. Coordination number 3

Several thienylmercury(II) polypyrazolylborates have been synthesised and characterized [91], and the structure of one, [Hg{(5-Me)Thien-2-yl}(pzTp)] (Fig. 38), has been determined by X-ray diffraction. In this compound the Hg atom has an approximately planar T-shaped coordination kernel with two almost collinear primary bonds, Hg–C and Hg–N, and a weak intramolecular Hg···N interaction. No intermolecular interactions are described.

Mahon et al. [92] prepared and studied the acylpyrazolone complex phenylmercury [HgPh(PMBP)]. The crystals of this compound are made up of discrete molecules in which the mercury atom is strongly bound to one C and one O atom.

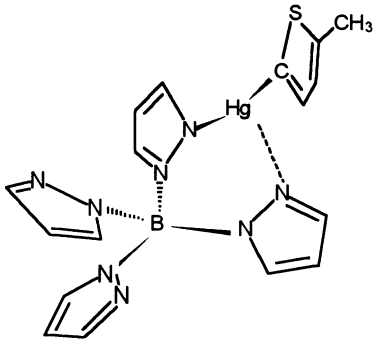

Fig. 38. Adapted from Ref. [91].

A relatively strong intramolecular secondary Hg···O interaction bends the C–Hg–O fragment about 11° from linearity.

In the phenylmercury xanthate [$HgPh(S_2COEt)$] [93], another organomercury derivative with an [$HgCS_2$] kernel, the Hg atom exhibits the usual linear primary coordination together with a weak secondary intramolecular Hg···S interaction.

Only one compound with an [$HgCCl_2$] kernel has been described during the period covered by this review, [Hg(Tpsi)Cl] (Tpsi = $(PhMe_2Si)_3C$) [94]. This complex is a dimer in the solid state, two chlorine atoms bridging between the two independent Hg atoms. Although the two primary bonds, Hg–C and Hg–Cl, are very similar in the two monomers, as is the C–Hg–Cl angle, the secondary bonds differ in length by at least 0.2 Å.

An interesting case of linkage isomerism is found in the 2-S-methylthiobarbiturate of phenylmercury, [$(HgPh)_2$TbSMe] [95]. The asymmetric unit consists of two independent molecules. In molecule 1, the two $HgPh^+$ moieties are coordinated to the N(1) and N(3) atoms of the pyrimidine ring; in molecule 2 the organometallic cations are bound to N(1) and one of the exocyclic oxygens. The Hg–O bond, which is rather uncommon in monoorganomercury(II) compounds other than carboxylates, is very short (2.088(10) Å), indicating a strong bond. The primary bonds (Hg–C and Hg–N or Hg–O) are roughly collinear. The four mercury atoms differ as regards their short intra- and intermolecular secondary interactions. In molecule 1, Hg(1) has only one secondary bond, an intermolecular interaction with an O atom (Hg···O = 2.627(10) Å), but Hg(2) has three: two intramolecular interactions, one with an oxygen and the other with the thioether S atom (Hg···O = 2.833(10) Å, Hg···S = 3.270(4) Å), and an intermolecular interaction with an oxygen belonging to a type 2 molecule. In molecule 2, Hg(3) has the same secondary Hg···O interactions as Hg(2), while Hg(4) has an intramolecular secondary Hg···N bond of length 2.707(11) Å and an intermolecular Hg···O interaction of length 2.617(9) Å with a neighbouring type 2 molecule.

A rare tautomer of 9-methyladenine (MeA) containing a protonated N(1) atom and an exocyclic imino group instead of the more usual amino group has been generated by mercuriation with [Hg(dimeU)(OAc] [96]. In [Hg(dimeU)-(MeA)(H_2O)]NO_3 the Hg is bound to N(6) of the 9-methyladenine and C(5) of the uracil ring. The slight deviation from linearity of the N–Hg–C angle (174.6(4)°) is attributed to weak interaction with the water molecule (Hg···O_w = 2.769(9) Å). The Hg···$N(7)_{MeA}$ distance, 2.87(1) Å, though shorter than the sum of the van der Waals radii, is not considered indicative of bonding because the N–Hg–C fragment bends away from O_w and towards N(7).

In crystals of the 2-chloromercurioferrocenylimine derivative, 2-chloromercurio-1-[(4-methoxyphenylimino)methyl]ferrocene, [Hg(ferrocenylimine-Me)Cl] (Fig. 39) [97], there are two primary bonds, Hg–C and Hg–Cl, and an intramolecular secondary interaction, Hg...N. The bond lengths and angles around the mercury atom are in the expected ranges.

Reaction of a saturated aqueous solution of mercury chloride with ethyl acetoacetate gives, upon recrystallization of the product from acetonitrile, the dimercuriated derivative [$Hg_2(C_6H_8O_3)Cl_2(0.5CH_3CN)$] (Fig. 40) [98]. The asymmetric unit

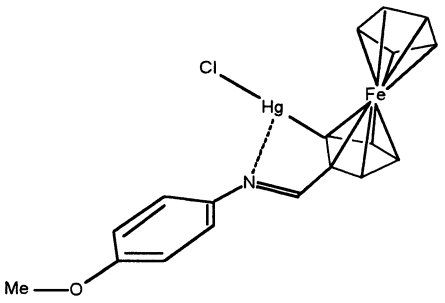

Fig. 39. Adapted from Ref. [97].

contains two different molecules, so there are four independent Hg atoms with four different environments, two of them (Hg(2) and Hg(3)) with an [HgCOCl] kernel, one (Hg(1)) with an [HgCNOCl] kernel and one (Hg(4)) with an [$HgCO_2Cl$] kernel. All four Hg atoms are involved in almost collinear Hg–C and Hg–Cl bonds (The C–Hg–Cl angles lie in the range 172.1(4)–177.1(5)°) with bond lengths ranging from 2.08(1) to 2.13(1) Å for Hg–C and from 2.30(1) to 2.35(1) Å for Hg–Cl. All the metal atoms are also involved in either intra- or intermolecular secondary Hg···O interactions, and Hg(1) additionally in a secondary Hg···N interaction with the acetonitrile molecule.

2.2.3. Coordination number 4

Reaction of [PPh_4][B_6H_7] with HgPh(OAc) in dichloromethane affords the phenylmercury derivative [PPh_4][$HgPh(\eta^3\text{-}B_6H_6)$] (Fig. 41) [99]. The geometry around the mercury atom can be described as a trigonal pyramid with the C atom in the apical position.

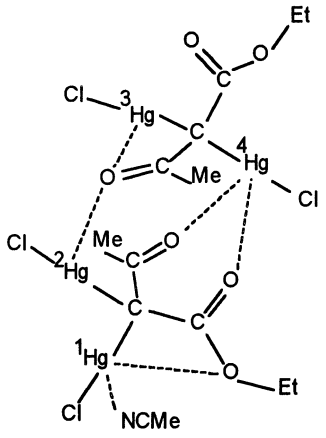

Fig. 40. Adapted from Ref. [98].

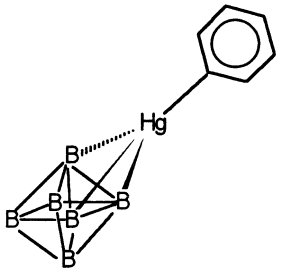

Fig. 41. Adapted from Ref. [99].

Tetramethylphenylenedimercury bistrifluoroacetate crystallizes from diethylformamide (Et_2F) as the complex $[\{(Hg_2TMPh)_2(OOCCF_3)_2\}_2(Et_2F)_3]$ [100]. This compound contains four independent mercury atoms per asymmetric unit, each of which forms primary Hg–C and Hg–O bonds, of lengths 2.012–2.089 Å and 2.023–2.104 Å respectively, that are almost collinear (the C–Hg–O angles range from 174.6 to 176.5°) [15]. Each mercury atom also has two secondary Hg···O bonds of lengths 2.64(2)–3.00(2) Å with two of the three diethylformamide molecules.

Concentrated sulphuric acid reacts with Hofmann's base, $[CHg_4O(OH)_2(H_2O)]_n$, to afford $[C(Hg(1)SO_4)_2(Hg(2)OH_2)_2]$ (Fig. 42) [101]. This compound contains slightly distorted tetrahedral CHg_4 units, and each Hg has a second primary bond with an oxygen atom. The oxygens bound to two of the four Hg atoms (Hg(1)) belong to monodentate sulphate anions (Hg–O = 2.104(9) Å), while those bound to the other two metal atoms (Hg(2)) belong to water molecules (Hg–O = 2.131(11) Å) (Fig. 42). As usual, the primary bonds are almost linear (C–Hg(1)–O = 171.3(3)°, C–Hg(2)–O = 173.6(3)°), the small deviation being attributed to the presence of secondary Hg···O interactions with neighbouring sulphate ligands (two in the case of Hg(1) and four in that of Hg(2)).

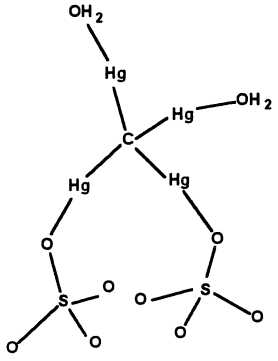

Fig. 42. Adapted from Ref. [101].

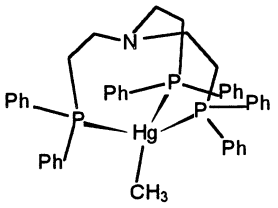

Fig. 43. Adapted from Ref. [102].

Although in monoorganomercury derivatives the mercury atom usually adopts a almost linear dicoordinate geometry (together with some secondary interactions), a few complexes with different geometry have also been described. One is the methylmercury complex of the tripodal ligand tris(2-diphenylphosphinoethyl)amine (np_3), $[HgMe(np_3)][CF_3SO_3]$.toluene [102]. The structure of the cation $[HgMe(np_3)]^+$ is shown in Fig. 43. Probably due to the rigidity of the ligand, the distance from the metal atom to the np_3 N atom is 3.50(2) Å, practically the sum of the van der Waals radii (3.55 Å). The mercury atom is tetracoordinated to the three np_3 phosphorus atoms and the methyl carbon. The coordination polyhedron is a distorted tetrahedron with angles ranging from 97.1(3) to 121.6(9)°.

In $[HgPh(S_2PEt_2)]$ [103] the mercury atom is strongly coordinated to a phenyl carbon atom and to one of the dithiophosphinate S atoms, and more weakly to the S of the same ligand molecule and to the corresponding S of a neighbouring ligand (Fig. 44). These secondary Hg···S interactions link the molecules in linear chains.

Reaction of benzoylmethylenetriphenylphosphorane with $HgCl_2$ and HgI_2 in methanol affords $[Ph_3PCHCOPh.HgCl_2] \cdot CH_3OH$ and $[Ph_3PCHCOPh \cdot HgI_2]$ [104]. Both compounds crystallize as centrosymmetric dimers. The mercury atoms have tetrahedral coordination involving an Hg–C bond, one short Hg–X bond and an asymmetric pair of bridging Hg–X bonds. No Hg···Hg interactions are described.

Metallation of (*p*-fluorophenyl)phenylethyne with $Hg(OAc)_2$ and further reaction with KCl has afforded [Hg(AcFPhEt)Cl], a crystalline solid containing the regioisomers (E)-1-acetoxy-2-chloromercurio-1-(4-fluorophenyl)-2-phenylethene and (E)-1-acetoxy-2-chloromercurio-2-(4-fluorophenyl)-1-phenylethene, in both of which the

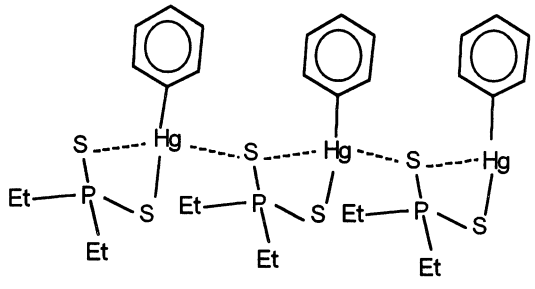

Fig. 44. Adapted from Ref. [103].

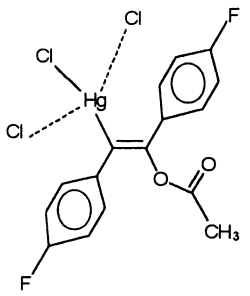

Fig. 45. Adapted from Ref. [105].

two phenyl groups are *trans* to each other (Fig. 45 is a combined representation of both isomers) [105]. The mercury atom has two strong bonds, Hg–C and Hg–Cl, which create an almost linear C–Hg–Cl fragment, and two weak Hg···Cl interactions (data from Ref. [15]).

The 3-mercuriated pyrrole derivative [Hg{$C_4H_3NSi(CHMe_2)_3$}Cl] has been obtained by reacting 3-bromo-*N*-(triisopropylsilyl)pyrrole, *n*-butyllithium and mercuric chloride in tetrahydrofuran [106]. Its Hg atoms are linearly coordinated to the ring C(3) and the Cl ligand (C(3)–Hg–Cl = 177.9°). Two intermolecular interactions with Cl atoms 3.206 and 3.268 Å away (data from [15]) give an effective coordination number of four.

Another organomercury derivative isolated by direct mercuriation is the bipyridyl (bpy) complex of the nitrate of monomercuriated propionic acid, [CH_3CH-{Hg(bpy)}COOH]NO_3 [107]. This compound contains the cation [CH_3CH{Hg(bpy)}-COOH]$^+$, in which the Hg atom forms a primary Hg–C bond with the α-carbon of propionic acid and a primary Hg–N bond with one the bpy nitrogens. A strong secondary Hg···N interaction with the second bpy N atom causes the primary bonds to deviate markedly from collinearity. A weaker secondary interaction with a propionic acid oxygen is also described.

Structural studies of the methylmercury derivative of azaindolylazaindole [Hg-Me(aza-aza)].CH_3OH and its phenylmercury analogue [HgPh(aza-aza)(CH_3OH)] (Fig. 46) reveal almost linear coordination by mercury atoms bound strongly to one C atom and one N atom [108]. In both compounds the metal atoms are also involved in two secondary interactions (Hg···N and Hg···O in the phenyl derivative and two Hg···O bonds in the methyl derivative).

The methylmercury complex of 4-amino-3-methyl-5-thione-1,2,4-triazole, [Hg-Me(AMMeT)], consists of molecules in which the triazolate anion is bound to mercury strongly via the S atom and weakly via the amine N [109]. There is also a weak intermolecular interaction between the endocyclic N and the Hg atom of a neighbouring unit. The S–Hg–C angle deviates by about 15° from linearity and the geometry around Hg is best described as T-shaped.

Chloro(diacetylmethyl)mercury(II) has been obtained by mercuriation of 2,4-pentanedione with $HgCl_2$ [110]. The mercury atom is coordinated to a Cl and to a γ-C

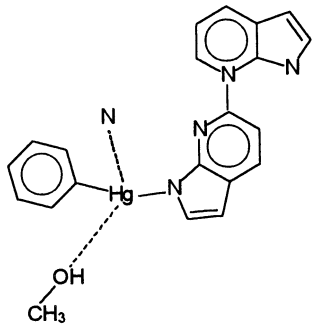

Fig. 46. Adapted from Ref. [108].

atom. Centrosymmetric dimers are created by further relatively strong intermolecular Hg···O interactions (Fig. 47). The strength of these secondary bonds makes the Cl–Hg–C angle deviate by about 19° from linearity.

An X-ray study of [Hg(PSTHFC)Cl], a poly(spirotetrahydrofuranyl)cyclohexyl compound containing an Hg–C bond, has shown that it crystallizes in two diastereomeric forms I and II (Fig. 48; only primary interactions were drawn), both of them containing two independent Hg atoms [111] (crystallographic data from CSD [15]). In both diastereomers the mercury forms strong, almost collinear Hg–C and Hg–Cl bonds. Weak secondary Hg···O and/or Hg···Cl interactions make the coordination number up to four or five.

Cyclometallation of 2,9-diphenyl-1,10-phenanthroline (dpphen) with mercury acetate and further reaction with lithium chloride give the dimeric complex $[Hg(dpphen)Cl]_2$ (Fig. 49) [112]. This compound crystallizes forming two structural units which differ in their conformation around the interannular bond between the phenyl ring and the phenanthroline system. The geometry around the mercury atom is described as an elongated tetrahedron in which two atoms, C and one of the chlorines, are closer than the other two, N and the other Cl, which may be considered as forming weak secondary interactions.

The crystal structures of the 2-chloromercurioferrocenylimine derivatives, 2-chloromercurio-1-[1-[(4-chlorophenyl)imino]ethyl]ferrocene [Hg(ferrocenylimine-

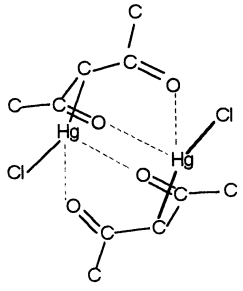

Fig. 47. Adapted from Ref. [110].

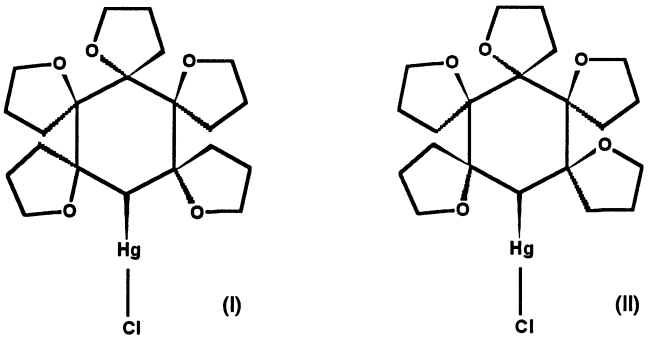

Fig. 48. Adapted from Ref. [111].

Et)Cl] [113] and 2-chloromercurio-1-[(phenylimino)phenylmethyl]ferrocene [Hg(ferrocenylimine-Ph)Cl] [114], are very similar to the chloromercurioferrocenylimine described previously [Hg(ferrocenylimine-Me)Cl] (Fig. 39) [97], with Hg–C and Hg–Cl primary bonds, and an intramolecular secondary interaction, Hg···N; but in the ethyl and phenyl derivatives there may also be a weak secondary Hg···Cl interaction that was not mentioned by the authors [15]. Of the three compounds, [Hg(ferrocenylimine-Et)Cl] has the shortest Hg···N and the longest Hg–Cl bonds.

A structural study of the halo{2-[1-(S)-(dimethylamino)ethyl]phenyl-C^1,N}mercury(II) compounds [Hg{$C_6H_4CH(Me)NMe_2$}X] (X = Cl, Br, I) [115] has shown that the mercury atom is bound to a phenyl C atom and a halogen (with C–Hg–X angles ranging from 174.0(3)° for X = I to 173.8(4)° for X = Br) and also to the amino N. Although the authors did not consider the intermolecular Hg···X distances as indicative of secondary interactions (they used a value of 1.50 Å for the van der Waals radius of the Hg atom), these distances do indicate interaction if a value in the range 1.73–2.00 Å given by Canty and Deacon [86] is used, which makes the coordination number of these compounds four.

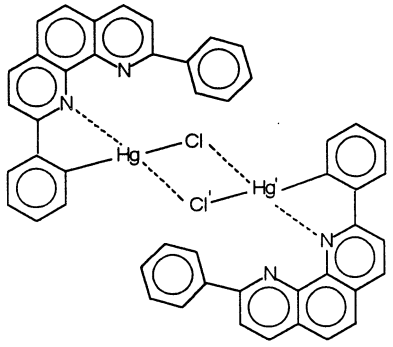

Fig. 49. Adapted from Ref. [112].

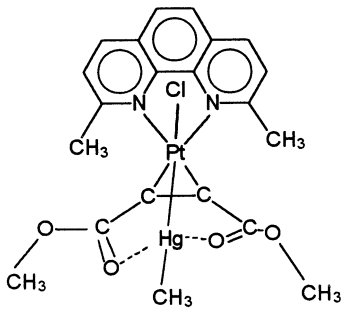

Fig. 50. Adapted from Ref. [117].

N-acetylpyrrole is selectively mercuriated at position 2 by treatment with mercury(II) chloride, giving [Hg(*N*-AcPyr)Cl] [116]. The Hg atom is coordinated linearly to C and Cl atoms (C–Hg–Cl 178.6(4)°), and also has a weak intramolecular Hg···O interaction [116], and a weak intermolecular Hg···Cl interaction [15].

Though few, some organomercury compounds have been studied in which the position *trans* to the carbon atom is occupied by another metal atom (see, for example, the Rh compound (Fig. 37) [90]). This is the case of the platinum derivative [PtCl(HgMe)(dmphen){$MeO_2CCH{=}CHCO_2Me$}] (Fig. 50), in which Hg is strongly bound to a C and a Pt atom in an almost linear C–Hg–Pt fragment as well as forming two weak bonds with the oxygen atoms of carboxylate groups [117].

The compound $[Hg_3O(dimeU)_3]NO_3 \cdot 2H_2O$ is obtained by hydrolysis of the uracil nucleobase complex (1,3-dimethyluracil-5-yl)mercury(II) nitrate [118]. An X-ray crystallographic study revealed that the colourless crystals contain two different forms of the $[Hg_3O(dimeU)_3]^+$ cation, **I** and **II** (Fig. 51), and that each individual of either kind is associated with a centrosymmetrically related individual of the same kind. Cation **I** has three mercury atoms bound to one O atom, defining a very flat pyramid with the oxygen in the apical position. Each Hg is also bound to the nucleobase at the C(5) position, and the Hg···Hg distances in the base of pyramid, 3.4705(5) –3.5859(5) Å, are shorter than the sum of the van der Waals radii (ca. 4 Å). Two of the Hg atoms are also involved in intermolecular metal–metal interactions with the two centrosymmetrically related counterparts (Hg···Hg = 3.5620(5) Å). In cation **II** the Hg_3O fragment is virtually planar, the Hg···Hg distances in the Hg_3 triangle range from 3.4552(6) to 3.5974(5) Å, and only one Hg atom has a weak intermolecular interaction with a metal atom belonging to the centrosymmetrically related partner. In both **I** and **II**, the primary Hg–O and Hg–C bonds have normal lengths, 2.05 Å for Hg–C and an average of 2.05 Å for Hg–O.

An X-ray study of the dimercuriated derivative of acetylacetone $[Hg_2(C_6H_5O_2)Cl_2] \cdot CH_3CN$ has shown that both Hg atoms are bound to C(3) of acetylacetone and that each is also strongly bound to a Cl atom [119]. Deviations from linearity in the C–Hg–Cl fragments are attributed to secondary Hg···O and Hg···N interactions.

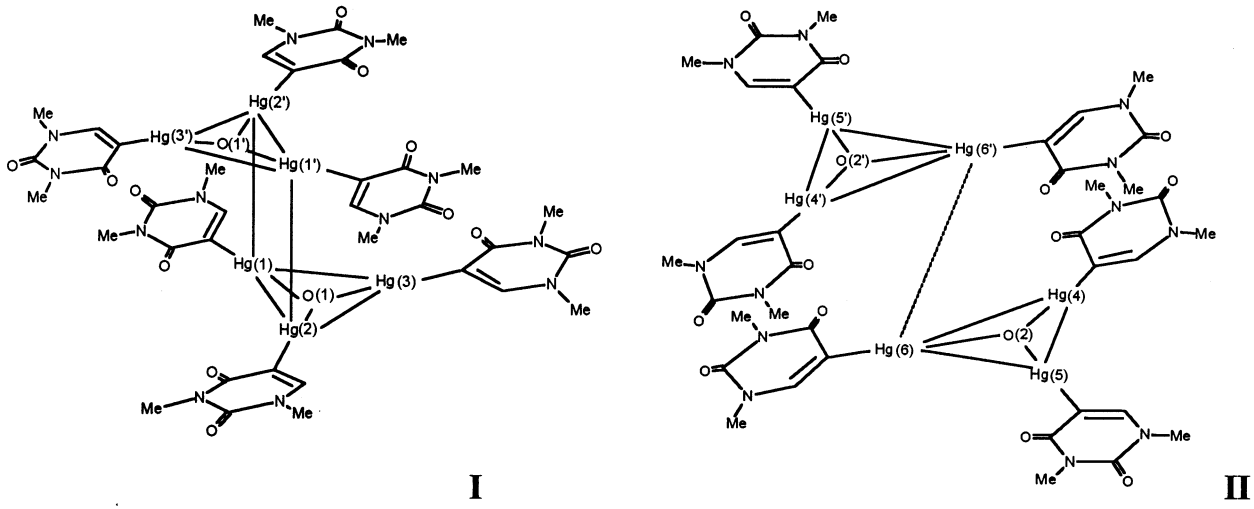

Fig. 51. Adapted from Ref. [118].

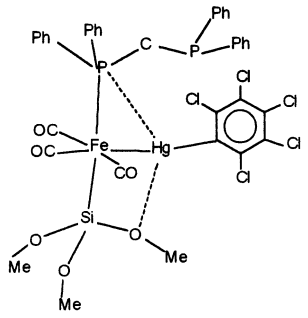

Fig. 52. Adapted from Ref. [120].

Another heterometallic organomercury derivative whose structure has been studied is $[(OC)_3\{MeO)_3Si\}Fe(\mu\text{-dppm})Hg(C_6Cl_5)]$ (Fig. 52), which contains strong Hg–Fe bonds [120]. The mercury atom is also bound to a C_6Cl_5 carbon atom and the Fe–Hg–C unit is slightly bent. P and O atoms are located at distances less than the sums of the van der Waals radii from Hg.

2.2.4. Coordination number 5

The complex $[HgPh(trenMe_6)][CF_3SO_3]$ is prepared by reacting $[(HgPh)(CF_3SO_3)]$ with tris(2-dimethylaminoethyl)amine and consists of $[HgPh(trenMe_6)]^+$ cations (Fig. 53) and $[CF_3SO_3]^-$ anions [121]. The geometry around the mercury atom is described as approximately a trigonal bipyramid, with a phenyl C and the central N in axial positions and the three dimethylamino nitrogens in the equatorial plane. The axial C–Hg–N fragment is practically linear (179.5(9)°) and the equatorial angles range from 105.1(9)° to 122.0(9)°. This stereochemistry contrasts with that of $[HgMe(np_3)]^+$ (Fig. 43 [102]), in which the Hg–N bond *trans* to the Hg–C bond disappears while the bonds with the three donor atoms belonging to the 'arms' of the tripoidal ligand (P atoms in np_3) are strengthened, possibly due to the 'soft' character of the HgR^+ cations.

Reaction of Hofmann's base with conc. nitric acid affords the compound $[C(HgNO_3)_4(H_2O)]$, which contains the tetrahedral unit CHg_4 [101]. The Hg–C distances range from 1.99(2) to 2.09(2) Å (mean value 2.06(2) Å). The other

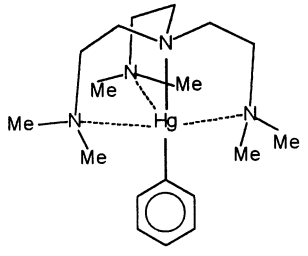

Fig. 53. Adapted from Ref. [121].

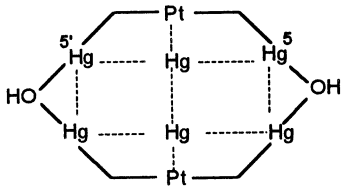

Fig. 54. Adapted from Ref. [123].

primary bond of each Hg is with a nitrate O atom at a distance in the range 2.09(2)–2.14(2) Å (mean value 2.11(1) Å). The C–Hg–O angles deviate slightly from linearity (mean value 174.7°). All the Hg atoms also have weak interactions with other oxygens: Hg(1) has three such secondary bonds (effective kernel [$HgCO_4$]), and Hg(2), Hg(3) and Hg(4) have four each (effective kernel [$HgCO_5$]).

Metallation of 1,3-dimethyluracil at C(5) using mercury acetate gives [Hg(dimeU)(OAc)], a 'bioorganometallic' species [122]. The mercury atom binds strongly to C(5) and to an acetate oxygen atom, and the Hg–C and Hg–O bonds are almost collinear. A weak intramolecular interaction with the other acetate oxygen and two intermolecular interactions with oxygens belonging to the acetate groups of neighbouring molecules complete the coordination sphere of the metal.

In the cyclic centrosymmetric cation $[Pt(CH_3NH_2)_2(MeC)_2Hg_3(OH)(NO_3)]_2^{4+}$ [123] the two Pt atoms and four of the Hg atoms occupy the sides of a 'compressed hexagon', while the two 'inorganic' Hg atoms lie on the line between the two Pt atoms (Fig. 54). The vertices of the hexagon located between Hg atoms are occupied by bridging OH groups, and those between Hg and Pt atoms by 1-methylcytosine bases bound to Hg through C(5) and to Pt through N(3). The Hg–C and Hg–O bond lengths of the 'organometallic' mercury atoms are normal (Hg(5)–C = 2.05(2) Å, Hg(5′)–C = 2.04(2) Å; Hg(5)–O = 2.09(1) Å, Hg(5′)–O = 2.06(1) Å), as are the bond angles (C–Hg(5)–O = 175.0(6), C–Hg(5′)–O = 178.6°). This primary kernel is supplemented by several weak intermolecular Hg···ONO_2 interactions: according to [15], Hg(5) has five Hg···O secondary bonds with lengths in the range 2.746 to 3.432 Å (the sum of the van der Waals radii is 3.5 Å), while Hg(5′) has only three, ranging in length from 2.678 to 3.073 Å. Note that Hg(5), which has the larger number of weak interactions, also has the longest primary Hg–C and Hg–O bonds and the C–Hg–O angle deviating most markedly from linearity. The distance between Hg(5) and Hg(5′) and the mercury atoms on adjacent sides of the hexagon is 3.540(1) Å.

The reaction in methanol of [2-(pyridin-2-yl)phenyl]mercury acetate with 2-thiouracil in 2:1 mole ratio affords the binuclear compound $[\{Hg(PhPy)\}_2(tuc)]$, the molecules of which are associated in centrosymmetric dimers (Fig. 55) [124]. In each HgPhPy unit the mercury atom is bound strongly to a phenyl C and more weakly to the pyridine N. Hg(1) coordinates to the thiouracil primarily through N(3), and Hg(2) through the sulphur atom. Hg(1) also has weak intramolecular bonds with the O and S atoms, while Hg(2) has an intramolecular secondary bond with the tuc N(1) atom (Hg(2)···N(1) = 2.99 Å) and also sustains the dimeric association by means of a weak intermolecular interaction with the pyridine N bound to Hg(2′).

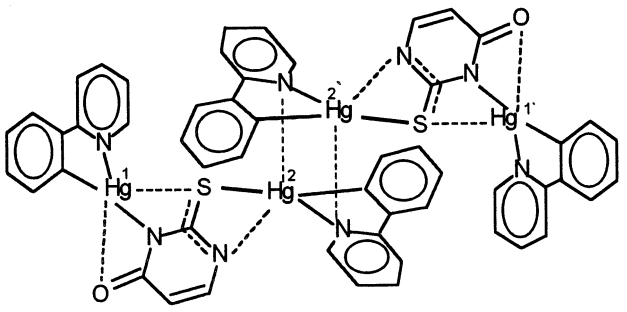

Fig. 55. Adapted from Ref. [124].

Crystals of methyl(*o*-nitrobenzenethiolato)mercury [125] contain two independent molecules. In both the ligand coordinates to the metal primarily through its exocyclic sulphur, and the stereochemistry of both mercury atoms is essentially linear, although there is also a complex series of three intermolecular interactions with exocyclic sulphur and nitro oxygen atoms. Taking the primary bonds and all three secondary interactions into account, the coordination polyhedron around the mercury atom can be described as a trigonal bipyramid.

Reaction of (2-lithio-1,3-xylylene)-18-crown-5 with $HgBr_2$ affords the organomercury compound [2-(bromomercurio)-1,3-xylylene]-18-crown-5, [Hg(X18C5)Br] (Fig. 56) [126]. X-ray study of this compound shows a C–Hg–Br fragment which deviates by about 5° from linearity, probably due to secondary interactions between the metal atom and three crown ether oxygen atoms.

The dimeric organomercuric compound $[Hg(CH_2COCH_3)(ClO_4)(Pyqx)]$ is obtained by mercuriation of acetone with mercury perchlorate in the presence of 2(2′-pyridyl)quinoxaline [127]. In this compound Hg forms two strong, almost collinear bonds with the oxopropyl carbon and the pyridyl nitrogen, and has three secondary interactions: one with a quinoxaline nitrogen, one with a perchlorate oxygen and one with the oxygen of a centrosymmetrically related oxopropyl group. If all these interactions are taken into account the coordination number is five and the coordination polyhedron can be described as a distorted trigonal bipyramid.

The methylmercury derivative $[HgMe\{S(O)PPh_2\}]$ has the supramolecular structure of a double-stranded ribbon (Fig. 57) [128]. In each monomer the mercury

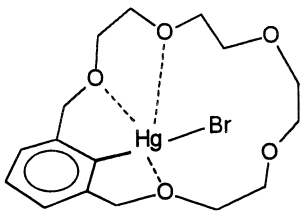

Fig. 56. Adapted from Ref. [126].

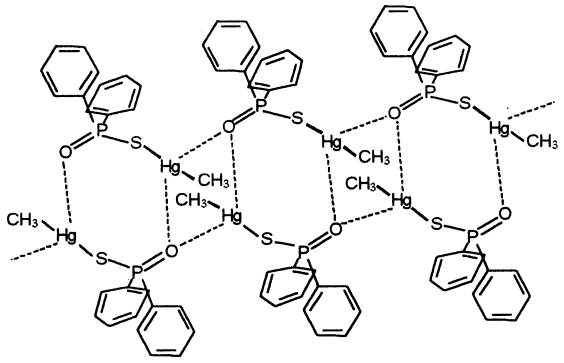

Fig. 57. Adapted from Ref. [128].

atom forms primary bonds with the methyl group and with the sulphur atom of $S(O)PPh_2$. The two primary bonds are basically collinear. Secondary Hg···O interactions link each monomer both with the neighbouring monomers of its own strand of the ribbon (Hg···O = 2.831(3) Å) and with a centrosymmetrically related monomer in the other strand (Hg···O = 2.897(4) Å). If these secondary bonds are taken into account but not a very weak intermolecular Hg···S interaction, the coordination polyhedron around the metal atom can be described as a distorted ψ-trigonal bipyramid, with the sulphur atom and methyl group in axial positions and two Hg···O secondary interactions in equatorial positions.

The organometallic derivative $(NBu_4)_2[(C_6F_5)_3Pt(\mu\text{-}OH)(\mu\text{-}HgC_6F_5)Pt(C_6F_5)_3]$ [129] contains a trinuclear complex anion (Fig. 58) which is considered as formed by the interaction of the anion $[(C_6F_5)_3Pt(\mu\text{-}OH)Pt(C_6F_5)_3]^-$ with the $[Hg(C_6F_5)]^+$ cation through two $Pt \rightarrow Hg$ donor – acceptor bonds. Although the authors describe the environment of the Hg atom as trigonal planar, formed by the C and Pt

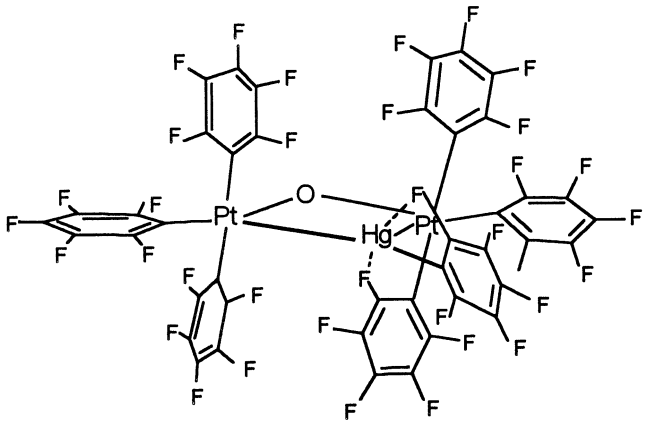

Fig. 58. Adapted from Ref. [129].

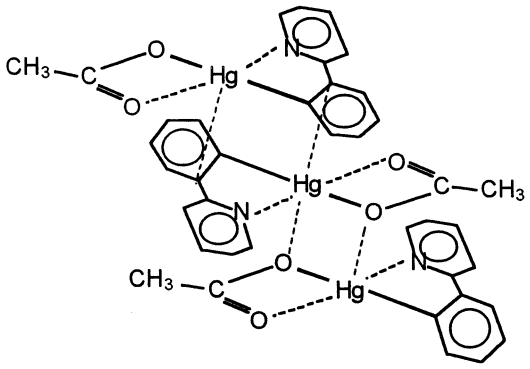

Fig. 59. Adapted from Ref. [130].

atoms, two weak *o*-F···Hg interactions make the Hg coordination number up to five.

2.2.5. Coordination number 6

Acetato[2-(pyridin-2′-yl)phenyl]mercury(II), [Hg(PhPy)(OAc)] (Fig. 59) [130], consists of molecules in which mercury is strongly bound to one of the acetate oxygens and to one of the phenyl carbons in an almost linear C–Hg–O fragment. These primary bonds are supplemented by two secondary intramolecular interactions, with the pyridine nitrogen and the other oxygen of the acetate group, and by two weak intermolecular interactions, Hg···C and Hg···O, with neighbouring molecules.

2.2.6. Coordination number 7

As was noted above in $[Pt(CH_3NH_2)_2(MeC)_2Hg_3(OH)(NO_3)]_2^{4+}$ [123] the Hg(5) mercury atoms have an $[HgCO_6]$ kernel.

2.3. Diorganomercury(II) compounds

Structural data for diorganomercury compounds are given in Table 5.

2.3.1. Coordination number 3

Bis(4-pyridylethynyl)mercury(II) is prepared by reacting mercuric acetate and 4-ethynylpyridine in methanol/1-butanol/acetic acid [131]. Structural analysis following recrystallization from dimethylformamide shows that the Hg atom has primary bonds with two ethynyl carbon atoms (both of length 2.02(3) Å), and that the deviation of these bonds from collinearity (C–Hg–C = 172(1)°) can be attributed to an intermolecular Hg–N bond of length 2.64(3) Å which makes the coordination around the metal atom T-shaped and interconnects the molecules in infinite zigzag polymeric chains.

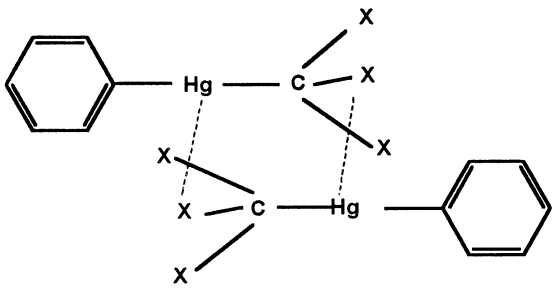

Fig. 60. Adapted from Ref. [132].

(Bromodichloromethyl)phenylmercury(II) (Fig. 60) is another example illustrating the residual Lewis acid character of mercury in diorganomercuric compounds. According to an X-ray study [132], the molecules of this compound are associated in dimers by secondary bonds between mercury and an unidentified halogen atom (both the relevant Hg···X distances, 3.468(3) and 3.516(4) Å, are less than the sums of the van der Waals radii for both Hg···Cl (3.70–3.90 Å) and Hg···Br (3.80–4.0 Å)). The small magnitude of the deviation of C–Hg–C from linearity (178.3(6)° for one of the molecules of the dimer, 179.5(6)° for the other) suggests that these secondary bonds are rather weak.

The four methyleneoxydiphenylphosphinate [$(mop)^-$] ligands in $[HgBr(mop)_2$-$Li(H_2O)(THF)]_2$ bridge between the metallic centres to create a 16-membered ring [133] (Fig. 61). The basically linear coordination of the mercury(II) (Hg–C = 2.105(6) and 2.110(6) Å, C–Hg–C = 176.9(3)°) is supplemented by a weak bond with a bromide ligand (Hg–Br = 3.127(1) Å) resulting in a T-shaped arrangement (C(1)–Hg–Br = 89.2(2), C(2)–Hg–Br = 92.6(2)°). The distribution of charge in the mop^- anion is not simple [133], and Fig. 61 must be considered as merely a structural scheme, not as representing bond orders.

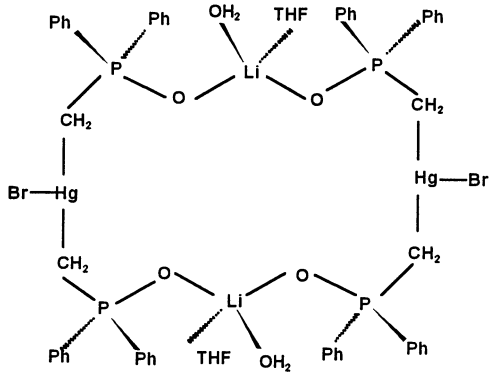

Fig. 61. Adapted from Ref. [133].

The similar anion mtp^-, in which the oxygen of mop^- is replaced by a sulphur atom, forms the trinuclear cation $[Hg_2(mtp)_4Pt]^{2+}$, which has been isolated as its PF_6^- and BPh_4^- salts [134]. In the hexafluorophosphate, each Hg is bound to two mtp^- ligands via their methylene C atoms (av. Hg–C = 2.10 Å, C–Hg–C 173.0(4)°) while the four S atoms of the two $Hg(mtp)_2$ units are bound to the Pt in a distorted square planar arrangement. The mtp^- bridges place the Pt and Hg centres 3.138(1) Å apart, with an Hg···Pt···Hg angle of 149.1(1)°. The structure of the cation in $[Hg_2(mtp)_4Pt](BPh_4)_2 \cdot CH_2Cl_2$ is similar, with just small changes in bond lengths and angles.

2.3.2. Coordination number 4

A good example of intramolecular secondary coordination in diorganomercury compounds is provided by bis[2-(pyridin-2′-yl)phenyl]mercury(II), $[Hg(PhPy)_2]$ [135]. This compound is formed by centrosymmetric molecules in which the mercury atom is bound to a C atom of each phenyl ring and also to the N atoms of the pyridine rings. Both the C–Hg–C and N–Hg–N angles are 180.0°, and the C–Hg–N angle is 70.7(3)°, so the metal coordination geometry can be described as distorted square-planar. The Hg–C bond length (2.098(8) Å) is normal, and the Hg–N distance (2.798(7) Å), though longer than those associated with strong primary bonds, is shorter than the sum of the van der Waals radii (although comparison with the length of Hg–N bonds in similar monoorganomercury compounds such as [Hg(PhPy)(OAc)] illustrates the weaker acceptor capacity of diorganomercuric derivatives; see Table 4).

The *N*-acetylpyrrole derivative [Hg(*N*–AcPyr)Cl] (see coordination number 4 in Table 4) symmetrizes to [Hg(*N*-AcPyr)$_2$] [116], which contains collinear Hg–C bonds (C–Hg–C = 180.0°) with bond lengths in the usual range (2.068(9) Å). The two centrosymmetrically related pyrrolyl rings are coplanar, and the oxygen atoms of the acetyl groups lie 2.87(1) Å from the metal atom, a distance indicative of secondary bonds that increase the coordination number of the mercury atom to four and create a distorted square-planar coordination geometry.

In the diarylmercury complex $[Hg(N^nBuPh)_2]$ the Hg forms collinear Hg–C bonds (C–Hg–C = 180.0°) with two C atoms belonging to the coplanar aryl groups (Fig. 62) [136]. The distance of the butoxyl O atoms from the metal, 3.015(2) Å, is probably determined by the rigidity of the ligand, but since it is shorter than the sum of the van der Waals radii (ca. 3.50 Å if the value of 2.0 Å for Hg is used) it nevertheless formally justifies the classification of this compound as tetracoordinate.

Symmetrization of [Hg(dimeU)(OAc)] (vide supra) gives $[Hg(dimeU)_2]$, in which the non-coplanar nucleobase rings (dihedral angle 64.9°) are both bound to the Hg atom through C(5) [137]. The Hg–C bond length and the C–Hg–C bond angle have unexceptional values, and there is an intermolecular interaction with an O atom of a neighbouring molecule [Hg···O = 2.901(8) Å]. The molecule is chiral, and both enantiomers are included in the crystal lattice. Like the preceding compound, $[Hg(dimeU)_2]$ is classified here as tetracoordinate even though the short intramolecular Hg···O distance, 3.180(8) Å, is probably imposed by the ligand geometry.

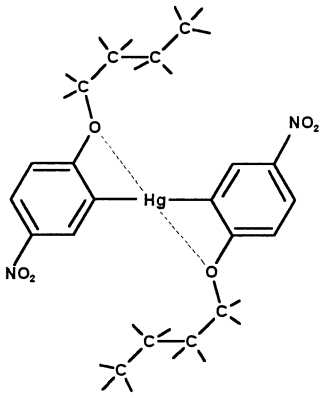

Fig. 62. Adapted from Ref. [136].

Viets et al. [138] have recently prepared and identified the first anionic fluoromercury compound, $Hg[(CF_3)_2F]^-$. X-ray structural analysis shows that in the solid state this compound exists as $[(CF_3)_2Hg(\mu\text{-}F)_2Hg(CF_3)_2]^{2-}$ dimers (Fig. 63).The authors suggest that the bridging Hg–F bonds of the four-membered Hg_2F_2 ring can be considered as involving the lone electron pair of the fluoride and the empty *p* orbitals of mercury atoms, whose acceptor capacity is increased by the inductive effect of the F_3C groups. These bonds modify the basic sp hybridization of the metal atom, resulting in a C–Hg–C bond angle of 162.1(5)°. The Hg–C bond length is normal, 2.086(14) Å, but this bond is nevertheless very labile after fluoride ion addition.

The ten-membered metallacycle $[HgC(CF_3)_2]_5$ (Fig. 64), another perfluoro derivative of mercury(II), reacts readily with tetraphenylphosphonium chloride or bromide in ethanol to give $[\{HgC(CF_3)_2\}_5X_2]^{2-}$ anions (X = Cl, Br) [139,140]. In the Cl derivative the two chloride ions are placed above and below the plane of the metallacycle at approximately equal distances from the mercury atoms, so that (CF_3 groups apart) the molecule is a distorted flattened decagonal bipyramid. The

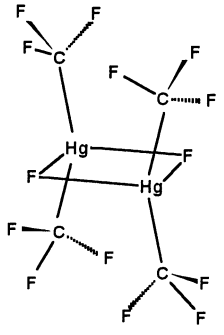

Fig. 63. Adapted from Ref. [138].

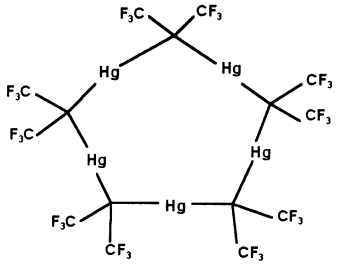

Fig. 64. Adapted from Ref. [139].

Cl···Cl distance, 3.25(1) Å, is unusually short, even shorter than the sum of the van der Waals radii for two chloride anions (ca. 3.6 Å). All the mercury atoms are tetracoordinated, with unexceptional Hg–C distances and C–Hg–C angles of 172.1–176.1°. The bromide derivative has the same structure except for minor differences in the Hg–C bond lengths and angles [140]. The bromide–bromide distance is very short, 3.616(5) Å.

The multidentate Lewis acid $[Hg(C_6F_4)]_3$ (see Fig. 65) is another diorganomercury compound that can bind anions using the residual acceptor capacity of the Hg atoms in its almost planar nine-membered metallacycle. For example, it reacts with $(^nBu_4N)^+SCN^-$ to afford the anionic complex $[\{Hg(C_6F_4)\}_3(SCN)]^-$, which has been isolated as its tetrabutylammonium salt [141]. The crystalline solid contains helical polymeric chains formed by alternating $[Hg(C_6F_4)]_3$ molecules and SCN^- anions, each of the latter being weakly *S*-bound to all six Hg atoms of the two non-parallel metallacycles between which it is sandwiched. The asymmetry of the coordination of the SCN^- anion is augmented by its lying off-centre with respect to each metallacycle, resulting in Hg···S bond lengths ranging from 3.06(1) to 3.87(1) Å.

The bimetallic sulphido complex $[PPh_4]_2[S_2WS_2HgCl_2]$ reacts with acetone to give the vinyl derivative $[Ph_4P]_2[S_2WS_2Hg(CH{=}CH_2)_2]\cdot 0.5Me_2CO$, which undergoes spontaneous dehydrogenation to afford the ethynyl complex

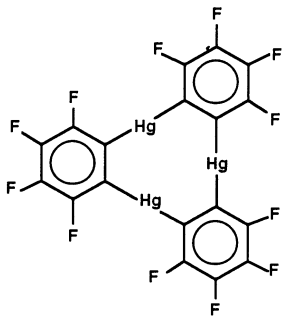

Fig. 65. Adapted from Ref. [141].

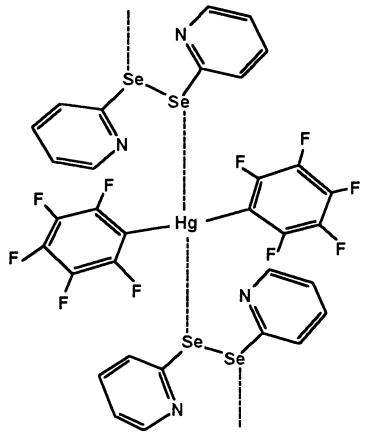

Fig. 66. Adapted from Ref. [143].

$[Ph_4P]_2[S_2WS_2Hg(C{\equiv}CH)_2]\cdot 0.5MeCHO$ [142]. The coordination kernels of this latter, WS_4 and HgC_2S_2, can be described as defining two tetrahedra with a common edge (S_2). The mercury atom has a rather distorted tetrahedral environment with C–Hg–C and S–Hg–S bond angles of 147(2) and 82.9(2)°, respectively.

In the adduct $[Hg(pFPh)_2(PySeSePy)]$, obtained by reaction of PySeSePy and $Hg(pFPh)_2$ in Et_2O [143], bis(pentafluorophenyl)mercury(II) and 2,2′-dipyridyldiselenide molecules are weakly bound by Hg···Se interactions, forming a 'staircase' in which the pyridine and pentafluorophenyl rings are almost parallel (Fig. 66). The geometry around the Hg atom is described as a plane tetragon with the two Hg–C bonds (slightly shorter than those of free $Hg(pFPh)_2$) and two long Hg···Se bonds.

2.3.3. Coordination number 6

Reaction of [Hg(X18C5)Br] and metallic Mg yields the symmetric compound $[Hg(X18C5)_2]$, in which the mercury is bound strongly to two carbon atoms in a linear C–Hg–C fragment and weakly to four crown ether oxygen atoms lying in a plane (Hg···O = 2.984(3)–3.064(3) Å) [126]. The coordination polyhedron around the mercury atom is a highly distorted octahedron.

$[Hg(DTDA)_2][AsF_6]$ is prepared by reacting $[SNS][AsF_6]$ and $Hg(CN)_2$ in 2:1 mole ratio [144]. It contains two dithiazolylium rings bound to Hg via the carbon atoms. Four weak Hg···F interactions with four different $[AsF_6]^-$ anions give rise to a distorted octahedral environment for the mercury atom.

The heteronuclear diorganomercury derivative $[Hg\{o\text{-}C_6H_4[InCl_2(THF)_2]\}_2]$ (Fig. 67) has been obtained by reaction of *ortho*-phenylenemercury with indium(I) chloride in THF [145]. The mercury atom is coordinated to two phenylene carbon atoms (C–Hg–C: 178.7(3)°), and weak Hg···O and Hg···Cl interactions (two each) may make the coordination number up to six and give rise to a distorted octahedral environment, although some of these weak interactions may be imposed by the coordination of Cl or THF to the indium atom.

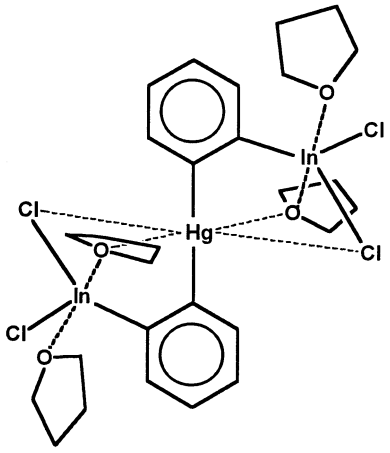

Fig. 67. Adapted from Ref. [145].

2.3.4. Coordination number 8

The coordination around the mercury atom in $[Hg(CHCl_2)_2]$ is as usual basically linear (C–Hg–C = 179.4(5)°) [146], but according to [15] there are also six weak Hg···Cl bonds ranging in length from 3.307 to 3.624 Å.

2.4. Conclusions

This review supplements that of Holloway and Melník [85], covering the literature up to and including 1997. Because special importance has been given to secondary bonds and effective coordination numbers, recent estimates of the van der Waals radius of the mercury atom have been used to identify the former. It must nervertheless be borne in mind that, as Kuz'mina and Struchkov have pointed out [83], it is difficult to establish a clear-cut boundary between a close interatomic contact imposed by the packing in the lattice and a 'real' secondary bond using interatomic distance as the only criterion; often, additional insight must be sought by analysis of changes in the sp hybridization of Hg or in the angle between the primary bonds. When the primary bonds are not collinear, a weak additional interaction must be suspected. On the other hand, although the primary kernel of mercury(II) compounds is usually not far from linear despite secondary interactions, sterically demanding ligands can significantly change this situation, as is illustrated by the complex $[HgMe(np_3)][CF_3SO_3]$ [102].

The structural data summarized in this review show that the primary bonds of monoorganomercury compounds leave the Hg atom with enough residual acidity for it to be able to reach a coordination number of seven when the donor atoms forming the secondary bonds are small. Diorganomercury compounds, though less acidic than monoorganomercury, can nevertheless also take part in several secondary interactions, especially if the primary bonds involve electron-withdrawing groups such as perfluorated radicals.

It may be noted that the common belief that Hg(II) has little affinity for oxygen atoms other than those of carboxylate groups may have to be revised in view of the very short Hg–O distance found in $[(HgPh)_2TbSMe]$ [95].

To sum up, even though the structures of more than four hundred organomercury compounds have been studied to date by X-ray diffraction, it seems that many features of the structural behaviour of organometallic cations remain to be found.

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