CHEMCOMM
Communication
www.rsc.org/chemcomm

Macrocyclic multi-telluranes with hypervalent Te–O apical linkages†

Kenji Kobayashi,*[a] Hiroyuki Izawa,[a] Kentaro Yamaguchi,[b] Ernst Horn[c] and Naomichi Furukawa[a]‡

[a] *Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan. E-mail: kenjinor@staff.chem.tsukuba.ac.jp*
[b] *Chemical Analysis Center, Chiba University, Inage-ku, Chiba 263-8522, Japan*
[c] *Department of Chemistry, Rikkyo University, Nishi-Ikebukuro, Toshima-ku, Tokyo 171-8501, Japan*

Received (in Cambridge, UK) 24th April 2001, Accepted 20th June 2001
First published as an Advance Article on the web 19th July 2001

Two types of macrocyclic multi-telluranes with hypervalent Te–O apical linkages in the main chain were prepared by the reaction of a telluronium salt or a cationic ditelluroxane with phthalate *via* [3 + 3] and [2 + 2] assembly, respectively.

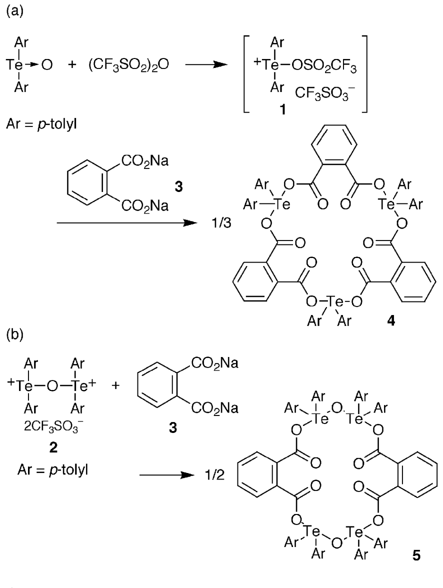
One of the characteristics of organic heteroatom chemistry is the formation of hypervalent compounds.[1] Telluranes have the trigonal bipyramidal geometry, in which the two apical ligands and the central Te atom construct a three-center–four-electron hypervalent bond with *ca.* 180° bond angle. A strategy for the formation of hypervalent telluranes is the use of $n \rightarrow \sigma^*$ orbital interaction, where the σ^* orbital of the Te–X bond of a telluronium salt interacts with the n orbital of a lone pair of electrons of a ligand.[1] In supramolecular chemistry, the field of macrocycles has advanced to the stage where self-assembly through transition-metal coordination has proved to be a reliable tool.[2] Hypervalent bonds *via* $n \rightarrow \sigma^*$ orbital interactions in heteroatoms may also be a viable alternative for self-assembled macrocycles.[3–7] Recently, we have found that the cationic ditelluroxane **2** interacts with triflate as a counter ion in the solid state and with telluroxide in solution to form a pseudo-macrocyclic multi-tellurane and oligotelluroxanes, respectively, with hypervalent Te–O apical linkages *via* $n \rightarrow \sigma^*$ orbital interaction.[8] Herein we report the synthesis of the macrocyclic multi-telluranes **4** and **5** by the reaction of the telluronium salt **1** or the cationic ditelluroxane **2** as building blocks with phthalate **3** as a convergent bidentate ligand. This is the first example of macrocycles composed of only hypervalent apical linkages in the main chain for group 13–17 elements, which are fully characterized both in solution and in the solid state.

The generation of the telluronium salt **1** *in situ* by the reaction of bis(4-methylphenyl) telluroxide with 1 equiv. of triflic anhydride in MeCN at −40 °C followed by the addition of 1 equiv. of sodium phthalate **3** at room temperature gave the hypervalent macrocycle **4** in 76% yield after recrystallization [Scheme 1(a)].§ Treatment of the cationic ditelluroxane **2** with 1 equiv. of **3** in MeCN at room temperature produced the hypervalent macrocycle **5** in 14% yield after recrystallization [Scheme 1(b)].§

The ^{125}Te NMR spectra of **4** and **5** in CD_2Cl_2 showed singlets at δ 997.0 and 1044.4, respectively, which are in the region of telluranes with hypervalent Te–O_2C apical bonds.[9] The ^{1}H NMR spectra of **4** and **5** exhibited doublet, double-doublet, double-doublet, and doublet peaks in the aromatic region in the integration ratios of 2 : 1 : 1 : 2 and 4 : 1 : 1 : 4, respectively. The IR spectrum of **5** showed the characteristic Te–O–Te stretching band at ν 639 cm^{-1}.[10] These data imply that **4** is the result of [3 + 3] assembly of **1** and **3** to give a 21-membered ring, and **5** is the result of [2 + 2] assembly of **2** and **3** to form an 18-membered ring; both structures are composed of the hypervalent Te–O apical linkages in the main chain. The FAB-MS spectra of **4** and **5** showed a parent peak at *m*/*z* 1423 ([M + H]$^+$) and at 1601 ([M + H]$^+$), respectively, the isotopic distribution patterns of which are consistent with the calculated ones. Distinctive fragment peaks also appeared at *m*/*z* 801 and 477 in both cases and at *m*/*z* 1509 and 1275 in **5**.

The ^{1}H and ^{125}Te NMR spectra of **4** and **5** in CD_2Cl_2 and CD_3CN remained unchanged in the range −90 to 80 °C. NOE experiments on **4** and **5** indicated −24 and −19% NOEs, respectively, at the *ortho*-hydrogens of the phthalate unit upon irradiation of the *ortho*-hydrogens of the *para*-tolyl unit. These results indicate that the cyclic structures of **4** and **5** are maintained in solution.

The molecular structures of the hypervalent macrocycles **4** and **5** were determined by X-ray crystallographic analysis, as shown in Fig. 1 and 2, respectively.¶|| The macrocycle **4** is composed of three Te atoms and three phthalates, and possesses Te–O_2C bond lengths of 2.133–2.166 Å, CO_2–Te–O_2C bond angles of 161.8–168.3° and C–Te–C bond angles of 96.2–100.3°. The macrocycle **5** consists of two ditelluroxanes and two phthalates, and the unit cell contains four independent molecules.|| The respective average bond lengths and angles are in the range of 2.23–2.29 Å for Te–O_2C, 1.99–2.03 Å for Te–O, 166.1–168.7° for O–Te–O_2C, 96–101° for C–Te–C and 114–126° for Te–O–Te. These data clearly indicate that both **4** and **5** have trigonal bipyramidal geometry for the Te atoms and hypervalent Te–O apical bonds.[11] In both cases, all the atoms of the respective macrocyclic rings are roughly coplanar. The halves of the carbonyl O atoms and the tolyl groups are directed inward and outward, respectively, to the respective macrocyclic rings. By contrast, the other halves of the carbonyl O atoms and the tolyl groups are vertically directed to the respective



Scheme 1 Synthesis of macrocyclic multi-telluranes (a) **4** and (b) **5**.

---

† Electronic supplementary information (ESI) available: characterization data and ORTEP diagrams for **4** and **5**. See http://www.rsc.org/suppdata/cc/b1/b103676a/

‡ Present address: Foundation for Advancement of International Science, 586-9 Akatsuka-Ushigahuchi, Tsukuba, Ibaraki 305-0062, Japan.

DOI: 10.1039/b103676a

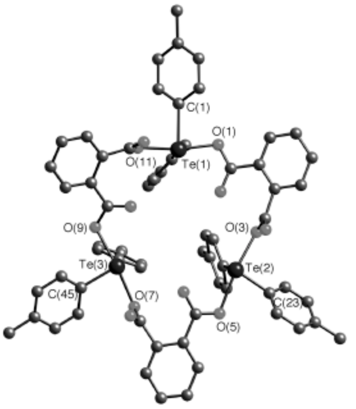


Fig. 1 Structure of **4** in the crystal; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Te(1)–O(1) 2.166(4), Te(1)–O(11) 2.133(4), Te(2)–O(3) 2.141(4), Te(2)–O(5) 2.163(4), Te(3)–O(7) 2.151(4), Te(3)–O(9) 2.144(4); O(1)–Te(1)–O(11) 161.8(2), O(3)–Te(2)–O(5) 168.3(2), O(7)–Te(3)–O(9) 165.6(2), C(1)–Te(1)–C(8) 100.3(2), C(23)–Te(2)–C(30) 96.2(2), C(45)–Te(3)–C(52) 98.9(2).

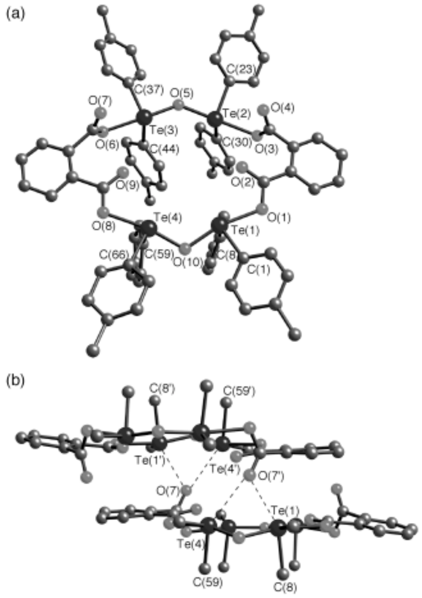


Fig. 2 (a) Structure of **5** and (b) its dimeric structure in the crystal; hydrogen atoms in (a) and (b) and *p*-tolyl groups in (b) are omitted for clarity. Selected average bond lengths (Å) and angles (°): Te(1)–O(1) 2.28(2), Te(2)–O(3) 2.23(2), Te(3)–O(6) 2.27(2), Te(4)–O(8) 2.29(2), Te(1)–O(10) 2.03(2), Te(4)–O(10) 2.01(2), Te(2)–O(5) 2.01(2), Te(3)–O(5) 1.99(2), O(7′)···Te(1) 2.95, O(7′)···Te(4) 3.20; O(1)–Te(1)–O(10) 166.6(7), O(3)–Te(2)–O(5) 167.2(7), O(5)–Te(3)–O(6) 168.7(7), O(8)–Te(4)–O(10) 166.1(8), C(1)–Te(1)–C(8) 96(1), C(23)–Te(2)–C(30) 101(1), C(37)–Te(3)–C(44) 98(1), C(59)–Te(4)–C(66) 98(1), Te(1)–O(10)–Te(4) 114(1), Te(2)–O(5)–Te(3) 126(1), O(7′)···Te(1)–C(8) 153, O(7′)···Te(4)–C(59) 149.

macrocyclic ring planes so as to be placed at the opposite side. It is noted that the Te(1) and Te(4) atoms in **5** interact with the carbonyl O(7′) atom of the adjacent molecule [O(7′)···Te(1) 2.95 and O(7′)···Te(4) 3.20 Å; O(7′)···Te(1)–C(8) 153 and O(7’)···Te(4)-C(59) 149°],[12] the contact distances of which are shorter than the sum of the van der Waals radii (3.60 Å) of the Te and O atoms. Thus, **5** forms a head-to-head type of dimeric structure in the solid state [Fig. 2(b)].

In summary, we have demonstrated the synthesis of macrocyclic multi-telluranes **4** and **5** with hypervalent Te–O apical linkages in the main chain. Hypervalent bonds *via* n→σ* orbital interaction in heteroatoms can serve as a new supramolecular synthon for molecular assembly. Studies on the synthesis of hypervalent polymers using the building blocks **1** and **2** with divergent bidentate ligands are underway.

Notes and references

§ *Representative data*: for **4**: mp 199–200 °C (decomp); ^{1}H NMR (270 MHz, CD_2Cl_2, 23 °C) δ 2.35 (s, 18H), 7.31 (d, *J* 8.3 Hz, 12H), 7.38 (dd, *J* 3.2 , 5.9 Hz, 6H), 7.48 (dd, *J* 3.2, 5.9 Hz, 6H), 7.78 (d, *J* 8.3 Hz, 12H); ^{125}Te NMR (85.2 MHz, CD_2Cl_2, 23 °C) δ 997.0; FAB-MS (2-nitrophenyl octyl ether matrix) *m*/*z* (%) 1423 (4, $[M + H]^+$), 801 (7, $[M - Ar_2Te - 2C_6H_4(CO_2)_2 + OH]^+$), 477 (43, $[1/3M + H]^+$), 329 (79, $[Ar_2TeO + H]^+$), 312 (100, $[Ar_2Te]^+$). For **5**: mp 172–174 °C (decomp); ^{1}H NMR (270 MHz, CD_2Cl_2, 23 °C) δ 2.32 (s, 24H), 7.13 (d, *J* 8.1 Hz, 16H), 7.31 (dd, *J* 3.2, 5.7 Hz, 4H), 7.50 (dd, *J* 3.2, 5.7 Hz, 4H), 7.76 (d, *J* 8.1 Hz, 16H); ^{125}Te NMR (85.2 MHz, CD_2Cl_2, 23 °C) δ 1044.4; FAB-MS (2-nitrophenyl octyl ether matrix) *m*/*z* (%) 1601 (8, $[M + H]^+$), 1509 (8, $[M - Ar]^+$), 1275 (18, $[M - Ar_2TeO + H]^+$), 801 (18, $[1/2M + H]^+$), 477 (37, $[1/2M - Ar_2TeO + H]^+$), 329 (98, $[Ar_2TeO + H]^+$), 312 (100, $[Ar_2Te]^+$).

¶ *Crystal data*: for **4**·0.5(*p*-xylene)·3(CH_3CN): $C_{76}H_{68}O_{12}N_3Te_3$, M = 1598.19, triclinic, space group $P\bar{1}$, a = 13.2525(8), b = 15.1873(9), c = 19.937(1) Å, α = 76.682(1), β = 75.167(1), γ = 65.688(1)°, U = 3499.3(4) Å^3, Z = 2, D_c = 1.517 g cm^{-3}, Bruker CCD/Smart 1000, μ(Mo-Kα) = 13.06 cm^{-1}, T = 173 K. Of 20229 measured and 14907 unique reflections (R_{int} = 0.062), the final least-squares refinement based on F for 12760 observed reflections with $I > 2.5\sigma(I)$ (767 variables) converged with R = 0.055 and R_w = 0.082. For **5**·1.5(*p*-xylene): $C_{84}H_{79}O_{10}Te_4$, M = 1758.94, triclinic, space group $P\bar{1}$, a = 18.150(2), b = 28.698(3), c = 30.804(3) Å, α = 86.630(2), β = 89.491(2), γ = 77.613(2)°, U = 15644(3) Å^3, Z = 8, D_c = 1.494 g cm^{-3}, Bruker CCD/Smart 1000, μ(Mo-Kα) = 15.33 cm^{-1}, T = 123 K. Of 93535 measured and 68077 unique reflections (R_{int} = 0.082), the final least-squares refinement based on F for 19579 observed reflections with $I > 3.0\sigma(I)$ (3527 variables) converged with R = 0.088 and R_w = 0.134. CCDC reference numbers 159004 and 159005. See http://www.rsc.org/suppdata/cc/b1/b103676a/ for crystallographic data in CIF or other electronic format.

‖ Compound **4** has some high thermal parameters for the solvent molecules. The structural parameters for compound **5** reported here are still preliminary. Even from the data collected at −150 °C we have not yet obtained satisfactory parameters because of the severe disorder. Although the final level of refinement has not yet been reached, we believe the data obtained here is significant enough to demonstrate the molecular structure of **5**.

1 J. Bergman, L. Engman and J. Sidén, in *The Chemistry of Organic Selenium and Tellurium Compounds*, ed. S. Patai and Z. Rappoport, Wiley, Chichester, 1986, vol. 1, p. 517; *Chemistry of Hypervalent Compounds*, ed. K.-y. Akiba, Wiley-VCH, New York, 1999; N. Furukawa, K. Kobayashi and S. Sato, *J. Organomet. Chem.*, 2000, **611**, 116.

2 *Comprehensive Supramolecular Chemistry*, ed. J.-P. Sauvage and M. W. Hosseini, Pergamon, Oxford, 1996, vol. 9; S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853.

3 For hypervalent pseudo-macrocyclic multi-telluranes with apical and equatorial linkages in the solid state *via* n→σ* orbital interactions, see: J. Jeske, W.-W. du Mont and P. G. Jones, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2219; P. D. Boyle, W. I. Cross, S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard, S. Sarwar and J. M. Sheffield, *Angew. Chem., Int. Ed.*, 2000, **39**, 1796.

4 For hypervalent multi-iodonium macrocycles with apical and equatorial linkages, see: P. J. Stang and V. V. Zhdankin, *J. Am. Chem. Soc.*, 1993, **115**, 9808.

5 For a macrocyclic multi-tellurane with equatorial linkages, see: Y. Takaguchi, E. Horn and N. Furukawa, *Organometallics*, 1996, **15**, 5112.

6 For a tellurium-containing macrocycle, see: S. C. Menon, H. B. Singh, R. P. Patel and S. K. Kulshreshtha, *J. Chem. Soc., Dalton Trans.*, 1996, 1203.

7 For macrocyclic imidazolylboranes with the sp^3-hybridized boron atoms *via* n→p$_\pi$ orbital interactions, see: A. Weiss, H. Pritzkow and W. Siebert, *Angew. Chem., Int. Ed.*, 2000, **39**, 547.

8 K. Kobayashi, N. Deguchi, E. Horn and N. Furukawa, *Angew. Chem., Int. Ed.*, 1998, **37**, 984; K. Kobayashi, N. Deguchi, O. Takahashi, K. Tanaka, E. Horn, O. Kikuchi and N. Furukawa, *Angew. Chem., Int. Ed.*, 1999, **38**, 1638.

9 Y. Takaguchi, H. Fujihara and N. Furukawa, *J. Organomet. Chem.*, 1995, **498**, 49.

10 N. W. Alcock and W. D. Harrison, *J. Chem. Soc., Dalton Trans.*, 1982, 1421; K. V. Domasevitch, V. V. Skopenko and E. B. Rusanov, *Z. Naturforsch, Teil B*, 1996, **51**, 832.

11 N. W. Alcock, W. D. Harrison and C. Howes, *J. Chem. Soc., Dalton Trans.*, 1984, 1709.

12 G. Schatte, T. Chivers, C. Jaska and N. Sandblom, *Chem. Commun.*, 2000, 1657.