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Recent developments in the ligand chemistry of tellurium

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Abstract

The synthesis and coordination chemistry of telluroether (including hybrid ones), anionic organotellurium and inorganic tellurium (halotellurium, telluride and polytellurides) ligands developed during the last decade are reviewed. The characterization of the metal–tellurium

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bond containing species by multinuclei NMR (particularly ^{125}Te-NMR) and X-ray diffraction on their single crystals are discussed more emphatically. The ligation of tellurium is compared with other donor sites. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Tellurium; Ligands; Metalloid

1. Introduction

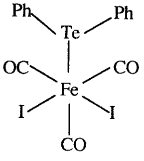
Tellurium is a noble metalloid which may act as a Lewis acid as well as Lewis base. Its coordination chemistry is dominated by sulfur ligands [1–5]. The ligand chemistry of tellurium, which acts as a 'soft' donor, was little explored before 1970, probably due to commercial non-availability of a wide variety of tellurium/organotellurium ligands and some misconception that they are air sensitive, foul smelling and toxic. In the last 3 decades many publications devoted to these ligands have appeared in the literature. This indicates considerable and continuing interest in tellurium ligands. Two reviews by Gysling [6,7] followed by that of Berry [8] on this subject were published in the 1980s. Thereafter, the ligand chemistry of polydentate organotellurium ligands was reviewed in 1992 by Singh and Srivastava [9] and of telluroethers by Hope and Levason [10]. However, even today few tellurium ligands are available commercially. With modern FT-NMR instruments there is a good possibility to use ^{125}Te-NMR to understand the solution behavior of metal–tellurium bond-containing systems. This coupled with the fact that metal complexes of organotellurium ligands [11] may be used as single source precursors for MOCVD of II–VI semiconductors, has enhanced interest in the ligand chemistry of tellurium. However, in the last decade no attempt has been made to review the overall current status of tellurium ligands. Some smaller fragments of this somewhat larger subject have been reviewed separately. The ligand chemistry of the polytelluride ion [12] was reviewed in 1994 covering literature up to early1 1993. Adamantane like tellurolate bridged cages of zinc group metals were reviewed in 1992 by Dean and Vittal [13]. The chemistry of inorganic halotellurium ligands, e.g. TeX_3^- was compiled by Beck [14] and of tellurometalates $[M_xTe_y]^{2-}$ by Ansari et al. [15]. Metal carbonyls [16] containing bridging tellurium ligands and metal tellurolates [17] have also been reviewed. In the present article a composite view of the current status of the ligand chemistry of tellurium is presented. Generally the recent research papers not covered in any of the above-mentioned reviews are incorporated here. The major objective of the present review is to promote interest in the subject of tellurium ligands.

2. Telluroether ligands

Several telluroether ligand types are known at present. They are potentially monodentate to hexadentate and have acyclic to macrocyclic structures. In addition to tellurium, many of them have other donor atoms viz. nitrogen, oxygen and sulfur. The latter ones are commonly referred to as hybrid telluroether ligands.

2.1. Monodentate acyclic telluroethers

Dialkyl as well as diaryl tellurides behave as monodentate 'soft' donors. Their ligand chemistry has been the subject of several publications. The last two reviews [9,10] covering this class of ligands were published in 1992 and 1993. Thereafter several interesting publications have appeared on these systems. In the recent past, success has been attained in obtaining a crystalline iron(II)–telluroether complex $[(Ph_2Te)Fe(CO)_3I_2]$ (**1**) [18] in 93% yield by reacting Ph_2TeI_2 with $Fe(CO)_5$ in THF at room temperature. The reaction occurs through oxidative addition of I_2 to Fe(0). The crystal structure of **1** shows Te···I interaction (3.423(2)–3.486(2) Å; I–Fe–I angle 83.55(7)°). Its IR spectrum has three (CO) bands at 2087, 2042 and 2025 cm^{-1} concurring with its unsymmetrical structure. A compound very similar to **1**, $[(MeTePh)Fe(CO)_3I_2]$ has been prepared by the sequence of reactions given in Eq. (1). These observations are significant in view of the fact that the complexes of telluroethers with Fe(II) are reported earlier [19–21] to have inherent instability and non-crystalline nature.



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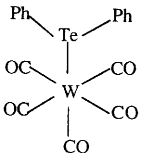

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On reacting $[W(CO)_5(THF)]$ with equimolar amounts of Ph_2Te, the tellurium ligand enters into the coordination sphere of tungsten resulting in $[Ph_2TeW(CO)_5]$ (**2**) [18], which has been structurally characterized and has an octahedral geometry.

$$[HFe(CO)_4]^- \xrightarrow{Ph_2Te_2} [PhTeFe(CO)_4]^- \xrightarrow{MeI} [(MeTePh)Fe(CO)_4] \xrightarrow{I_2} (MeTePh)Fe(CO)_3I_2] \quad (1)$$

The crystal structure of a Re(I) species $[(PhTeMe)Re(CO)_5]BF_4$ is similar to that of **2** [22]. However, it has been synthesized by methylation of $[PhTeRe(CO)_5]$ with $[Me_3O]BF_4$. The complexes of Cu(I) with Me_2Te and Ph_2Te viz. $[Cu(Me_2Te/Ph_2Te)_4][O_3SCF_3]$ and $[Cu(Ph_2Te)_4]BF_4$ were synthesized by Black and Levason [23], using the reaction of $[\{Cu(O_3SCF_3)\}_2(C_6H_6)]$ with these tellurides. The copper complex of Ph_2Te was also obtained by reacting it with $[Cu(MeCN)_4]BF_4$. The low frequency coordination shift has been observed in ^{125}Te-NMR signals of Me_2Te (δ -37 ppm; free Me_2Te, δ 0) and Ph_2Te (δ 578 ppm; free Ph_2Te, δ 685 ppm; reference Me_2Te) on complex formation with Cu(I), a d^{10} system. The Cu-complex of Me_2Te exhibits a ^{63}Cu-NMR resonance (reference $[Cu(MeCN)_4]^+$), at δ -56 ppm and of Ph_2Te at δ -153 ppm (both in the presence of excess of the ligand).

Recently extremely moisture sensitive adducts $[SnX_4{\cdot}(Me_2Te)_2]$ (X = Cl or Br) have been reported but only with spectroscopic characterization [24]. Attempts to record $^{119}Sn\{^1H\}$- or $^{125}Te\{^1H\}$-NMR spectra of these adducts were not fruitful. The ν(Sn–Cl) has been reported at 312 cm^{-1} for solid $[SnCl_4{\cdot}(Me_2Te)_2]$, consistent with its *trans* geometry, but in solution *cis* and *trans* isomers probably coexist at 180 K. On reacting dialkyltelluride [25] with $RMn(CO)_5$, a CO ligand is inserted into the R–Mn bond, resulting in $RCOMn(CO)_4(TeR_2)$ (R = Me, Et). When R = benzyl (Bz) this product is unstable and undergoes decarbonylation resulting in $BzMn(CO)_4(TeR_2)$. Only spectral data of these complexes are reported in the support of octahedral geometry of Mn and its *cis* stereochemistry. A novel diorganotelluride $[\eta^1\text{-}\{(Me_3Si)_3C_5H_2\}]_2Te$ and its adduct $[\eta^1\text{-}\{(Me_3Si)_3C_5H_2\}]_2TeW(CO)_5$ [26] contain a ligand which was synthesized by reacting bis(diethyldithiocarbamate)tellurium(II) with lithium tris(trimethylsilyl)-cyclopentadienide.

2.2. Bidentate telluroethers

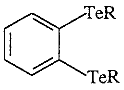
Interest in the three bidentate telluroether ligands **3**–**5** has continued, for the tellurium analog of dppm (**3**), a very clean and high yield (~ 80%) synthesis based on the reaction of $CHCl_3$ with $ArTe^-$ (in situ generated in ethanol by $NaBH_4$ reduction of Ar_2Te_2) was recently reported [27].

$RTeCH_2TeR$

3

$RTe(CH_2)_3TeR$

4



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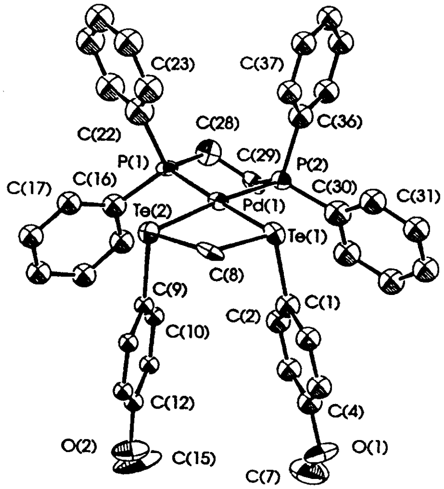
$R = CH_3, C_6H_5, 4\text{-}MeOC_6H_4$

The pathway proposed for the reaction is given in Eq. (2).

$$CHCl_3 \overset{OH^-}{\rightarrow} :CCl_3^- \rightarrow :CCl_2 \overset{ArTe^-}{\rightarrow} (ArTe)_2C \overset{BH_4^-}{\rightarrow} (ArTe)_2CH^- \underset{solvent}{\overset{H^+}{\rightarrow}} (ArTe)_2CH_2 \qquad (2)$$

The first structurally characterized complexes [28] of a chelating C_1 linked ditelluroether **3** are $[\{meso(4\text{-}MeOC_6H_4Te)_2CH_2\}(dppe)Pd(II)](ClO_4)_2{\cdot}4H_2O$ (**6**) and $[meso(4\text{-}MeOC_6H_4Te)_2CH_2\}Pd(II)Cl_2]$ (**7**) (dppe = diphenylphosphinoethane). The platinum(IV) complexes of **3** viz. $[(PtIMe_3)_2(RTeCH_2TeR)]$, $[(PtIMe_3)(RTeCH_2TeR)]$ and $[PtIMe_3(RTeCH_2TeR)_2$ have also been reported but not characterized structurally [29]. The synthesis of **6** and **7** is contrary to the claim of Chiffey et al. [30], that **3** always make polymeric complexes with Pd(II). The solubility of **7** in common organic solvents is of course very poor. The structurally characterized first examples in which S and Se analogs of **3** function as a chelating ligand, ($[SnCl_4(MeSCH_2SMe)]$ and $[SnCl_4(MeSeCH_2SeMe)]$), were also reported very recently [31]. The $^{125}Te\{^1H\}$-NMR spectrum of **6** has only one prominent signal at δ 509 (signal of free **3**; δ 571 ppm) favoring the presence of the *meso* invertomer [32].



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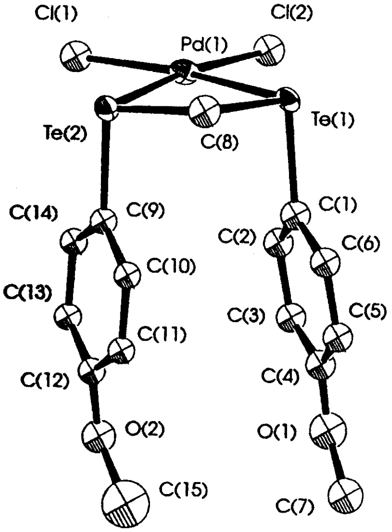

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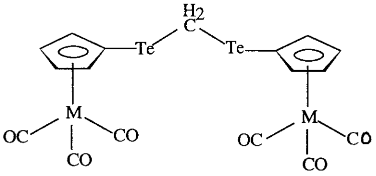
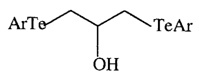
Complex **3a** shown below is essentially similar to **3** and has been synthesized very recently [33] but its coordination has not been studied so far. The adducts of **4** and **5** with $SnCl_4/Br_4$ have been reported.



3a

However, only the crystal structure of the adduct made with **5**, is solved. In this adduct the geometry of tin is distorted octahedrally with the chelating ligand **5** in a *meso* conformation. The variable temperature (180–300 K) ^{125}Te{^{1}H}- and ^{119}Sn{^{1}H}-NMR spectra of these adducts, even in the presence of free **5**, exhibit resonances which are unobservably broad, due to fast exchange on the NMR time scale, between free and coordinated ligand molecules. The broad ^{1}H-NMR resonances of these adducts also remain unaffected on cooling for similar reasons. The adduct of **4** with $SnCl_4$ can be stored for several weeks in a dry box but its solubility is reported to be unsuitable for recording NMR. $GeCl_4$ and $SiCl_4$ do not show any adduct formation with **4** or **5**. The complex $(PhTe(CH_2)_3TePh)Re(CO)_3Br$ [22], synthesized by reacting $Re(CO)_5Br$ with the ditelluroether ligand has been characterized. It is interesting to note that Te donors substitute CO ligands. In the Cu(I) complex of **4**, $[Cu\{MeTe(CH_2)_3TeMe\}_2]PF_6$, the ^{63}Cu-NMR spectrum exhibits a broad resonance at 300 K which is further broadened on cooling, but its chemical shift is insensitive to temperature. However, in the ^{63}Cu-NMR spectrum of $[Cu\{PhTe(CH_2)_3TePh\}_2]PF_6$, only a broad signal appears on cooling to 273 K which merges to base line at <220 K. However, in the NMR spectrum of $[Cu\{PhS(CH_2)_3SPh\}_2]PF_6$ no ^{63}Cu resonance could be observed, indicating a very high sensitivity of rate of quadrupolar relaxation of ^{63}Cu nuclei to small changes in its environment. The ^{109}Ag-NMR spectrum of $[Ag(RTe(CH_2)_3TeR)_2]BF_4$, [34] exhibits resonance at $\delta+1053$ and $+989$ ppm, when R is Me and Ph, respectively. The signal disappears on cooling below 250 K. In the ^{125}Te-NMR spectrum of this Ag complex, only one signal (80–105 ppm shielded with respect to that of free ligand) has been noticed, suggesting that both Te donor sites are involved in ligation. Most probably **4** in this silver complex is coordinating in a chelating mode like its selenium analog, making the geometry of Ag^+ tetrahedral. The Cu(I) and Ag(I) complexes of **5**, having composition $[M\{o\text{-}C_6H_4(TeMe)_2\}_2]PF_6/BF_4$, are reported [36] but only the first one is structurally characterized, in which Cu has a flattened tetrahedral geometry (Te–Cu–Te angle of chelate ring 95.59(1)°) due to the restricted bite of the ligand **5**, which has a *meso* configuration. The ^{125}Te resonances of complexes of copper and silver with **5** appear as a singlet and deshielded (~ 130 ppm for Cu; 57 ppm for Ag) with respect to that of the free ligand. This is in consonance with the chelating ligation mode of **5**, but on cooling, the single resonance observed in the spectrum of this copper complex at 300 K resolves into several resonances, attributed to invertomers. However, the signal in the ^{63}Cu-NMR spectrum of the copper complex of **5** disappears below 240 K due to quadrupolar relaxation. The ^{125}Te-NMR spectra recorded on addition of ligand **5** to the solution of its either Cu or Ag complex suggest that there is a fast exchange between free and coordinated ligands. The ^{109}Ag resonance of $[Ag\{o\text{-}C_6H_4(TeMe)_2\}_2]^+$ appears at $\delta+1128$ ppm and shifts to $\delta+1164$ ppm on adding the ditelluroether ligand.

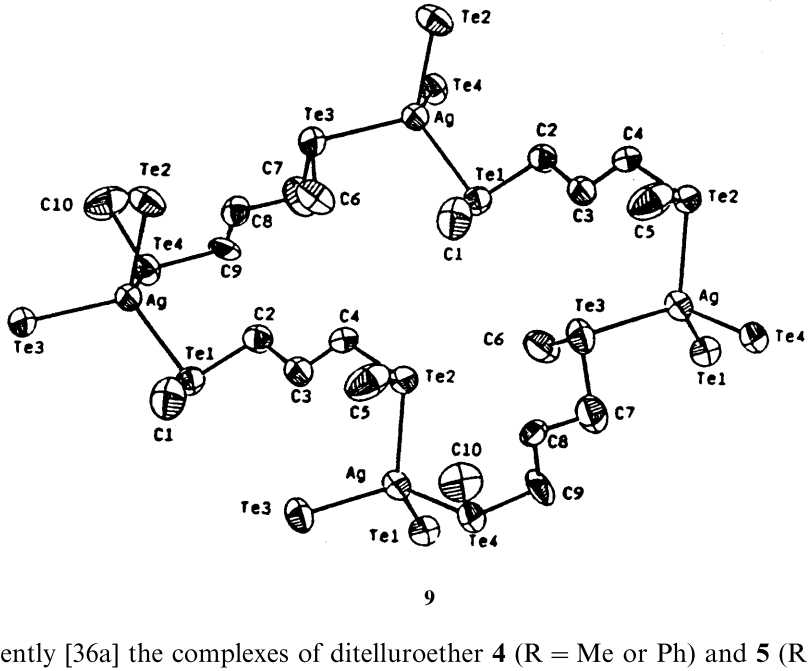
A ligand **8**, which is similar to **4**, has been synthesized [37] by reacting ArTeNa with $ClCH_2CH(OH)CH_2Cl$. Its Hg(II), Pd(II) and Pt(II) complexes have been characterized by spectroscopic methods.



Ar = 4-MeOC$_6$H$_4$

8

The OH remains non-participating in these complexes and consequently it exhibits a ligation mode similar to that of **4**. The ^{125}Te-NMR spectra of Pd(II) and Pt(II) complexes of **8** have two signals due to coexistence of *meso* and *dl* invertomers. Attempts to synthesize [Pd(**8**)$_2$](ClO$_4$)$_2$ and [Pd(**8**)L](ClO$_4$)$_2$ (L = ArTeCH$_2$COOH) by reacting [Pd(**8**)Cl$_2$] with AgClO$_4$ and the second ligand molecule resulted in elemental tellurium, Ar–Ar and CH$_2$=CH–CH$_2$OH. Liaw et al. [35a] have synthesized and characterized structurally a complex [Ag(MeTe(CH$_2$)$_3$TeMe)$_2$]$_n$[BF$_4$]$_n$ (**9**), a polymeric species in which all telluroether ligands bridge Ag atoms having distorted tetrahedral geometry. In this complex, non-interacting [BF$_4$]$^-$ anions are situated between the cationic layers of [Ag(MeTe(CH$_2$)$_3$TeMe)$_2$]$_n^{n+}$. Alternatively the Ag(I) polymer bridged by MeTe(CH$_2$)$_3$TeMe ligands can be envisaged as containing the repeat unit of a Ag$_4$(MeTe(CH$_2$)$_3$TeMe)$_4$ ring. The donor set around each Ag is of four tellurium atoms of four bridging MeTe(CH$_2$)$_3$TeMe chains. The Ag–Te bond lengths are of two types: shorter distances 2.789(2) and 2.785(2) Å and longer distances 2.820(2) and 2.837(2) Å. The shorter ones are close to normal values known for silver tellurolates [35b], [Ag$_4$(TeR)$_6$]$^{2-}$.



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Recently [36a] the complexes of ditelluroether **4** (R = Me or Ph) and **5** (R = Me) with Mn(I) and Re(I) carbonyl halides, having composition [MX(CO)$_3$(L–L)]

(L–L = **4** or **5**, X = Cl or Br, M = Mn or Re) were reported. Crystal structures of $[MCl(CO)_3\mathbf{5}]$ have shown the ditelluroether adopting a *meso*-2 arrangement with complexes in a distorted six coordinate geometry. The ^{55}Mn- and ^{125}Te-NMR data of these complexes in comparison with similar data for Se and S analogs of ditelluroethers **4** and **5** have revealed that ^{55}Mn chemical shift moves progressively to lower frequency as the Group 16 donor is changed; S → Se → Te. This increased

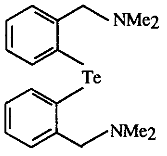
Table 1
Important hybrid telluroether ligands

	Hybrid telluroether	Metals with which complexation explored	Ref.
1	$1\text{-}(TePh)\text{-}2\text{-}(PPh_2)C_6H_4$ (**9a**)	Pt(II)	[38]
2	$1\text{-}(NMe_2)\text{-}2\text{-}(TeAr)\text{-}4\text{-}MeC_6H_3$(**10**) $Ar = 4\text{-}MeOC_6H_4$, $4\text{-}EtOC_6H_4$	Hg(II), Pd(II), Pt(II) Ni(II), Rh(I, III)	[39,40,56]
3	$\{2\text{-}(Me_2N)CH_2C_6H_4\}_2Te$ (**11**)	Cr(0)	[41]
4	$1\text{-}(Me_2NCH_2)\text{-}2\text{-}(TeR)C_6H_4$ (**12**)		[43]
5	$\{4\text{-}RC_6H_4TeCH_2CH_2\text{-}2\text{-}C_5H_4N\}$ (**13**) R = 4-Me/EtO, Me	Pd/Pt(II), Cu(I/II), Co(II/III)	[44,45]
6	$Te\{CH_2CH_2\text{-}2\text{-}(C_5H_4N)\}_2$ (**14**)	Pd/Pt(II)	[26]
7	$1\text{-}(NMe_2)\text{-}2\text{-}(TeMe)C_6H_4$ (**15**)	–	[46]
8	$H_2NCH_2CH_2TeAr$ (**16**)	Hg(II)	[47]
9	$Me_2NCH_2CH_2TeAr$ (**17**)	Pt(IV)	[49]
10	$H/MeN(CH_2CH_2TeAr)_2$ (**18**)	Hg(II), Pd(II), Pt(II), Rh(I, III)	[50,51,56]
11	$N(CH_2CH_2TeAr)_3$(**19**)	Hg(II)	[52]
12	$Te(CH_2CH_2NR_2)_2$ (**20**)	–	[53]
13	$Te_2(CH_2CH_2NR_2)_2$ (**21**)	–	[53]
14	$(ArTeCH_2CH_2)_2$ $NCH_2CH_2N(CH_2CH_2TeAr)_2$ (**22**)	–	[53]
15	$NH_2(CH_2)_3TeAr$ (**23**) $Ar = Ph$, $4\text{-}MeOC_6H_4$	–	[54]
16	$ArTeCH_2CH_2OMe$ (**24**)	–	[53]
17	$ArTeCH_2COOH$ (**25**)	Hg(II), Pd(II), Pt(II)	[57,58]
18	$ArTeCH_2CH_2OH$ (**26**)	Hg(II), Pd(II), Pt(II)	[59]
19	$ArTeCH_2CHOHCH_2OH$ (**27**)	Hg(II), Pd(II), Pt(II)	[60]
20	$(ArTeCH_2CH_2)_2O$ (**28**)	–	[53]
21	$(ArTeCH_2CH_2O\text{–}CH_2)_2$ (**29**)	–	[53]
22	$1\text{-}(ArTe)\text{-}2\text{-}OH\text{-}5\text{-}MeC_6H_3$ (**30**)	Hg(II), Pd(II), Pt(II)	[61]
23	$(5\text{-}Me\text{-}2\text{-}OH\text{–}C_6H_4)_2Te_2$ (**31**)	–	[57]
24	$\overline{CH_2CH_2CH_2CH_2OC}HCH_2TeAr$ (**32**)	Pd(II), Pt(II)	[62]
25	$\overline{OCH_2CH_2CH_2OC}HCH_2CH_2TeAr$ (**33**)	Pd(II), Pt(II)	[62]
26	$\overline{CH_2CH_2CH_2OC}HCH_2TeAr$ (**34**)	Pd(II), Pt(II)	[63]
27	$\overline{OCH_2CH_2OC}HCH_2CH_2TeAr$ (**35**)	Pd(II), Pt(II)	[63]
28	$ArTeCH_2CH_2SMe$ (**36**)	Pd(II), Pt(II)	[42,64]
29	$(RSCH_2CH_2)_2Te$ (**37**) (R = Me/Ph)	Hg(II), Pd(II), Pt(II)	[67,68]
30	$1\text{-}(ArTe)\text{-}2\text{-}(HSCH_2)C_6H_4$ (**38**)	Hg(II), Pd(II)	[69]
31	$2\text{-}Y\text{-}1\text{-}(MeTe)C_6H_4$ (**39**) Y = SMe, SeMe, PMe_2, $AsMe_2$, $SbMe_2$	–	[46]
32	Schiff bases containing Te (**40**)	–	[70,71]
33	$N\text{-}[2\text{-}(4\text{-}MeOC_6H_4TeCH_2CH_2]C_8H_4NO_2$ (**41**)	–	[72]

shielding parallels the decrease in ν(CO). The ^{125}Te chemical shifts of these complexes are found much more positive than expected and δ(Te):δ(Se) ratio (obtained by using ^{77}Se chemical shifts of analogous complexes) ranges from 2.1 to 2.9 (usual range for comparable organoselenium and -tellurium compounds: 1.7–1.8). These observations support the hypothesis that telluroethers show significantly enhanced σ-donation compared to the lighter analogs. The crystal structure [36b] of *fac*-isomer of octahedral Mn(I) complex of tritelluroether $MeC(CH_2TeMe)_3$ has recently been reported.

2.3. Hybrid telluroethers

The complexation of a hybrid telluroether ligand of (Te, P) type, was first reported by Gysling and Luss [38]. Thereafter ligation of several such ligands has been investigated. In Table 1 various hybrid ligands explored so far are listed. The chemistry of these ligands, known up to 1992, was first reviewed by Singh and Srivastava [9] and later by Hope and Levason [10]. Several research papers describing new ligands of this kind and their coordination behavior then appeared. Moreover, research papers reporting the new ligand chemistry of already known hybrid organotellurium ligands appeared. Both these types of publications are covered in this section. The new complexes [39,40] of an earlier known ligand 1-(NMe_2)-2-(TeAr)-4-MeC_6H_3 (**10**) viz. of the type [(**10**)M(ClO_4)$_2$], [(**10**)$_2$M](ClO_4)$_2$, [(**10**)$_2$MCl_2] (M = Pd or Pt), [(**10**)Pd(μ-SePh)$_2$PtCl_2], [(**10**)Pt(μ-TePh)$_2$PdCl_2], [(dppe)Pt(μ-TeAr)$_2$Ni(**10**)](ClO_4)$_2$, [(dppe)Pt(μ-Cl)$_2$Ni(**10**)](ClO_4)$_2$, [Cl_2Pd(μ-**10**)$_2$Ni(ClO_4)$_2$], [Cl_2Pt(μ-**10**)$_2$Ni(ClO_4)$_2$], [Co(**10**)$_2$$Br_2$]$BPh_4$, [Cu(**10**)$_2$Br] BPh_4, [Co(**10**)$_2$$Br_2$] and [Cu(**10**)$_2$Br] were reported, but none of them are structurally characterized. Moreover, the spectroscopic data given are not enough to support the proposed structures unequivocally, particularly the dimeric ones. A new potentially tridentate ligand of (N, Te, N) type (**11**) was synthesized by Kaur et al. [41] by reacting $C_6H_5CH_2NMe_2$ lithiated at the *ortho* position, with TeI_2.



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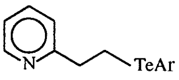

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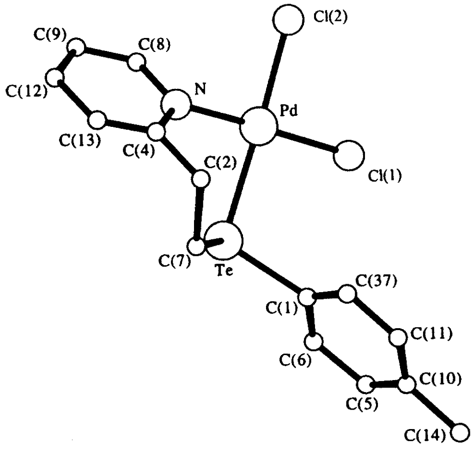
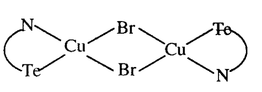
In the octahedral complex [$Cr(CO)_5$·**11**] in which **11** ligates only through Te, the CO *trans* to tellurium has a slightly longer bond length (1.162(7) Å) than the other CO groups (bond lengths, 1.140(7)–1.144(5) Å), due to a marginally higher *trans* influence of the tellurium ligand in comparison to CO or stronger σ-donation by the tellurium ligand. A very similar observation was made for a neutral Te donor versus a similar S donor [42]. A bidentate ligand **13** (Table 1) having a pyridine nitrogen as a donor in conjunction with a tellurium donor site, was designed by reacting ArTe$^-$ with 2-(2-chloroethyl)pyridine [44]. The complexes of **13** with Pd(II) [26,44], Pt(II) [44], Co(II, III) [45] and Cu(I, II) [45] are reported. An *endo* puckered chelate ring [26,44,45] is formed by (Te, N) ligand **13** when forming a square planar complex with Pd/Pt (see **13a**). The Pd–Cl *trans* to Te (2.352(3) Å) in the palladium(II) complex of **13** is longer in comparison to other Pd–Cl of the same complex (2.287(3) Å), also ascribed to a stronger *trans* influence than pyridine for the Te donor, or σ-donation by tellurium. The cobalt and copper complexes were characterized spectroscopically. The μ_{eff} of [Co(**13**)Br$_2$] is 3.5–3.7 B.M. [45], suggesting that it should be formulated as [Co(**13**)$_2$][CoBr$_4$]. Molecular weight and conductance data of the cobalt complex also suggest the existence of equilibrium of Eq. (3) in solution.

$$2[Co(\mathbf{13})Br_2] \rightleftharpoons [Co(\mathbf{13})_2][CoBr_4] \quad (3)$$

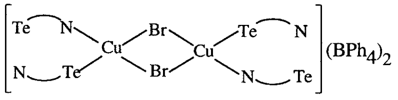


13a

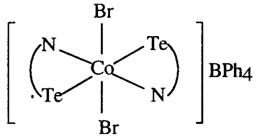
IR, ^{1}H- and ^{125}Te-NMR, ESR and electronic spectra in conjunction with ESCA, molar conductance, molecular weight and magnetic susceptibility data for species [Co(**13**)$_2$Br$_2$]BPh$_4$, [Cu(**13**)Br]$_2$ and [Cu(**13**)$_2$Br]$_2$(BPh$_4$)$_2$ are in agreement with the following proposed structures of these species.



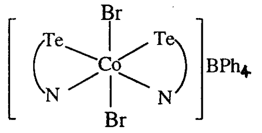
[Cu(**13**)Br]$_2$



[Cu(**13**)$_2$Br]$_2^{2+}$



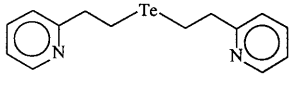
trans



cis

[Co(**13**)$_2$Br$_2$]$^+$

A (N, Te, N) type of ligand **14** has been synthesized [27] by reacting Na_2Te with 2-(2-chloroethyl)pyridine. Deshielded CH_2N and pyridine signals (with respect to free **14**) in the ^{1}H-NMR spectra of the Pd(II) or Pt(II) complexes ([MCl·**14**]Cl) are observed, which indicate a tridentate coordination mode of **14**.



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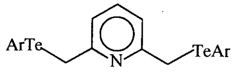
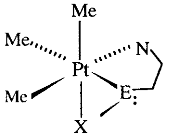
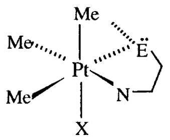


14a

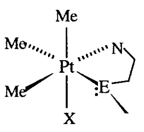
However, an attempt to design **14a** by an reacting appropriate organic halide with ArTeNa/ArTeLi did not succeed. It is not possible to synthesize $RTeCH_2CH_2TeR$ [48], consequently $RTeCH_2CH_2Y$ ($Y = NH_2$, NR_2, OR, SR) is closest to this skeleton. The first (Te, N) ligand of this kind $ArTeCH_2CH_2NH_2$ was designed by Singh and Srivastava [47]. Its dimethyl derivative $Me_2NCH_2CH_2TeAr$ was reported later [53]. Jain et al. [49] have also synthesized this dimethyl derivative and its complexes of the type *fac*-$Me_3PtX(Me_2NCH_2CH_2TePh)$; (X = Cl, Br, I), have been shown by ^{1}H-NMR, to exist in solution in different forms **17a**–**17d** at temperatures below −60°C.



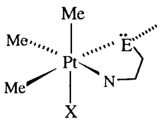
17a



17b



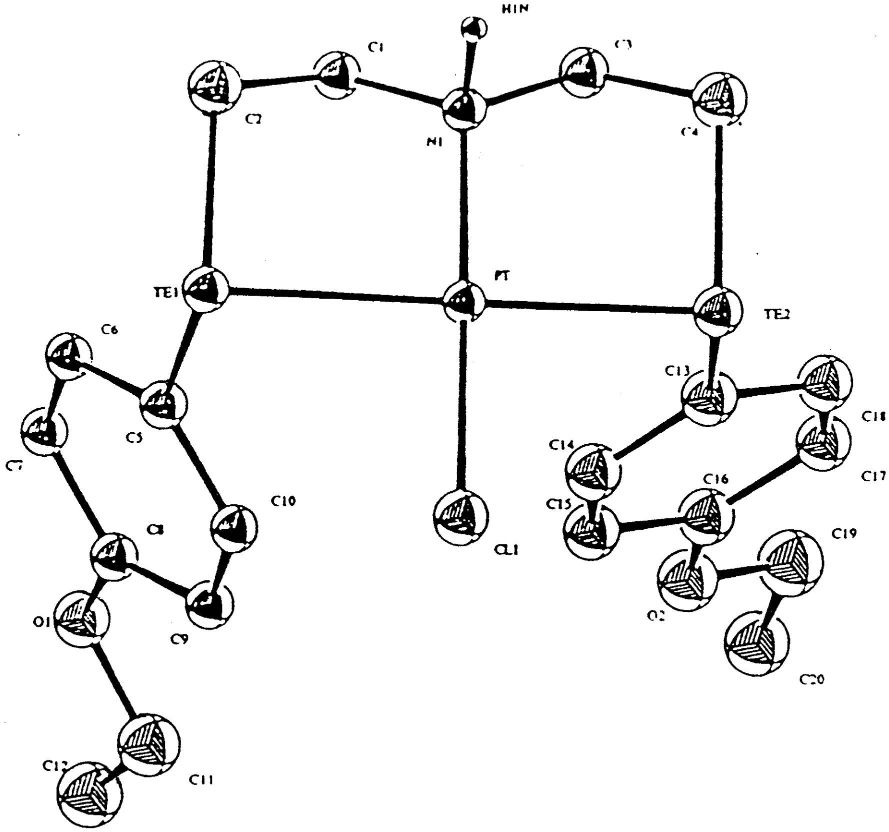
17c



17d

E = Te

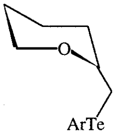
The (Te, N, Te) ligand **18** (Table 1) was first explored by Singh et al. [50] in 1990. Thereafter the crystal structure of $[Pt\{(2\text{-}(4\text{-}EtOC_6H_4Te)CH_2CH_2)_2NH\}_2Cl_2]\cdot CHCl_3\cdot H_2O$ was reported [51]. The cationic complex has a square planar geometry (**18a**). The Pt–Te bond length is 2.557(2)/2.564(2) Å. Very recently multidentate hybrid telluroether ligands **20**–**22**, **24**, **28** and **29** (Table 1) were designed by Srivastava et al. [53], by reacting ArTeNa or Na_2Te with appropriate organic halides but results of investigations on their ligand chemistry are yet to be reported. The ligation [54] of $NH_2CH_2CH_2CH_2TeAr$ (**23**), which is a homolog of **16**, with Pd(II) and Pt(II) is almost parallel to its selenium analog. The ligand **23** coordinates through both NH_2 and ArTe groups as revealed by ^{1}H-, $^{13}C\{^1H\}$- and $^{125}Te\{^1H\}$-NMR spectra, except in [MePdCl(**23**)$_2$] where bonding is proposed only through Te and the two ligands are presumably *trans* to each other. The ^{31}P chemical shift of [PtCl(**23**)PPh_3] is reported upfield with respect to that of *cis*-$[PtCl_2(PPh_3)_2]$, along with a decrease in the value of ${}^1J$(Pt–P). The reason assigned to this observation is strong σ-donation by Te as the ^{125}Te chemical shift of **23** (δ 460–473 ppm) undergoes a deshielding of 233 ppm on ligation. A ligand closely related to **23**, bis(3-aminopropyl)telluride and its Pd(II) and Pt(II) complexes were also reported [55], but without structural characterization. However, this ligand is proposed to behave as a tridentate (N, Te, N) donor on the basis of spectroscopic data. Rh(I, III) complexes [56] of **10** and **18** were characterized spectroscopically. They have stoichiometry $[RhCl(L)]_2$ or $[RhCl_3(L)_n]$ ($n = 2$ for **10** and $n = 1$ for **18**) and exhibit broad ^{1}H-NMR spectra due to dissociation and recombination equilibria of the various ligands including chloride.



18a

Aryltelluroacetates of Pd(II) and Pt(II) were reported [57] very recently whereas the synthesis of 2-aryltelluroacetic acid was published in 1990 [58]. These acetates are formulated as chloro-bridged dimers on the basis of IR, ^{1}H- and ^{13}C-NMR spectral data. The metal complexes of (Te, O) ligands are generally difficult to crystallize as a single crystal suitable for X-ray diffraction. Therefore, no single crystal structure of a metal complex of any (Te, O) ligand is so far known. However, tellurium is capable, like phosphorus, in stabilizing [59] alkoxides of Pd(II) or Pt(II) which are otherwise highly prone to β-elimination. Complexes of **27** (Table 1; synthesized by reacting $ClCH_2CHOHCH_2OH$ with $ArTe^-$), having composition $[MX_2 \cdot \mathbf{27}]_2$, $[MX_2(\mathbf{27})_2]$, $[(PPh_3)_2MCl(\mathbf{27})]ClO_4$ and $[(PPh_3)_2M(\mathbf{27})](ClO_4)_2$ (M = Hg(II), Pd(II), Pt(II); X = Cl, Br) were reported [60]. Their IR, ^1H-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR data suggest that the Te ligand exhibits monodentate character, bonding through tellurium only in all the complexes, except in the last, where the metal is proposed to coordinate also through an OH group, but without its deprotonation.

Four new (Te, O) ligands **32**–**35** (Table 1) have been designed [62,63] and their complexes having composition $[MCl_2(L)_2]$, $[M(L)_2](ClO_4)$, $[M(dppe)(L)_2](ClO_4)_2$, $[M(PPh_3)_2(L)_2](ClO_4)_2$ and $[M(phen)(L)_2](ClO_4)_2$ (M = Pd(II) or Pt(II), L = **32**–**35**) were reported. The formation of a chelate ring when $[MCl_2(L)_2]$ reacts with $AgClO_4$ to give $[M(L)_2](ClO_4)_2$, results in a chelate or coordination shift in ^{125}Te resonance, which is downfield and of the order of 120 ppm when the chelate ring is five-membered but upfield and small (~ 12 ppm) when the ring size is six-membered. Most of the earlier reported coordination shifts do not involve the same hemilabile ligand in monodentate and chelating mode, but are based on the use of two different ligands [10].



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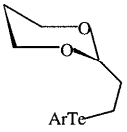

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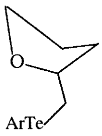

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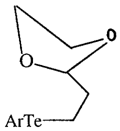
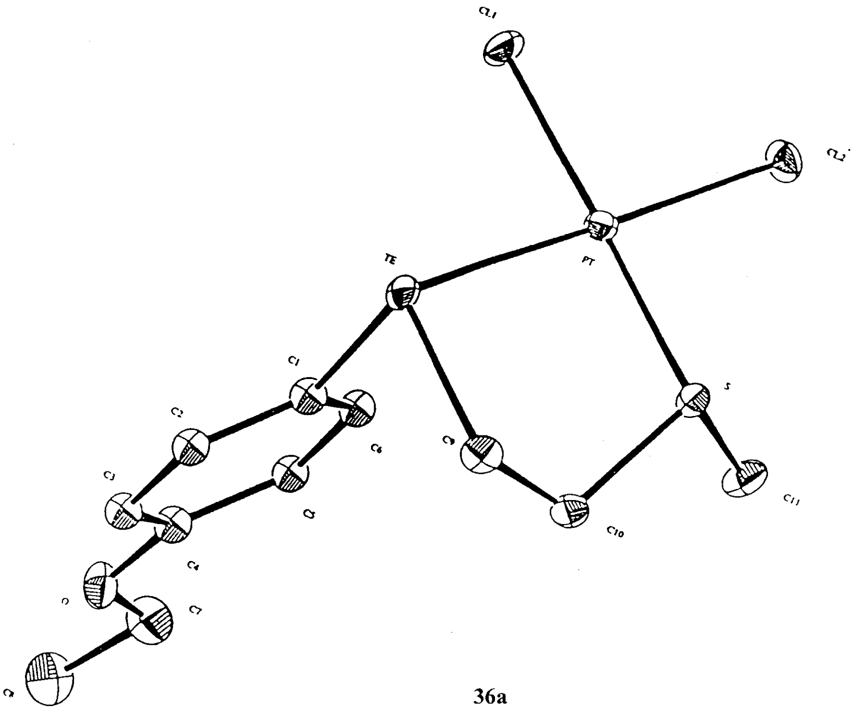


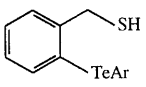
35

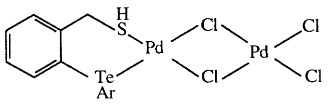
The *trans* configuration has been found favorable for complexes of **32**–**35**. The coordinated ligands are readily oxidized by singlet oxygen. The quenching of $^1O_2$ follows first-order kinetics, as monitored spectrophotometrically, in the case of the palladium complex having 1,10-phenanthroline as a co-ligand. The ligand $MeSCH_2CH_2TeAr$ (**36**) was the first (Te, S) ligand [64]. In its platinum(II) complex (**36a**) was [42] the Pt–Cl *trans* to Te is 2.336(3)) Å whereas the one *trans* to S is shorter (2.324(2) Å). Moreover, in this square planar complex both Pt–Cl bond lengths are typical of those *trans* to a π-bonding ligand. Its Pt–Te bond length 2.514(1) Å is shorter than those reported earlier, when Te is *trans* to another Te [65] or a P atom [38] (2.575(1) or 2.553(1) Å). The mixed ligand complexes [66] of **36** with $Me_2NCH_2CH_2TeAr$ and $MeSCH_2CH(OH)CH_2SMe$ (L) having composition

$[Pd(\mathbf{36})(L)](ClO_4)_2$ and a 1:2 complex with **36**, $[Pd(\mathbf{36})_2](ClO_4)_2$ were studied. The ^{125}Te resonance of $[Pd(\mathbf{36})_2](ClO_4)_2$ appearing in a fresh solution at δ 589 ppm is split into two signals (other appears at δ 668 ppm) after 3 h. Similarly for $[Pd(\mathbf{36})(Me_2NCH_2CH_2TeAr)](ClO_4)_2$, an additional ^{125}Te resonance appears at δ 686 ppm along with other two already present at δ 569 and 610 ppm. These observations imply that these mixed complexes originally *cis*, change partially in solution to the *trans* form, resulting in an equilibrium mixture. The reaction of Na_2Te with $RSCH_2CH_2Cl$ ($R = Ph/Me$) results in $(RSCH_2CH_2)_2Te$ (**37**) which is unstable [67,68]. It is possible to stabilize the methyl derivative [67] by reacting with $[(PPh_3)_2M(ClO_4)_2]$, M = Pd(II), Pt(II) or Hg(II). The multiple signals observed in the ^1H-NMR spectra of these complexes are interpreted by presuming the coordination of **37** in a bidentate mode (through Te and S) and an exchange of sulfur of pendent arm with the coordinated sulfur in solution. However, attempts to stabilize a phenyl derivative [68] did not succeed. 2-(Aryltelluro)benzyl mercaptan (**38**) [69] is an interesting (Te, SH) donor which acts as a bidentate ligand without deprotonation in its Pd(II) complex (**38a**). The reaction of $HgCl_2$ with **38** results in ArTeHgCl. After the synthesis of ligand **39** [46], no report on its complexation has so far appeared. A Schiff base **40** and its Co(II) complexes of stoichiometries $[CoBr_2(\mathbf{40})]$, $[CoBr_2(\mathbf{40})_2]$, $[CoBr(\mathbf{40}\text{-}H)]$ and $[CoBr(\mathbf{40})_2]BPh_4$ were reported [70] along with a Co(III) species $[CoBr_2(\mathbf{40})_2]BPh_4$. However, the reported coexistence of both bridging and chelating modes of **40** in $[Co(\mathbf{40})_2Br_2]$ is not substantiated, except for the IR spectral data. The palladium(II) complex, $[PdCl_2(\mathbf{41})_2]$, of a Schiff base **41** [71] have also been reported.



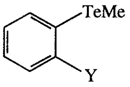
36a

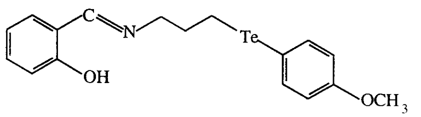




Ar = C_6H_5, 4-$MeOC_6H_4$, 4-$EtOC_6H_4$

38 **38a**

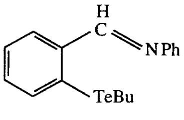


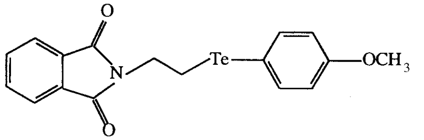


Y = SMe, SeMe, PMe_2, $AsMe_2$ $SbMe_2$

39 **40**

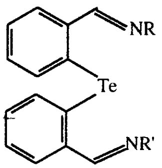
The first (Te, N, O) ligand **42** [72] exhibits Pd(II) complexes, where the ligand **42** behaves as (Te, N) as well as a (Te, N, O) donor on the basis of ^{1}H-NMR and IR data.

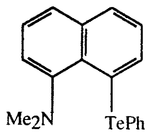




41 **42**

Some organotellurium compounds (**43** and **44**) [73,94] could act as interesting hybrid organotellurium ligands, but no reports on their ligand chemistry have appeared.



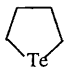


43 **44**

R =R' = *$CH(CH_3)C_6H_5$
*$CH(CH_3)$*$CH(OH)C_6H_5$; R' = Bu

2.4. Cyclic telluroethers

Morgan and Burstall first reported [75] a complex of a cyclic telluroether, $[HgCl_2L_2]$ (L = tellurocyclopentane (**45**) in 1931. The complexation of cyclic telluroethers reported up to 1981 is largely covered in the review of Gysling [6]. The ligands **46**–**55** represent some such cyclotelluroethers. Thereafter, Russian workers reported complexes of 10-alkylphenotellurazine [76] and 9H-telluraxanthane [77] with Hg(II), Pd(II), Ag(I) and Rh(I/III). A series of square planar Pd(II) complexes of cyclic telluroethers **45**, **52** and **53**, having stoichiometry $[PdX_2L_2]$ (X = Cl, Br, I; L = **45**, **52** or **53**) has been reported by Khanna and Singh [78]. On the basis of ^{1}H-NMR, far-IR and UV–vis spectra, *trans* geometries are proposed for all the complexes, except those of **45**.



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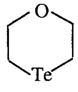

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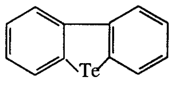

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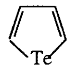

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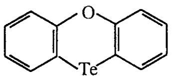

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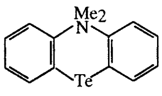

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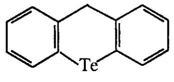

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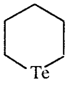

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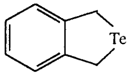

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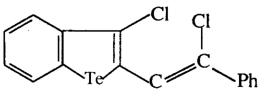

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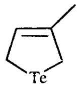
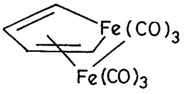


55

The complexes of **45** are mixtures of both *cis* and *trans* isomeric forms. The Rh(III) complexes [79] of **45**, **46**, **54**, **55**, chloro and dimethyl chloro derivatives of **55** (stoichiometry $[RhCl_3{\cdot}L_3]$) were synthesized along with [(COD)RhCl(**45**)]. Their ^{1}H-NMR and IR spectra were used mainly to conclude that these Rh(III) complexes are *fac* isomers. The cyclotelluroether ligands can be easily substituted by carbonyl groups. The synthesis of $[(\eta^5\text{-}C_5H_5)Nb(CO)_3($**45**$)]$ by such a strategy and kinetics of substitution of tellurocyclopentane with phosphine were reported by Freeman and Basolo [80]. The substitution of **45** is slowest in comparison to its other chalcogen analogs (order Te < Se < S < O), suggesting the strongest σ-donation characteristics of Te among chalcogens. The first structurally characterized [81a] Pd(II) complex of tellurocyclopentane(**45**) is *trans*-$[PdCl_2($**45**$)_2]$, in which Pd–Te is 2.593(3) Å and Pd–Cl 2.319(8)/2.326(8) Å The complexes $[PtCl_2($**45**$)_2]$ and $[RhCl_3($**45**$)_3]$ are isomeric mixtures (*cis*–*trans* and *fac*–*mer*, respectively) in solution on the basis of spectral data, including ^{125}Te- and ^{195}Pt-NMR, but the Pt(II) complex in the solid state is predominantly a *cis* isomer. However, $[MBr_2($**45**$)_2]$ or $[MI_2($**45**$)_2]$ (M = Pd/Pt(II)) are only *trans* isomers. The complexes having composition $[M($**53**$)_4]BF_4/PF_6$, where M = Cu or Ag were reported [81b] recently. They adopt distorted tetrahedral structures at the metal centers, with the tellurophene ligated via a Te-based lone pair, the Cu–Te 2.587(2)–2.596(2); Ag–Te 2.767(7)–2.810(5) Å. Singh et al. [82] examined reactions of **47**, **48** and **53** with $Fe_3(CO)_{12}$. In the first two cases FeTe is formed along with **56** and **57**. In the reaction of **53**, the product is a novel dimer of a detellurated C_8H_8 fragment which is coordinated to an $Fe(CO)_3$ unit as shown in **58**. The released tellurium is isolated as $[Fe_3Te_2(CO)_9]$. The reaction [83] of $[\{Rh(\eta^5\text{-}C_5Me_5)Cl_2\}_2]$ with tellurophene **48** in the presence of $Ag(O_3SCF_3)$ gives $[Rh(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_4H_4Te](O_3SCF_3)_2$ which, on reaction with $[Co(\eta^5\text{-}C_5H_5)_2]$, gives **58a**. The reaction of $Fe_3(CO)_{12}$, with **58a** gives another novel compound **58b**.



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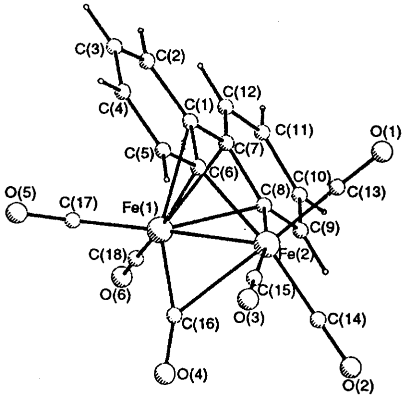

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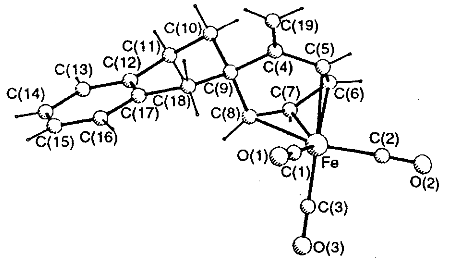

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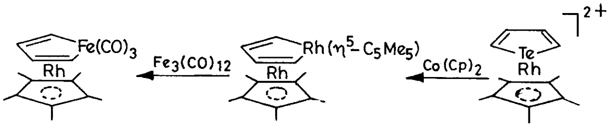
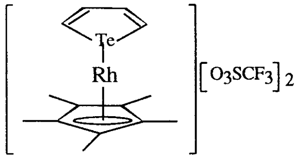


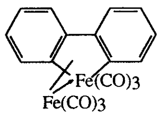
58b

58a

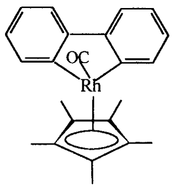
The reaction of **51** with $[\{Rh(\eta^5\text{-}C_5Me_5)Cl_2\}_2]$ in the presence of $Ag(O_2SCF_3)$ gives $[Rh(\eta^5\text{-}C_5Me_5)$ (**51**)$](O_3SCF_3)_2$ (**58c**) in which **51** is bonded, only through Te. The reaction of **58c** with $Co(Cp)_2$ and $Fe_3(CO)_{12}$ gives **58d** along with **58e**. In the absence of $Ag(O_2SCF_3)$ the reaction of **51** results in **58f**. The reaction of $Fe_3(CO)_{12}$ with benzoisotellurazole yields $(C_6H_4CHNTe)_2Fe_3(CO)_7$ (**58g**). The detelluration of 2-methylbenzotellurazole on reaction with $Fe_3(CO)_{12}$ has also been reported [84a] and the two crystalline products identified are $C_{18}H_7NFe_3O_{10}$ (**58h**) and $C_{14}H_7NFe_2O_6$ (**58i**). The 2-telluraphthalide [84b] reacts with $Fe_3(CO)_{12}$ resulting in a novel compound **58j** whereas the reaction of 2-telluraphthalic anhydride with $Fe_3(CO)_{12}$ results in **58k**.



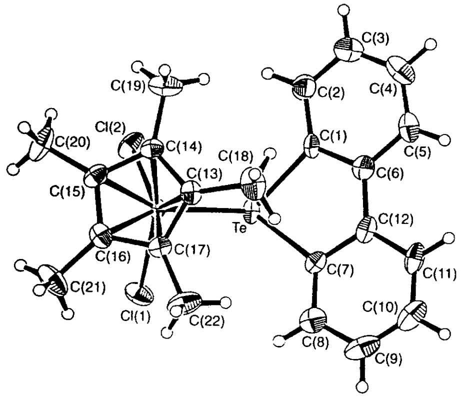
58c



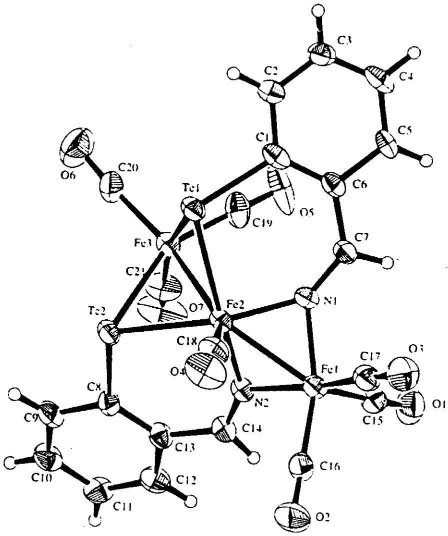
58d



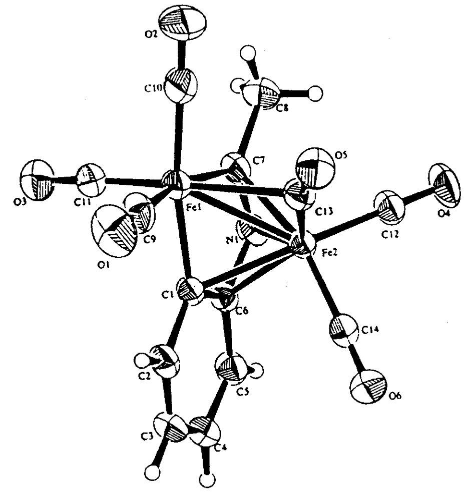
58e



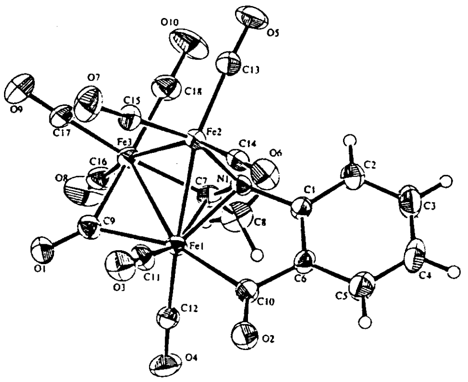
58f



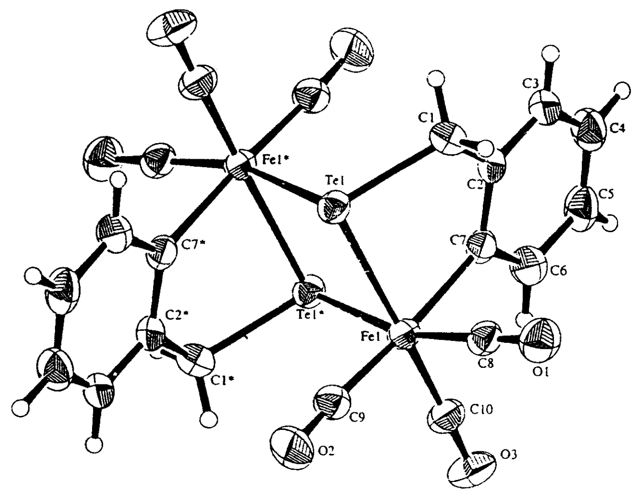
58g



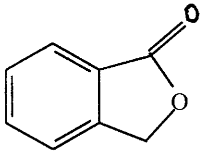
58h



58i

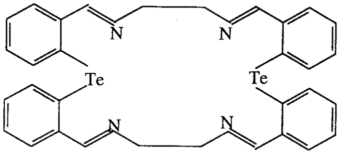


58j



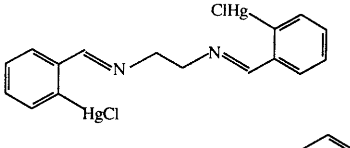
58k

A macrocyclic Schiff base [85] **59** was synthesized by the reaction of bis(2-formylphenyl)telluride with ethane-1,2-diamine. Its reduction with $NaBH_4$ reduces the azomethane groups resulting in a tetrazamacrocycle. The reaction of $HgCl_2$ breaks the ligand **59** resulting in **60** and **61**. However, $[PdCl_2(C_6H_5CN)_2]$ reacts with **59** giving a 2:1 (M:L) complex in which each $PdCl_2$ unit is linked with one (Te, N) pair as the ^{125}Te resonance of the complex appears as a deshielded singlet at, δ -77.5 ppm with respect to that of free **59** (δ -226.5 ppm).



59

The tellurocrown ethers such as 10-tellurobenzo-15-crown-5, 19-tellurodibenzo-24-crown-8,10-tellurabenzo-18-crown-6 and 11-tellurabenzo-16-crown-5 form [86] by reaction of bis(2-hydroxymethyl)telluride with diolditosylates.



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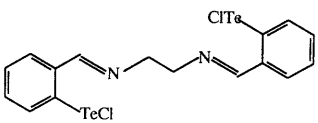
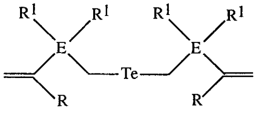


61

The platinum complex of the first of these telluracrown ethers was studied for its catalytic activity [87] for hydrosilation of olefins by triethoxysilane. However, the activity was found to be lower in comparison to the corresponding selenacrown ethers. Recently tellurium-containing heterocycles are reviewed by Detty and O'Regan [88].

2.5. Other neutral organotellurium ligands

The tellurated olefins and alkynes and diorgano ditellurides are organotellurium ligands, which have gained some attention in the recent past. Abel et al. [89] reported dialkenyl telluroethers, **62** and their platinum(II) and rhodium(I) complexes. The ligands synthesized by the reaction of Na_2Te with alkenyl halide, exhibit a bidentate coordination mode (binding through Te and one alkene function) in the square planar platinum complex, but act as a tridentate with Rh(I).

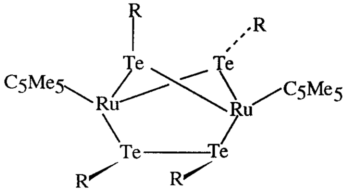


E = C, Si; R = R^1 = H; R = Me, R^1 = H

62

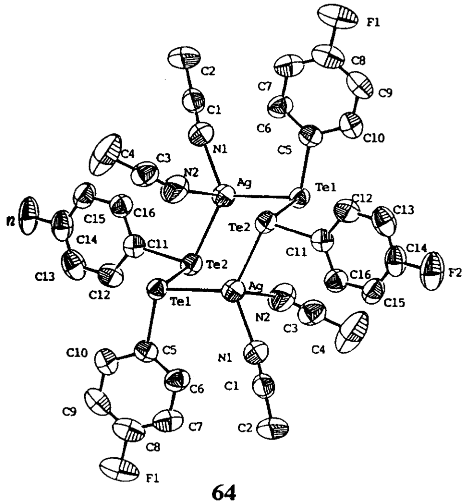
In the crystal structure of *cis*-dibromo(3,3,7,7-tetramethyl-5-tellura-3,7-disilanone-1,8-diene)platinum(II), the Pt–Te bond length is 2.544(1) Å whereas Pt–Br is 2.472(1) Å when *trans* to Te and 2.444(1) Å when *trans* to a double bond. The platinum complexes are fluxional, exhibiting exchange of the alkene moieties (energy barrier $\Delta G^{\ddagger}_{T}$ 37.0–49.3 kJ mol^{-1}). The chelation parameter in the ^{125}Te-NMR of the Pt(II) complexes is ~75 ppm as expected for such a chelate ring that due to fluxional nature has a time averaged ring structure of further enlarged size. The tellurated alkynes, synthesized by reacting $(2,4,6\text{-}Me_3C_6H_2)TeBr$ with $LiC{\equiv}CR$ (R = C_6H_5, $SiMe_3$), on reaction with $Co_2(CO)_8$ give side on coordinated complex $[(\eta^2\text{-}((2,4,6\text{-}Me_3C_6H_2)TeC{\equiv}CR)Co_2(CO)_6]$ in which there is no interaction between cobalt and tellurium [90]. In the complexes $Li[W(OMe)_5(EtTeC{\equiv}CTeEt)]$ and $[WCl_4(PhC{\equiv}CTeC_4H_9)(THF)]$ [91,92], the alkyne ligand is coordinated in a metallacyclopropane like fashion, without invoking tellurium. In the second complex the alkyne bonding mode is similar, resulting in a seven coordinated W (surrounded by four Cl, THF and two C donor atoms).

The ligand chemistry of diorganoditellurides has also received attention in the recent past. In the reaction of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$ with Me_3SiTeR (R = $4\text{-}MeC_6H_4$, C_6H_5), R_2Te_2 is generated at the metal center, resulting finally in $(\eta^5\text{-}C_5Me_5)Ru(\mu_2\text{-}RTeTeR)(\mu_2\text{-}TeR)_2Ru(\eta^5\text{-}C_5Me_5)$ (**63**) [93], when the bridging by ditelluride ligand is very symmetrical (both Ru–Te = 2.540(3) Å). Liaw et al. [35a] have reported an interesting coordination mode of diorganoditelluride in $[Ag_2(NCCH_3)_4(\mu_2\text{-}(p\text{-}C_6H_4F)\ Te\text{–}Te(p\text{-}C_6H_4F))_2]$ (**64**); the two silver atoms are bridged by two ditellurides resulting in a six-membered Ag_2Te_4 ring system. The Te–Te bond length observed in this complex is 2.752(1) Å, longer than PhTeTePh (2.712 Å) [35c] but shorter than the value observed in the case of **63** (2.794(5) Å).



63

All Ag–Te bond lengths are nearly equal. A polymeric $[(\mu_2\text{-MeTeTeMe})Cu(\mu\text{-Cl})]_n$ (**65**) contains copper atoms bridged by MeTeTeMe units, resulting in chains, which are linked with each other through chlorobridges. The geometry of Cu(I) in **65** is distorted tetrahedral. The Te–Te distance (2.755(1) Å) in this copper complex is close to that of other intact Te–Te distance observed in case of **64**. The Cu–Te bond length is 2.529(2) or 2.565(2) Å. The presence of bridging diorganoditelluride was also reported in the complex $[(PtIMe_3)_2(p\text{-MeOC}_6H_4Te)_2]$ [29]. The Te–Te distance is 2.749(2) Å and the two Pt–Te bond distances are similar.



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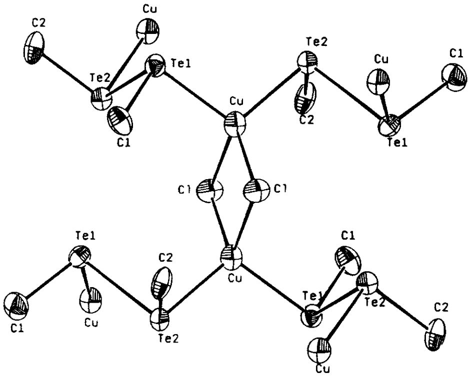
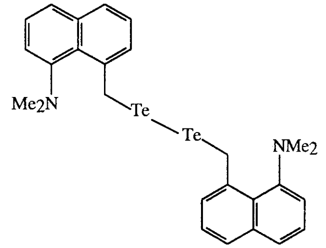
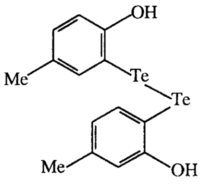


65

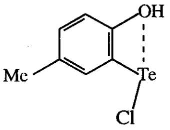
The functionalized diorganoditellurides **66** [94] and **67** [57a] were synthesized by oxygen oxidation of ArTeLi and metabisulfite reduction of $ArTeCl_3$, respectively.





66 **67**

The reaction of **66** with Pd($C_6H_5CN)_2Cl_2$ resulted in elemental tellurium [94]. The reaction of **67** with $CuCl_2$ gives **68** and with $HgCl_2$ a material of composition $ArTeHgCl_2$, which is proposed to be **69**.



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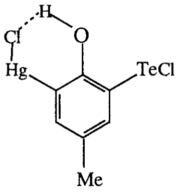
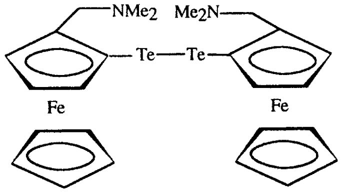


69

A novel diorganoditelluride **69a**, which is a potentially tetradentate hybrid organotellurium ligand has been synthesized [74] but its ligation has not been explored. 4′-(2-Pyridylmethyleneamino)benzo-10-tellura-15-crown-5 (**69b**) and its Cu(I) complex [Cu($PPh_3)_2$(**69b**)] has been recently synthesized [57b], but only Se and S analogs of the complex are structurally characterized. The crown ether part remains as a dormant arm. The encapsulation of metal ions by the crown ether cavity present in these complexes, has been explored by electronic absorption and emission spectra. Cd^{2+} ions are bound in preference to Na^+, indicating that the hard–soft acid–base factor plays a dominant role rather than size–match selectivity in governing the ion binding properties.



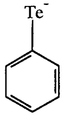
69a

3. Anionic organotellurium ligands

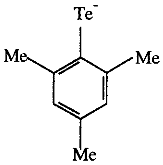
The chemistry of metal tellurolates was reviewed in 1995 by Arnold [17], covering literature largely up to 1994. Dean and Vittal [13] have reviewed (in 1992) the developments in adamantane-like tellurolate bridged cages of the zinc group elements. An overview of tellurolates of coinage metals is also included in a review on thiolates published by Grove and van Koten [95]. Several research papers have been published in the recent past on anionic organotellurium ligands. Their main focus is on four types of tellurolates **70**–**73**. The organic tellurolates are generated from R_2/Ar_2Te, R_2/Ar_2Te_2, $ArTeSiMe_3$ and $LiSi(SiMe_3)_3$ (via Te insertion).

RTe^-

70



71



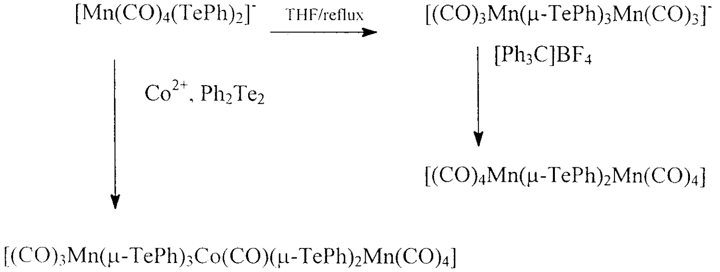
72

R_3Si-Te

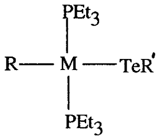
R= Me / $SiMe_3$

73

Both terminal and bridging modes have been reported for these ligands. The reaction of $Re(CO)_5Cl$ with NaTePh yielded a structurally characterized octahedral complex $PhTeRe(CO)_5$ [22]. Oxidative addition of Ph_2Te_2 to $[Mn(CO)_5]^-$ gives *cis*-$[Mn(CO)_4(TePh)_2]^-$ which may be crystallized as *cis*-$[Na(18\text{-crown-}6)(THF)]_2[Mn(CO)_4(TePh)_2]$ (**74**) [96]. The anion of **74** undergoes a variety of reactions shown in Scheme 1. The metal ions have a geometry very close to octahedral. The reaction of ditelluride Ph_2Te_2 with Me_3N adduct of alane or gallane gives a product $[Me_3N{\cdot}Al/Ga(TePh)_3]$. The aluminum derivative has been shown to be a four coordinated monomeric species in the solid state by X-ray crystallography [97]. The diphenyltelluride(Ph_2Te) [98] and silyl/germyl/stannyl telluride [99] on oxidative addition to $M(PEt)_n$ ($n = 3$ or 4 $M = Pt$, Pd or Ni) results in **74a**. However, in the case of Ni the complex could not be isolated as a pure product. When an unsymmetrical telluride is oxidatively added, the probability of the lighter group remaining with tellurium has been found to be greater.



Scheme 1.



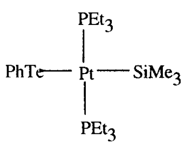
$$\begin{array}{c} PEt_3 \\ | \\ R\!-\!M\!-\!TeR' \\ | \\ PEt_3 \end{array}$$

R = Ph, $SiMe_3$, $GeMe_3$, $SnMe_3$

R' = Ph, 4-biphenyl, Bu

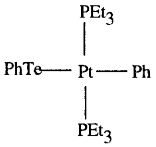
74a

The *cis* isomer of **74a** is probably formed in the beginning, but it is readily converted to the *trans* form. The silyl group-containing complex **74b** decomposes at room temperature into **74c**, **74d**, $PhSiMe_3$ and $(Me_3Si)_2Te$.



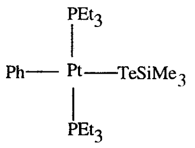
$\mathrm{PhTe{-}\underset{PEt_3}{\overset{PEt_3}{Pt}}{-}SiMe_3}$

74b



$\mathrm{PhTe{-}\underset{PEt_3}{\overset{PEt_3}{Pt}}{-}Ph}$

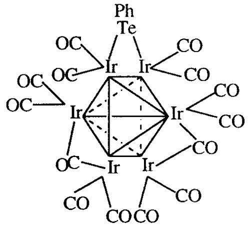
74c



$\mathrm{Ph{-}\underset{PEt_3}{\overset{PEt_3}{Pt}}{-}TeSiMe_3}$

74d

The clusters **75**–**79** of Ag and Cu given in Table 2 have been designed [100,101] by reacting AgCl or CuCl with PEt_2Ph, PPh_3 or PMe_3 and $PhTeSiMe_3$. The cluster **80** is obtained by photochemical activation of **79**. The reagent $MeTeSiMe_3$ is an equally good source of the RTe^- group and high nuclearity copper–tellurium clusters **82**–**83** have been synthesized from it [102]. However, cluster formation is very much dependent on the ancillary phosphine used. Iridium clusters $[PPh_4][Ir_6(CO)_{12}(\mu\text{-}CO)_2(\mu\text{-}TePh)]$ (**84**) and $[Ir_6(CO)_{12}(\mu\text{-}CO)(\mu\text{-}TePh)_2]$ (**85**) were synthesized [103] by refluxing $[Ir_6(CO)_{15}]^{2-}$ with Ph_2Te_2 in THF.



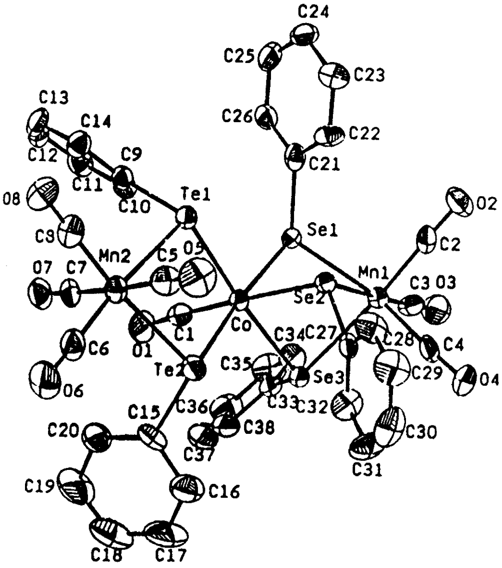
84

In these clusters there is an octahedral Ir_6 core. Each Ir has two terminal CO groups. The structure of **85** is similar to that of **84**, except one bridging CO is replaced by a PhTe bridging group. The coordination around the Te atoms is

Table 2
Tellurolate clusters

Metal	Cluster	Ref.
Ag	$Ag_9(\mu_3TePh)_9(PEt_2Ph)_6$ (**75**)	[100]
	$[Ag_{14}(\mu_3\text{-}TePh)_{12}(\mu_6\text{-}Te)(PEt_2Ph)_8]$ (**76**)	
	$[Ag_{14}(\mu\text{-}TePh)_2(\mu_3\text{-}TePh)_6(\mu_4\text{-}TePh)_4(\mu_6\text{-}Te)(PMe_3)_8]$ (**77**)	
	$[Ag_{10}(\mu_3\text{-}TePh)_{10}(PMe_3)_2]_\infty$ (**78**)	
Cu	$[Cu_6(TePh)_6(PetPh_2)_5]$ (**79**)	[101]
	$[Cu_{50}(\mu_3\text{-}TePh)_{20}(Te)_{17}(PEtPh_2)_8][PEtPh_3]_4$ (**80**)	
	$[Cu_{12}(\mu_6\text{-}Te)_3(\mu_3\text{-}TePh)_6(PPh_3)_6]$ (**81**)	
	$[Cu_{11}(\mu_3\text{-}TeBu^n)(\mu_4\text{-}TeBu^n)_2(\mu\text{-}Te)(PPh_3)_5$ (**82**)	[102]
	$[Cu_{18}(\mu_4\text{-}TeBu^n)_6Te_6(PPr^n_3)_8]$ (**83**)	
Ir	$PPh_4[Ir_6(CO)_{12}(\mu\text{-}CO)_2(\mu\text{-}TePh)]$ (**84**)	[103]
	$[Ir_6(CO)_{12}(\mu\text{-}CO)(\mu\text{-}TePh)_2]$ (**85**)	

pyramidal. On the basis of cyclic voltammetric studies it is shown that addition of $PhTe^-$ occurs upon oxidation of the parent cluster and the mechanism of reaction of Ph_2Te_2 is through the monoanion $[Ir_6(CO)_{15}]^-$, in contrast to that of Ph_2S_2 which is said to involve $[Ir_6(CO)_{15}]$.



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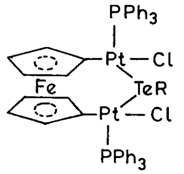
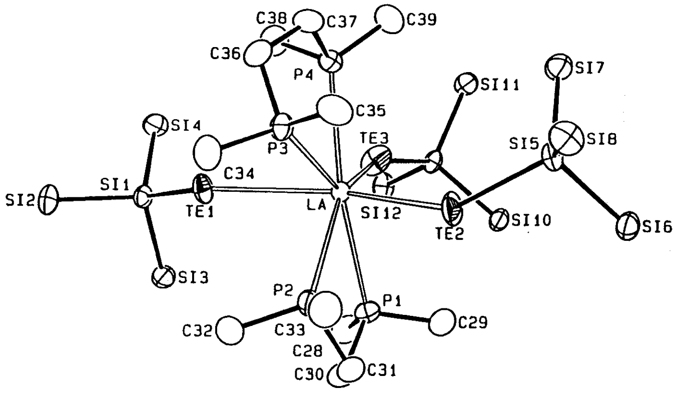
The complexes having a bridging RTe^- group were synthesized by using a metalloligand $[Mn(CO)_4(TePh)_2]^-$ which on reaction [104] with $BrMn(CO)_5$ gives $[(CO)_3BrMn(\mu\text{-}TePh)_2Mn(CO)_4]^-$ and $[Mn_2(\mu\text{-}TePh)_2(CO)_8]$. In the presence of $[Mn(CO)_4(SePh)_2]^-$ and $[Mn(CO)_4(TePh)_2]^-$ oxidation of Co^{2+} to Co^{3+} by Ph_2Se_2 results in a novel complex $[(CO)_4Mn(\mu\text{-}TePh)_2Co(CO)(\mu\text{-}SePh)_3Mn(CO)_3]$ (**86**) [105]. The cation $Me_2TeTeMe^+$ also acts as a source of $MeTe^-$ and its reaction with $Mn(CO)_5^-$ results first in $[MeTeMn(CO)_5]$ which dimerizes to $Mn_2(\mu\text{-}TeMe)_2(CO)_8$. A very novel organotellurol bridged complex **87** was reported by Onitsuka et al. [106]. The source of RTe^- in the reaction giving **87** is diorganoditelluride. The $MeTe^-$ group is generated [107] in a methanothermal reaction between $M_3(CO)_{12}$ (M = Fe, Ru) and Na_2Te_2 carried out in 0.5 ml of CH_3OH in the presence of Me_4NBr in a sealed Pyrex tube, and gives the cluster $[M_4(Te_2)_2(Te)_2(TeMe)_2(CO)_8]^{2-}$. The sterically demanding arenetellurol (**72**) forms complexes $[Mn(\mu\text{-}(\mathbf{72})]_n$ and $[Zn(\mu\text{-}\mathbf{72})_2]_n$ by protolysis of $Mn\{N(SiMe_3)_2\}_2(THF)]$ and $[Zn\{N(SiMe_3)_2\}_2]$ respectively with 2,4,6-MeC_6H_2TeH.



R = Me, Et, Ph

87

These complexes are structurally characterized [108,109]. The reaction [110] of Hg with $(2,4,6\text{-}Me_3C_6H_2Te)_2$ also gives $Hg(TeC_6H_2\text{-}2,4,6\text{-}Me_3)_2$. Arnold [17] has published several papers on the ligation of sterically hindered tellurol ligands $(Me_3Si)_3SiTe^-$ and Ph_3SiTe^-. A novel complex recently characterized structurally is $La\{TeSi(SiMe_3)_3\}_3(dmpe)_2$ (**88**) [111] (dmpe = 1,2-bis(dimethylphosphino)ethane). The Ce and Y analogs of **88** are also known. The three coordinate vanadium(III) complexes (**89**) [112] of the type $[(Me_3Si)_2N]_2VTeR]$ (R = $Si(SiMe_3)_3$ or $SiPh_3$ were synthesized in 60–80% yield by reacting $[(Me_3Si)_2N]_2V(Br)(THF)$ with $(THF)_2$-LiTeR. There is an agostic interaction between two C–H groups of amidotrimethylsilyl ligand at the vacant apical coordination site of V. Synthesis of homoleptic vanadium and molybdenum tellurolates of stoichiometry $[M\{TeSi(SiMe_3)_3\}_4]$ (**90**) and their structural characterization are reported [113].



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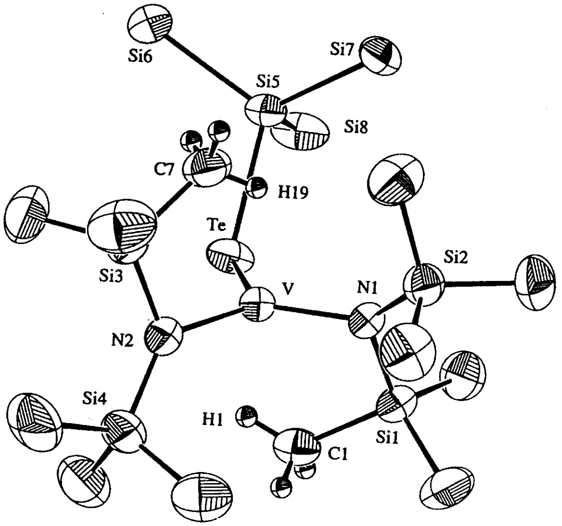

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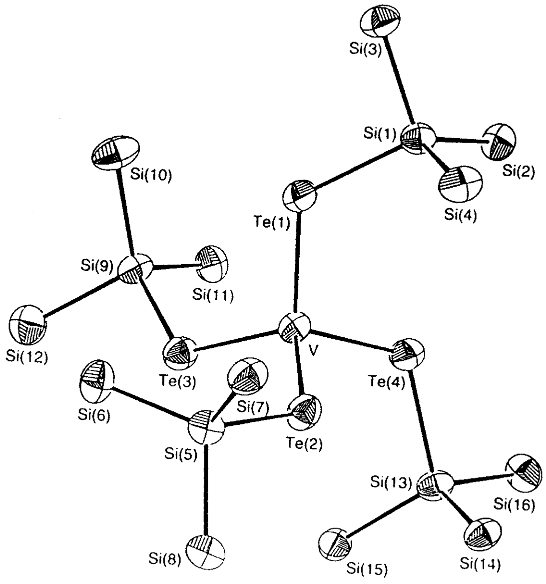

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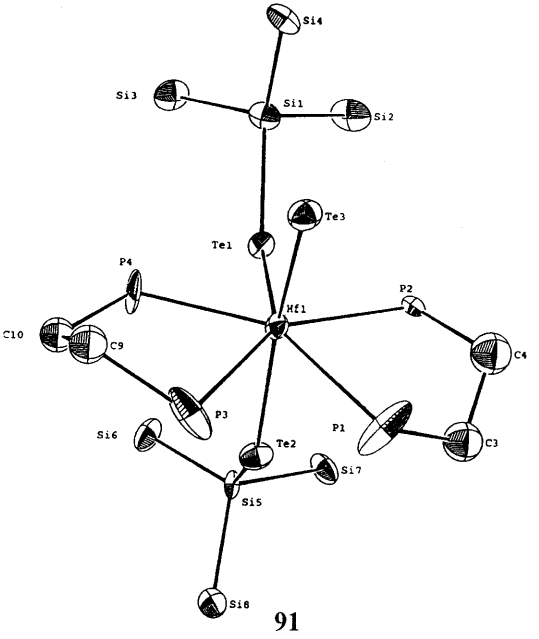
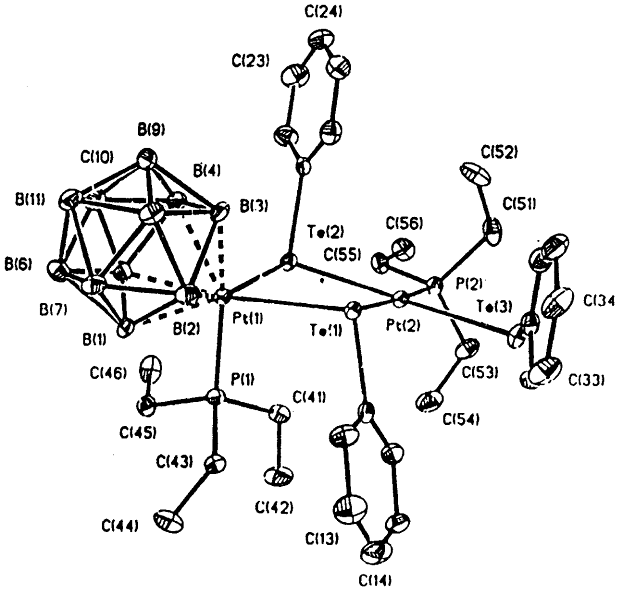
Metathesis reaction between $ZrCl_4$ or $HfCl_4$ and $(THF)_2LiTeSi(SiMe_3)_3$ or chalcogenolysis reaction between $M(CH_2Ph)_4$ and $HTeSi(SiMe_3)_3$ also gives $M[TeSi(SiMe_3)_3]_4$ types of derivative [114], which form adducts, $M[TeSi(SiMe_3)_3]_4 \cdot (NCAr)_2$ (Ar = xylyl) and $\{M[TeSi(SiMe_3)]_4(dmpe)\}$.



91

The second adduct on further reaction with dimethylphosphinoethane (dmpe) eliminates two $[TeSi(SiMe_3)_3]^-$ entities and gives seven-coordinate complex **91**. A novel stannyl tellurolate R_2SnTe^- was generated by reacting $[Cp^*Ti]_2(\mu\text{-}Te)$ or $Cp_2^*Ti(\eta^2\text{-}Te_2)$ with stoichiometric amounts of R_3SnH, which probably first results in an unstable compound $Cp_2^*Ti(H)TeSnR_3$ and finally $Cp_2^*TiTeSnR_3$ (R = Bu, Ph) which contains [115] a three coordinate complex of Ti. The Te insertion in $Cp_2^*TiSnPh_3$ prepared from Ph_3SnH and Cp_2^*TiH also results in the same product. The RTe^- ligand is known to generate cage type structures reviewed by Dean and Vittal [13] in 1992. Recently novel cages $[Ag_6(\mu_3\text{-}TeBu^n)_4(\mu\text{-}TeBu^n)_2(PEt_3)_4]$, $[Ag_{32}(\mu_3\text{-}TeBu^n)_{18}Te_7(PEt_3)_6]$, $[Ag_{48}(\mu_3\text{-}TeBu^n)_{24}Te_{12}(PEt_3)_{14}]$, $[Ag_{30}(TePh)_{12}Te_9(PEt_2R)_{12}]$ (R = Et or Ph) and $[Ag_{46}\{Te(mes)\}_{12}Te_{17}(PEt_3)_{16}]$ were designed [116] by reacting $RTeSiMe_3$ (Bu^n, Ph, mesityl, or $SiMe_3$) with AgCl in the presence of PEt_3/PEt_2R. The reaction [194] between $Na[Pt(PEt_3)_2(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ and PhTeI in THF has yielded a mixture of $[Pt(PEt_3)_2\{\eta^5\text{-}9\text{-}Te(Ph)CH_2Cl\text{-}7\text{-}CB_{10}H_{11}\}]$ (**91a**) and $[Pt_2(TePh)(\mu\text{-}TePh)_2(PEt_3)_2(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**91b**). Complex **91a** is a charge-compensated platinacarborane with a $Pt(PEt_3)_2$ and with the nido-7-CB_{10} framework carrying a $Te(Ph)CH_2Cl$ moiety at the boron vertex situated in the β site with respect to the carbon in the CB*B*BB ring ligating the platinum. Complex **91b** is a diplatinum species in which TePh bridges two Pt atoms as shown below.



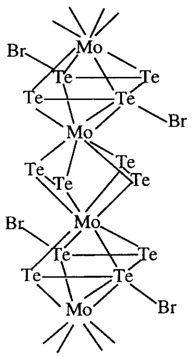
91b

4. Inorganic tellurium ligands

The chemistry of inorganic tellurium ligands is more diverse than that of the organotellurium ligands, as they have ligating abilities towards a larger number of metal ions and their complexes are characterized by extensive structural diversity. Until 1987 very few reports on metal complexes of these ligands appeared in the literature.

4.1. Halotellurium ligands

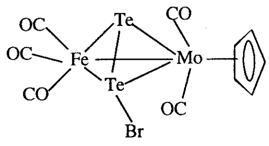
The metal chalcogenide halides, a class of ternary compound, e.g. NbS_2Cl_2 or $NbTe_2I_6$ are known [14]. Similarly $[TeX_3]^+$ ($X = Cl$, Br, I) ions have also been used as ligands [117–119], but in these instances they do not form a metal–tellurium bond. However, in the present article an emphasis is placed on those metal/tellurium/halide ternary systems, which have a metal–tellurium as well as a tellurium–halogen bond or interaction. Beck [14] has reported several crystals **92**–**94** which have, along with a M–Te bond, a Te–X interaction very close to that of a covalent bond, e.g. Te–Br ~ 260–303 pm, whereas the sum of covalent radii for Te and Br is 251 pm. The $Mo_4Te_7X_8$ ($X = Cl$ or Br) cluster is another example of a similar kind in which Te–Br = 260 pm and Te–Cl = 244 pm.



$MoTe_4Br$

Te-Br = 303 pm

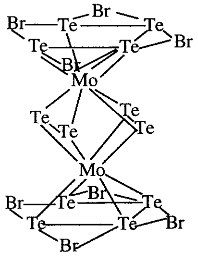
92



$(C_5H_5)(CO)_2MoFe(CO)_3(Te_2Br)$

Te-Br = 281 pm

93



$MoTe_6Br_3$

Te-Br = 281 pm

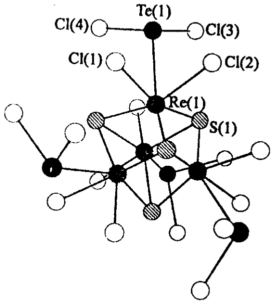
94

Eveland and Whitmire [120] have synthesised two novel clusters containing $TeCl_2$ or TeCl bonded through tellurium by the reaction given in Eq. (5).

$$[Te_2Fe_3(CO)_9] \xrightarrow[\text{in } CH_2Cl_2]{SOCl_2/SO_2Cl_2} [Fe_2(CO)_6(\mu\text{-}Cl)(\mu\text{-}TeCl)_2]_2[\eta^2,\mu_2,\mu_2\text{-}Te_2Cl_{10}]$$
$$\xrightarrow{\text{1 week}} [Fe_2(CO)_6(\eta^2,\mu_2,\mu_2\text{-}Te_4)(\mu\text{-}TeCl_2)] \quad (5)$$

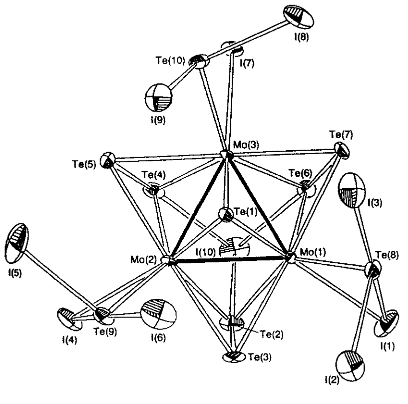
In the solid state cluster [121] $Re_6Te_{16}Cl_{18}$ and $Re_6Te_{16}Cl_6$ which contain $[Re_6Te_8]^{2+}$ units, the chlorotellurato ligand, $[TeCl_3]^-$, has a multidimensional structure. Lang et al. [122] have reported the synthesis of $Re_4(\mu_3\text{-}Te)_4(TeBr_2)_4Br_8$

from the elements and its structural characterization. Re_4Te_4 makes the inner skeleton of a heterocubane (Re–Re = 277/283 pm). To each Re atom is coordinated a $TeBr_2$ unit, resulting in the formal oxidation state of Re as IV. Mironov et al. [123] have synthesized clusters $Re_6Te_6Cl_6(TeCl_2)_2$ and $Re_6Te_8(TeBr_2)_6Br_2$ by reaction of $ReCl_5$ or Re_3Br_9 with Te at 450°C. In the first cluster a Re_6 octahedron resides inside the Te_6Cl_2 cube and the second in a Te_8 cube. The neutral $TeCl_2$ and $TeBr_2$ ligands are coordinated to the Re center (Re–TeCl/Br_2, 2.634(3)–2.667(3) Å). The Te–Cl and Te–Br bond lengths are in the ranges 2.330(9)–2.363(10) and 2.484(6)–2.503(6) Å, respectively. Three Re_4 clusters $Re_4(\mu_3\text{-}Q)_4(TeCl_2)_4Cl_8$ were synthesized [124] by reaction of $ReCl_5$ with elemental Q (Q = S, Se, or Te) at 400°C (350°C for Te). In these clusters there is a Re_4Q_4 cubane core. Each Re atom is coordinated with a neutral $TeCl_2$ ligand (Re–$TeCl_2$ = 2.634–2.738 Å) and two Cl.



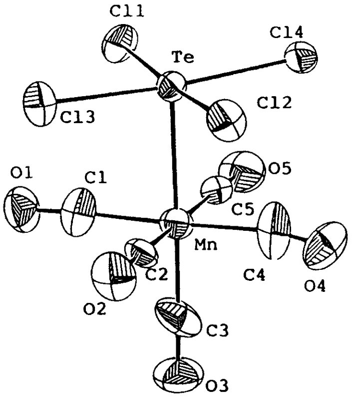
$Re_4(\mu_3\text{-}Q)_4(TeCl_2)_4Cl_8$ (95a)

Very recently a TeI_2 ligand-containing cluster $[Re_6Te_8(TeI_2)_6]I_2$ was reported by Fedin et al. [125]. It was synthesized by reacting Re_6Te_{15} with I_2 in a 1:9 ratio at 400°C. In this cluster neutral TeI_2 ligand coordinates also with Re (Re–TeI_2 = 2.670(1)–2.672(1) Å). The reaction of Pd, Te and $TeBr_4$ gives black air stable crystals of composition $PdTe_2Br_6$, which has been formulated on the basis of the crystal structure [126] as *cis*-$PdBr_2(TeBr_2)_2$. The presence of a TeI_3^- ligand has been shown in the cluster $[Mo_3(\mu_3\text{-}Te)(\mu_2\text{-}Te_2)_3(TeI_3)_3]I$ [127] synthesized from elemental Mo, Te and iodine. The Mo–TeI_3 bond length is 2.787–2.791 Å.



$[Mo_3(\mu_3\text{-}Te)(\mu_2\text{-}Te_2)_3(TeI_3)_3]I$ (95b)

A novel cluster containing the $Te_2I_6^{2-}$ ligand, $Nb_2(\mu_2\text{-}Se_2)(Te_2I_6)_2$ was synthesized [128] recently by reacting $Nb_2(\mu_2\text{-}Se_2)_2I_4$ with Te and I_2 in a 1:4:4 ratio at 500°C. The inner skeleton of the cluster is the dinuclear species $[Nb_2(\mu\text{-}Se_2)_2]^{4+}$ (Nb–Nb = 2.926(2); Se–Se = 2.310(2)/2.311(2) Å). Each Nb is ligated by $Te_2I_6^{2-}$ (Terminal Te–I = 2.735(2)–2.786(2); bridging Te–I = 3.175(1) to 3.261(2) Å). The species $[Cl_4TeMn(CO)_5]^-$ (**95c**) is formed [195] in the reaction of $[Mn(CO)_5]^-$ with $TeCl_4$. The Mn–Te bond length is 2.665(5) Å whereas Te–Cl is from 2.549(7) to 2.569(7) Å. The geometry around Mn is close to octahedral.



$[Cl_4TeMn(CO)_5]^-$ (95c)

4.2. Tellurido ligands

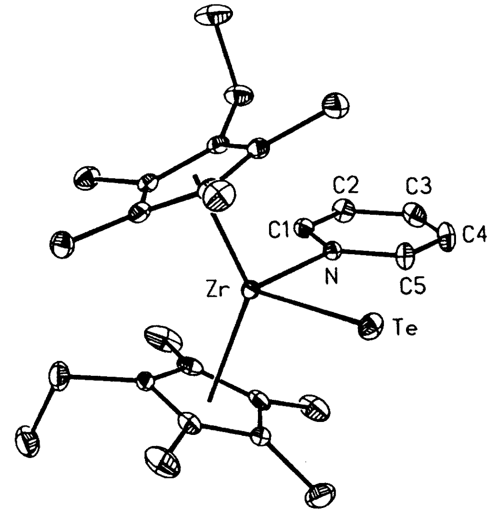
The chemistry of sulfide and selenide ligands is much more developed [12,129] than that of the tellurido ligand (Te^{2-}). The tellurido ligand is known in a terminal as well as a bridging form. The first example having a terminal tellurido ligand, $W(PMe_3)_4(Te)_2$ was reported in 1991 [130]. Important examples of tellurido complexes are summarized in Table 3. The compounds **96**–**101** were reported before the review of Roof and Kolis [129] and Kanatzidis and Huang [12] and, therefore, are not discussed here in detail. Elemental tellurium is a good source of tellurido ligand. Insertion of tellurium in a Sc–C bond of $\{meso\text{-}Me_2Si[(tert\text{-}C_4H_9)C_5H_3]_2\}Sc(CH_2SiMe_3)$ (DpScR) results in a tellurolate complex [136], which on heating is converted into DpSc–Te–ScDp which may also be synthesized (~ 74% yield) by the reaction of DpScH with $TePBu_3$. The $(DpSc)_2Te$ has been crystallized as a benzene solvate of its adduct with PMe_3 (Table 3, **102**). The Sc–Te–Sc coordination is linear (Sc–Te = 2.875(5) Å). Complex **103** (Table 3) was synthesized by the reaction [137] of $Pd^{2+}/Pt^{2+}/Ni^{2+}$ with dppe and NaTeH in CH_3CN/DMF. The platinum complex has two $\mu_3\text{-}Te^{2-}$ ligands and each platinum is coordinated with two Te and P atoms. (Pt–Te = 2.634(3), Te···Te = 3.432(2), Pt···Pt = 3.456(6) Å). The reaction [138] of $(\eta^5\text{-}C_5Me_4R)_2Zr(CO)_2$ (R = Me/Et) with elemental Te in

Table 3
Complexes of the tellurido ligand[a]

	Complexes	Ref.
1	$W(PMe_3)_2(Te)_2(\eta^2\text{-OCHR})$ (**96**)	[131]
2	$Fe_3(CO)_{10}(\mu\text{-Te})_2$ (**97**)	[132]
3	$(dmpe)_2M(TeR)_2(Te)$ (**98**) $M = Zr, Hf; R = Si(SiMe_3)_3$ (**99**)	[133]
4	$Cp^*Nb(PMe_3)(NAr)(Te)$ (**100**) $Ar = 2,6\text{-}C_6H_3Pr^i_2$	[134]
5	$[\{(Me_3Si)_2NCH_2CH_2\}_3NtaTe]$ (**101**)	[135]
6	$\{(CH_3)_2Si[t\text{-}C_4H_9)C_5H_3]_2Sc(PMe_3)\}_2(\mu\text{-Te})\cdot C_6H_6$ (**102**)	[136]
7	$[M_3(\mu_3\text{-Te})_2(dppe)_3](BPh_4)_2$ (**103**) $M = Pd, Pt, Ni$	[137]
8	$(\eta^5\text{-}C_5Me_4R)_2Zr(Te)(NC_5H_5)$ (**104**)	[138]
9	$Cs_{4.5}[Mo_3(\mu_3\text{-Te})(\mu_2\text{-Te}_2)_3(CN)I_{2.5}\cdot 3H_2O$ (**105**)	[139]
10	$[(C_5Me_5)_2Ti]_2(\mu\text{-Te})$ (**106**)	[140]
11	$M(PMe_3)_4(Te)_2$ (**107**) $M = Mo, W$	[141]
12	$Me_3N(H)Al(\mu\text{-Te})_2$ (**108**)	[142]
13	$[Co_6(\mu_3\text{-Te})_8(PEt_3)_6^{n+}(PF_6)_n$ (**109**) $n = 1$ or 2	[143]
14	$C_5R_5(CO)_2WPH(t\text{-Bu})Te$ (**110**) $R = H, Me$	[137]
15	$Pd_5(\mu_3\text{-Te})_4(dppe)_4]^{2+}$ (**111**)	[138]
16	$FeMo_2(\mu_3\text{-Te})(CO)_7(\eta^5\text{-}C_5H_5)_2$ (**112**)	[146]
17	$[\eta^4\text{-}Me_8taa]MTe$ (**113**) $M = Ti, V$	[147]
18	$[Fe_3(CO)_9Te]^{2-}$ (**114**)	[149]
19	$(Ph_4P)_2[Fe_2M(Te_2)(Te)(CO)_{11}]$ (**115**) $M = Mo, W$	[150]
20	$Na(Et_4N)_2[Fe_3W_2(Te_2)_3(Te)_2(TeMe)(CO)_{12}]$ (**116**)	[150]
21	$[M_4Te_4(Epr^i)_4]^{x-}$ (**117**) $[M = Fe; E = S; x = 2/3, M = Mn; E = Te; x = 4]$	[131]

[a] dppe, dimethylphosphinoethane; dmpe, dimethylphosphinoethane.

the presence of pyridine forms **104** (Table 3) The $(\eta^5\text{-}C_5Me_5)ZrTe(NC_5H_5)$ on reaction with Na_2O gives an oxo derivative$(\eta^5\text{-}C_5Me_5)ZrO(NC_5H_5)$ and with $Ph(CO)CH_3$ forms $(\eta^5\text{-}C_5Me_4R)_2ZrTeH(\eta^1\text{-OC(Ph)=CH}_2)$. The Zr=Te bond length is 2.729(1) Å, as predicted on the basis of covalent radii. The double bond covalent radius of Zr has been concluded as 0.07 Å shorter than that of a single bond. Complex **105** of C_{3v} symmetry (Table 3), was synthesized [139] by the reaction of aqueous KCN with Mo, Te and I_2 at 380°C. The reaction of elemental tellurium with Cp_2^*TiH results in paramagnetic $[(C_5Me_5)Ti]_2(\mu\text{-Te})$ (**106**) [140]. The Ti–Te bond length is 2.697(3) and 2.705(3) Å.



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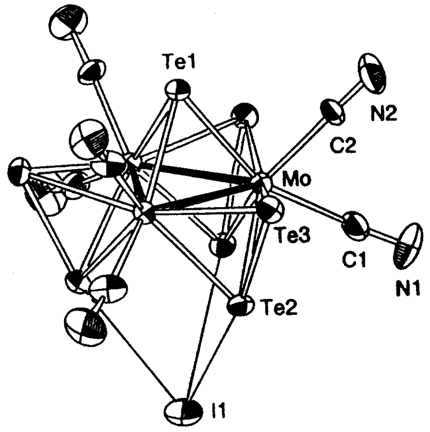

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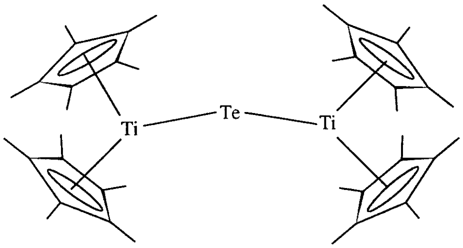
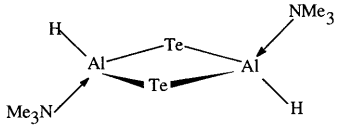


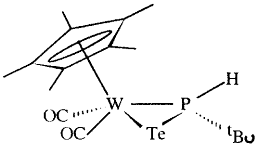
106

The tellurido ligand can be converted to Te_2^{2-}. The reaction [140] of **106** with $TePBu_3$ results in $[Cp_2^*Ti(Te_2)]$, which acts as an efficient 'Te' or 'Te_2' transfer agent. Its reaction with Hg gives back **106** and with RX the products are $Cp_2^*TiX_2$ and R_2Te_2. Another conversion of terminal Te^{2-} to Te_2^{2-} has been reported [141] and involves $W(PMe_3)_4(Te)_2$ (**107**) which reacts with RCHO (R = H, Ph) and Bu^tNC to give $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$. The adduct $[Me_3NaAlH_3]$ on reaction [142] with elemental Te results in **108** (Table 3). The tellurido clusters can be sometimes oxidized into mono or dicationic clusters without their disintegration.



108

For example $[Co_6(\mu_3\text{-}Te)_8(PEt_3)_6]$ can be easily oxidized [143] to **109** (Table 3). The tellurido ligand can bridge [144] metal and P donor linked to metal as in **110** which is formed by a [2 + 1] cycloaddition of Te to $C_5R_5(CO)_2W{=}PH(^tBu)$ (R = H or Me). The NaTeH also inducts the tellurido ligand in cluster formation. The $Pd(OAc)_2$ reacts with dppe, NaTeH, Et_3N and $NaBH_4$ resulting in $[Pd_5(\mu_3\text{-}Te)_4(dppe)_4][BPh_4]_2\cdot dmf\cdot MeCN\cdot EtOH\cdot H_2O$ (**111**) [145]. The Pd–Te bond length is 2.595(2)–2.619(2) Å. The $TeBu^n(SiMe_3)$ is also a good source of the Te^{2-} ligand. The synthesis of $[Co_6(\mu_3\text{-}Te)_8(PPh_2Pr^n)_6]$, $[Cu_{11}(\mu_3\text{-}TeBu^n)_7\text{-}(\mu_4\text{-}TeBu^n)_2(\mu_7\text{-}Te)(PPh_3)_5]$, $[Cu_{18}(\mu_3\text{-}TeBu^n)_6Te_6(PPr^n)_8]$, $[Cu_{58}Te_{32}(PPh_3)_{16}]$ and $[Cu_{23}Te_{18}(PEt_3)_{12}]$ was reported [102] using this source. The alkali metal tellurides are capable of introducing a tellurido ligand directly. The reaction of $Fe(CO)_5$ with Te^{2-} ligand gives a higher nuclearity cluster [149] $[Fe_3(CO)_9Te]^{2-}$ (**112**) whose Fe···Fe bond is quite reactive as addition of protons may occur across it.



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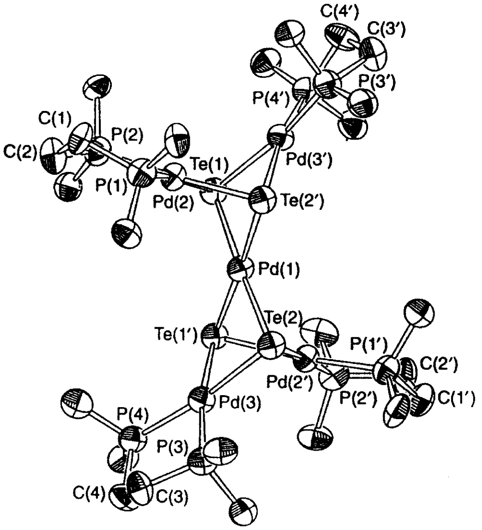
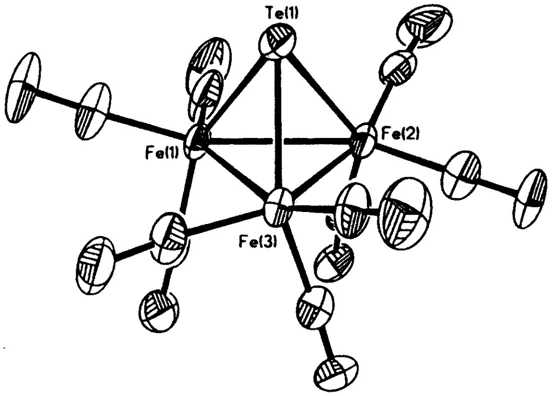


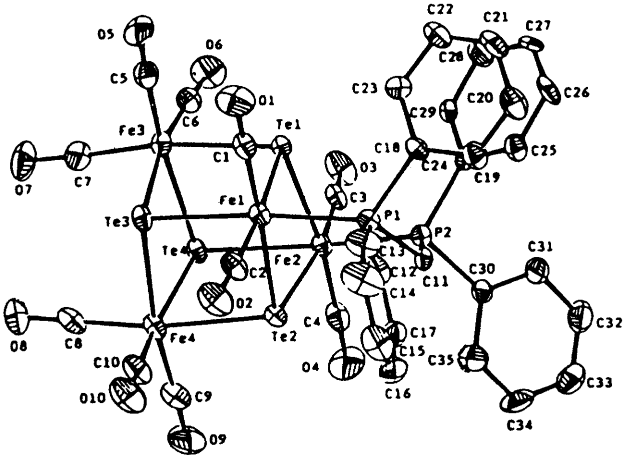
111

Similarly electrophiles $(PPh_3)Au^+$ and $PhHg^+$ also add to a Fe···Fe edge and not the apical Te. The reaction of I_2 with **112** gives $[Fe_3Te_2(CO)_9I]^-$ which is isostructural with $Fe_3Te_2(CO)_{10}$. The aerial oxidation of mixture of $Fe(CO)_5$ and Te^{2-} gives $[(Fe(CO)_4)_2Te]^{2-}$.



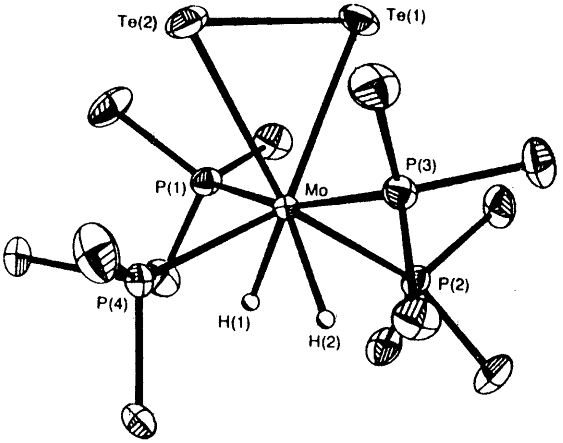
112

The alkylation [199] of $[TeFe_3(CO)_9]^{2-}$ with methyl triflate or MeI occurs at the metal framework (Fe–Me = 2.226(9) Å), like its Se analog but contrary to the sulfur one, which is alkylated at S itself. The tetrahedral cluster $[TeFe_3(CO)_9]^{2-}$ on successive treatment [200] with $Te_2Fe_3(CO)_9$ results in $[Te_4Fe_5(CO)_{14}]^{2-}$, $[Te_6Fe_8(CO)_{24}]^{2-}$ and $[Te_{10}Fe_8(CO)_{20}]^{2-}$. The last, on reaction with $[Cu_2(dppm)_2(MeCN)_4][BF_4]_2$, results in a cubic cluster $[Te_4Fe_4(CO)_{10}(dppm)]$ (**112b**). The Fe–Te bond length is 2.605(2)–2.625(2) Å.



112b

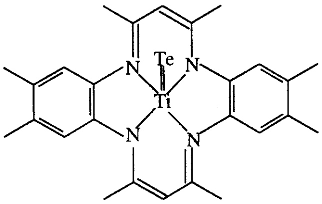
The oxidative cleavage of the Te–Te bond [141] also results in a tellurido complex, as complex **107** (Table 3) is formed from the decomposition of $M(PMe_3)_4(\eta^2\text{-}Te_2)H_2$ (M = Mo, W), which involves oxidative cleavage of the ditelluride ligand at the metal center.



$M(PMe_3)_4(\eta^2\text{-}Te_2)H_2$ (M = W or Mo)

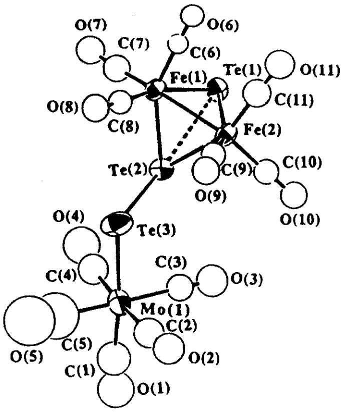
Complex $(Bu^tMe_2Si)_2Te$ generates the tellurido ligand via the reaction [147] with $[\eta^4\text{-}Me_8taa]MCl_2$ (Me_8taa = octamethyldibenzotetraaza[14]annulene dianion, M = Ti or V) to yield **113**. The tellurido ligand of **113** can be substituted by an oxygen ligand, when it reacts with N_2O or O_2. The Ti=Te and V=Te bond lengths are

2.484(2) and 2.433(1)/2.435(1) Å, respectively. The $TePEt_3$ has also been used as source of tellurido ligand [148].

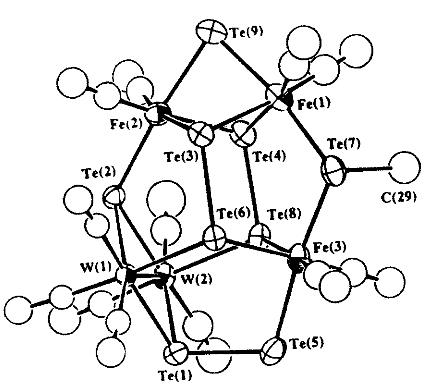


113

Its reaction with tetrakis[bis(trimethylsilyl)methyl]digallane results in $R_2Ga–Te–GaR_2$ species (where $R = CH(SiMe_3)_2$) containing a μ_2-Te^{2-} ligand. The sodium ditelluride has been used as a source of tellurido ligand. The methanothermal reaction [150] of $Fe_3(CO)_{12}$, $M(CO)_6$ (M = Mo or W), Na_2Te_2 and Ph_4PBr or $Et_4NCl \cdot H_2O$ results in **115** and **116**.

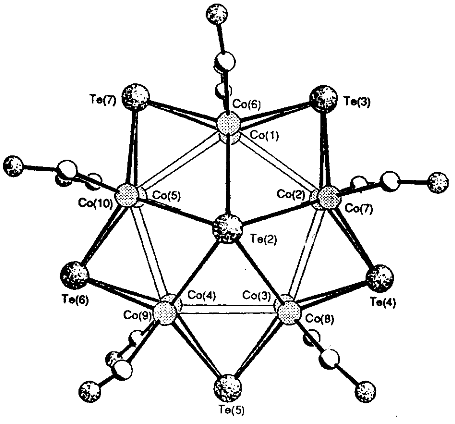


115

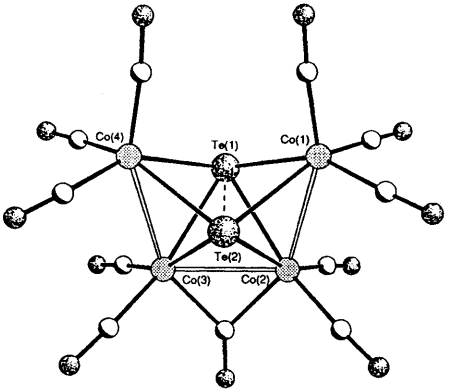


116

A similar reaction [151] of $Co_2(CO)_8$, Na_2Te and Ph_4PCl in methanol gives clusters $(Ph_4P)_2[Co_{11}Te_7(CO)_{10}]$ (**116a**) and $Co_4Te(CO)_{11}$ (**116b**), when the reactants are in the molar ratio 3:2:3 and 4:2:1, respectively. The first cluster has a slightly elongated pentagonal prismatic array of cobalt atoms, which has one Co atom at the center. Each Co_4 square is capped by a μ_4-Te^{2-} ligand (mean Co–Te 2.510(3) Å). There are two μ_6-Te^{2-}, one at the center of each pentagonal Co face (mean Co–Te(3) 2.569 Å; Co(central)–Te 2.642(2)/2.647(2) Å). The formal core framework of this cluster is $[Co_{10}Co(\mu_6\text{-}Te)_2(\mu_4\text{-}Te)_5]$. The two μ_4-Te ligands make the core framework of $Co_4Te_2(CO)_{11}$. The tellurido bridged cubane core [152] M_4Te_4, M = Mn or Fe was synthesized by stabilizing it with Pr^iS^- or Pr^iTe^-. The resulting complex anion $[M_4Te_4(SPr^i)_4]^{2-}$ were structurally characterized. The $Sn_2Te_6^{4-}$ cluster [153] containing two bridging and four terminal ligands was prepared by the reaction of Li_2Te, Te, $NaBH_4$ and $SnCl_2$ in DMF. It was structurally characterized as $(Et_4N)_4[Sn_2Te_6]$.

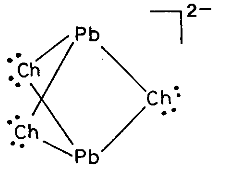


116a



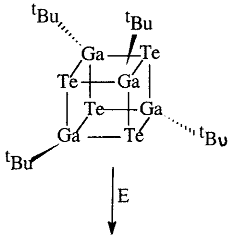
116b

The Sn_2Te_2 rings and adamantane like Sn_4Te_6 cages have also been generated [154] with the tellurido ligand. The reaction of R_2SnCl_2 (R={Cp(CO)$_2$Fe}, {Cp(CO)$_3$Mo}) with $Te(SiMe_3)_2$ forms $R_4Sn_2Te_2$ and $R_4Sn_4Te_6$. The reaction of W_6Cl_{12} with Na_2Te/Na_2Te_2 in the presence of ligand pyridine/piperidine/PEt_3 (L) results in the cluster $W_6Te_8L_6$ [155] which has an octahedron of W atoms, whose face is capped by a triply bridging tellurido ligand, each W is also linked to L. A related anionic cluster $[W_6Te_8L_6]^-$ was synthesized [156] by using similar reactants. It also has a W_6 octahedron capped by a tellurido ligand. The $PbTe_3^{4-}$ anion containing tellurido ligand Te^{2-} [157] was synthesized by reduction of $PbTe_2$ alloy with potassium in ethylenediamine, and characterized structurally. A series of anions $Pb_2S_nTe_{3-n}^{2-}$ ($n = 0$–3) and Pb_2SSeTe^{2-} were obtained [178] by extraction of the alloys of the type $KPb_xS_yCh_2$ (Ch = Se and/or Te) in ethylenediamine and characterized in solution. They have two lead atoms bridged by chalcogenido ligands as shown below.



The tellurido ligand (Te^{2-}) based clusters were found to grow [158] further on reacting lower clusters with $TePEt_3$, as a source of such ligands. $Pd_2Te_2(PEt_3)_4$ gives $Pd_6Te_6(PEt_3)_8$ in such a reaction whereas $Ni_9Te(PEt_3)_8$ results in $Ni_{20}Te_{18}(PEt_3)_{12}$. Several ternary solid phases [159] like Hf_8Te_6M (M = Mn, Fe) which may be considered as formally containing Te^{2-} ligand are known but are not within the scope of the present review. Very recently [160] clusters of composition

$[Me_4N]_4[Re_6(Te_{8-n})(Se_n)(CN)_6]$ ($n = 0$–4) were designed by reacting Re_6Te_{15} with NaCN and Se at 600°C followed by cation exchange with Me_4NBr. Each face of the Re_6 octahedron of this cluster is capped by a μ_3-Te or Se ligand. Similarly the cluster [161] $Cs_3K[Re_6(\mu_3\text{-}S)(\mu_3\text{-}Te_{0.66}S_{0.34})_2(CN)_6]$ prepared by reacting Re_6Te_{15} with molten KSCN and subsequent treatment with an aqueous CsCl, has μ_3-S and/or μ_3-Te ligands on the faces of the Re_6 octahedron. The reaction of $Mo_3Te_7I_4$ or WTe_2 with KCN at 450°C gave species $K_7[Mo_4(\mu_3\text{-}Te)_4(CN)_{12}]\cdot 11H_2O$ and $K_6[W_4(\mu_3\text{-}Te)_4(CN)_{12}]\cdot 5H_2O$, which have a M_4Te_4 cubane based structure [196]. In the reaction of $[(^{t}Bu)Ga(\mu_3\text{-}Te)]_4$ with elemental sulfur and selenium, a facile chalcogenide exchange [197] was reported very recently as shown below.



$[(^{t}Bu)_4Ga_4(\mu_3\text{-}E)(\mu_3\text{-}Te)_3]$

↓

$[(^{t}Bu)_4Ga_4(\mu_3\text{-}E)_2(\mu_3\text{-}Te)_2]$ E = S/Se_8 or S/Se_x

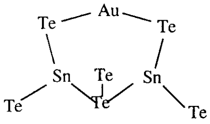
↓

$[(^{t}Bu)_4Ga_4(\mu_3\text{-}E)_3(\mu_3\text{-}Te)]$

↓

$[(^{t}Bu)_4Ga_4(\mu_3\text{-}E)(\mu_3\text{-}Te)_3]$

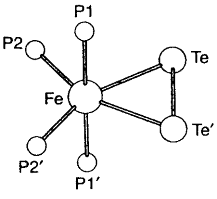
The exchange follows first-order kinetics with respect to the cubane. The $(^{n}Bu_4N)_3AuSn_2Te_6$ (**116c**) was synthesized very recently [198]. Its anion has Te^{2-} and Te_2^{2-} units as shown below.



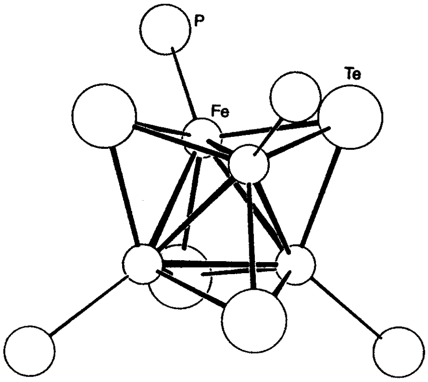
116c

4.3. Polytelluride ligand

The chemistry of polytelluride ligands has been reviewed by Roof and Kolis [129] in 1993 and Kanatzidis and Huang [12] in 1994. The last review covered the literature of 1993 scantily. The last 5–6 years have witnessed reasonably intense activity in this area and most of the papers published during this period are included here. The main group and transition metal ions both form homoleptic complexes with polytelluride ions. The transition elements also form organometallic species containing polytelluride ligands. The polytelluride anions and cations have been both explored as ligands in the recent past, and their complexes have diverse structural features. The first member of the polytelluride series Te_2^{2-} has been further explored as a ligand. The homoleptic complex cation $[Ta(Te_2)_2]^+$ was isolated [162] as $[TaTe_4]_4[PtI_6]I_2$, and consists of $Ta(Te_2)_2$ chains separated by PtI_6 and I. The reaction of $Fe(C_8H_8)_2$ with $TePR_3$ resulted [163] in $FeTe_2(dmpe)_2$ and $FeTe_2(depe)_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$; depe = $Et_2PCH_2CH_2PEt_2$) which contain a Te_2^{2-} ligand.



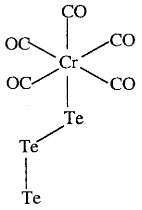
$FeTe_2(depe)_2$



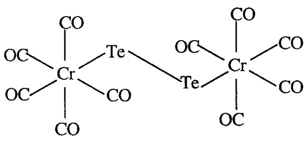
$Fe_4Te_4(PPr^i_3)_4$

This reaction also results in $Fe_4Te_4(PEt_3)_4$, $Fe_4Te_4(PPr^i_3)_4$, $Fe_6Te_8(PMe_3)_6$ and $Fe_4Te_6(dmpe)_4$ in which tellurium is present as a μ_3-Te^{2-} ligand, except in the last case when μ_2-Te^{2-} is also present. The homoleptic polyselenide complexes $(PPh_4)_2[M(Se_4)_2]$ (M = Ni/Pt) react with $TePEt_3$ in DMF resulting in $[PPh_4]_4[Ni_4Te_4(Te_2)_2(Te_3)_4]$ and $[PPh_4]_4[Pt_4Te_4(Te_3)_6]$ [164]. Both these clusters have a M_4Te_4 cubane core, whose metal atoms are bridged by Te_2^{2-} and Te_3^{2-} ligands. Indium tellurides $[M(en)_3]In_2Te_6$ (M = Fe, Zn) and $[Mo_3(en)_3(\mu_2\text{-}Te_2)(\mu_3\text{-}Te)(\mu_3\text{-}O)]In_2Te_6$ were synthesized [165] by solvothermal reactions at temperature below 200°C. In_2Te_6 unit has chains of fused five-membered (In_2Te_3) rings which have two indium atoms bridged by Te_2^{2-} and Te^{2-}. The Mo cluster has three Mo atoms, each pair bridged by a Te_2^{2-} ligand and all the three by a Te^{2-} ligand. Each Mo is also chelated by an ethylenediamine ligand. Recently the syntheses and structures of $[K(2,2\text{-crypt})]_2[Cr(CO_5)Te_3]\cdot(0.5en)$ (**118**) and $[K(2,2\text{-crypt})]_2[\{Cr(CO)_5\}_2Te_2]$

(**119**) were reported [166]. In the first case a Te_3 chain is bonded through one end and in the second two $Cr(CO)_5$ units are bridged by Te_2^{2-}.

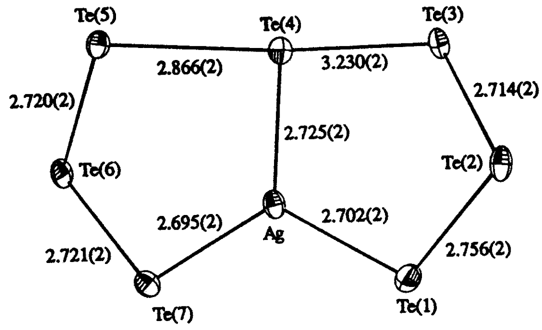


118



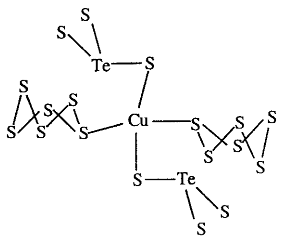
119

A M_3Te_7 cluster core was obtained [167] by reaction of aqueous cyanide with the product of a solid state (temperature, 380°C) reaction of Mo, Te and iodine (ratio = 3:7:4). One compound having this core $Cs_{4.5}[Mo_3(\mu_3\text{-}Te)(\mu_2\text{-}Te_2)_3(CN)_6]I_{2.5}\cdot 3H_2O$ (**120**) has been characterized structurally. A cluster anion $[AuTe_7]^{3-}$ having a chelated Te_3^{2-} and monodentate Te_2^{2-} ion, was synthesized [168] by reacting AuCN with Te_n^{2-} (in situ generated by Li_2Te and Te powder) in DMF in the presence of PEt_3 and NEt_4Cl. The reaction of $M(OAc)_2$ (M = Zn or Hg) in DMF at low temperature (0 or -50°C) with K_2Te_3 also results in the $[MTe_7]^{2-}$ anion [169] as $[K(15\text{-crown-}5)]_2[MTe_7]$. The $[HgTe_7]^{2-}$ consists of two condensed five-membered rings and $[ZnTe_7]^{2-}$ a Zn^{2+} ion, chelated with Te_4^{2-} and bonded with Te_3^{2-} through one terminal Te atom. The interest in ligand chemistry of Te_4^{2-} continues, as it is known to make chelate rings with metal ions. The reactions of CuCl and $AgNO_3$ with Na_2Te_3 in DMF (in the presence of $[PPh_4]Br$) results in complexes of composition $[PPh_4]_4[M_2Te_{12}]$ [170]. The anion is composed of two five membered chelate $[MTe_4]^-$ units, which are linked by a Te_4^{2-} chain. The $[Ag_2Te_{12}]^{4-}$ anion was also characterized structurally as $[NEt_4]_4[(Te_4)Ag(\mu\text{-}Te_4)Ag(Te_4)]$ by Ansari et al. [171], after its synthesis through a different route, i.e. silver compound $[Ag(Me_3P)I]_4$ was reacted with $Li_2Te + Te$ in DMF. The copper analog of this anion made by reacting CuCl in THF with Li_2Te and Te powder dissolved in DMF has also been structurally characterized. The Zn(II), Cd(II) and Hg(II) chelates of the ligands Te_4^{2-} having composition $[Ph_4P]_2[M(Te_4)_2]$, were synthesized by Bollinger et al. [172], by reaction of $Cd(xan)_2$, $Zn(xan)_2$ (xan = xanthate) or $HgCl_2$ with $Li_2Te + Te$ in DMF. The Te_4^{2-} chelates of all these metal ions having tetrahedral geometry. The ^{125}Te resonances of $[M(Te_4)_2]^{2-}$ anion reveal that while Te linked to metal appears highly shielded, δ -337 to -478 ppm, other tellurium appears in the spectrum in the range δ 198–224 ppm. The reaction of Rb_2CO_3 with Te in MeOH at 160°C [173] yields $RbTe_6$. The structure consists of chains of Te_6^- rings which have a chair conformation and connected via Te–Te bonds. The discrete Te_7^{4-} anion [174] is shown as chelated with Hg(II) and Ag(I). The structure of $[AgTe_7]^{3-}$ is shown below and is similar to that of its Hg analog. However, the $AuTe_7^{3-}$ [168] contains the combination of $\eta^3\text{-}Te_5^{4-}$and $\eta^1\text{-}Te_2^{2-}$ ligand or $\eta^2\text{-}Te_3^{2-}$and two Te_2^{2-} ligands (Te(3)–Te(4) distance is 3.120(3) Å, only slightly larger than Te(2)–Te(3) = 2.927(2) Å). To generate the Te_7^{4-} anion in situ in DMF, Li_2Te and Te were reacted. The oxidation of K_2Te_3 solution with $FeCl_3$ in DMF in the presence of 15-crown-5 gives $[K(15\text{-crown-}5)]_2Te_8$ [175] which contains the discrete Te_8^{2-} anion. The Te_8^{2-} anion has a cyclic structure in which the Te^{2+} ion is chelated in a planar fashion by Te_3^{2-} and Te_4^{2-} ions. A molecular cluster [176] $Cr_6Te_8(PEt_3)_6$ has a Cr_6 octahedron, Te_8 cube and $(PEt_3)_6$ octahedron which are cocentric.

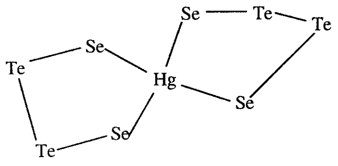


$[AgTe_7]^{3-}$

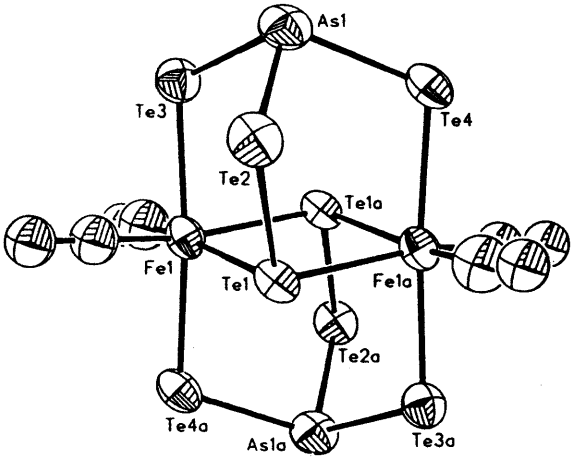
It does not have a discrete Te_8 unit but each face of the Cr_6 octahedron has a cap of triply bridging tellurium. Several new copper–tellurium clusters, $[Cu_4Te_4(P(CHMe_2)_3)]$, $[Cu_{23}Te_{13}(P(CHMe_2)_3)_{10}]$, $[Cu_{16}Te_9L_8]$ (L = phosphine), $[Cu_{28}Te_{17}(PPhEt_2)_{12\}}]$, $Cu_{26}Te_{16}\{(P(CMe_3)_3\}_{10}]$ and $Cu_{29}Te_{16}\{(P(CHMe_2)_3\}_{12}]$ were synthesized [177] by reacting CuCl with $Te(SiMe_3)_2$ and phosphine. Mixed polytelluride ions, containing other elements like S, Se, etc., exhibit interesting features. The reaction of Cu or Ag with mixed polychalcogenide flux $A_2S_xTe_y$ (A = K, Rb, Cs) has yielded $RbCuTeS_3$, $CsCuTeS_3$, $KAgTeS_3$ (α and β form) $RbAgTeS_3$ and $CsAgTeS_3$. The $[MTeS_3]_n^{n-}$ has a large layer structure [179] and alkali metal/counter ions are present between the layers. The TeS_3^{2-} units bridge the copper atoms via sulfur. The reaction of copper with excess of Cs_2S_x and $Cs_2S_xTe_y$, gives the $Cs_6Cu_2(S_6)_2(TeS_3)_2$ cluster [180] containing trigonal pyramidal TeS_3^{2-} ligands bridging two copper atoms via sulfur. The layered solids $A_2Mn(TeS_3)_2$, (A = Cs/Rb) based on pyramidal TeS_3^{2-} were synthesized recently by Zhang and Kanatzidis [181]. Similarly a layer structure solid Cu_2TeS_3 has been synthesized [182]. The discrete complex anions containing TeS_3^{2-} ligand in bridging mode, $[Au_2(TeS_3)_2]^{2-}$ and $[Ag_2Te(TeSe_3)_2]^{2-}$ [183] were characterized as a salt of PPh_4^+, $(Ph_3P)_2N^+$ and Me_4N^+ cations. The reaction of $TePEt_3$ with $[M(Se_4)_2]^{2-}$ results in mixed polychalcogenide ions [184] $[Hg(Te_2Se_2)_2]^{2-}$, $[Hg(TeSe_3)(Se_4)]^{2-}$ and $[Hg(Te_2S_2)(Se_4)]^{2-}$. The $Te_xSe_{4-x}^{2-}$ anions are similar to Te_4^{2-}, Te is partially replaced by Se. The iron pentacarbonyl reacts with $As_2Te_6^{2-}$ (prepared by reducing As_2Te_3 with K in dry DMF) resulting in $[Fe_2(AsTe_4)(CO)_4]^{2-}$, which is, characterized structurally [185]. The Te–Fe bond lengths are in the range 2.570(7)–2.6226(8) Å.



$[Cu_2(S_6)_2(TeS_3)_2]^{6-}$

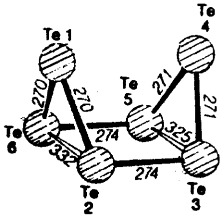


$[Hg(Te_2Se_2)_2]^{2-}$

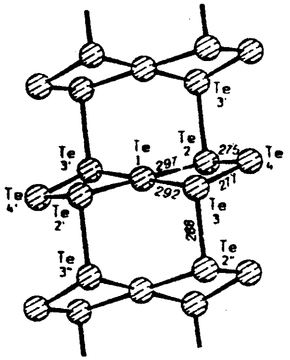


$Fe_2(AsTe_4)(CO)_4]^{2-}$

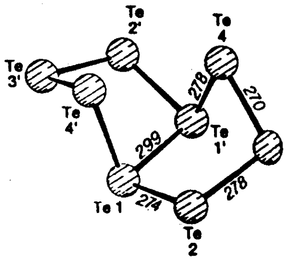
The cationic polytellurides have also been explored [14]. The important species are Te_4^{2+}, Te_6^{2+}, Te_7^{2+} and Te_8^{2+} Recently $Te_8[VOCl_4]_2$ and $Te_6[WOCl_4]$ were synthesized and characterized structurally [186,187].



Te_6^{2+}



Te_7^{2+}



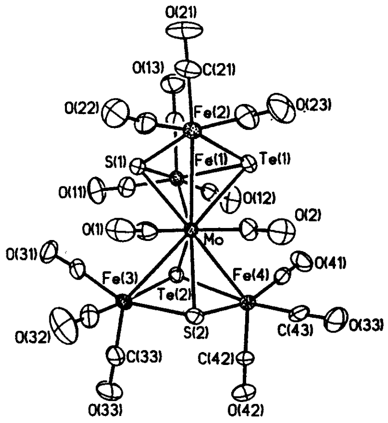
Te_8^{2+}

5. Tellurium ligands in cluster design

The application of tellurium ligands in the design of organometallic clusters has been reviewed very recently [16]. The facile addition of coordinatively unsaturated transition metal species to the reactive Te–Te bond of $[Fe_2(CO)_6(\mu\text{-}Te_2)]$ was found to be a convenient method to obtain mixed metal clusters. Recently an 'hour-glass' cluster, e.g. $[Fe_4Mo(CO)_{14}(\mu_3\text{-}S/Se)(\mu_3\text{-}Te)_2]$ was designed by a similar synthetic strategy [188], viz. the reaction of $[Fe_2(CO)_6(\mu\text{-}STe)]$ with $[Mo(CO)_5(THF)]$.

6. Miscellaneous tellurium ligands

The metallatelluroborane complexes $[2,2\text{-}(PR_3)_2\text{-}$*closo*$\text{-}2,1\text{-}PdTeB_{10}H_{10}]$ [189] $[2\text{-}X\text{-}2\text{-}(PPh_3)\text{-}$*closo*$\text{-}2,1\text{-}PdTeB_{10}Hg(PPh_3)]$ [189] ($X = Cl$, $PR_3 = PPh_3$, $PMePh_2$, PMe_2Ph), $[2\text{-}L\text{-}2\text{-}(PPh_3)\text{-}$*closo*$\text{-}2,1\text{-}PdTeB_{10}Hg(PPh_3)]BF_4$ [190] and $[2,2\text{-}(PR_3)_2\text{-}1\text{-}$*closo*$\text{-}2,1\text{-}PdTeB_{10}Hg(PPh_3)]$ [191] ($PR_3 = PMe_3$, PMe_2Ph) have been reported. A poly(gold)telluronium salt [192] $[(Ph_3P)Au]_3Te^+BF_4^-$ has been prepared from the corresponding oxonium salt and $(^tBuMe_2Si)_2Te$ in CH_2Cl_2 at $-78°C$. A stable telluroketone, 1,1,3,3-tetramethylindanetellone reacts with $W(CO)_5(THF)$ to give an adduct characterized structurally. The telluroketone group is in η^1, σ-complexation [193] mode.



$[Fe_4Mo(CO)_{14}(\mu_3\text{-}S/Se)(\mu_3\text{-}Te)_2]$

7. Conclusions

Very diverse types of systems containing a metal–tellurium bond have been studied, making a novel contribution to the chemistry of tellurium ligands. However, there is a greater need to solve crystal structures of complexes of organotellurium ligands, so that uses of this class of tellurium ligands may be better envisaged. The cluster formation with tellurido, polytellurido and tellurolato ligands is still not easily controlled. Some attempts to develop strategies for the synthesis of clusters of predetermined design are definitely required. For the successful use of metal–tellurium bond containing systems as a single source precursor for MOCVD, there is a need to pay attention to improve the volatility of such systems. The use of ^{125}Te-NMR in exploring the solution behavior of tellurium ligands is sometimes restricted due to solubility problems, but is still less exploited in comparison to ^{31}P-NMR for phosphines. The most notable contribution made in this area in the recent past are, the four membered chelate ring formed by $ArTeCH_2TeAr$ with Pd(II), adduct of ditelluroethers with $SnCl_4$, the chemistry of halotellurium ligands, Te ligand based organometallic cluster designing and mixed polychalcogenide ligands.

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