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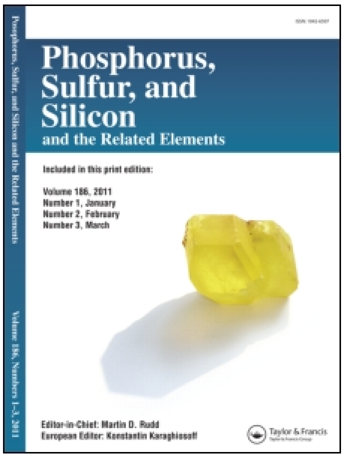

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RECENT DEVELOPMENTS IN TELLURIUM-NITROGEN CHEMISTRY

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This paper summarizes developments in the synthesis, structural characterization and reactions of tellurium-nitrogen compounds that have occurred during the last five years.

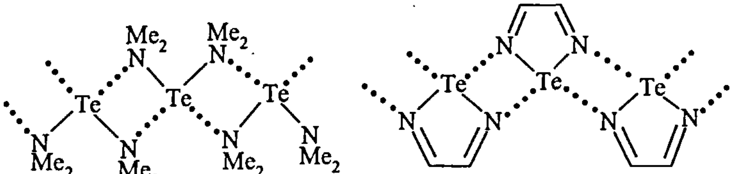
Keywords: tellurium; nitrogen; synthesis; structures

INTRODUCTION

The explosive nature of compounds such as Te_3N_4 and potassium triimidotellurite (IV), $K_2Te(NH)_3$, has been a deterrent to the study of tellurium-nitrogen (Te-N) compounds, particularly multiply bonded derivatives.[1] However, significant progress has been made recently in the synthesis and characterization of tellurium amides and imides. Many of these reagents have unique structures and/or differ in their reactivities compared with their S or Se analogues. Two previous reviews cover the Te-N literature up to 1992.[2,3] In this account attention will be focussed on developments during the last five years placed, where appropriate, in the context of earlier work.

TELLURIUM(II)-NITROGEN COMPOUNDS

The reaction of $TeCl_4$ with $Li[N(SiMe_3)]_2$ or $LiNMe_2$ results in reduction to give the tellurium(II) derivatives $Te[N(SiMe_3)_2]_2$ (**1**)[4] and $[Te(NMe_2)_2]_n$ (**2**),[5] respectively, as thermally stable, but very moisture-sensitive, yellow crystals. In contrast to the monomeric structure of $Te[N(SiMe_3)_2]_2$ [|d(Te-N)| = 205 pm],[4] complex **2** has a polymeric structure reminiscent of 1,2,5-telluradiazole (see Fig. 1).[6] The Te-N distances in the monomer units of **2** are also 205 pm while the intermolecular Te···N contacts are 296 pm (*cf.* 276 pm for **3**).



2 **3**

FIGURE 1 Association of monomer units in $[Te(NMe_2)_2]_n$ (**2**) and $(C_2H_2N_2Te)_n$ (**3**).

The polar tellurium(II)-nitrogen bond is readily susceptible to protolysis by weakly acidic reagents. For example, the reaction of $[Te(NMe_2)_2]_n$ with two equivalents of Ph_3CSH produces

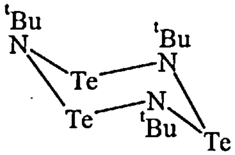
$Te(SCPh_3)_2$, which has a bent (S-Te-S 110.8°) monomeric structure.[4]

Alkynyl tellurides may be prepared by the reaction of terminal acetylenes with arenetellurenamides [Eq. (1)].

$$C_6H_5TeN(^iPr)_2 + RC{\equiv}CH \rightarrow RC{\equiv}CTeC_6H_5 + HN^iPr_2 \quad (1)$$
$$(R = Ph, {}^nBu)$$

Dialkynyl tellurides are obtained in moderate yields by the reaction of $TeCl_4$ with $LiN(SiMe_3)_2$ followed by the addition of a terminal acetylene,[8] presumably by the formation of **1**, as an intermediate.

The cyclic tellurium(II) imide $(TeN^tBu)_3$ (**4**) has been isolated as a minor product in the preparation of the tellurium diimide dimer $^tBuNTe(\mu\text{-}N^tBu)_2TeN^tBu$ from $TeCl_4$ and $LiNH^tBu$ (*vide infra*).[9] The complex **4** exists as a six-membered Te_3N_3 ring in the chair conformation with mean Te-N distances of 203 pm. The geometry at the three nitrogen atoms is essentially planar. There are no precedents in chalcogen-nitrogen chemistry for a six-membered E_3N_3 ring.

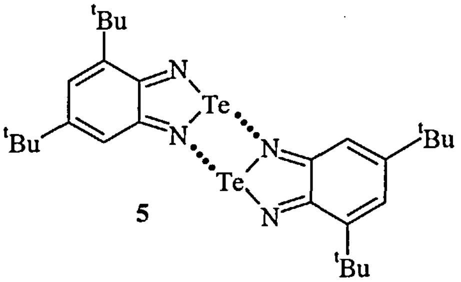


4

The oxidation of $Te[N(SiMe_3)_2]_2$ with AsF_5 produces the remarkable Te(III) cation radical $\{Te[N(SiMe_3)_2]_2\}[AsF_6]$ as blue crystals. This salt is monomeric in the solid state with d(Te-N) = 197 pm consistent with multiple bonding.[9] The ESR spectrum indicates that the unpaired electron is located primarily on the Te atom.

TELLURADIAZOLES

The telluradiazole $[{}^tBu_2C_6H_2N_2Te]_2$ (**5**) is the unexpected product from the reaction of $Ph_2P(NSiMe_3)_2Te(Cl)NPPh_2NSiMe_3$ [10] with ${}^tBu_3C_6H_2NHLi$ in a process that must involve C(aryl)-$C(CH_3)_3$ bond cleavage.[11] The intramolecular Te···N interactions (263 pm) are apparently stronger than those in the parent telluradiazole polymer (**3**). The bulky *tert*-butyl groups prevent further association in the case of **5**. The other geometrical parameters for **5** [d(Te-N) = 200 pm], < N-Te-N 85.8°] indicate that the tellurium(II) resonance form **A** is a more important contributor than **B** [tellurium (IV)] to the overall structure.[11] By contrast, a monomeric structure of type **B** has been postulated for tetrafluoro-2,1,3-benzotelluradiazole (**6**), which is prepared from $TeCl_4$ and tetrafluoro-1,2-phenylenediamine in a high boiling solvent, on the basis of spectroscopic data.[12]



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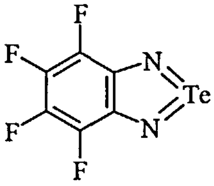

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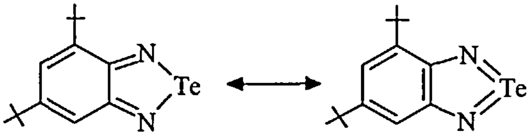
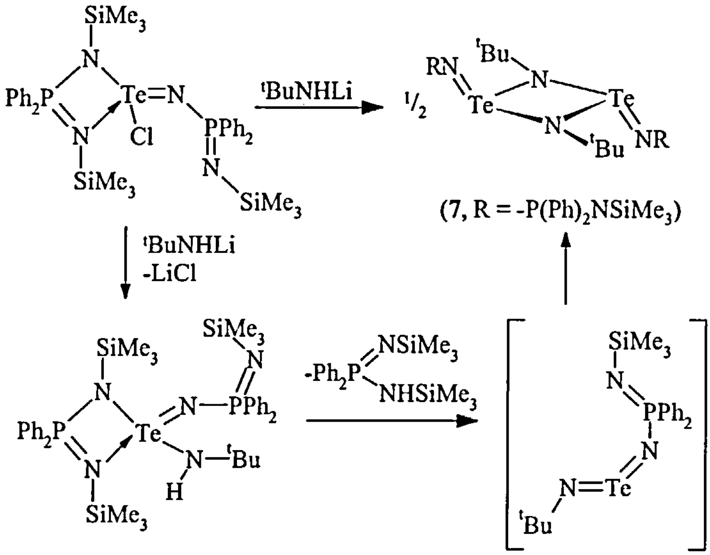


A **B**

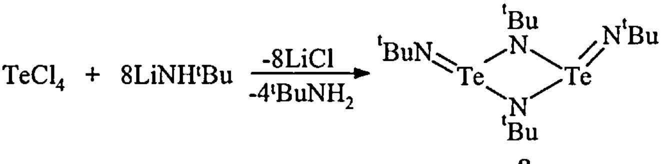
TELLURIUM(IV)-NITROGEN COMPOUNDS

Although there is an extensive chemistry of sulfur diimides, RN=S=NR, and the Se analogues have been known for more than 20 years, the corresponding tellurium diimides proved elusive until 1994.[13] The first example of a tellurium diimide was obtained by the unexpected route illustrated in Scheme I. Complex 7 has a dimeric structure with short exocyclic Te-N distances (190 pm). Although the *trans* isomer was characterized in the solid state, multinuclear (^{1}H, ^{31}P and ^{125}Te) NMR studies revealed that isomerisation to the corresponding *cis* isomer occurs slowly in solution at 25°C.[11]



SCHEME I

Subsequently, it was shown that **8**, the dimer of the symmetrical tellurium diimide $^tBuN{=}Te{=}N^tBu$, can be obtained in yields of up to 56% by the reaction of $TeCl_4$ with $LiNH^tBu$ in toluene at -78°C [Eq. (2)]. The cyclic tellurium(II) imide **4** is a minor product.[14,15]

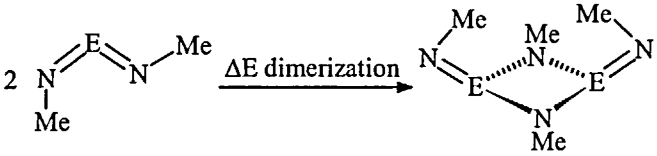


8

(2)

The dimer **8** is obtained as thermally stable, orange crystals which sublime at *ca.* 80°C/10^{-2} Torr.[14] The endocyclic and exocyclic Te-N distances are 208 and 188 pm respectively, and exocyclic N^tBu groups are in a *cis* orientation with respect to the folded Te_2N_2 ring. There is no exchange between terminal and bridging N^tBu groups in solution even at 100°C (^1H NMR).

Since dimeric structures are not found for sulfur or selenium diimides,[16] density functional theory calculations (DFT) have been performed to investigate the dimerization process shown in Eq. (3).



(3)

The calculated dimerization energies show that the process is endothermic ($\Delta E = 34.9$ kJ mol^{-1}) for E = S, approximately thermoneutral ($\Delta E = -2.8$ kJ mol^{-1}) for E = Se, and strongly exothermic ($\Delta E = -82.9$ kJ mol^{-1}) for E = Te consistent with the expected trend to lower π-bond energies for chalcogen-nitrogen (np-2p)π-bonds along the series S (n=3), Se (n=4), Te (n=5). The frontier orbitals for $[Te(NMe)_2]_2$ are illustrated in Fig. 2. A bonding combination of two monomer LUMOs is populated to provide the bridge bonding in the dimer.

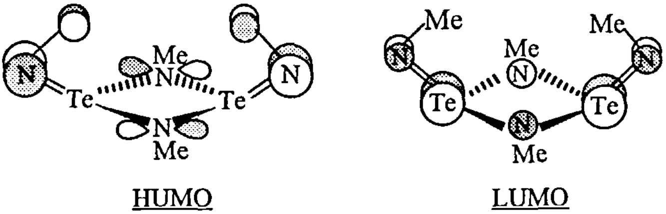
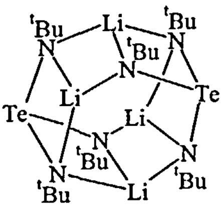


FIGURE 2 Frontier orbitals of $[Te(NMe)_2]_2$.

The LUMO of the dimer $[Te(NMe)_2]_2$ is Te-N π-antibonding with a large coefficient on tellurium. Consequently, reactions with nucleophiles are expected to occur at Te with cleavage of the Te-N bridge bonds. Indeed, the reaction of $[Te(N^tBu)_2]_2$ with four equivalents of $LiNH^tBu$ produces the triazatellurite $Li_2[Te(N^tBu)_3]$ which exists as the centrosymmetric dimer **9** with a hexagonal prismatic (cyclic ladder) structure.[18] The selenium analogue $[Li_2Se(N^tBu)_3]_2$, prepared from $^tBuN{=}Se{=}N^tBu$ and two equivalents of $LiNH^tBu$, has a similar structure.[19] The production of the $[Te(N^tBu)_3]^{2-}$ dianion involves the intermediate formation of the monoanion $[Te(N^tBu)_2(NH^tBu)]^-$, which is also obtained as the salt $\{Li[Te(N^tBu)_2(NH^tBu)]_2LiCl\}_2$ (**10**) by protonation of **9** with the stoichiometric amount of HCl.[15] The isoelectronic monoanion $[Te(N^tBu)_2(O^tBu)]^-$ is found in the complex $[K(THF)Te(N^tBu)_2(O^tBu)]_2$ (**11**) prepared by the treatment of $[Te(N^tBu)_2]_2$ with two equivalents of potassium *tert*-butoxide.[20]



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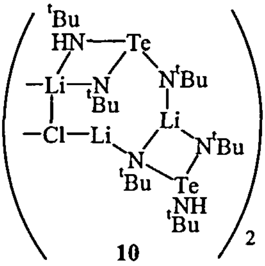

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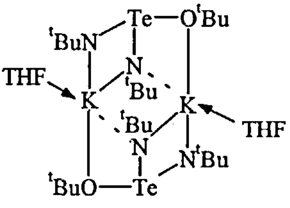
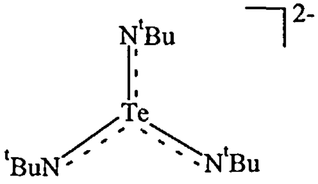
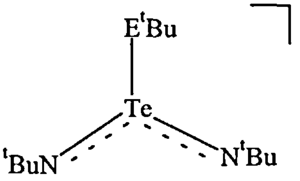


11

The pyramidal azatellurite anions $[Te(N^tBu)_3]^{2-}$, $[Te(N^tBu)_2(NH^tBu)]^-$ and $[Te(N^tBu)_2(O^tBu)]^-$ present in **9**, **10** and **11** exhibit mean Te-N bond lengths of 198, 194 and 192 pm, respectively. In the context of TeN single and double bond distances of 205 and 183 pm, respectively, these values are consistent with the resonance hybrids **C** (dianion) and **D** (monoanions).

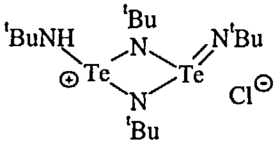


C



D (E = NH, O)

The HOMO of the dimer $[Te(NMe)_2]_2$ is primarily a π-lone pair localised on the terminal nitrogen atoms. Thus reactions with electrophiles are expected to occur at these exocyclic centres. Consistently, the reactions of **7** with HCl or $MeSO_3CF_3$ result in the protonation or methylation, respectively, of one of these nitrogen atoms.[15] The X-ray structure of [Te$_2$(^{t}BuNH)(^{t}BuN)$_3$]Cl (**12**) reveals the shortest known TeN distance (184 pm).[14] Unlike the dimer **8** itself, variable temperature ^{1}H NMR studies show that rapid exchange of bridging and terminal N^{t}Bu occurs in the protonated derivative **11**. This fluxional process presumably involves rapid 1,3-proton shifts between terminal and bridging N atoms followed by exchange of the resultant bridging ^{t}BuNH and terminal ^{t}BuN groups.[15] Although it has not been possible to generate diprotonated or dimethylated derivatives of **8**, the dimer does act as an N,N′-chelating ligand in the Ag$^+$ complex **13**.



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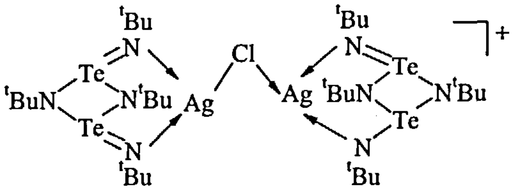
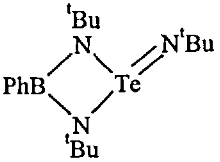


13

The dimer **8** also reacts readily with weak protic reagents to provide a variety of tellurium(IV) complexes. For example, the reaction of **8** with eight equivalents of *tert*-butanol produces Te(O^{t}Bu)$_4$ as thermally stable, colourless crystals.[22]

REACTIONS OF [Li$_2$Te(N^{t}Bu)$_3$]$_2$

The novel cage compound **9** contains the first structurally characterized triazatellurite, [Te(N^{t}Bu)$_3$]$^{2-}$, which is a potentially versatile building block for the incorporation of other p-block elements or transition metals into Te-N rings or cages. For example, the reaction of **9** with $PhBCl_2$ produces the four-membered (BN_2Te) ring compound **14**.[18] However, the cyclic tellurium(II) imide **4** is also obtained as a minor product suggesting that simple metathesis is accompanied by a redox process. Redox behaviour is observed exclusively in the reaction of **9** with $PhPCl_2$, which yields the spirocyclic tellurium(IV)/phosphorus(V) system **15** and elemental tellurium.[18]



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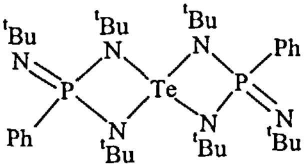
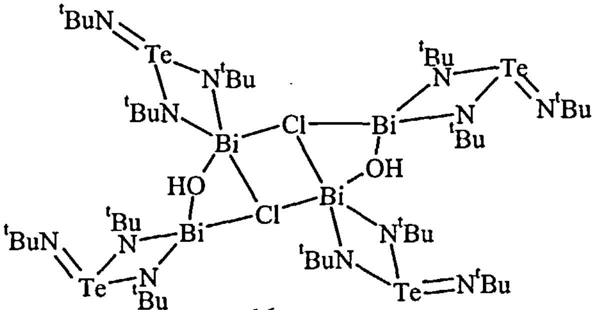


15

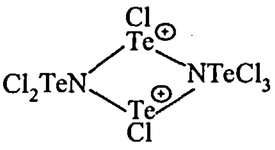
The reaction of **9** with $BiCl_3$ produces the partial hydrolysis product **16**, which contains a cluster of four BiN_2Te rings bridged by two Cl^- and two OH^- ions.[21]



16

TELLURIUM-NITROGEN-CHLORINE SYSTEMS

The reaction of $TeCl_4$ with $N(SiMe_3)_3$, in a 2:1 molar ratio in CH_3CN followed by treatment of the product with AsF_5 in liquid SO_2, gives $[Te_4N_2Cl_8][AsF_6]_2 \cdot 2SO_2$.[23] The dication $Te_4N_2Cl_8^{2+}$ (**17**) in this salt is the dimer of $[Cl_3Te\text{-}N{=}Te\text{-}Cl]^+$, another illustration of the self-association of multiply bonded TeN species. The compound $[Te_{11}N_6Cl_{26}]_2 \cdot 9C_7H_9$ was isolated from the reaction of $TeCl_4$ with $N(SiMe_3)_3$ carried out in boiling toluene.[24] Each half of this centrosymmetric dimer contains a $[Te_5N_3Cl_{10}]^+$ cation (**18**) and a $[Te_5N_3Cl_{12}]^-$ anion linked to a $TeCl_4$ molecule. A planar Te_5N_3 structural motif (**18**) is common to both the anion and cation in this complex structure.



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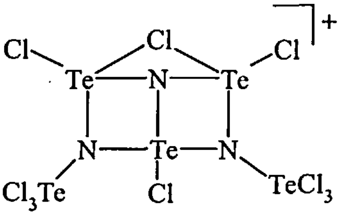

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SUMMARY

During the last three years significant progress has been made in the synthesis and structural characterization of "user-friendly" Te-N compounds. These include the tellurium(II) amide $[Te(NMe_2)_2]_n$, a dimeric telluradiazole, and the first examples of (a) a cyclic tellurium imide, $[Te(N^tBu)]_3$ (b) tellurium diimide dimers, e.g. $[Te(N^tBu)_2]_2$ and (c) a triazatellurite, $[Li_2Te(N^tBu)_3]_2$. The versatile reactivity of the latter two reagents holds considerable promise for the future development of Te-N chemistry.

Acknowledgements

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