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Tellurium compounds of the main-group elements: progress and prospects†

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The discovery of tellurium (Latin *tellus*, earth) in ores mined in Transylvania in 1782 predated the isolation of selenium by 35 years.[1] Despite this historical precedence, investigations of tellurium compounds have lagged behind developments in selenium chemistry. There is, however, an increasing interest in tellurium chemistry that is reflected in the number of recent reviews dealing with various aspects of the subject. These include tellurium-rich tellurides,[2] the co-ordination chemistry of telluride ligands,[3] the synthesis and structures of tellurium–nitrogen compounds,[4] stereochemical aspects of tellurium complexes with sulfur ligands,[5] intramolecular co-ordination in tellurium chemistry,[6] tellurium polycations,[7] and electrochemically generated tellurium-containing polyanions.[8]

The major consumers of tellurium (worldwide production *ca.* 260 tonnes in 1991)[1b] have traditionally been the metallurgical and rubber industries, but electronic applications of tellurides, particularly of the Zn/Cd/Hg triad, in solar cells, IR detectors, and optical fibre communication devices are attracting increasing attention. The potential uses of transition-metal tellurides have been the source of much of the extensive recent work on the co-ordination chemistry of telluride ligands.[3] Many main-group element tellurides, *e.g.* SnTe, GaTe anions and Bi_2Te_3, also have desirable properties for applications in optical or magnetic devices and in the semiconductor industries.[8a] The present technology for the preparation of these tellurides includes aqueous precipitation, gas-phase deposition, or the reaction of the elements at elevated temperatures. A major focus of recent work[8b] has been the development of alternative routes to these interesting materials.

From the viewpoint of fundamental chemistry, the synthesis of multiply bonded tellurium derivatives represents a considerable, but worthwhile, challenge since such compounds exhibit unusual reactivities. At the same time inorganic tellurium compounds generate excitement for the synthetic chemist because unique structural features are often encountered. The intention of this article is to reflect upon these three aspects of the chemistry of main-group element–tellurium compounds with emphasis on significant developments during the past 5 years.

Structural Chemistry of Tellurium Compounds

Inorganic chemistry textbooks, with one notable exception,[1a] accord scant attention to tellurium compounds. Consequently, most chemistry students are unaware of the remarkable polymeric structures of the tellurium subhalides Te_3Cl_2, Te_2X (X = Br or I) and TeI. The fascinating structural chemistry of elemental tellurium is highlighted by recent discoveries of polyanions and polycations with unique frameworks. For example, the Te_{12}^{2-} ion,[9] which consists of a puckered chain [*d*(Te–Te) 2.71–2.78 Å, *cf.* 2.75 Å for a Te–Te single, bond][10] interconnected by weak Te–Te interactions [*d*(Te–Te) 3.16–3.50 Å] to give a two-dimensional network [Fig. 1(*a*)] is the longest structurally characterized polychalcogenide ion. The S_{12}^{2-} ion has been claimed as the product of the reaction of sulfur and K_2CO_3 in acetone, but the characterization relied on chemical analyses.[14] Attempts to prepare Se_{12}^{2-} from selenium under similar conditions yielded the novel $[Se_5C(Se)COMe]^-$ anion in which the six-membered Se_5C ring adopts a chair conformation.[15] The unbranched structure of Te_{12}^{2-} is particularly surprising in view of the disposition of the heavier chalcogens to form 'non-classical' anions,[2b] *e.g.* in polyselenides with bicyclic (Se_{10}^{2-})[16] and spirocyclic (Se_{11}^{2-} and Se_{16}^{2-})[17,18] structures. Indeed the most common structural motifs for polytellurides are the T-shaped $[TeTe_3]^{n-}$ or square $[TeTe_4]^{n-}$ arrangements as found, for example in the spirocyclic Te_8^{2-} anion [Fig. 1(*b*)].[11] In contrast, the S_8^{2-} anion has an unbranched chain structure.[19,20]

The anions in tellurium-rich polytellurides form two-dimensional infinite networks, *e.g.* $(Te_6^{-})_n$ in $RbTe_6$[12] and $(Te_6^{3-})_n$ in Cs_3Te_{22}.[13] The polytelluride in the former consists of Te_6 rings in a chair conformation connected by four Te–Te bonds in a layer structure. T-Shaped $TeTe_3$ units are apparent in this structure [Fig. 1(*c*)]. The layer anions $(Te_6^{3-})_n$ in Cs_3Te_{22} contain two crystallographically independent Te atoms with linear or T-shaped co-ordination geometries connected to give Te_4 and Te_{12} squares [Fig. 1(*d*)]. The remarkable structure of Cs_3Te_{22} also incorporates Cs^+ ions co-ordinated to a cubic arrangement of eight tellurium atoms from two crown-shaped Te_8 rings [Fig. 2(*b*)].[13] Cyclic allotropes of tellurium have not previously been characterized, although there is NMR evidence for *cyclo*-TeS_7 in sulfur–tellurium melts.[21] This discovery suggests the prospect of interesting developments in the chemistry of homocyclic Te rings.

Like the other chalcogens tellurium also forms polycations with weakly nucleophilic anions in highly electrophilic media. The square planar Te_4^{2+} and trigonal prismatic Te_6^{4+} cations have been known for many years.[7] More recently, the oxidation of tellurium by high oxidation state transition-metal halides has emerged as an alternative to the use of more traditional oxidizing agents, *e.g.* MF_5 (M = As or Sb) or $S_2O_6F_2$, for the generation of novel tellurium polycations.[7] As indicated in Fig. 2 a plethora of structural types has been discovered, including examples of polycations for which several isomers exist. For example, the monomeric square-planar cation Te_4^{2+}[27] also exists as a dimer in the Te_8^{4+} cation [Fig. 2(*a*)][22a] and in a one-dimensional polymeric form $(Te_4^{2+})_n$ [Fig. 2(*b*)].[22b] In Te_8^{4+} the Te_4 squares [|*d*(Te–Te)| 2.76 Å] are linked by two Te • • • Te interactions of 3.01 Å and the elongated Te_8 cubes form strands.

In addition to Te_6^{2+} [Fig. 2(*c*)],[23] with a boat conformation, and $(Te_{10}^{2+})_n$,[22b] three isomers of Te_8^{2+} [Fig. 2(*d*), 2(*e*) and 2(*f*)][22b,c,24] and two isomers of Te_7^{2+} [Fig. 2(*g*) and 2(*h*)][25,26] have been structurally characterized. A comparison of the frameworks of these new polycations reveals some interesting structural patterns that may be indicative of additional possibilities. The tricyclic Te_8^{2+} [Fig. 2(*d*)] is derived from Te_6^{2+} by the formal insertion of a Te–Te bridge. The infinite chain structures of $(Te_7^{2+})_n$ [Fig. 2(*g*)] and $(Te_8^{2+})_n$ [Fig. 2(*f*)] involve Te_6 rings bridged by one or two Te atoms, respectively. The polymeric structures of $(Te_7^{2+})_n$ [Fig. 2(*h*)] and $(Te_{10}^{2+})_n$ [Fig. 2(*i*)] are closely related and, reminiscent of

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† *Non-SI unit employed:* Torr ≈ 133.322 Pa.

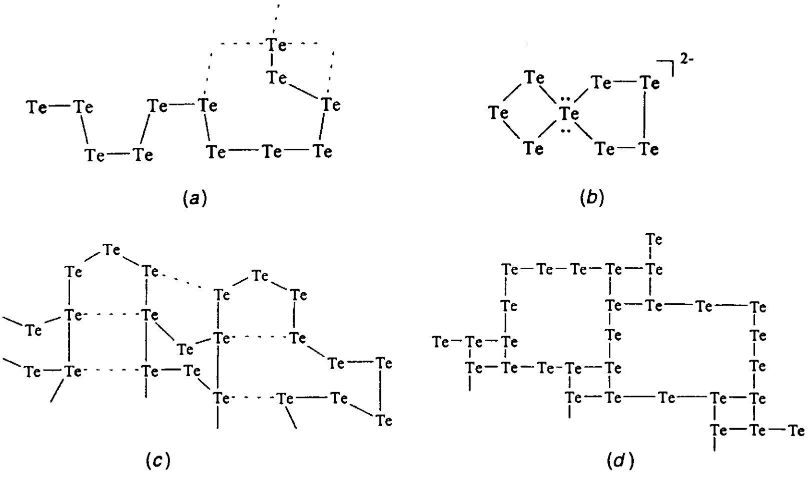


Fig. 1 Structures of tellurium polyanions: (*a*) Te_{12}^{2-} in $(NEt_4)_2Te_{12}$,[9] (*b*) Te_8^{2-} in $[K(15\text{-crown-}5)_2]_2Te_8$ (15-crown-5 = 1,4,7,10,13-pentaoxacyclopentadecane),[11] (*c*) $(Te_6^{-})_n$ in $RbTe_6$[12] and (*d*) $(Te_6^{3-})_n$ in Cs_3Te_{22}[13]

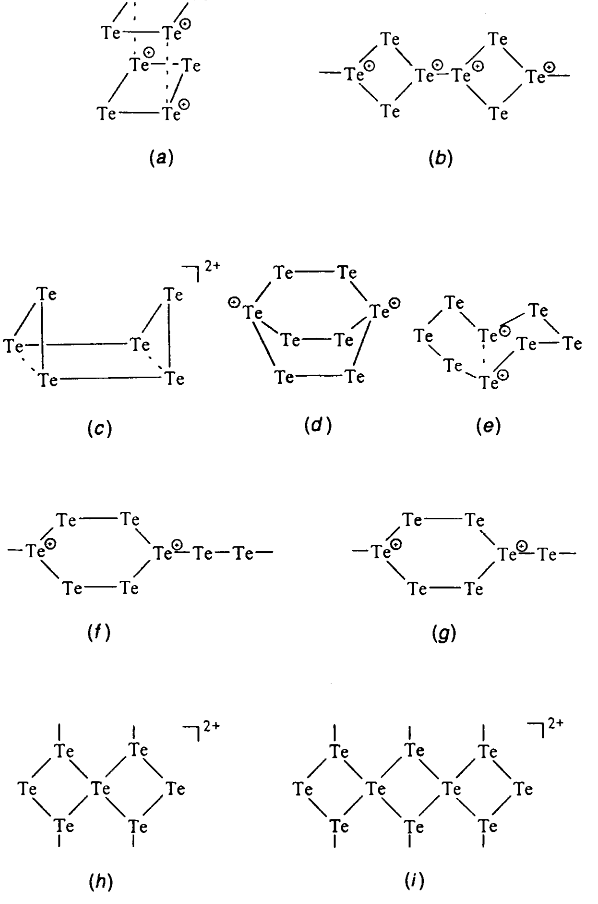


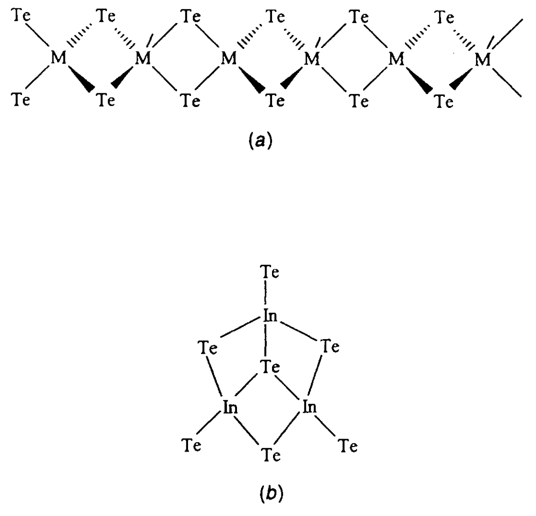
Fig. 2 Structures of tellurium polycations: (*a*) Te_8^{4+} in $[\{Te_8(VOCl_4)_2\}_n]$,[22a] (*b*) $(Te_4^{2+})_n$ in $(Te_{10})_n(Te_4)_n(Bi_4Cl_{16})_n$,[22b] (*c*) Te_6^{2+} in $Te_6(WOCl_4)_2$,[23] (*d*) Te_8^{2+} in $(Te_8)(Te_6)(WCl_6)_4$,[22c] (*e*) Te_8^{2+} in $Te_8(WCl_6)_2$,[24] (*f*) $(Te_8^{2+})_n$ in $(Te_8)_2(Bi_4Cl_{14})$,[22b] (*g*) $(Te_7^{2+})_n$ in $Te_7(AsF_6)_2$,[25] (*h*) $(Te_7^{2+})_n$ in $Te_7(MOX_5)$ (M = Nb, X = Cl or Br);[26a] (M = W, X = Cl[26b]) and (*i*) $(Te_{10}^{2+})_n$ in $(Te_{10})_n(Te_4)_n(Bi_4Cl_{16})_n$[22b]

Te_7^{2-}, display spirocyclic Te centres. For example, the Te_7 unit in $(Te_7^{2+})_n$ consists of a central tellurium co-ordinated *via* four long Te–Te bonds (mean value 2.95 Å) to two Te_3 units in which the Te–Te distances are 2.76 Å. The Te_7 units are connected by covalent Te–Te bonds of 2.88 Å to give the one-dimensional strands. The bicyclic structure of Te_8^{2+} [Fig. 2(*e*)] resembles that of the well known S_8^{2+} and Se_8^{2+} cations, but the transannular interaction in Te_8^{2+} [*d*(Te–Te) 2.99 Å] is stronger than those in S_8^{2+} or Se_8^{2+}. Thus a wide variety of polycationic alternatives to Te_4^{2+} now exist as potential sources of polytellurium fragments or rings in metal complexes.[3b]

Polyanions that incorporate tellurium and other p-block elements, especially those of Group 15, exhibit tremendous structural variety. This field originated with the pioneering work of Zintl and co-workers in the 1930s.[1b] It has experienced a rebirth in view of the possible applications of ternary main-group element tellurides, *e.g.* MM'_2Te_4 (M = Cd or Hg, M′ = Ga or In)[28,29] in the semiconductor industries resulting from their optical, thermal and electrophysical properties. The traditional methods for the synthesis of Ga/In–Te anions, *e.g.* $K_6Ga_2Te_6$,[30] involve either the high temperature fusion of the elements or hydrothermal techniques. A milder approach to these materials involves the exploitation of Zintl's electrochemical method. This approach is potentially very versatile.[8] For example, the cathodic dissolution of a Ga_2Te_3 electrode in an ethylenediamine (en) solution of $[PPh_4]Br$ yields $[PPh_4][GaTe_2(en)]$[31] and a similar electrochemical synthesis has been used to prepare $[NBu^n_4][InTe_2]$,[32] which consists of one-dimensional chains of $InTe_4$ tetrahedra. The structurally related polymer $RbInTe_2$ has been prepared by high temperature fusion of Rb_2Te_2, In and Te at 400 °C.[33] The isoelectronic polymeric anion $(GeInTe_4^{-})$ in $[PPh_4][GeInTe_4]$ also forms one-dimensional chains [Fig. 3(*a*)].[33] An alternative, low temperature route to telluridometalates involves the reduction of main-group element tellurides with potassium in liquid ammonia in the presence of an encapsulating ligand, *e.g.* 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane).[34,35] This procedure has been used to generate the $[GaTe_3]^{3-}$ ion which, in $K[K(18\text{-crown-}6)]_2[GaTe_3]\cdot 2MeCN$, has a somewhat distorted trigonal planar structure and the novel $In_3Te_7^{5-}$ ion.[34] The latter consists of a cubic $[In_3Te_4]^{+}$ framework (where one corner is vacant) with a terminal Te^{2-} ion attached to each In^{3+} centre [Fig. 3(*b*)].

The best known examples of Group 14 element–tellurium anions are of the type $[M_2Te_3]^{2-}$ (**1**, M = Sn or Pb) for the +2 oxidation state of the metal and $[SnTe_4]^{4-}$ (**2**) for Sn in the +4 oxidation state. The trigonal-bipyramidal structure of **1** (M = Sn[36a] or Pb[35,36b]) is well established. The anion in M_2GeTe_4 (M = Rb or Cs) consists of $GeTe_4$ tetrahedra linked by Te–Te bonds.[37]

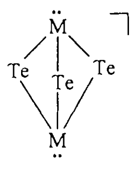
The known arsenic telluride ions include $[As_2Te_4]^{4-}$ (**3**),[38] $[As_2Te_5]^{2-}$ (**4**),[39] $[As_4Te_6]^{4-}$ (**5**),[39] $[As_2Te_6]^{2-}$ (**6**)[38,40] and $[As_{10}Te_3]^{2-}$ (**7**).[41] These As–Te anions adopt structures with three-co-ordinate As, two-co-ordinate Te and terminal (unidentate) Te atoms (Fig. 4), which can readily be rationalized by a two-centre two-electron bonding description. The $[As_2Te_4]^{4-}$ ion (**3**) adopts a staggered (C_{2h}) structure,



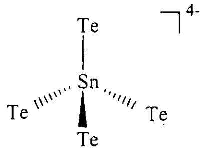
(*a*)

(*b*)

Fig. 3 (*a*) One-dimensional chain in $[\{In_2Te_4{}^{2-}\}_n]$ or $[\{GeInTe_4{}^{-}\}_n]$[33] and (*b*) the $[In_3Te_7]^{5}$ ion in $[NEt_4]_5[In_3Te_7]\cdot0.5Et_2O$[34]



1 M = Sn or Pb



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reminiscent of the isoelectronic P_2I_4, with a normal As–As bond length whereas the $[As_2Te_5]^{2-}$ ion (**4**) exists as infinite one-dimensional chains.[39]

The electrochemical approach is a particularly fruitful source of the unique antimony–tellurium anions $[SbTe_4]^{3-}$ (**8**),[42] $[Sb_2Te_5]^{4-}$ (**9**),[43] $[Sb_4Te_4]^{4-}$ (**10**),[44] $[Sb_6Te_9]^{4-}$ (**11**)[43] and $[Sb_9Te_6]^{3-}$ (**12**)[44] (Fig. 4). These anions are all prepared by the cathodic dissolution of an Sb_2Te_3 electrode in ethylenediamine in the presence of tetraalkylammonium cations, $NR_4{}^+$ (R = Me, Et or Pr), which facilitate the isolation of crystalline salts. The pyramidal Sb atom in $[SbTe_4]^{3-}$ is attached to a $Te_2{}^{2-}$ and two Te^{2-} ligands.[42] Interestingly, the closely related pyramidal $[SbTe_5]^{3-}$ ion (two $Te_2{}^{2-}$ and one Te^{2-} ligands) is found in the ternary polytelluride ion $[Cu_4SbTe_{12}]^{3-}$.[45] The $[Sb_2Te_5]^{2-}$ anion consists of two $SbTe_3$ trigonal pyramids that share a corner Te atom[43] while $[Sb_4Te_4]^{4-}$ adopts a folded four-membered Sb_4 ring with terminal Te atoms in equatorial positions.[44] The $[Sb_6Te_9]^{4-}$ ion involves the weak co-ordination of a Te^{2-} ion in a square-pyramidal fashion to the four Sb atoms of the central Sb_4Te_2 ring of the tricyclic $[Sb_6Te_8]^{2-}$ ion.[43] The unusual structure of the $[Sb_9Te_6]^{3-}$ ion defies a simple description. One of the Sb atoms is four-co-ordinate with a weak interaction of 3.205 Å (dashed line) to a terminal Te atom and an unusually long terminal Sb–Te bond (2.994 Å, *cf.* typical values of 2.65–2.75 Å). In view of the extensive range of frameworks already established for As– or Sb–Te anions (Fig. 4), it is remarkable that, as yet, none of these structural types is known for both As and Sb.

The ability of tellurium to accommodate high co-ordination numbers (*i.e.* seven or eight) in ions such as $[TeF_6O]^-$, $[TeF_7]^-$ and $[TeF_8]^{2-}$[46,47] is another important feature of the structural chemistry of tellurium compounds. The ^{125}Te NMR spectrum of $[TeF_7]^-$ at 25 °C consists of a binomial octet indicating a stereochemically non-rigid pentagonal-bipyramidal structure (D_{5h}) like the isoelectronic IF_7 molecule.[46,47] The $[TeF_8]^{2-}$ ion has not been obtained in a pure state but, on the basis of vibrational spectroscopy, it exists as a square antiprism (D_{4d}).[46a] Although the octahedral structure of $TeMe_6$, determined by a gas-phase electron diffraction study,[48a] is unremarkable, the high thermal stability of this unique hexaalkylated derivative of a main-group element is noteworthy.[48b]

Multiple Bonding in Main-group Element–Tellurium Compounds

Multiple bonding involving the heavier p-block elements has been a topic of considerable interest in recent years and tellurium is no exception. The reluctance of tellurium to engage in p(π)–p(π) bonding with other main-group elements is evident, however, from the observations that Te=C=Te and RN=Te=NR (R = alkyl or aryl) are unknown while $(TeO_2)_n$ is a three-dimensional polymer. By contrast, the corresponding sulfur compounds are stable, multiply bonded monomers with a very extensive chemistry. Although tellurocarbonyls $R_2C{=}Te$ (*e.g.* R = H) can be stabilized by co-ordination to a transition metal, no example of a stable telluroaldehyde or telluroketone was known until recently.[49] The dimer **13a** is obtained from the treatment of adamantanone with the tellurium-transfer reagent $Me_2AlTeAlMe_2$.[50] The reaction of $Hg[Te(CF_3)]_2$ with $AlEt_2$ in the absence of a solvent produces a deep violet, amorphous material, presumably $Te{=}CF_2$, at −196 °C,[51] but the dark red 1,3-ditelluretane **13b** is formed upon warming. The first telluroketone that is sufficiently stable to be characterized spectroscopically in solution, 1,1,3,3-tetramethylindantellurone (**14**), exhibits a weak visible absorption band at 825 nm, attributed to the n $\longrightarrow$ π* transition of the C=Te bond and remarkably deshielded ^{13}C and ^{125}Te NMR resonances (δ ^{13}C 301, δ ^{125}Te 2858).[49]

Although stable compounds containing [Si=Te] multiple bonds are unknown, it is possible that the silatellurone $Cp^*{}_2Si{=}Te$ ($Cp^* = C_5Me_5$) is an intermediate in the formation of the cyclodisilatellurolane **15** from the reaction of $Cp^*{}_2Si$ and $Te{=}PBu_3$.[52] The remarkable macrocyclic germanium complex **16**, in which a terminal telluride ligand is stabilized by the tetramethyldibenzotetraaza[14]annulene dianion, has been reported recently.[53] The Ge–Te bond distance of 2.466(1) Å in **16** suggests that the bonding involves contributions from both the $Ge^+{-}Te^-$ and Ge=Te resonance structures (*cf.* predicted values of 2.59 and 2.39 Å for single and double bonds, respectively).[53] The molecular structure of **16** differs from that of the corresponding selenide or sulfide complexes in that the benzo groups of the macrocyclic ligand are tilted away from the [GeTe] moiety (as opposed to towards the [GeE] group when E = S or Se). Attempts to make the Sn analogue of **16** were unsuccessful, although the corresponding Sn sulfide and selenide have been structurally characterized.[54] Recent successes in the generation and characterization of other kinetically stabilized 'heavy ketones' involving the [Ge=Se],[55a] [Sn=Se][55b] or [Pb=S][56] groups suggest that tellurones $R_2M{=}Te$ (M = Si, Ge or Sn) may be accessible for extremely bulky R groups, at least *in situ*.

The thermal instability of multiply bonded tellurium–nitrogen compounds is manifested by the explosive nature of Te_3N_4[57,58] and potassium triimidotellurite(IV), $K_2Te(NH)_3$.[58] Although the formula of Te_3N_4, the only known binary tellurium nitride, represents an obvious difference from that of the most common nitrides of sulfur and selenium, *i.e.* S_4N_4 and Se_4N_4, it is the expected composition for a tellurium(IV) nitride. Both S_4N_4 and Se_4N_4 are known to adopt a cradle-shaped (D_{2d}) structure with weak, transannular chalcogen–chalcogen interactions, but the structure of Te_3N_4 is unknown. However, the unusual framework of derivatives of the type $N(XTeNSN)_3$ (**17**, X = F or Cl)[59] consists of a twelve-membered $Te_3N_6S_3$ ring with a central nitrido ligand co-ordinated to three tellurium atoms. It is conceivable that Te_3N_4 also incorporates the μ_3-nitrido structural motif and that it

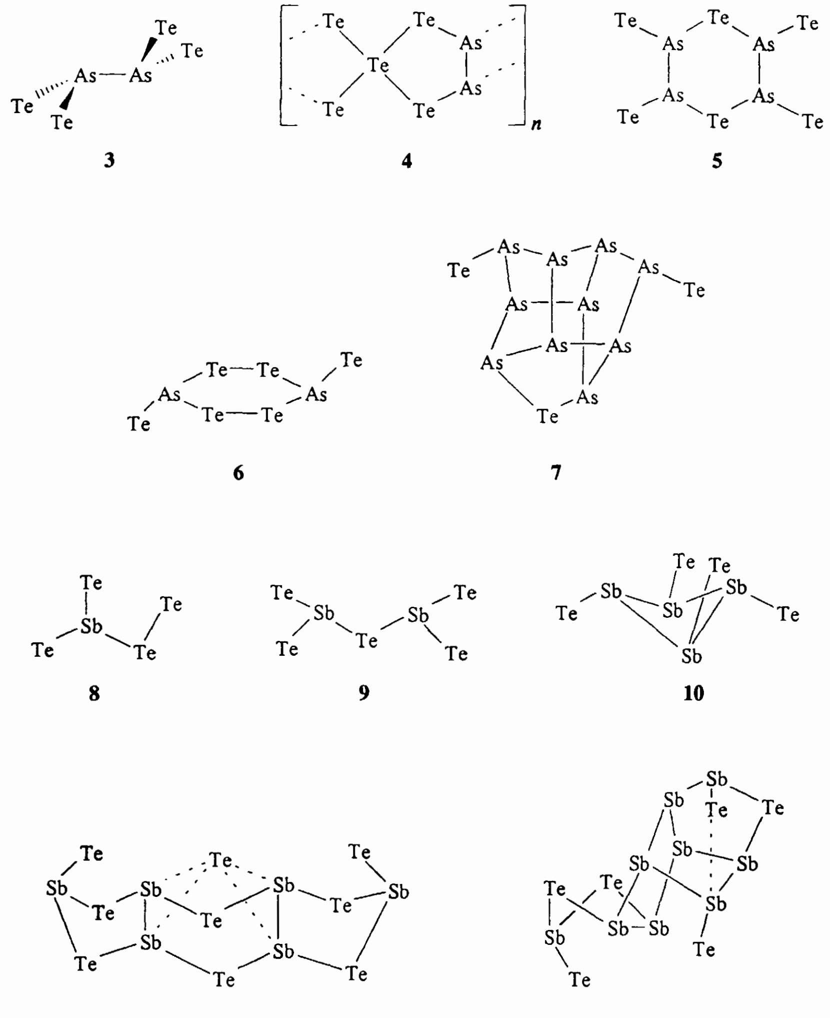
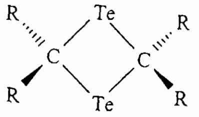
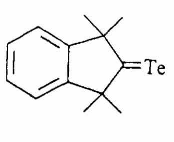


Fig. 4 Structural frameworks of arsenic– and antimony–tellurium polyanions (see text for negative charges on the anions **3**–**12**)



13a R = adamantyl
13b R = F



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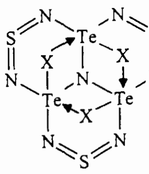

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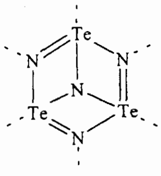

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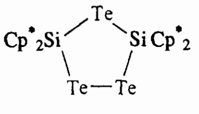

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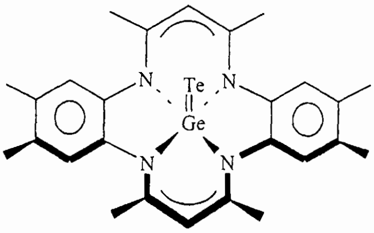

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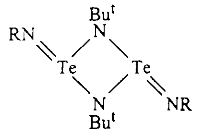
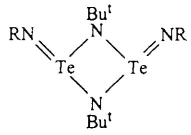
has a highly associated structure (*e.g.* **18**) as a result of intermolecular Te···N interactions, *cf.* telluradiazoles,[4a,60] accounting for its insoluble nature.

Diorganotellurimides $R_2Te{=}NR'$ formally contain a tellurium–nitrogen double bond, but the Te–N bond distance of 1.98 Å in $(4\text{-}MeOC_6H_4)_2Te{=}NSO_2C_6H_4Me\text{-}4$[61] [*cf.* *d*(Te–N) 2.05 and 1.83 Å for single and double bonds, respectively] indicates predominantly dipolar character for this bond.

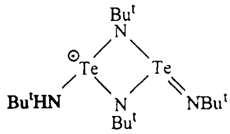
Compounds formulated as tellurium diimides '$RN{=}Te{=}NR$' (R = COMe or $ArSO_2$) have been reported,[62] but their insolubility and high melting points imply highly associated structures. The search for genuine Te–N double bonds has intensified recently[63–65] and the first structural determination of a tellurium diimide was reported in 1994.[66] The derivative **19** is a dimer with exocyclic Te–N bond lengths of 1.90 Å. The exocyclic imido substituents are in a *trans* orientation with respect to the Te_2N_2 ring, but ^1H, ^{31}P and ^{125}Te NMR studies indicate that conversion to the *cis* isomer **20a** occurs slowly in solution at 23 °C.[60,66] The *cis* isomer **20b**, with exocyclic Te–N distances of 1.88 Å, and the cyclic tellurium(II) imide $(Bu^tNTe)_3$, which is a six-membered ring in the chair conformation, are obtained from the reaction of $TeCl_4$ with $LiNHBu^t$ in a 1:4 molar ratio in toluene at −78 °C.[67] When this reaction is carried out in a 2:7 molar ratio, the major product is **21**, a protonated derivative of **20b**, in which the exocyclic $Te{=}NBu^t$ bond length of 1.84 Å is very close to the predicted double bond value.[67] The dimer **20b** sublimes at 85 °C, 10^{-3} Torr and melts at 100–102 °C without decomposition. This high thermal



19 R = PPh$_2$NSiMe$_3$



20a R = PPh$_2$NSiMe$_3$
20b R = Bu^t



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stability is in marked contrast to that of the corresponding selenium diimide Bu^{t}N=Se=NBu^t, which decomposes at room temperature.[68] On the basis of spectroscopic evidence selenium diimides are monomeric in solution,[68] but the solid-state structures are unknown.

The facile synthesis of the tellurium diimide dimer **20b** provides a unique opportunity to investigate the reactivity of Te=N double bonds. A characteristic reaction of sulfur diimides is the quantitative formation of sulfinimidamates Li[RN-S(R')NR], whose dimeric structures have only recently been established,[69] upon treatment with organolithium reagents, LiR'. Surprisingly, the product of the reaction of the tellurium diimide dimer **20b** with phenyllithium contains no Ph groups.[70] It was identified by X-ray crystallography as the dimer $[\{Li_2Te(NBu^t)_3\}_2]$, **22**, which can be obtained in much better yields (> 90%) from **20b** and four mol equivalents of LiNHBu^t.

The $Te_2N_6Li_4$ cage in **22** consists of a distorted hexagonal prism containing two pyramidal tris(*tert*-butylimido)tellurite ions $[Te(NBu^t)_3]^{2-}$. The essentially equal Te–N bond lengths of *ca.* 1.98 Å are consistent with the delocalized structure **23**. In contrast to the parent $[Te(NH)_3]^{2-}$ ion,[58] the *tert*-butyl derivative **22** can be handled without fear of explosion. The monoanionic tellurite analogues $Te(NBu^t)_2(EBu^t)$ (**24a**, E = O; **24b**, E = NH) have also been structurally characterized recently in the clusters $[\{K(thf)[Te(NBu^t)_2(OBu^t)]\}_2]$ (thf = tetrahydrofuran) (**25**) and $[\{[LiTe(NBu^t)_2(NHBu^t)_2]LiCl\}_2]$ (**26**), respectively. The structural parameters for these isoelectronic anions are consistent with a Te–E single bond [*d*(Te–O) 2.049(5) Å in **24a** and |*d*(Te–N)| 2.057(6) Å in **24b**] and a Te–N bond order of *ca.* 1.5 [*d*|(Te–N)| 1.915(5) Å and 1.943(5) Å in **24a** and **24b**, respectively]. The cluster **25** is prepared by the reaction of the tellurium diimide dimer **20b** with potassium *tert*-butoxide, while the centrosymmetric dimer **26** is obtained when the cage **22** is treated with 2 equivalents of dry HCl gas.[71]

The pyramidal trithiotellurite ion, $[TeS_3]^{2-}$,[72] is a versatile ligand for transition metals. The bonding modes that have been established to date [see Fig. 5(*a*)] give some indication of the potential ligand behaviour of the isoelectronic ions, **23**, **24a** and **24b**. For example, the dimeric anion $[Cu_2(TeS_3)_2(S_6)_2]^{6-}$ consists of two CuS_6 rings bridged by two monodentate $[TeS_3]^{2-}$ anions.[73] The ability of the $[TeS_3]^{2-}$ ligand to generate novel two- or three-dimensional materials is illustrated by compounds of the type $AMTeS_3$ (A = K, Rb or Cs; M = Cu or Ag)[74a] and $A_2Mn(TeS_3)_2$ (A = Cs or Rb).[74b] The complex $CsCuTeS_3$ has a three-dimensional structure in which the $[TeS_3]^{2-}$ ions bridges three trigonal planar Cu^+ atoms. By contrast, the other complexes of the type $AMTeS_3$ adopt structures with alternating layers of $(A^+)_n$ cations and $(MTeS_3)_n{}^{n-}$ anions comprised of $[TeS_3]^{2-}$ ligands bridging four tetrahedral Cu^+ or Ag^+ centres. A layer structure is also observed for $Cs_2Mn(TeS_3)_2$, but the $[TeS_3]^{2-}$ ligands in this complex bridge three octahedral Mn^{2+} cations. A different bonding mode is observed for $[TeS_3]^{2-}$ in the anion $[Au_2(TeS_3)_2]^{2-}$.[75] In this complex the linearly co-ordinated Au^+ centres are bridged by two bidentate $[TeS_3]^{2-}$ ligands to give an eight-membered ring. Interestingly, the reaction of $[TeS_3]^{2-}$ or $[TeSe_3]^{2-}$ with $AgNO_3$ generates the new ligands $[Te(TeE_3)_2]^{4-}$ (E = S, Se) in which a tellurium atom bridges two $[TeE_3]^{2-}$ ions [Fig. 5(*b*)]. In the isostructural anions $[Ag_2Te(TeE_3)_2]^{2-}$ (E = S or Se) this ligand gives rise to a novel cage structure in which a triangular Ag_2Te plane is sandwiched by two pyramidal $[TeE_3]^{2-}$ ligands. Significantly, co-ordination of the lone pair on Te to a metal centre has not been observed in any of these complexes.

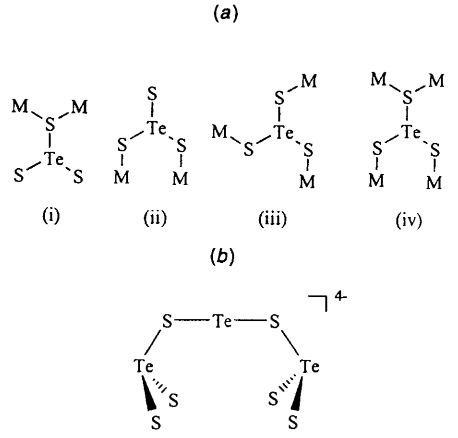
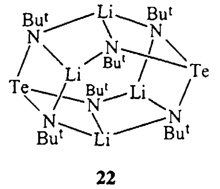


Fig. 5 Bonding modes of (*a*) the $[TeS_3]^{2-}$ ligand[73–75] and (*b*) the $[Te(TeS_3)_2]^{4-}$ ligand[75]



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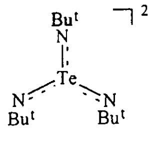

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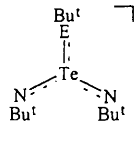
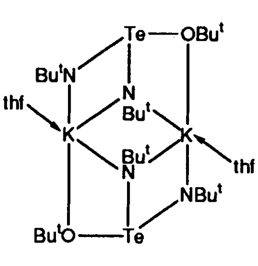


24a
24b



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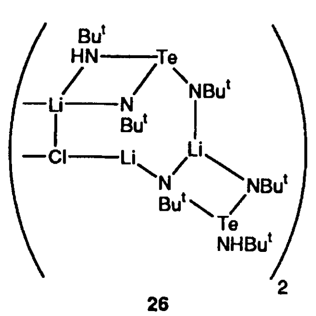
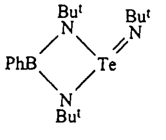


26

The $[Te(NBu^t)_3]^{2-}$ dianion (**23**) and the tellurium diimide dimer $Te_2(NBu^t)_4$ (**20b**) are isoelectronic with the recently described Sb–N anions, $[Sb(NR)_3]^{3-}$ (R = $PhCH_2CH_2$),[76] and $[Sb_2(NR)_4]^{2-}$ (R = cyclohexyl),[77] respectively. Parallels between the chemistry of Te–N species and their isoelectronic Sb–N counterparts can be anticipated. The dianion $[Sb_2(NR)_4]^{2-}$ has been used to incorporate metals into an Sb–N cage, *e.g.* $[Cu_4\{Sb_2(NC_6H_{11})_4\}_2]$,[78] and it seems likely that $[Te(NBu^t)_3]^{2-}$ will also prove to be a useful building block for incorporating other elements into Te–N rings and cages. Indeed the usefulness of the reagent **22** has already been established by reactions with BCl_2Ph and PCl_2Ph which produce the four-membered ring **27** containing an exocyclic Te=N double bond and, *via* a redox process, the spirocycle **28**, respectively.[70]

The recently reported cation $[Te_4N_2Cl_8]^{2+}$, **29**,[79] the dimer of $[Cl_3Te\text{-}N{=}Te\text{-}Cl]^+$, provides another example of the tendency of multiply bonded tellurium–nitrogen compounds to dimerize.



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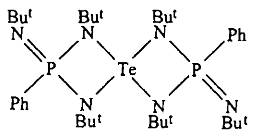

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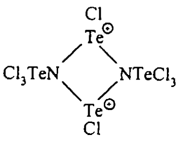

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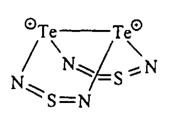

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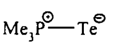
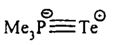


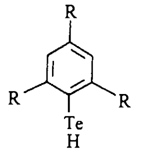
$Me_3\overset{\oplus}{P}-\overset{\ominus}{Te}$

31a



$Me_3\overset{\ominus}{P}\equiv\overset{\oplus}{Te}$

31b



32a R = Me
32b R = Pr^i
32c R = Bu^t

In contrast, the related selenium–nitrogen–chlorine cation $[Cl_2SeNSeCl_2]^+$ is monomeric in the solid state.[80]

Two other examples from Te–N chemistry illustrate the unique structural features or unusual reactivity of tellurium compounds. The bicyclic structure of $[Te_2S_2N_4]^{2+}$ [*d*(Te–Te) 2.88 Å][81] is of interest in comparison with the planar, delocalized 10 π-electron ring system $[S_4N_4]^{2+}$. Presumably, the folded structure of **30** is a reflection of the weakness of Te(5p)–N(2p) π bonding and the pronounced tendency for tellurium to catenate (*cf.* tellurium polycations). The dark blue tellurium(III) cation radical $[Te\{N(SiMe_3)_2\}_2]^{\bullet+}$ $[AsF_6]^-$ is monomeric in the solid state with |*d*(Te–N)| 1.97 Å[82a] {*cf.* 2.05 Å for $Te[N(SiMe_3)_2]$}[82b] consistent with some multiple bond character. The ESR spectrum of a $CDCl_3$ solution of this radical indicates that the unpaired electron is located primarily on tellurium.

Triorganophosphine tellurides $TePR_3$ were first prepared more than 30 years ago by the combination of phosphines with Te powder in boiling toluene,[83] but the nature of the bonding in these (and other) four-co-ordinate phosphorus(V) chalcogenides is still a matter of debate.[84] X-Ray structural determinations of $TePR_3$ derivatives reveal almost identical P–Te distances [*d*(P–Te) 2.368 Å for $TePBu^t{}_3$,[85a] 2.365 Å for $TePPr^i{}_3$,[85b] and 2.371 Å for $Bu^t{}_2P(Te)NH(C_6H_{11})$.[86] It was suggested that these bond lengths imply a bond order of 1.5.[85] However, solution and solid-state ^{125}Te NMR and ^{125}Te Mössbauer spectroscopic data have been interpreted to indicate the absence of multiple bonding in $TePR_3$ compounds.[87] Recent density functional theory (DFT) calculations on $TePMe_3$ reveal contributions from resonance structures **31a** and **31b**, consistent with substantial multiple bonding.[88] As indicated in Fig. 6, structure **31a** involves σ donation from PMe_3 to Te, while the π interactions in **31b** are due to negative hyperconjugation from the filled p orbitals on Te to the degenerate σ* orbitals of the PMe_3 fragment. The back donation is enhanced by the synergic effect and, in the series $EPMe_3$ (E = O, S, Se or Te), becomes more important relative to σ donation, as one descends the series.[88]

Although the thermal instability of $TePR_3$ has been an impediment to the development of the chemistry of phosphine tellurides, and very few metal complexes are known,[89] this property has been exploited imaginatively in the use of these reagents as a more reactive source of tellurium than Te metal.[90] Foremost in this development has been the low-temperature generation of transition-metal–tellurium clusters, which may subsequently be pyrolysed to yield binary metal tellurides, by the reaction of $TePR_3$ reagents with low-valent transition-metal compounds. Examples of clusters prepared in this way include $[Fe_4Te_4(PEt_3)_4]$,[90a] $[Co_6Te_8(PEt_3)_6]$,[90b] $[Pd_6Te_6(PEt_3)_8]$,[90c] $[Ni_9Te_6(PEt_3)_8]$ and $[Ni_{20}Te_{18}(PEt_3)_{12}]$,[90d] and the ditelluride $[\{Co_3MnTe(PEt_3)_2\}_2]$.[90e] Other important applications of $TePR_3$ as Te transfer reagents involve the preparation of terminal transition-metal tellurides, *e.g.* $[W(PMe_3)_4(Te)_2]$,[91] chalcogen-exchange reactions to produce tellurometalates from selenometalates,[92] and insertions into metal–carbon[93,94] or metal–metal bonds.[95]

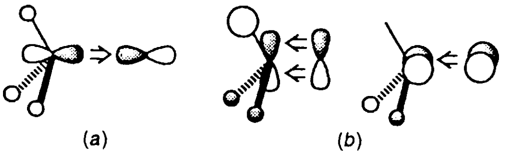


Fig. 6 Bonding contributions in $TePMe_3$ (*a*) σ donation and (*b*) π-back donation (negative hyperconjugation)

Single Source Precursors of Metal Tellurides

Tellurides of the Group 12 metals (Zn, Cd or Hg), including cadmium mercury telluride, are important semiconductors with applications in infrared, solar cell and optoelectronic devices. The technique of MOCVD (metal-organic chemical vapour deposition) applied to single source precursors is a potential source of thin films at temperatures significantly lower than those used in the traditional methods for producing such materials. Tellurolates are important precursors for the generation of tellurides. For example, the thermolysis of mercury tellurolates at 200 °C produces HgTe.[96] The phosphine telluride $TePEt_3$ serves as a source of tellurium in combination with $HgEt_2$ or, preferably, $HgPh_2$ to give pure HgTe in toluene at reflux, presumably *via* the insertion of Te atoms into Hg–C bonds [equation (1)].[97]

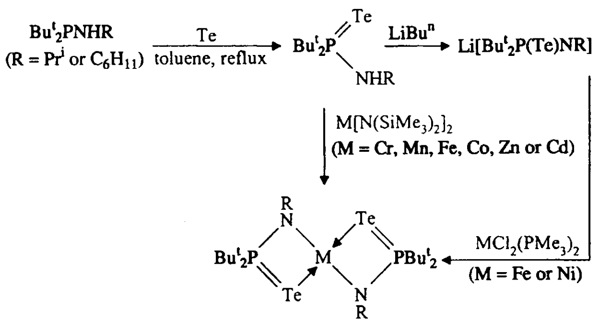
$$HgPh_2 + 2TePEt_3 \longrightarrow Hg(TePh)_2 \longrightarrow HgTe + TePh_2 \quad (1)$$

Generally tellurols RTeH (R = Ph or alkyl) are considered to be undesirable reagents on account of their foul smell, toxicity and thermal instability. However, important advances have been made recently with the discovery of the remarkably stable tellurol $[(Me_3Si)_3Si]TeH$ (m.p. 128–130 °C)[98] and sterically hindered benzenetellurols **32a**–**32c** which, unlike PhTeH, can be isolated as colourless, low melting solids.[99a] These new reagents have been used for the preparation of tellurolates *via* tellurolysis of M–C or M–N bonds [equations (2) and (3)].[98,99a] The Cd tellurolate $[\{Cd[Te(mes)]_2\}_n]$ (mes = 2,4,6-$Me_3C_6H_2$) is a one-dimensional polymer with bridging Te(mes) ligands and tetrahedrally co-ordinated Cd.[99a] The monomeric adduct $[Zn\{Te(mes)\}_2(NC_5H_5)_2]$ has also been structurally characterized.[99b]

$$2[(Me_3Si)_3Si]TeH \xrightarrow[\text{or } Zn[N(SiMe_3)_2]_2]{ZnEt_2} Zn[Te\{Si(SiMe_3)_3\}]_2 + 2C_2H_6 \quad (2)$$

$$[\text{or } 2NH(SiMe_3)_2]$$

$$(mes)TeH + Cd[N(SiMe_3)_2]_2 \longrightarrow [\{Cd[Te(mes)]_2\}_n] + 2NH(SiMe_3)_2 \quad (3)$$



Scheme 1

The gas-phase pyrolysis of $M[Te\{E(SiMe_3)_3\}]_2$ (M = Zn, Cd or Hg; E = C or Si) produces crystalline thin films of the corresponding tellurides;[100,101] CdTe may also be formed by the decomposition of the polymer $[\{Cd[Te(mes)]_2\}_n]$ in boiling mesitylene.[99]

A promising new strategy for the generation of binary metal tellurides films from single source precursors involves the synthesis, and subsequent thermolysis, of chelate complexes of phosphine tellurides of the type $Bu^t_2P(Te)NHR$ (R = Pr^i or C_6H_{11}).[86] The general approach is summarized in Scheme 1. This method provides an alternative to the tellurolate-based routes to metal tellurides, since it produces thermally stable metal complexes sublimable in the temperature range 115–200 °C.

The technique of MOCVD has been widely investigated for the generation of Group 13–15 semiconductors, *e.g.* GaAs and InP,[102] from organometallic precursors. In the last 4–5 years an interest has developed in complexes containing Al, Ga or In bonded to tellurium as potential precursors for generating films of the corresponding tellurides with useful optoelectronic properties. A variety of mono-, di- and tetra-meric complexes have been prepared and structurally characterized.

The monomeric aluminium tellurolate $Bu^i_2AlTeBu^n$, a useful reagent in organic synthesis, has been generated from $Bu^nTeTeBu^n$ and $AlHBu^i_2$.[103,104] The metal–hydride cleavage of ditellurides has also been used to prepare the monomeric adduct $Al(NMe_3)(TePh)_3$ [equation (4)].[105]

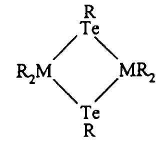
$$AlH_3(NMe_3) + \tfrac{3}{2}\,Te_2Ph_2 \longrightarrow Al(NMe_3)(TePh)_3 + \tfrac{3}{2}\,H_2 \quad (4)$$

The monomeric gallium tellurolate $[(Me_3Si)_2CH]_2GaTe[Si(SiMe_3)_3]$ has been prepared by two routes [equations (5) and (6)][106] and the homoleptic complex $Ga[Te\{Si(SiMe_3)_3\}]_3$ has also been obtained by the metathetical approach.[107] In general, the M–Te distances are significantly shorter (*ca.* 0.15 Å for Al and *ca.* 0.20 Å for Ga) in monomeric compared to dimeric (bridged) Group 13 tellurolate complexes.

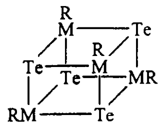
$$GaBr[CH(SiMe_3)_2]_2 + LiTe[Si(SiMe_3)_3] \xrightarrow{-LiBr} [(Me_3Si)_2CH]_2Ga{-}Te[Si(SiMe_3)_3] \quad (5)$$

$$\tfrac{1}{2}[(Me_3Si)_2CH]_2GaGa[CH(SiMe_3)_2] + \tfrac{1}{2}(Me_3Si)_3SiTeTeSi(SiMe_3)_3 \longrightarrow [(Me_3Si_2)CH]_2Ga{-}Te[Si(SiMe_3)_3] \quad (6)$$

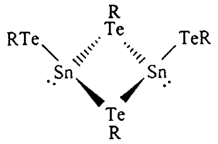
Dimers of the type **33** have been obtained by the reaction of (*a*) $GaCl(CH_2CMe_3)_2$ with LiTePh,[108] (*b*) trimesitylindium with ditellurides TeR_2 (R = Pr^n or Ph)[109] and (*c*) tri-*tert*-butylaluminium or -gallium with elemental tellurium.[110,111] The dimers **33a** and **33b** adopt a butterfly arrangement for the four-membered M_2Te_2 ring[112,113] whereas the Al_2Te_2 ring in **33c** is planar.[110] The latter dimer was shown to be an intermediate in the formation of the tetramer $(Bu^tAlTe)_4$.[110] Tetramers of the type **34**, which have cubane structures,[110,112,113] may be obtained from (*a*) tri-*t*-butylgallium and elemental tellurium,[110,111] (*b*) $(AlCp^*)_4$ and elemental tellurium[114] and (*c*) $(GaCl_2Cp^*)_2$ and $Te(SiMe_3)_2$.[113] Interestingly, the Cp* ligand in the Ga complex **34c** is σ bonded[113] whereas the corresponding Al complex **34b** exhibits η^5 co-ordination of the Cp* rings.[112]



33a M = Ga, R = CH_2CMe_3
33b M = In, R = Pr^n or Ph
33c M = Al, R = Bu^t
33d M = Ga, R = Bu^t



34a M = Ga, R = Bu^t
34b M = Al, R = Cp*
34c M = Ga, R = Cp*



35 R = $Si(SiMe_3)_3$

Although impure In_2Te_3 is produced by heating $[\{(mes)_2In(\mu\text{-}TePh)\}_2]$ at 600 °C,[109] the conversion of the organometallic complexes **33** or **34** to pure Group 13 tellurides by MOCVD techniques has not yet been achieved. Clearly there is a need for further investigations of suitable low-temperature precursors of binary tellurides of Group 13 and other main-group elements.

Several groups have investigated organometallic and inorganometallic Sn–Te complexes as potential single source precursors for SnTe, which is a narrow band gap semiconductor of interest for use in infrared detectors. The homoleptic tin(II) and lead(II) tellurolates $M[Te\{Si(SiMe_3)_3\}]_2$ (M = Sn or Pb) are conveniently prepared by protonolysis using the bulky tellurol $[(Me_3Si)_3Si]TeH$ [equation (7)].[114]

$$[(Me_3Si)_3Si]TeH + M[N(SiMe_3)_2]_2 \longrightarrow M[Te\{Si(SiMe_3)_3\}]_2 + 2NH(SiMe_3)_2 \quad (7)$$
$$(M = \text{Sn or Pb})$$

The tin(II) compound **35** is dimeric in the solid state with a butterfly-shaped Sn_2Te_2 ring and exocyclic substituents in a *cis* orientation. Pyrolysis of the complexes $M[Te\{Si(SiMe_3)_3\}]_2$ (M = Sn or Pb) at 250 °C proceeds cleanly to give cubic SnTe and PbTe [equation (8)] containing small amounts of carbon and hydrogen.[114]

$$M[Te\{Si(SiMe_3)_3\}]_2 \longrightarrow MTe + Te[Si(SiMe_3)_3]_2 \quad (8)$$
$$(M = \text{Sn or Pb})$$

Bis(triphenylstannyl) telluride is readily obtained from the reaction of $SnClPh_3$ with anhydrous Na_2Te in thf.[115] Pyrolysis of this organometallic telluride at 450 °C under N_2 produces cubooctahedral SnTe (containing 1–5% carbon) according to equation (9).[115] This transformation may occur *via* the terminal telluride $Ph_2Sn{=}Te$, which trimerizes to the unstable six-membered ring $(Ph_2SnTe)_3$. Surprisingly, in view of the reducing nature of tellurolates, the reaction of $Sn^{II}X_2$ (X = Cl or Br) with K[Te(mes)] yields the Sn^{IV} derivative $Sn[Te(mes)]_4$, which generates SnTe rather than $SnTe_2$ upon pyrolysis.[116]

$$3Te(SnPh_3)_2 \xrightarrow{450\,^{\circ}C} 2SnTe + 4SnPh_4 + TePh_2 \quad (9)$$

The tellurides M_2Te_3 (M = As or Sb) and, especially, bismuth–telluride-based alloys are the most efficient semiconductor materials for thermoelectric cooling devices. They are also of interest for their optoelectronic properties. These alloys are typically made by comelting the constituent elements, in appropriate amounts, above 600 °C. A remarkably facile process for the generation of Sb_2Te_3 films by MOCVD has been reported recently.[117] Polycrystalline Sb_2Te_3 films can be grown at room temperature under reduced pressure ($\sim$0.25 Torr) by the combination of $Sb(NMe_3)_3$ and $Te(SiMe_3)_2$ in a gas-phase MOCVD reactor. When this reaction is carried out in hexanes solution, polycrystalline powders of Sb_2Te_3 (or Bi_2Te_3) are precipitated at temperatures as low as -30 °C [equation (10)].[117]

$$2M(NMe_2)_3 + 3Te(SiMe_3)_2 \longrightarrow M_2Te_3 + 6NMe_2(SiMe_3) \quad (10)$$
$$(M = Sb \text{ or } Bi)$$

The thermally unstable organometallic Bi–Te compounds $Te(BiR_2)_2$ (R = Me or mes), which are prepared by the insertion of Te into the Bi–Bi bond of Bi_2R_4, decompose to give Bi_2Te_3 and BiR_3.[118] The corresponding antimony compound $Et_2SbTeSbEt_2$, prepared in a similar manner from Sb_2Et_4 and Te, is not a useful source of Sb_2Te_3.[119] Antimony tellurolates are obtained in high yields by the disportionation of distibanes and ditellurides [equation (11)] or, in the case of $Et_2SbTeEt$,

$$R_2SbSbR_2 + R'TeTeR' \longrightarrow 2R_2SbTeR' \quad (11)$$
$$(R = Me \text{ or } Et)\ (R' = Me, Et \text{ or } p\text{-}CH_3C_6H_4)$$

from $SbBrEt_2$ and LiTeEt. However, the thermal degradation of $Et_2SbTeEt$ produces an Sb-rich film.

Polycrystalline Bi_2Te_3 may also be prepared at room temperature by a two-step process involving the aqueous reaction of Bi_2O_3 with $[TeO_3]^{2-}$ (generated by dissolving Te in 6 mol dm^{-3} nitric acid) followed by hydrogen reduction of the precipitate so formed.[120] Alternatively, Bi_2Te_3 may be synthesized from the complex formed by adding tartaric acid and ethylene glycol to a mixture of Bi_2O_3 and $[TeO_3]^{2-}$.[121] The product is heated to 350 °C to remove carbonaceous material and then reduced under an H_2 atmosphere to give Bi_2Te_3. The mechanism of this transformation merits further investigation.

Conclusion

The chemistry of tellurium compounds of the main-group elements is still relatively unexplored, but recent studies reinforce the notion that tellurium is often unique among the chalcogens in its structural chemistry. Moreover, multiply bonded tellurium compounds, particularly those involving nitrogen or phosphorus, exhibit unusual reactivity. The prospect of discovering novel chemistry should provide a strong incentive for future studies of tellurium compounds which, in certain cases, will be aided by NMR studies (^{125}Te, $I = \frac{1}{2}$, 7%).[122] In addition, the unique solid-state properties of many binary or ternary tellurides is likely to lead to an increasing interest in organometallic or inorganometallic tellurium compounds as single-source precursors for the generation of thin films of these desirable materials. Finally, there is an exciting possibility of controlling the design of novel materials with specific electronic properties based on layered polytelluride structures.[2b] The blending of the pure and applied aspects of the subject will undoubtedly result in the most significant advances.

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