Synthesis of intramolecularly coordinated heteroleptic diorganotellurides and diorganotelluroxides: Isolation of monomeric diorganotelluroxide [{2,6-(Me2NCH2)2C6H3}2TeO] and diorganohydroxytelluronium chloride [{2,6-(Me2NCH2)2C6H3}2Te(OH)]Cl

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Abstract
A series of heteroleptic diorganotellurides (2-NMe2CH2C6H4)(R)Te, where R = C6H5 (5), 2-MeC6H4 (6), 2,6-MeC6H3 (7) and 2,6-iPrC6H3 (8) was synthesised from N,N-dimethylbenzylamine via the ortho-lithiation route. Reactions of 5–8 with SO2Cl2 followed by alkaline hydrolysis afforded diorganotelluroxides (2-NMe2CH2C6H4)(R)TeO, where R = C6H5 (10), 2-MeC6H4 (11), 2,6-MeC6H3 (12) and 2,6-iPrC6H3 (13) respectively. A similar alkaline hydrolysis of homoleptic diorganotellurides, {2,6-(Me2NCH2)2C6H3}2Te (9), afforded a co-crystal of [{2,6-(Me2NCH2)2C6H3}2TeO] (14a) and disordered [{2,6-(Me2NCH2)2C6H3}2Te(OH)]Cl (14b) or a completely ordered diorganohydroxytelluronium chloride [{2,6-(Me2NCH2)2C6H3}2Te(OH)]Cl (14c). Heteroleptic diorganotellurides 7–8 and telluroxides 10–14a–b and diorganohydroxytelluronium chloride 14c were characterised by single crystal X-ray diffraction studies. In the molecular structures, the N-donor substituent made five-membered chelating ring with the tellurium atom via Te—N secondary bonding interactions. Diorganotelluroxide 10 existed in dimeric form exhibiting both intramolecular Te—N and intermolecular Te—O secondary interactions. Due to the strong intramolecular Te—N secondary bonding interactions from the three N-donor substituents, diorganotelluroxide 14a was stabilised in the monomeric form. This is, in fact, the only second example of a discrete monomeric diorganotelluroxide. Again, because of the presence of intramolecular Te—N secondary bonding interactions, the diorganotelluroxides 10–14a–b and diorganohydroxytelluronium chloride 14c exhibited downfield 125Te NMR chemical shift as compared with the earlier reported oligomeric or polymeric diorganotelluroxides.

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1. Introduction

Organotelluroxanes, a class of tellurium derivatives containing Te—O covalent bond, have become an important research area in organometallic chemistry with respect to their promising applications in various aspects such as in, catalysis [1–3], oxygen transfer reactions [4–6], developing supramolecular synthons [7–9], synthesis of biologically active compounds [10–13], and CO2 fixation [14,15] to name a few. Within this broad context, diorganotelluroxide (R2TeO), a class of tellurium(IV) compounds have gained significant attention with respect to their structural heterogeneity [16–19], stabilisation by intramolecular secondary bonding interactions [20,21] and more importantly with their diverse reactivity [1,2,4–6,14,15,22,23]. Due to the presence of polar Te—O bond, one of the promising reactions of diorganotelluroxide in organometallic chemistry is the oxidation reaction, where it acts as a mild oxidant. In particular, the oxidizing properties of various diorganotelluroxides towards the conversion of different alcohols, xanthates, phosphines, thiobezoates, etc. to their corresponding oxo derivatives have been comprehensively studied in literature [22,24–28].

Although, the synthesis of first diorganotelluroxide, Ph2TeO was

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reported in 1894 [29], its structural elucidation remained elusive for a long time, until Alcock et al. reported the molecular structure of Ph₂TeO in dimeric form [16]. In fact, it is worth noting that most of diorganotelluroxides exist in aggregated form (dimer or polymer) in their solid states, which is accountable to their polar Te=O bonds [16–19,21,30]. Oba et al. have incorporated bulky aryl groups namely, 2,4,6-trisopropylphenyl (Tip) and 2,4,6-trimethylphenyl (Mes) and reported the synthesis of diorganotelluroxides, Tip₂TeO, 1 and Mes₂TeO, 2 (Chart 1) [30]. (Chart 1 should be ideally placed before Scheme 1.) Diorganotelluroxides 1 and 2 exist in the dimeric form originating from the intermolecular Te…O secondary interactions. Klapötke et al., fortuitously, isolated the first mono-meric telluroxide, (2-Me₂NCH₂C₆H₄)₂TeO, 3 stabilised by intramolecular Te…N secondary bonding interactions from the N donor atoms of the side arms to the Te atom [20]. Recently, our group has reported the synthesis of bist[2-phenylazophenyl-C,N’]tellurium(IV) oxide, 4 by alkaline hydrolysis of bist[2-phenylazophenyl-C,N’]tellurium(IV) dichloride in ethanolic solution [21]. Due to the steric constraints from the bulky azo groups, only one of the two sp³ N-donor substitutions was involved in secondary bonding interactions to the tellurium atom. Consequently, telluroxide 4 was stabilized in dimeric form consisting of both intramolecular Te…N and intermolecular Te…O secondary interactions. Interestingly, when (2-phenylazophenyl-C,N’)tellurium(IV) trichloride was subjected to alkaline hydrolysis in THF solution, it underwent condensation to afford heptatellurium covalent cluster stabilized by extensive Te…N secondary bonding interactions [31]. One of the interesting aspects of diorganotelluroxide (R₂TeO) is that, due to the polar and basic nature of Te=O bond, it readily undergoes hydrolysis in presence of moisture to afford diallyltellurium dihydroxide, [R₂Te(OH)]₂ [32–34]. The diallyltellurium dihydroxide, being unstable by nature, can further undergo dissociation resulting in the formation of diallyldi oxytellurium(IV) cation, [R₂Te(OH)]⁺. Beckmann et al. have synthesized intramolecularly coordinated diorganotelluroxide, (8-Me₂NC₆H₄)₂TeO and reacted with triflic acid (HOT₃SCF₃). It was observed that diorganotelluroxide (8-Me₂NC₆H₄)₂TeO underwent protonation and afforded diaryldi oxytellurium triolate, [(8-Me₂NC₆H₄)₂Te(OH)](O₃SCF₃) [33]. Similar results were also observed when (p-MeOC₆H₄)₂TeO was treated with HO₃SCF₃ or diphenylphosphinic acid (HO₂PPh₂) [34]. From the literature studies, it is perceived that most of the diorganotelluroxides reported so far are ‘homoleptic’ i.e., both the ‘R’ group in R₂TeO are identical. Herein, in the present work, we report the synthesis of a series of intramolecular interaction stabilized ‘heteroleptic’ diorganotelluroxides, 10–13, where one of the ‘R’ groups contains ‘one coordinating group’ with sp³ N-donor atom. Recently we have reported the ligation behavior of homoleptic diorganotelluride namely bist[2,6-(dimethylamino)methyl] phenyltelluride, 9 containing four coordinating sp³ N-donor atoms [35]. In this paper, we envisaged to explore the oxidation reaction of 9 and report the synthesis of the ‘second’ example of a monomeric diorganotelluroxide, 14a and its protonated derivatives 14b–c. The structures of the synthesized diorganotelluroxides, 10–14a–b and diorganohydroxytellurium chloride 14c were thoroughly studied both in solution states as well as solid states (telluroxide 10 and 14a–b and diorganohydroxytellurium chloride 14c) and are compared with the similar reported diorganotelluroxides and diorganohydroxytellurium salts.

2. Results and discussion

In order to synthesize diorganotellurides 10–13, first diorganotellurides 5 [36–8] were synthesized by the otho-lithiation route as reported in the literature (Scheme 1) [36,37]. In particular, N,N-dimethylbenzylamine was treated with n-BuLi to afford the aryllithium intermediate. When aryllithium bromides, R₄Br (generated in situ by slow addition of dry benzene solution of Br₂ to the Et₂O solution of R₂Te₂ at -114 °C; R = C₆H₅, 2-MeC₆H₄, 2,6-Me₂C₆H₃, 2,6-Pr₂C₆H₃) were added to the lithiated intermediates, nucleophilic substitution reactions took place at the tellurium centers to afford diorganotellurides, 5–8. Diorganotellurides 5–8 were purified by column chromatography using petroleum ether (60–80%) as eluent. The first fraction was isolated as the corresponding diorganoditellurides (R₂Te₂) and the second fraction obtained was the desired diorganotellurides 5–8. The yield of the diorganotellurides ranged from 42 to 45% in all the cases. It is

![Chart 1. Examples of monomeric and dimeric diorganotelluroxides.](image-url)
worth-mentioning that the formation of corresponding ditellurides significantly reduced the yield of the desired tellurides. Diorganotelurid, 9 was synthesized from 2-bromo-1,3-bis(2-methylamino)methyl]benzene by the treatment of n-Buli followed by addition of Te(dtc)₂ (dtc = diethylidithiocarbamate) [35]. The synthesis of diorganoteluridoxanes 10–13 from the corresponding diorganotelurid 5–8 was achieved by chlorination followed by alkaline hydrolysis. In detail, when tellurides 5–8 were chlorinated by SO₂Cl₂, the corresponding diorganotelurid(IV) chlorides were obtained. The diorganotelurid(IV) chlorides on alkaline hydrolysis by NaOH afforded the desired diorganoteluridoxides 10–13 (Scheme 1).

Interestingly, the oxidation reaction of 9 with SO₂Cl₂/NaOH was not as straightforward and provided varied oxidized products from preparation to preparation (Scheme 2). The initial oxidation experiment provided a co-crystal of novel monomeric telluridoxide 14a and zwitterionic telluroxane 14b (as evident by single crystal X-ray diffraction studies, vide infra). In order to check the reproducibility of the experiments, when the experiment was repeated, it offered completely ordered diorganohydroteluridoxide chloride 14c (vide infra).

The ¹H NMR spectra of diorganoteluridoxanes 5–8, recorded in CDCl₃ at room temperature, showed sharp singlet at ~2.2 ppm corresponding to the -N(CH₃)₂ protons from the N,N-dimethylbenzylamine moiety. The benzylic protons attached to the -N(CH₃)₂ showed a sharp singlet at ~3.4 ppm for all the tellurides. The aromatic protons and the protons corresponding to the substituent(s) on the ancillary phenyl ring showed resonances in the expected regions with appropriated integration values (vide infra). Interestingly, in the corresponding ¹H NMR spectra of telluridoxides 10–13, due to the geminal coupling, the two benzyl protons resolved in to two discrete diastereotopic signals. The splitting of the benzyl protons in the telluridoxides in comparison to that of the corresponding tellurides might be attributed to the more restricted rotation of the side arms around the tellurium center due to the presence of Te=Y bond.

The ¹²⁵Te NMR chemical shifts for the synthesized tellurium derivatives are given in Table 1. The ¹²⁵Te NMR spectra of all the synthesized tellurium derivatives exhibited single resonance signals suggesting the desired purity and stability of the compounds. In particular, the ¹²⁵Te NMR signals for tellurides 5–9 appeared in the region 633–350 ppm (Table 1). These chemical shifts are considerably downfield shifted in comparison to other related diorganoteluridoxides which lacked intramolecular coordinating N-donor substituents [38]. The ¹²⁵Te NMR signals for the telluridoxanes 10–14b-c were significantly downfield shifted in comparison to the corresponding tellurides and appeared in the region 1223–1256 ppm. The significant downfield shifts of the telluridoxanes 10–14 in comparison to that of the tellurides, 5–9, are attributed to the presence of polar Te=Y bonds in the former. These chemical shifts in 10–14 are in agreement with the values reported in the literature for similar telluridoxides. For example, telluridoxide 4 exhibited ¹²⁵Te NMR chemical shift at 1228 ppm [21]. Similarly (8-Me₂NC₆H₄)₂TeO exhibited chemical shift at 1255 ppm (in CD₂OD) and 1272 ppm (in CDCl₃) [33].

The High Resolution Electrospray Ionization Mass Spectrometry (HRMS) also aided validation of the synthesized telluridoxides 5–9 and telluridoxanes 10–14. In the mass spectra taken in the positive ion mode, the molecular ion peaks at m/z 342.0495 (Calc. 342.0497 [M+H]+) (5), 356.0654 (Calc. 356.0653 [M+H]+) (6), 370.0811 (Calc. 370.0810 [M+H]+) (7), 426.1436 (Calc. 370.1436 [M+H]+) (8) substantiated the formation of the tellurides. Similarly, in cases of the mass spectra of telluridoxides 10–14, the molecular ion peaks at m/z 358.0445 (Calc. 358.0446 [M+H]+) (10), 372.0601 (Calc. 372.0602 [M+H]+) (11), 386.0758 (Calc. 386.0759 [M+H]+) (12), 442.1385 (Calc. 442.1385 [M+H]+) (13) confirmed the formation of the respective compounds. It is worth noting that the observed patterns in HRMS of all the compounds were in agreement with the simulated isotopic patterns.

Interestingly, in the ¹²⁵Te NMR spectrum of telluridoxide 14a-b, a single resonance was observed at 1119 ppm. This observation is probably due to the rotation of the side arms around the tellurium center due to the geminal coupling, the two benzyl protons resolved in to two discrete diastereotopic signals. The splitting of the benzyl protons in the telluridoxides in comparison to that of the corresponding tellurides might be attributed to the more restricted rotation of the side arms around the tellurium center due to the presence of Te=Y bond.

In the ¹H NMR spectrum of 14a and 14b, all the signals appeared

| Table 1 ¹²⁵Te NMR chemical shifts for tellurides 5–9 and telluridoxides 10–14. |
| Telluride Chemical shift (δ) in ppm | Telluridoxide Chemical shift (δ) in ppm |
| 5 | 633 | 10 | 1223 |
| 6 | 549 | 11 | 1214 |
| 7 | 410 | 12 | 1240 |
| 8 | 350 | 13 | 1256 |
| 9 [37] | 367 | 14 | 1119 |

Scheme 2. Synthesis of monomeric diorganoteluridoxides 14a-b and diorganohydroteluridoxide chloride 14c.
broad, which in turn, could not be adequately integrated. The broadening of the signal could be probably due to the fluxional nature of the proton and interconversion of 14a ↔ 14b in the solution state. In fact, from the solid state structural analysis, it was revealed that in compound 14b, another equilibrium is present where 14b and 14c existed as tautomer in the ratio 72.2(1):27.8(1) (vide infra). Such broadening of signals in $^1$H spectrum of 14a-b is not unusual, as similar complexity in $^1$H spectra of intramolecularly coordinated diorganotelluroxanes has been observed in the literature [33,34], as these molecules are prone to fluxional behavior in solution state. In comparison to the $^1$H NMR spectrum of 14a-b, the corresponding $^1$H NMR spectrum of 14c was well-resolved. The aromatic protons showed resonances in the range 7.1–8.1 ppm. The chemical shifts for the benzylic protons were observed in the range 2.5–4.5 ppm. Out of the four methylene groups one showed AB pattern and appeared in the down field region. This might be due to the interactions of the corresponding nitrogen atom to the tellurium center. In the IR spectrum of compound 14c, the absorption at $\tilde{\nu}=3417$ cm$^{-1}$ corresponded to the O–H stretching vibration involved in hydrogen bonding interactions. It is worth mentioning that the formation of diorganotelluroxides 14aa-b and diorganohydroxytellurium chloride 14c from telluride under similar conditions might be attributed to the generation of varying amounts of HCl during hydrolysis. Interestingly, in both the reactions only one HCl molecule is trapped.

3. Crystal structures

To confirm the proposed formulations of the synthesized compounds, we obtained single crystals for X-ray diffraction experiments. The molecular structure of monotelluride 7 is shown in [Fig. 1a]. In the molecular structure, the unit cell contains two molecules of compound 7. The spatial arrangement around Te atom is distorted T-shaped, taking the Te···N intramolecular interaction in to account. The tellurium atom is bonded to two carbon atoms with Te1–C1 and Te1–C10 distances of 2.123(4) Å and 2.156(5) Å respectively. It is worth mentioning that due to the hypervalent interaction, the Te1–C10 bond, which trans to the amino group, is elongated in comparison to that of Te1–C1 bond. These distances are in agreement with the sum of the single bonded covalent radii for Te–C (2.11 Å) bond, as suggested by Pauling [39]. The N1···Te1–C10 bond angle 165.1(1)$^\circ$ deviates from linearity, whereas N1···Te1–C1 angle is 71.2(1)$^\circ$. The intramolecular Te1···N1 bond lengths of 2.786 (4) Å is much shorter than $\Sigma_{vdw}$(Te, N) i.e. 3.58 Å but are longer than $\Sigma_{cov}$(Te, N) i.e. 2.09 Å [39,40]. This Te···N bond distance is in close agreement with the values observed in telluride 5 [36] and other related compounds, namely bis[2-(phenylazo)phenyl]-CN$^-$telluride [2.62(2) Å] [21], bis[2-(4’-methoxyphenyl)iminomethinylphenyl]telluride [2.702(3) Å] [41], bis[2-isopropyl-iminomethinylphenyl]telluride [2.720(2) Å] [41], 8-(dimethylamino)naphthyltelluride [2.713(1) Å] [42]. The C1–Te1–C10 angle is 93.93 (16)$^\circ$ and is close to the related diorganotellurides [21, 36, 41–42].

The molecular structure of compound 8 [Fig. 1b] is similar to that of 7, except the fact that in the place of phenyl ring, diisopropylphenyl unit is bonded to the tellurium atom. The intramolecular Te1···N1 distance is 2.844 (2) Å, is slightly longer than that observed for compound 7. The N1···Te1–C10, N1···Te1–C1, C1–Te1–C10 bond angles are 165.91 (7)$^\circ$, 70.64 (7)$^\circ$ and 95.41 (8)$^\circ$ respectively. All these bond angles are in line with that of the previous structure, 7. Again, Te1–C1 and Te1–C10 distances of 2.122(2) Å and 2.167(2) Å respectively closely resemble with the respective bond distances observed in compound 7.

The molecular structure of telluroxide 10 is shown in [Fig. 2]. In the unit cell of telluroxide 10, two asymmetric units are connected to a water solvent molecule via H-bonding. Compound 10 exists as a dimer consisting of a Te$_2$O$_2$ core with two different Te–O distances, one characteristic Te–O double bond and other one is elongated coordinative bond. The structure of the compound essentially resembles to that of the previously reported dimeric diaryltellurium(IV) oxides [16–18,30]. The geometry around each tellurium atom is distorted square pyramidal. The Te–O double bond

![Fig. 1](image1.png) Molecular structures of (a) 7 and (b) 8 at 50% probability level.

![Fig. 2](image2.png) Molecular structure of dimeric telluroxide, 10 at 50% probability level.
bond distance is 1.872 (3) Å, which is in agreement with the corresponding Te–O bond distances observed in similar dimeric telluroxides such as Ph₂TeO [1.871(2) Å] [16], (C₆F₅)₂TeO [1.872 (2)/1.87(1) Å] [17], 1 [1.853(5)], 2 [1.855(4)] [30], 4 [1.864 (12) Å] [21]. Similarly, the secondary intermolecular Te…O distance of 2.525(3) Å is close to that observed for Ph₂TeO [2.563(21), 2.545(22) Å] [16], 1 [2.536(5) Å, 2.518(4) Å], 2 [2.613(4) Å, 2.647(4) Å] [30] and 4 [2.623(12) Å] [21]. The intramolecular Te…N secondary bonding distance of 2.819(3) Å is considerably longer than that of 3 [2.755(6) and 2.565(4) Å] [20], 4 [2.714(1) Å] [21]. The Cl₁–Te₁–C₁₀ bond angle in 10 is 94.27(16)°, which is again in the same range of the corresponding bond angles found in Ph₂TeO [90.6(6)°, 91.8(6)°] [16], 1 [94.7(2)°], 2 [94.1(2)°, 96.8(2)°] [30] and 4 [90.69(6)°] [21].

The title compound 14 was a co-crystal of a salt, [C₂₂H₃₉N₄OTe]⁺Cl⁻ (14b) and the neutral molecule, [C₂₂H₃₈N₂TeO] (14a) as well as a water solvent molecule at full occupancy. The occupancy factors were 0.9059(7) for the salt and 0.0941(7) for the neutral molecule (Fig. 3). Each component will be discussed separately but it is notable that both contain rare examples of a monomeric telluroxide moiety. Even in the major component, i.e., in 14b, the H-atom is distributed between the telluroxide O-atom and the proximal N-atom. In the major component, it is attached to N1B with occupancy of 0.6545(15) and in the minor component it is attached to O1A with occupancy of 0.2514(15) [both values add up to 0.9059 which is the occupancy of the major component overall and the ratio between the major component and minor component within 14b is 72.2(1):27.8(1)]. For the major tautom, there is a very strong hydrogen bond between N1B and O1A [N1B–O1A separation of only 2.621(4)]. In the major component, i.e., the salt 14b (Fig. 3a), the central Te is six coordinate with a coordination sphere made up of a terminal Te–O (with H delocalized between O1A and N1B), 2 C donors from two phenyl rings and three of the possible 4 N donor atoms. This results in a very distorted octahedral arrangement where the trans angles range from 156.74(11)° to 174.30(8)° and the cis angles range from 69.48(8)° to 116.97(9)°. In the coordination sphere, the terminal Te–O bond at 1.943(3) Å is longer than that observed in previous telluroxides containing Te–O bonds [16–21] while the Te–C distances at 2.1229(18) Å and 2.1756(18) Å are in the normal range. The Te–N distances at 2.665(3) Å, 2.676(3) Å and 2.755(3) Å, while longer than typical Te–N single bonds, are much shorter than the sum of the van der Waals radii for these atoms [40]. The two phenyl rings occupy cis position in the Te coordination sphere and are twisted with respect to each other making a dihedral angle of 60.0(1)°.

![Fig. 3. Molecular structures of (a) 14a and (b) cation of 14b (major tautomer only) and (c) cation of 14c.](image-url)
There is no evidence of either π…π stacking or C–H…π interactions, thus the major influence on the packing arrangement is a hydrogen bonding scheme (see in Supporting Information, Fig. S36) which involves both intra- and interspecies hydrogen bonds. There is a strong intra-species hydrogen bond involving the N⁺–H and the Te–O moieties [N…O distance of 2.626(5) Å and N–H…O angle of 174.3(4)°]. The major influence in the packing results from the cations, chloride anion and water molecules linked into ribbons in the 1 0 1 direction by O–H…Cl, C–H…Cl and O–H…O hydrogen bonds. In the minor tautomer the O–H group forms a weaker hydrogen bond with N1A.

The minor component, [C24H38N4OTe], 14a is only at 0.0941(7) occupancy and thus the esd’s on its metrical parameters are significantly larger than those of the major component. In addition, the coordination sphere about the central Te is significantly different from that in the cation as in this case the Te is five coordinate with a distorted square pyramidal geometry (τ = 0.287) (Fig. 3b). The coordination sphere is made up of the terminal O, 2 C donors from two phenyl rings and two N donors (one each from the two ligands). The terminal Te–O distance is 1.83(3) Å, a value which is much closer to those found in other telluroxides [16–21] and significantly shorter than that observed in the cation, 14b. The Te–C [2.084(5) Å, 2.222(5) Å] and Te–N [2.678(5) Å, 2.763(5) Å] distances are similar to those observed in the cation. As is observed for the cation, the two phenyl donors occupy cis positions in the coordination sphere and are significantly twisted with a dihedral angle of 57.1(1)°.

Obviously the packing arrangement for the neutral molecule cannot be the exactly the same as that observed for the salt. However, since they are co-crystals (or alternatively considered as a 9% doping into the major lattice), the packing arrangement looks quite similar as observed from an examination of the two packing diagrams (see in Supporting Information, Fig. S37). There is no N⁺–H group or Cl⁻ anion but the H2O molecule is still present and dominates the packing arrangement. The major packing interactions involve O–H…O(terminal) and C–H…O(water) within the stoichiometric unit with no interactions between units. Thus in the absence of both the N⁺–H group and Cl⁻ anion there are no ribbons in the 1 0 1 direction.

In order to test the reproducibility of this reaction, it was repeated under identical conditions and new crystals were obtained. Even though the cell constants for the new sample were identical to those previously obtained (within experimental errors), a new structure was obtained (14c). In this case there was no disorder, no minor component and only the salt was obtained, which had metrical parameters which were identical to the major component in 14b but with a better overall result (i.e. lower esd’s). Unlike the previous case, in 14b where the H was only partially attached to O (ca. 27.8%) in 14c it is completely localized on O confirming that both 14a-b and 14c are hydroxyltelluroxide cations (for these metrical parameters for both 14b and 14c along with figures of all species present see ESI). Thus 14c can be considered to be a pseudo-polymorph as well as a tautomer of 14b.

4. Conclusion

As an extension of our previous work for the synthesis of diorganotelluroxides stabilized by secondary bonding interactions [21], here we have reported the synthesis of a series of intramolecularly coordinated heteroleptic diorganotelluroxides. To overcome the steric constraints observed in the previous work due to the presence of two bulky azo groups, in the present work we have used heteroleptic diorganotellurides as a precursors that contain flexible sp³ N-donor arm(s). When diorganotellurides with one coordinating group are used, similar to our earlier observations, we have obtained dimeric diorganotelluroxides stabilized by both intramolecular Te–N and intramolecular Te–O secondary interactions. However, when a pincer type substrate is used where each aryl substrate contains two coordinating groups, we have succeeded in isolating the second example of monomeric, heteroleptic diorganotelluroxide, 14a and its protonated derivative 14b. Interestingly, in order to check the reproducibility of the reaction, when the oxidation of 9 was carried out under identical conditions, the tautomer of 14b, where the proton was located on oxygen was isolated and the structure was completely orders. In diorganotelluroxide, 14 the N-donor substituents offered extensive intramolecular Te–N secondary bonding interactions to the Te atom and thereby sufficing the coordination environment around Te center. This results in the isolation of a monomeric telluroxide entity.

5. Experimental section

5.1. Materials and methods

All manipulations were performed under a N₂ atmosphere using standard Schlenk techniques. Solvents were dried by following standard methods. The starting materials and solvents were purchased from commercial sources. ¹H (400 and 500 MHz), ¹³C (100 and 125 MHz) and ¹²⁵Te (126 MHz, 158 MHz) NMR spectra were recorded on Bruker AV 400 MHz and Bruker AV 500 MHz spectrometers at 25 ºC. Chemical shifts were referenced to TMS (¹H,¹³C) as internal and Me₄Te (¹²⁵Te) as external standard. Electron spray mass spectra (ESI-MS) were performed on a Q-Tof micro (YA-105) mass spectrometer. Melting points were recorded in capillary tubes on a Veego VMP-1 instrument and are uncorrected.

5.2. General procedure for synthesis of diaryltelluride (5–8)

A stirred solution of N,N-dimethylaniline (1.95 mL, 1.78 g, 13.16 mmol) in dry Et₂O (50 mL) was treated dropwise with 1.6 M solution of n-ButLi in hexane (8.23 mL, 13.16 mmol) at 0 ºC under nitrogen atmosphere for 30 min. The reaction mixture was allowed to stir for 24 h at room temperature to give a white suspension of the lithiated product. A solution of ArTeBr (Ar = C₆H₅, 2-MeC₆H₄, 2,6-Me₂C₆H₃, 2,6-Pr₂MeC₆H₃) was prepared in situ by slow addition of solution of Br₂ in benzene (10 mL) at −114 ºC to the solution of Ar₂Te₂ (Ar = C₆H₅, 2-MeC₆H₄, 2,6-Me₂C₆H₃, 2,6-Pr₂MeC₆H₃) in 150 mL of Et₂O. The solution was stirred for 30 min in an ice bath. The white suspension of the lithiated product was transferred via a cannula to the dark red RTeBr reagent at −114 ºC and the resulting suspension was stirred for 2 h at the same temperature and at room temperature for 6 h. After completion of the reaction (monitored by TLC), saturated NH₄Cl aqueous solution (100 mL) was added. The reaction mixture was extracted with Et₂O (25 mL x 3) and the organic phase was washed with H₂O, dried over anhydrous Na₂SO₄ and concentrated over rotary evaporator. The resulting semi-solid was purified by column chromatography using petroleum ether (60–80%) as eluent. The first fraction isolated was Ar₂Te₂ and second fraction was desired diorganotellurides 5–8.

Synthesis of 5 [36]. Reagents used were C₆H₅TeBr, prepared by Br₂ (1.05 g, 6.58 mmol), 1,2-diphenyldimethanoxide (2.69 g, 6.58 mmol). A yellowish liquid which solidified upon cooling to give crystalline solids (yield: 0.75 g, 42%); m.p. 77–80 ºC (lit 77 ºC [36]). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.80 (d, 2H, Ar–H), 7.29–7.27 (m, 1H, Ar–H), 7.20–7.16 (m, 2H, Ar–H), 7.08 (d, 1H, Ar–H), 7.02–7.00 (d, 2H, Ar–H), 6.84 (t, 1H, Ar–H), 3.46 (s, 2H, ArCH₂), 2.18 (s, 6H, NMe₂).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 140.84, 140.53, 134.73, 129.32, 128.73, 128.01, 127.97, 125.94, 122.91, 121.11, 66.38, 43.89. ¹²⁵Te NMR
(126 MHz, CDCl3): δ (ppm) 633. ESI-MS (positive mode): [M+H]+ m/z = 342.0495 (observed), 342.0497 (calculated).

**Synthesis of 6.** Reagents were used 2-MeC6H4TeBr (in situ) prepared by Br2 (1.05 ml, 6.58 mmol), 1,2-di-o-tolylditelluride (2.88 g, 6.58 mmol). A Yellowish liquid which solidified upon cooling. Yield: 0.80 g (45%). 1H NMR (400 MHz, CDCl3): δ (ppm) 7.88 (d, 1H, Ar-H), 7.20 (s, 2H, Ar-H), 7.00—6.94 (m, 4H, Ar-H), 6.81 (t, 1H, Ar-H), 3.43 (s, 2H, Ar-CH2), 2.37 (s, 2H, Ar-CH3), 2.17 (s, 6H, NMe2). 13C NMR (100 MHz, CDCl3): δ (ppm) 142.71, 141.20, 141.07, 134.51, 129.09, 128.99, 128.81, 128.01, 126.50, 125.93, 124.13, 122.56, 66.55, 44.00, 27.22. 125Te NMR (126 MHz, CDCl3): δ (ppm) 549. ESI-MS (positive mode): [M+H]+ m/z = 356.0654 (observed), 356.0653 (calculated).

**Synthesis of 7.** Reagents were used 2,6-Me2C6H4TeBr (in situ) prepared by Br2 (1.05 ml, 6.58 mmol) [1,2-bis(2,6-dimethylphenyl)ditelluride] (3.06 g, 6.58 mmol). White solid, yield: 0.78 g (44%); m.p. 88—90 °C. 1H NMR (400 MHz, CDCl3): δ (ppm) 7.17—7.14 (m, 1H, Ar-H), 7.13—7.11 (m, 1H, Ar-H), 7.05 (d, 2H, Ar-H), 6.98 (t, 1H, Ar-H), 6.85 (t, 1H, Ar-H), 6.61 (d, 1H, Ar-H), 3.42 (s, 2H, Ar-CH2), 2.35 (s, 6H, CH3), 2.20 (s, 6H, NMe2). 13C NMR (100 MHz, CDCl3): δ (ppm) 143.82, 138.74, 135.95, 132.55, 132.49, 132.35, 129.00, 128.44, 128.00, 129.17, 125.24, 64.67, 45.07, 24.49. 125Te NMR (126 MHz, CDCl3): δ (ppm) 140.83. ESI-MS (positive mode): [M+H]+ m/z = 370.8011 (observed), 370.8010 (calculated).

**Synthesis of 8.** Reagents were used 2-Pr2C6H3TeBr (in situ) prepared by Br2 (1.05 ml, 6.58 mmol) [1,2-bis(2,6-diisopropylphenyl)ditelluride] (3.80 g, 6.58 mmol), provided a white solid. Yield 0.76 mg (43%); m.p. 95—97 °C. 1H NMR (400 MHz, CDCl3): δ (ppm) 7.18 (t, 1H, Ar-H), 7.14 (t, 1H, Ar-H), 7.01 (d, 1H, Ar-H), 6.94 (t, 1H, Ar-H), 6.83 (d, 1H, Ar-H), 6.77—6.73 (m, 1H, Ar-H), 3.69 (sept, 2H, Ar-CH2), 3.46 (s, 2H, Ar-CH3), 2.21 (s, 6H, NMe2). 13C NMR (100 MHz, CDCl3): δ (ppm) 155.53, 140.91, 134.67, 129.77, 128.73, 128.68, 128.74, 125.60, 123.93, 122.93, 66.84, 44.20, 39.51, 24.83. 125Te NMR (126 MHz, CDCl3): δ (ppm) 350. ESI-MS (positive mode): [M+H]+ m/z = 426.1436 (observed), 426.1436 (calculated).

5.3. General procedure for the oxidation of tellurides 10—14 by halogenation followed by hydrolysis

A solution of tellurides 5—9 in CCl4 (15 ml) was chlorinated by gradual addition of SO2Cl2 in CCl4 solution (10 ml) at 0°C under inert atmosphere and the solution was stirred for an additional 30 min and was then permitted to stir at room temperature for additional 3 h. The precipitate formed was filtered and washed with hexane (2x10 ml). The resulting solid was dried under vacuum to afford white solids of the corresponding diorganotellurium(IV) chlorides and was used as such for the next step without any further purification. A suspension of the chlorinated compound in 2 M NaOH (10 ml) was refluxed for 3 h. A few drops of ethanol were added until the product had entirely dissolved and the solution was filtered in hot condition. The organic component was extracted with CH2Cl2 and the combined organic layer was dried over anhydrous Na2SO4 and concentrated by rotary evaporator to afford white solids. The white solids were washed with hexane (2x10 ml) to give the pure product in ~80% yield. Single crystals of 10 and 14 suitable for single-crystal diffraction analysis were obtained by slow diffusion of hexane in CH2Cl2 solution of the respective compounds at room temperature.

**Synthesis of 10.** The reagents used are 5 (0.5 g, 1.47 mmol) in CCl4 (35 ml), SO2Cl2 (0.2 g, 1.47 mmol, 119 µl) in CCl4 (5 ml) and 2 M NaOH aqueous solution (5 ml). Yield 0.65 g (76.2%), m.p. 194 °C. 1H NMR (500 MHz, CDCl3): δ (ppm) 8.11 (d, 1H, Ar—H), 8.05 (d, 1H, Ar—H), 7.49 (s, br, 1H, Ar-H), 7.38 (s, br, 1H, Ar—H), 7.33 (s, br, 1H, Ar—H), 7.21 (d, br, 1H, Ar—H), 4.64 (dd, 1H, Ar—CH3), 4.13 (dd, 1H, Ar—CH3), 3.38 (t, 1H, Ar—CH3), 2.32 (d, 2H, Ar—CH3), 2.30 (d, 1H, Ar—CH3), 2.99 (d, 1H, Ar—CH3), 2.79 (d, 1H, Ar—CH3), 2.28 (s, 8H, CH3), 2.09 (s, br, 4H, CH3), 1.75 (s, br, 12H, CH3). 125Te NMR (126 MHz, CDCl3): δ (ppm) 529.2183 (observed), 529.2182 (calculated).

**Synthesis of 14a—14c.** The reagents used are 9 [37] (0.75 g, 1.46 mmol) in CCl4 (10 ml), SO2Cl2 (0.2 g, 1.47 mmol, 119 µl) in CCl4 (5 ml) and 2 M NaOH aqueous solution (5 ml). Yield 0.65 g (76.2%), m.p. 194 °C. 1H NMR (500 MHz, CDCl3): δ (ppm) 8.11 (d, 1H, Ar—H), 8.05 (d, 1H, Ar—H), 7.49 (s, br, 1H, Ar—H), 7.38 (s, br, 1H, Ar—H), 7.33 (s, br, 1H, Ar—H), 7.21 (d, br, 1H, Ar—H), 4.64 (dd, 1H, Ar—CH3), 4.13 (dd, 1H, Ar—CH3), 3.38 (t, 1H, Ar—CH3), 2.32 (d, 2H, Ar—CH3), 2.30 (d, 1H, Ar—CH3), 2.99 (d, 1H, Ar—CH3), 2.79 (d, 1H, Ar—CH3), 2.28 (s, 8H, CH3), 2.09 (s, br, 4H, CH3), 1.75 (s, br, 12H, CH3). 125Te NMR (126 MHz, CDCl3): δ (ppm) 529.2188 (observed), 529.2182 (calculated).

6. X-ray crystallographic study

The single crystal X-ray diffraction measurements were performed on a Rigaku Saturn 724 diffractometer and an Oxford Diffraction Gemini diffractometer. The data were corrected for Lorentz, polarization, and absorption effects. The structures were determined by routine direct methods using SHELXT [43] and Fourier methods and refined by full-matrix least squares with the
anisotropic non-hydrogen atoms and hydrogen atoms with fixed isotropic thermal parameters of 0.07 Å² using the SHELXL-2018 [44] program. The hydrogens were partially located from difference electron density maps, and the rest were fixed at pre-determined positions. Scattering factors were from common sources [45]. For 14, the metrical parameters of the minor component were constrained to be similar to those of the cation using the SAME command in Shelxl-2018. The occupancy within 14b was refined using the SUMP command: sump 0.90595 .001 1 3 1 4; FVVAR 1.02308 0.90595 0.25145 0.65448, free variable 3 and 4 refined with good esd's. [Final values were 0.251(1) for 14c and 0.654(1) for 14b. If these are expressed as percentages the values would be 27.8(1) % (14c) and 72.2(1) % (14b)]. X-ray structural parameters for compounds 7, 8, 10, 14a-b and 14c are given in Supporting Information (Table S1). CCDC 1501265 (7), 1501266 (8), 1501267 (10), 1885841 (14a-b), and 1903831 (14c) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures-beta/.

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Appendix A. Supplementary data

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References