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Article

Tellurasiloxane Cages Containing $Te_6Si_4O_{12}$ and $Te_6Si_6O_{15}$ Frameworks

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Reaction of the silanetriol t-$BuSi(OH)_3$ with $(p\text{-}Me_2NC_6H_4)_2TeO$ in a 4:6 ratio resulted in the formation of $[((p\text{-}Me_2NC_6H_4)_2Te)_6(t\text{-}BuSiO_3)_4]\cdot 1.5\ C_7H_8$ ($\mathbf{1}\cdot 1.5C_7H_8$). In contrast, the reaction of tetrahydroxy-1,3-disiloxane, $[t\text{-}BuSi(OH)_2]_2O$ with $(p\text{-}MeOC_6H_4)_2TeO$ in a 3:6 ratio afforded $[((p\text{-}MeOC_6H_4)_2Te)_6(t\text{-}BuSi)_6O_{15}]\cdot 2\ C_7H_8$ ($\mathbf{2}\cdot 2C_7H_8$). **1** possesses a tetrahedron cage structure in which the vertices of the tetrahedron are occupied by silicon atoms. Each pair of silicon atoms is connected to each other by a R_2TeO_2 motif. The six O–Te–O bridges occupy the edges of the tetrahedron. In contrast to **1**, the structure of **2** can be described as a trigonal prismatic cage. The latter consists of two $Te_3Si_3O_6$ rings that are interconnected to each other through three Si–O–Si linkages. The structure of **2** is reminiscent of a double-six-ring (D6R) secondary building unit (SBU) framework found in zeolites such as faujasite. Reaction of $(p\text{-}Me_2NC_6H_4)_2TeO$ or $(p\text{-}MeOC_6H_4)_2TeO$ with the disiloxane-1,3-diol, $[Ph_2Si(OH)]_2O$ in a 2:2 ratio afforded $[((p\text{-}Me_2NC_6H_4)_2Te)(OPh_2Si{-}O{-}SiPh_2O)]_2$ (**3**) and $[((p\text{-}MeOC_6H_4)_2Te)(OPh_2Si{-}O{-}SiPh_2O)]_2\cdot CH_3CN$ ($\mathbf{4}\cdot CH_3CN$). In contrast to **1** and **2**, the compounds **3** and **4** contain puckered 12-membered $Te_2Si_4O_6$ rings.

Introduction

Molecular compounds containing Si–O–M (metallasiloxanes)[1] and P–O–M linkages (metallaphosphonates[2] and metallaphosphates[3]) have attracted considerable interest in recent years because of their large structural diversity. Another reason for interest in these compounds is their utility as structural models for secondary building units (SBUs) that occur in naturally occurring or synthetically accessible metallasilicates including zeolites.[4]

In contrast to the well-studied examples of metallasiloxanes containing Group 13[5] and Group 14[6] metals there has been almost no work on the corresponding compounds containing Group 16 metal atoms.[7] Very recently, Beckmann

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and co-workers have reported a 12-membered tellurasiloxane ring, *cyclo*-[(p-MeOC$_6$H$_4$)$_2$TeOSi(t-Bu)$_2$O]$_3$.[7a] Previously, [(t-Bu)$_2$SiO$_2$(TeCl$_2$-μ-Cl$_2$−TeCl$_2$)] was reported by Roesky and co-workers.[7c] To the best of our knowledge, tellurasiloxanes possessing cage structures are completely unknown. To assemble such compounds, we have utilized a rational synthetic design. Accordingly, we have used (p-Me$_2$NC$_6$H$_4$)$_2$TeO or (p-MeOC$_6$H$_4$)$_2$TeO as the tellurium precursor while varying the silicon reagent. Reaction of the silanetriol t-BuSi(OH)$_3$ with (p-Me$_2$NC$_6$H$_4$)$_2$TeO in a 4:6 ratio resulted in the formation of [((p-Me$_2$NC$_6$H$_4$)$_2$Te)$_6$(t-BuSiO$_3$)$_4$]·1.5C$_7$H$_8$ (**1**·1.5C$_7$H$_8$). On the other hand, the reaction of tetrahydroxy-1,3-disiloxane, [t-BuSi(OH)$_2$]$_2$O with (p-MeOC$_6$H$_4$)$_2$TeO in a 3:6 ratio afforded [((p-MeOC$_6$H$_4$)$_2$Te)$_6$(t-BuSi)$_6$O$_{15}$]·2C$_7$H$_8$ (**2**·2C$_7$H$_8$). **1** and **2** represent unprecedented structural types for tellurasiloxanes and possess cage structures. Whereas the cage structure of **1** can be described as a tetrahedron, **2** possesses a cage structure reminiscent of a double-six-ring (D6R) secondary building unit (SBU) framework[8] found in zeolites such as faujasite. Reaction of (p-Me$_2$NC$_6$H$_4$)$_2$TeO or (p-MeOC$_6$H$_4$)$_2$TeO with the disiloxane-1,3-diol, [Ph$_2$Si(OH)]$_2$O in a 2:2 ratio afforded [((p-Me$_2$NC$_6$H$_4$)$_2$Te)(OPh$_2$Si−O−SiPh$_2$O)]$_2$ (**3**) and [((p-MeOC$_6$H$_4$)$_2$Te)(OPh$_2$Si−O−SiPh$_2$O)]$_2$·CH$_3$CN (**4**·CH$_3$CN). In contrast to **1** and **2**, the compounds **3** and **4** contain 12-membered Te$_2$Si$_4$O$_6$ rings.

Experimental Section

Reagents and General Procedures. Solvents and other general reagents used in this work were purified according to standard procedures.[9a] Tellurium tetrachloride and *tert*-butyltrichlorosilane were purchased from Aldrich Chemical Co. and used as such. Potassium hydroxide (RANKEM) was purchased from RFCL Limited, New Delhi, India and was used as such. *N*,*N*′-dimethylaniline and anisole were purchased from s. d. Fine. Chem. Ltd., Mumbai, India, and purified by well-known procedures.[9a] The starting materials bis(*N*,*N*′-dimethylaminophenyl)telluroxide, bis(p-methoxyphenyl)telluroxide,[9b] *tert*-butylsilanetriol,[9c] 1,3-bis(*tert*-butyl)-1,1,3,3-tetrahydroxydisiloxane,[9d] and 1,1,3,3-tetraphenyl-1,3-dihydroxydisiloxane[9e] were synthesized according to literature procedures.

Instrumentation. Melting points were measured using a JSGW melting point apparatus and are uncorrected. Elemental Analyses of the compounds were obtained using a Thermoquest CE instrument CHNS-O, EA/110 model. IR spectra were recorded as KBr pellets on a Bruker Vector 22 FTIR Spectrophotometer operating from 400 to 4000 cm^{-1}. ^{1}H, ^{29}Si, and ^{125}Te NMR spectra were obtained on a JEOL DELTA2 500 model spectrometer operating at 500, 99, and 158 MHz, respectively. The chemical shifts were referenced with respect to tetramethylsilane (^{1}H, ^{29}Si) and dimethyltelluride (^{125}Te) respectively. ESI-MS analyses were performed on a Waters Micromass Quattro Micro triple quadrupole mass spectrometer. Electrospray ionization (positive, full scan mode) mass spectra were obtained for compounds **1** (CH$_2$Cl$_2$/CH$_3$OH), **2**−**4** (acetonitrile) with cone voltage at 31−34 kV.

X-ray Crystallography. Single crystals of **1**−**4**, suitable for X-ray crystallographic analyses, were obtained by slow diffusion of toluene/hexane (**1** & **2**) and slow evaporation of acetonitrile solution for **3** and **4** (Table 1). Crystal data for **1**−**4** were collected on a Bruker SMART CCD diffractometer using a Mo Kα sealed tube. The program SMART[10a] was used for collecting frames of data, indexing reflexions and determining lattice parameters, SAINT[10a] for integration of the intensity of reflections and scaling, and SADABS[10b] for absorption corrections. All structures were solved by direct methods using the program SHELXS-97[10c] and refined by full-matrix least-squares methods against F^2 with SHELXL-97.[10c] Hydrogen atoms were fixed at calculated positions and refined isotropically. All non-hydrogen atoms were refined with anisotropic displacement parameters. The program SQUEEZE/PLATON[10d] was used to remove the high thermal ellipsoid present in solvent molecules of compound **1**. PLATON program shows the compound **1** contains the solvent-accessible void 3234.2 Å^3 and the electron count per cell is 302. This shows that it contains six toluene molecules present in the unit cell. We have found that five phenyl groups were severely disordered over two/three positions and fixed satisfactorily. The figures have been generated using Diamond 3.1e software.[10e]

Synthesis of Compounds 1−4

A mixture of the appropriate organosilanol, (p-Me$_2$NC$_6$H$_4$)$_2$TeO or (p-MeOC$_6$H$_4$)$_2$TeO and 100 mL of toluene were refluxed using a Dean−Stark apparatus for 24 h. The reaction mixture was cooled to room temperature, filtered, and evaporated to afford a creamy solid (**1**) or an oil (**2**−**4**). Crystals of **1** were obtained by diffusing *n*-hexane into its toluene solution. Treatment of **2** with diethyl ether followed by evaporation of the solvent afforded a solid that was recrystallized from its toluene solution by allowing diffusion of *n*-hexane. **3** and **4** were triturated with 10 mL of acetonitrile to afford a solid material. This was recrystallized from hot acetonitrile to afford pure crystals of **3** and **4**, respectively.

[((p-Me$_2$NC$_6$H$_4$)$_2$Te)$_6$(t-BuSiO$_3$)$_4$]·1.5 C$_7$H$_8$ (1·1.5C$_7$H$_8$). Reagents: Bis(*N*,*N*′-dimethylaminophenyl)telluroxide (0.21 g, 0.55 mmol), *tert*-butylsilanetriol (0.05 g, 0.37 mmol). Yield: 0.22 g (84%). Mp: 238−239 °C. Anal. Calcd for **1**·1.5C$_7$H$_8$ (2878.65): C, 51.11; H, 5.88; N, 5.84. Found: C, 50.96; H, 5.79; N, 5.79. IR (KBr, cm^{-1}): 2882 (s), 2801 (s), 1591 (s), 1502 (s), 1354 (s), 926 (br,s). ^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 7.63 (d, 24H, J = 9 Hz, Ar), 6.19 (d, 24H, J = 9 Hz, Ar), 2.84 (s, 72H, −NCH$_3$), 0.93 (s, 36H, t-Bu). ^{29}Si NMR (99.4 MHz, CDCl$_3$, ppm): δ −53.5 (s). ^{125}Te NMR (158 MHz, CDCl$_3$, ppm): δ 872 (s). ESI-MS m/z (%): 387.0751 [(p-Me$_2$NC$_6$H$_4$)$_2$TeOH]$^+$ (21), 401.0813 [(p-Me$_2$NC$_6$H$_4$)$_2$TeOCH$_3$]$^+$ (100), 887.1740 [{((p-Me$_2$NC$_6$H$_4$)$_2$Te)$_2$O}{t-BuSiO(OH)$_2$}]$^+$ (8), 1253.2114 [{(p-Me$_2$NC$_6$H$_4$)$_2$Te}$_3$O

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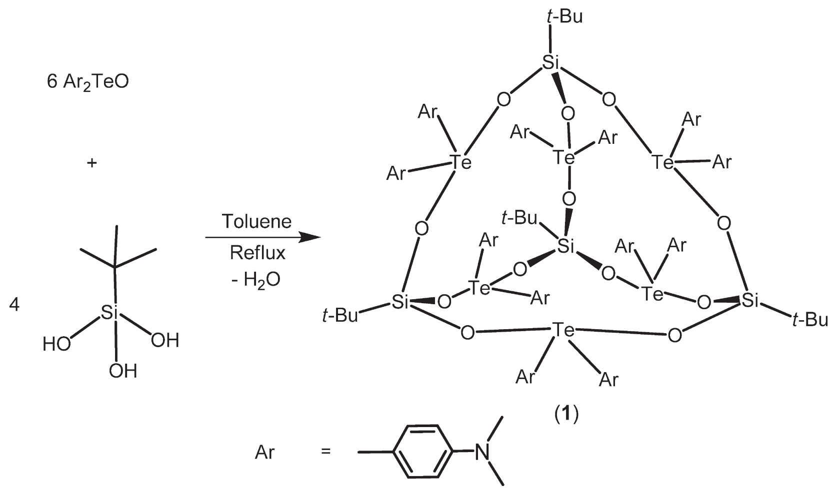
Table 1. Crystal and Refinement Data for **1**−**4**

empirical formula	**1**·1.5 C_7H_8	**2**·C_7H_8	$C_{80}H_{80}N_4O_6Si_4Te_2$	**4**·CH_3CN
fw	2878.65	3170.86	1561.04	1549.92
T (K)	100(2)	100(2)	153(2)	153(2)
wavelength (Å)	0.71073	0.71073	0.71069	0.71069
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	$P2(1)/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	26.274(5)	26.871(2)	12.778(5)	12.963 (5)
b (Å)	17.708(4)	18.933(2)	12.818(5)	15.505(5)
c (Å)	30.953(6)	28.711(3)	12.993(5)	18.489(5)
α (deg)	90	90	105.406(5)	89.053(5)
β (deg)	96.28(3)°	107.086(2)	97.549(5)	75.640(5)
γ (deg)	90	90	114.546(5)	86.924(5)
V (Å^3)	14315(5)	13963(2)	1793.9(12)	3595 (2)
Z	4	4	1	2
density calcd (g cm^{-3})	1.336	1.508	1.445	1.432
absorp coeff (mm^{-1})	1.295	1.357	0.937	0.937
F(000)	5804	6392	796	1572
cryst size (mm^3)	0.30 × 0.20 × 0.20	0.30 × 0.25 × 0.20	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10
θ range (deg)	2.10 to 25.00	2.15 to 27.00	2.12 to 27.00	2.13 to 27.00
limiting indices	$-31 \le h \le 24$, $-19 \le k \le 21$, $-36 \le l \le 36$	$-34 \le h \le 29$, $-24 \le k \le 16$, $-36 \le l \le 36$	$-15 \le h \le 16$, $-16 \le k \le 8$, $-15 \le l \le 16$	$-16 \le h \le 16$, $-16 \le \mathrm{k} \le 19$, $-21 \le l \le 23$
no. of reflns collected	72943	41063	10797	21721
no. of independent reflns	25153 [R(int) = 0.0643]	15115 [R(int) = 0.0451]	7579 [R(int) = 0.0315]	15204 [R(int) = 0.0366]
completeness to θ (%)	99.8	99.2	96.6	96.7
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	25153/6/1302	15115/0/806	7579/0/437	15204/0/861
GOF on F^2	1.011	1.132	1.126	1.096
final R indices [$I > 2\theta(I)$]	$R_1 = 0.0569$, $wR_2 = 0.1442$	$R_1 = 0.0393$, $wR_2 = 0.0934$	$R_1 = 0.0592$, $wR_2 = 0.1475$	$R_1 = 0.0596$, $wR_2 = 0.1355$
R indices (all data)	$R_1 = 0.0809$, $wR_2 = 0.1583$	$R_1 = 0.0548$, $wR_2 = 0.1225$	$R_1 = 0.0797$, $wR_2 = 0.1931$	$R_1 = 0.0913$, $wR_2 = 0.1820$
largest diff. peak and hole (e Å^{-3})	2.065 and −1.911	1.184 and −0.838	1.805 and −1.039	1.267 and −1.266

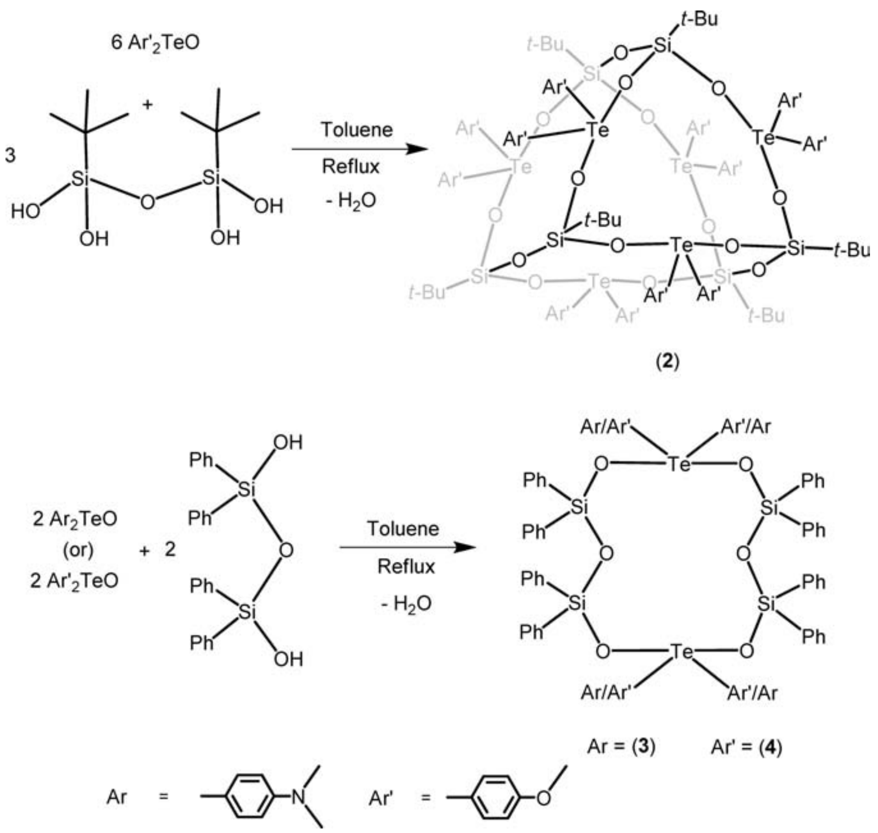
Scheme 1



{t-BuSiO$_3$}]$^+$ (1), 1285.2399 [{(p-Me$_2$NC$_6$H$_4$)$_2$Te}$_3$O-{t-BuSiO$_3$} + CH$_3$OH]$^+$ (2).

[((p-MeOC$_6$H$_4$)$_2$Te)$_6$(t-BuSi)$_6$O$_{15}$]·2C$_7$H$_8$ (2). Reagents: Bis(p-methoxyphenyl)telluroxide (0.23 g, 0.71 mmol), 1,3-bis($tert$-butyl)-1,1,3,3-tetrahydroxydisiloxane (0.09 g, 0.35 mmol). Yield: 0.27 g (72%). Mp: 230 °C (dec). Anal. Calcd for **2**·2C$_7$H$_8$ (3170.86): C, 51.51; H, 5.40. Found: C, 51.34; H, 5.33. IR (KBr, cm^{-1}): 3002 (m), 2956 (w), 2850 (m), 1589 (sh), 1493 (s), 1297 (m), 1254 (s), 1177 (sh), 1053 (s), 911 (s, br). ^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 7.74 (d, 12H, J = 9 Hz, Ar), 7.52 (d, 12H, J = 9 Hz, Ar), 6.43 (d, 12H, J = 9 Hz, Ar), 6.22 (d, 12H, J = 9 Hz, Ar), 3.73 (s, 18H, -OCH$_3$), 3.59 (s, 18H, -OCH$_3$), 0.99 (s, 54H, t-Bu). ^{29}Si NMR (99.4 MHz, CDCl$_3$, ppm): δ −61.9 (s). ^{125}Te NMR (158 MHz, CDCl$_3$, ppm): δ 922 (s). ESI-MS m/z (%): 360.9952 [(p-MeOC$_6$H$_4$)$_2$TeOH]$^+$ (100), 597.0919 [(p-MeOC$_6$H$_4$)$_2$Te{(t-BuSi)$_2$(OH)$_3$(O)$_2$}]$^+$ (30), 953.0822 [((p-MeOC$_6$H$_4$)$_2$-Te)$_2$((t-BuSi)$_2$(OH)(O)$_4$)(OH$_2$)]$^+$ (26), 1887.1429 [((p-MeOC$_6$H$_4$)$_2$Te)$_4$(O){((t-BuSi)$_2$(OH)$_4$(O))-5H}]$^+$ (26), 2821.1780 [{((p-MeOC$_6$H$_4$)$_2$Te)$_6$(t-BuSi)$_6$O$_{15}$} + H + H$_2$O]$^+$ (1).

Scheme 2



[((*p*-$Me_2NC_6H_4)_2$Te)(OPh_2Si−O−$SiPh_2$O)]$_2$ (3). Reagents: Bis(*N*,*N*′-dimethylaminophenyl)telluroxide (0.23 g, 0.60 mmol), (HO)$Ph_2SiOSiPh_2$(OH) (0.25 g, 0.60 mmol). Yield: 0.41 g (88%). Mp: 208−209 °C. Anal. Calcd for $C_{80}H_{80}N_4O_6Si_4Te_2$ (1561.04) (**3**): C, 61.55; H, 5.17; N, 3.59. Found: C, 61.44; H, 5.09; N, 3.52. IR (KBr, cm^{-1}): 3065 (w), 2997 (w), 2812 (w), 1589 (s), 1503 (s), 1442 (m), 1363 (s), 1169 (w), 1068 (s), 928 (s, br). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.82 (d, 8H, *J* = 9 Hz, Ar), 7.41 (d, 16H, *J* = 7 Hz, *o*-H-Ph), 7.39 (t, 8H, *J* = 7 Hz, *p*-H-Ph), 7.12−7.10 (m, 16H, *m*-H-Ph), 6.38 (d, 8H, *J* = 9 Hz, Ar), 2.91 (s, 24H, -NCH_3). ^{29}Si NMR (99.4 MHz, $CDCl_3$, ppm): δ −44.9 (s). ^{125}Te NMR (158 MHz, $CDCl_3$, ppm): δ 944 (s). ESI-MS *m*/*z* (%): 387.0695 [(*p*-$Me_2NC_6H_4)_2$TeOH]$^+$ (100), 769.1324 [((*p*-$Me_2NC_6H_4)_2$Te)$_2$(O)(OH)]$^+$ (10), 783.1638 [(*p*-$Me_2NC_6H_4)_2$Te(OPh_2Si-OH-Ph_2SiO)]$^+$ (21), 1165.2216 [((*p*-$Me_2NC_6H_4)_2$Te)$_2$(OH)(OPh_2Si−O−Ph_2SiO)]$^+$ (22), 1563.3197 [{((*p*-$Me_2NC_6H_4)_2$Te)(OPh_2Si−O−$SiPh_2$O)}$_2$ + H]$^+$ (3).

[((*p*-$MeOC_6H_4)_2$Te)(OPh_2Si−O−$SiPh_2$O)]$_2$·CH_3CN (**4**·CH_3CN). Reagents: Bis(*p*-methoxyphenyl)telluroxide (0.23 g, 0.71 mmol), (OH)$Ph_2SiOSiPh_2$(OH) (0.29 g, 0.70 mmol). Yield: 0.44 g (88%). Mp: 180−182 °C. Anal. Calcd for **4**·CH_3CN (1549.92) (**4**): C, 60.44; H, 4.61; N, 0.90. Found: C, 60.32; H, 4.52; N, 0.79. IR (KBr, cm^{-1}): 3067(w), 2925 (w), 2839 (w), 1587 (m), 1491 (sh), 1252 (s), 1070 (m), 919 (s). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.87 (d, 8H, *J* = 9 Hz, Ar), 7.36 (d, 16H, *J* = 7 Hz, *o*-H-Ph), 7.27 (t, 8H, *J* = 7 Hz, *p*-H-Ph), 7.09−7.12 (m, 16H, *m*-H-Ph), 6.64 (d, 8H, *J* = 9 Hz, Ar), 3.75 (s, 12H, -OCH_3). ^{29}Si NMR (99.4 MHz, C_6D_6, ppm): δ −43.1 (s). ^{125}Te NMR (158 MHz, $CDCl_3$, ppm): δ 931 (s). ESI-MS *m*/*z* (%): 360.9922 [(*p*-$MeOC_6H_4)_2$TeOH]$^+$ (100), 717.0038 [((*p*-$MeOC_6H_4)_2$Te)$_2$(O)(OH)]$^+$ (10), 757.0966 [(*p*-$MeOC_6H_4)_2$Te(OPh_2Si-OH-Ph_2SiO)]$^+$ (33), 1113.0911 [((*p*-$MeOC_6H_4)_2$Te)$_2$(OH)(OPh_2Si−O−Ph_2SiO)]$^+$ (30), 1509.2031 [{((*p*-$MeOC_6H_4)_2$Te)(OPh_2Si−O−$SiPh_2$O)}$_2$ + H]$^+$ (4).

Results and Discussion

The reaction of *t*-BuSi$(OH)_3$ with (*p*-$Me_2NC_6H_4)_2$TeO in a 4:6 ratio afforded [((*p*-$Me_2NC_6H_4)_2$Te)$_6$(*t*-$BuSiO_3)_4$]·1.5 C_7H_8 (**1**·1.5C_7H_8) in 84% yield (Scheme 1). Similarly, a 3:6 reaction of [*t*-BuSi$(OH)_2]_2$O with (*p*-$MeOC_6H_4)_2$TeO afforded [((*p*-$MeOC_6H_4)_2$Te)$_6$(*t*-BuSi)$_6O_{15}$]·2C_7H_8 (**2**·2C_7H_8) in 72% yield (Scheme 2). The reaction of disiloxane-1,3-diol [Ph_2Si(OH)]$_2$O with (*p*-$Me_2NC_6H_4)_2$TeO or (*p*-$MeOC_6H_4)_2$TeO in a 2:2 stoichiometry afforded the 12-membered rings, [((*p*-$Me_2NC_6H_4)_2$Te)(OPh_2Si−O−$SiPh_2$O)]$_2$ (**3**) and [((*p*-$MeOC_6H_4)_2$Te)(OPh_2Si−O−$SiPh_2$O)]$_2$·CH_3CN (**4**·CH_3CN) in excellent yields (Scheme 2) (both 88%). The ESI-MS analyses of **1**−**4** reveal that under positive ion mode in acetonitrile solutions, compounds **2**−**4** retain their solid-state structures in solution as evidenced by the observation of molecular ion peaks at 2821.1780, 1563.3197, and 1509.2031, respectively (see the Supporting Information). Although the parent ion peak for **1** could not be detected in its ESI-MS spectrum, peaks at 1285.2399 could be detected that correspond to species [{(*p*-$Me_2NC_6H_4)_2$Te}$_3$O{*t*-$BuSiO_3$} + CH_3OH]$^+$ (see the Supporting Information). The ^{29}Si{^{1}H} and ^{125}Te{^{1}H} NMR spectra of **1**−**4** reveal that all the silicon and tellurium atoms present in these compounds are equivalent (see the Supporting Information).

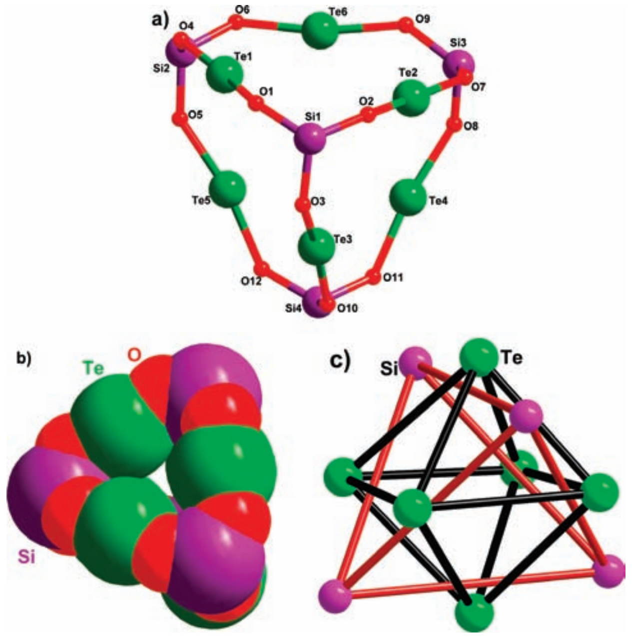


Figure 1. (a) Tetrahedron core of **1**; *N*,*N'*-dimethylaminophenyl and *tert*-butyl groups are omitted for clarity. (b) Space-filling model of $Te_6Si_4O_{12}$ core. (c) Octahedron in a tetrahedron arrangement in **1**.

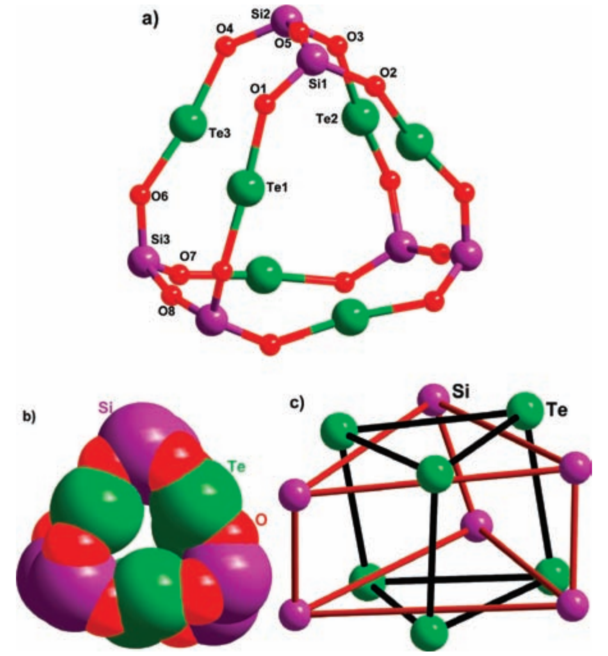


Figure 2. (a) Trigonal prismatic core of **2**; *p*-methoxyphenyl, *tert*-butyl groups, and solvent molecules are omitted for clarity. (b) Space-filling model of $Te_6Si_6O_{15}$ core. (c) Trigonal prismatic arrangement in **2**.

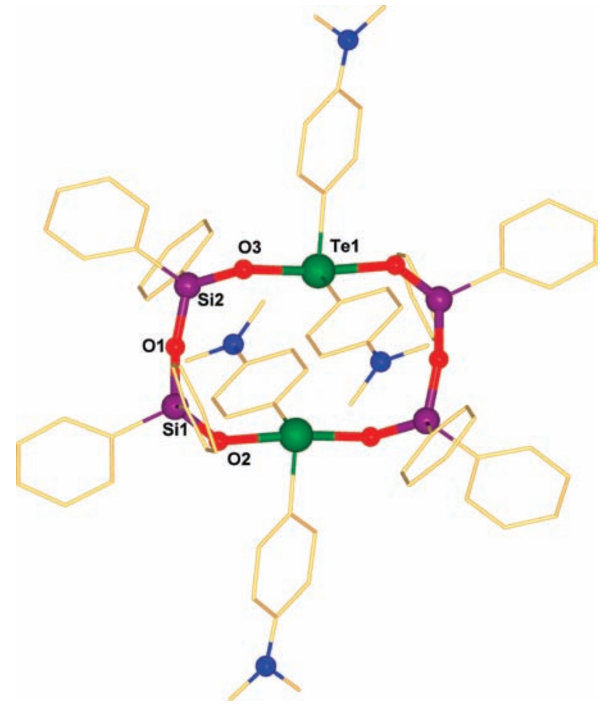


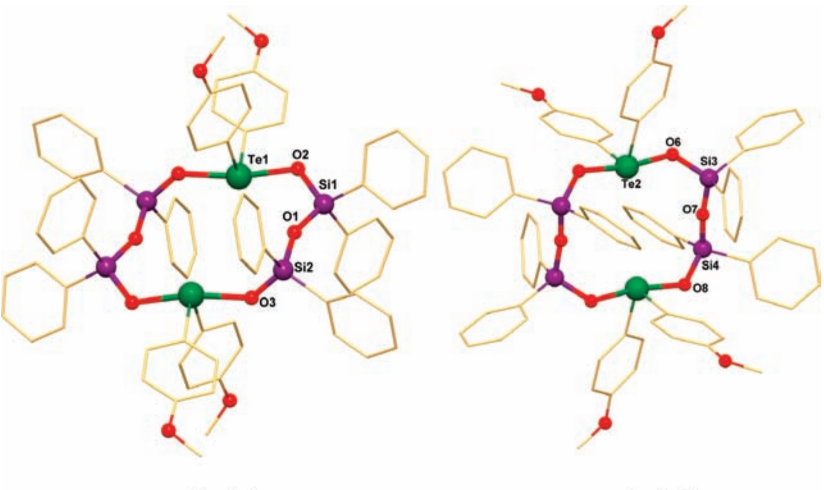
Figure 3. Molecular structure of **3**. Hydrogen atoms are omitted for clarity.

X-ray Crystal Structures of 1−4

Molecular Structures. The molecular structure of **1** (Figure 1) contains a tetrahedron as its core. The four silicon atoms occupy the vertices of a tetrahedron while its six edges are bridged by O−Te−O linkages. The formation of this unprecedented cage is facilitated by the attachment of each *t*-$BuSiO_3$ motif to three (*p*-$Me_2NC_6H_4)_2Te$ units. The six tellurium atoms present occupy the vertices of an octahedron with the four silicon atoms occupying opposite faces of the Te_6 octahedron (Figure 1). Thus, the $Te_6Si_4O_{12}$ of **1** contains four triangular faces containing $Te_3Si_3O_6$ motifs and six Si−O−Te−O edges. This structure, thus represents an example of an octahedron in a tetrahedron (Figure 1c). The average Te−O bond distance in **1** is 2.046 (4) Å. This distance is comparable to that found in *cyclo*-[(*p*-$MeOC_6H_4)_2TeOSi$(*t*-$Bu)_2O]_3$ (2.057 (2) Å).[7a] The geometry around tellurium can be described as trigonal bipyramidal if one considers the stereochemically active lone pair. The average O−Te−O angle is 168.93(17)°, whereas the average Si−O−Te angle is 136.1(3)°.

Compound **2** is a dodecanuclear compound containing a $Te_6Si_6O_{15}$ core (Figure 2). The molecular structure of **2** is approximately in the shape of a trigonal prism. The top and bottom faces of this cage are made up of two $Te_3Si_3O_6$ 12-membered rings. Each of the three pairs of silicon atoms present in the top and bottom faces are connected to each other by an oxygen atom. The resulting Si−O−Si bond is close to being linear (~166°). All six silicon and tellurium atoms present in **2** occupy the vertices of two Si_6 and Te_6 trigonal prisms respectively (Figure 2). The overall $Te_6Si_6O_{15}$ core of **2** resembles the double-six-ring (D6R) SBU of zeolites such as faujasite and chabazite.[11] The average Te−O bond distance in **2** is 2.059(3) Å, which is similar to that found in *cyclo*-[(*p*-$MeOC_6H_4)_2TeOSi$(*t*-$Bu)_2O]_3$ (2.057 (2) Å),[7a] whereas the average Si−O bond distance is 1.615 (3) Å, which is comparable to that found in [(*t*-$BuSi)_4$-($CH_2{=}CHC_6H_4B)_4O_{10}$] (1.616 Å).[5e]

Compounds **3** and **4** are isostructural and crystallize in a $P\bar{1}$ space group of the triclinic system. Although the asymmetric unit of **3** contains one-half of a molecule, that of **4** contains two independent halves. The molecular structures of **3** and **4** possess a 12-membered $Te_2Si_4O_6$ ring (Figures 3 and 4) that is structurally similar



molecule 1 **molecule 2**

Figure 4. Molecular structure of **4**. Two independent molecules are present in the crystal structure. Hydrogen atoms and the solvent molecules are omitted for clarity.

to a single-six-ring (S6R) SBU of a zeolite such as sodalite.[11c,12] In contrast to *cyclo*-[(*p*-MeOC$_6$H$_4$)$_2$TeOSi(*t*-Bu)$_2$O]$_3$, which contains a Si:Te ratio of 1:1 in **3** and **4**, this ratio is 2:1. The 12-membered rings present in **3** and **4** are nearly planar, with only one atom in each case deviating significantly from the mean plane (see the Supporting Information). The Si−O−Si bond angle found in **3** is 164.0(3)°, whereas for **4** it is 155.2(3)° (molecule 1) and 170.1(3)° (molecule 2). The average Te−O bond distance in **3** and **4** are 2.069(4) and 2.073(5) Å, whereas the average Si−O bond distances are 1.607(5) and 1.614(5) Å. The overall dimensions of the ring may be gauged by the inter-tellurium and inter-oxygen distances (cf. for **3** Te1···Te1, 4.2908 (12) Å; O1···O1, 6.8908 (72) Å). It may be mentioned that two other compounds, [Cr(O)$_2${(Ph$_2$SiO)$_2$O}]$_2$[12a] and *cyclo*-[(CpFeC$_5$H$_4$)$_2$Sn(OSiPh$_2$OSiPh$_2$O)$_2$Sn(C$_5$H$_4$FeCp)$_2$],[6b] contain a M$_2$Si$_4$O$_6$ core as in **3** and **4**.

Concluding Remarks

In conclusion, we have been able to synthesize tellurasiloxanes possessing cage and ring structures using a rational synthetic design. The (*p*-Me$_2$NC$_6$H$_4$)$_2$TeO unit is a difunctional reactant; combination of this with a silicon reagent containing three reactive centers affords a product whose core is a tetrahedron (see the Supporting Information). Changing the silicon precursor to [*t*-BuSi(OH)$_2$]$_2$O, where a pair of silicon atoms possess two reactive centers, leads to a trigonal prismatic cage (see the Supporting Information). In this case, the cage structure is formed because of the fact that in the silicon precursor the two difunctional silicon atoms are attached to each other by an oxygen atom. Finally, choosing a simple difunctional silicon precursor in the form of disiloxane-1,3-diol leads to a ring structure. Interestingly, products arising from Si−OH condensation were not observed in this work.[13]

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Supporting Information Available: Mass and multinuclear NMR spectra of compounds **1**−**4**, additional figures, and Tables **1**−**4** (PDF); CIF File for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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