

Octameric molecular aggregates of cyclic tellurane ($C_5H_{10}TeCl_2$) assisted by Te---Cl secondary bonds and long Cl---Cl contacts

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The supramolecular association in the cyclic tellurane [1,1,2,3,4,5,6-heptahydro-1,1-dichloro tellurane] ($C_5H_{10}TeCl_2$) is described. It exists as tetrameric molecular aggregates assisted by Te---Cl secondary bonds. The tetramers are further associated through long Cl---Cl contacts to yield octameric molecular aggregates. The supramolecular association in $C_5H_{10}TeCl_2$ is compared with the supramolecular associations (trimeric molecular aggregates) present in $C_5H_{10}TeBr_2$ and $C_5H_{10}TeI_2$.

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Organotelluriums have received considerable attention in recent years in the field of: (a) semiconductors¹ (b) nuclear medicine² (c) photo imaging agents³ (d) single source precursors for metal organic chemical vapour deposition⁴ (MOCVD) (e) organic superconductors⁵ and (f) organic synthesis^{6,7}. Supramolecular associations are useful in the field of non-linear optics⁸, solid-state electrical conductivity⁹ and molecular sieves¹⁰. Supramolecular associations in organotellurium compounds¹¹ are a growing field of recent interest in pursuit of engineering of organotellurium crystals with desired structures and properties. We are developing supramolecular chemistry based on Te---X (X = O, I) secondary bonds¹²⁻¹⁷ and C-H---O hydrogen bonds¹⁸ in acyclic and cyclic organotellurium compounds.

Among organotelluriums (cyclic telluranes) the studies on $C_5H_{10}Te$ () systems are limited. Morgan *et al.*¹⁹ reported synthesis and characterization of $C_5H_{10}TeI_2$ as early as in year 1928 and after

half a century, its derivatives $C_5H_{10}TeX_2$ (X = F, Cl, Br, CN, NCO, NCS, NCSe, N₃) were reported, from our laboratory, by Srivastava *et al.*²⁰ The conformation of $C_5H_{10}Te$ cycle in $C_5H_{10}TeBr_2$ was reported by Lambert *et al.*²¹ through NMR studies. We for the first time¹², described the conformation of $C_5H_{10}Te$ cycle in $C_5H_{10}TeI_2$ through single crystal X-ray diffraction studies and discussed supramolecular association (trimeric molecular aggregates assisted by Te---I secondary bonds) in $C_5H_{10}TeI_2$. Recently, we²² were able to obtain trimeric molecular aggregates assisted by Te---Br secondary bonds in $C_5H_{10}TeBr_2$. The supramolecular associations assisted by Te---Cl secondary bonds in acyclic telluranes have been reported by De Matheus *et al.*²³ in *cis*-[(4-PhOC₆H₄)₂TeCl(μ-Cl)]₂, Alcock *et al.*²⁴ in Ph₂TeCl₂ and Ziolo *et al.*²⁵ in α-Me₂TeCl₂ whereas, to our knowledge, there is no report of Te---Cl secondary bonds assisted supramolecular associations in cyclic telluranes (*cf.* Te---I assisted supramolecular assemblies in cyclic telluranes^{11c,12,22,26} resulting in the formation of oligomers, stairs, ribbons, ladders and zig-zag chains).

In the present note, we discuss the supramolecular associations in (cyclic tellurane) $C_5H_{10}TeCl_2$ assisted by Te---Cl secondary bonds and long Cl---Cl contacts resulting in the formation of octameric molecular aggregates and compare it with the supramolecular associations (trimeric molecular aggregates) present in already reported (cyclic telluranes) $C_5H_{10}TeBr_2$ ²² and $C_5H_{10}TeI_2$ ¹².

Experimental

$C_5H_{10}TeI_2$ was prepared by the literature method¹⁹. Tellurium, 1,5-pentanediol, potassium iodide, *o*-phosphoric acid, P₂O₅ and silver nitrate were commercially obtained from Aldrich. Acetone and petroleum ether (60-80 °C) were dried by standard procedures and freshly distilled before use. Elemental analyses, FT-IR and ¹HNMR spectroscopy were carried out as already reported¹³. The single crystal X-ray diffraction studies were carried out at Howard University, USA.

Preparation of 1,1,2,3,4,5,6- heptahydro-1,1-,dichloro tellurane (C₅H₁₀TeCl₂)

Based on the method of Srivastava *et al.*²⁰, solid C₅H₁₀TeCl₂ was prepared. Single crystals of C₅H₁₀TeCl₂ were obtained by the reaction of C₅H₁₀TeI₂ (5.56 mmol, 2.51 g) and freshly prepared AgCl (11.15 mmol, 1.60 g) in 25 mL of acetone. The reaction mixture was stirred for 24 h at room temperature. Precipitated AgI and excess of AgCl were filtered. The reaction mixture was reduced to ~10 mL and a layer of petroleum ether (60-80 °C) was put on it. After a day, a large crop of needle shaped colourless crystals of C₅H₁₀TeCl₂ (yield 45%) were obtained. [M.P.=75°C, Anal. C₅H₁₀Cl₂Te. Calcd.: C, 22.34; H, 3.72; Te, 47.50. Found: C, 22.28; H, 3.70; Te, 47.46]. Selected FT-IR (ν/cm⁻¹): 530 (Te-C), 280 (Te-Cl). ¹H NMR(ppm)/CDCl₃: 3.55(t, Te-CH₂), 2.16(m, C-CH₂), 1.88 (m, C-CH₂).

Table 1 — Selected bond lengths (Å) for C₅H₁₀TeCl₂

Te(1)-C(5A)	2.09(2)	C(4A)-C(5A)	1.50(2)
Te(1)-C(1A)	2.13(2)	C(1B)-C(2B)	1.51(2)
Te(1)-Cl(1A)	2.48(3)	C(2B)-C(3B)	1.51(2)
Te(1)-Cl(2A)	2.49(3)	C(3B)-C(4B)	1.53(2)
Te(2)-C(5B)	2.10(1)	C(4B)-C(5B)	1.48(2)
Te(2)-C(1B)	2.12(2)	C(1C)-C(2C)	1.52(2)
Te(2)-Cl(2B)	2.49(3)	C(2C)-C(3C)	1.53(2)
Te(2)-Cl(1B)	2.49(3)	C(3C)-C(4C)	1.50(2)
Te(3)-C(1C)	2.10(1)	C(4C)-C(5C)	1.49(2)
Te(3)-C(5C)	2.11(1)	C(1D)-C(2D)	1.50(2)
Te(3)-Cl(2C)	2.49(4)	C(2D)-C(3D)	1.52(2)
Te(3)-Cl(1C)	2.52(4)	C(3D)-C(4D)	1.51(2)
Te(4)-C(1D)	2.09(2)	C(4D)-C(5D)	1.52(2)
Te(4)-C(5D)	2.11(1)	Te(1)---Cl(1B)	3.602
Te(4)-Cl(2D)	2.49(3)	Te(2)---Cl(1A)	3.816
Te(4)-Cl(1D)	2.50(3)	Te(3)---Cl(1A)	3.543
C(1A)-C(2A)	1.49(2)	Te(4)---Cl(1B)	3.505
C(2A)-C(3A)	1.55(2)	Cl(1A)---Cl(1A)	3.315
C(3A)-C(4A)	1.50(2)	Cl(1B)---Cl(1A)	3.362

Determination of crystal structure

A colourless crystal having dimensions of 0.10 × 0.25 × 0.95 mm³ was mounted on a Bruker P4 diffractometer using graphite monochromated Mo-K_α (0.71073 Å) radiations. The data were collected at a temperature of 103(2) K to maximum θ value of 29.09°. The unit cell was determined from 25 randomly selected reflections using the automatic search index and least squares refinement. The crystal structure belongs to triclinic, space group *P*-1 with cell dimensions: *a*=12.265(3), *b*=12.873(3), *c*=13.196(3) Å, α=62.202(4), β=63.988(4), γ=87.986(4)°, *V*=1618.4(6) Å³, *Z*=8, *D*_{calcld}=2.205 Mg/m³, *F*(000)=1008. The data were corrected for Lorentz, polarization and absorption effects. The data were monitored by measuring three standard reflections at every 97 reflections. The structure was solved by the routine heavy atom method SHELXS-97²⁷ and Fourier methods and refined by full-matrix least-squares using the SHELXL-97 program²⁷ with the non-hydrogen atoms anisotropic and hydrogen atoms having fixed isotropic thermal parameters of 0.08 Å. Final *R* indices [*I*>2σ (*I*)] *R*₁ = 0.0766 and *wR*₂=0.1936 and *R* indices (all data) *R*₁=0.1137, *wR*₂=0.2204 for 7498 independent reflections [*R*_{int}=0.0706]. Selected bond lengths and bond angles for C₅H₁₀TeCl₂ are listed in Tables 1 and 2.

Results and discussion

The structure of C₅H₁₀TeCl₂ contains four independent molecules in the asymmetric unit (Fig. 1). In each molecule, the tellurium atom completes a cyclohexane ring with other five atoms and the ring has chair conformation due to the staggered situation of C-H bonds on neighbouring carbon atoms. In all the four molecules, tellurium atom of each molecule forms two normal bonds with the two neighbouring carbon atoms Te(1)-C(1A)=2.13(2)Å, Te(1)-C(5A)=2.09(2)Å, C(1A)-Te(1)-C(5A)=97.3(6)° in molecule A; Te(2)-C(1B)=2.12(2)Å, Te(2)-C(5B)=2.10(1)Å, C(1B)-Te(2)-C(5B)=96.1(5)° in molecule B; Te(3)-C(1C)=2.10(1)Å, Te(3)-C(5C)=2.11(1)Å, C(1C)-Te(3)-C(5C)=96.9(6)° in molecule C and Te(4)-C(1D)=2.09(2)Å, Te(4)-C(5D)=2.11(1)Å, C(1D)-Te(4)-C(5D)=98.3(6)° in molecule D. Two axial bonds are formed with chlorine atoms with bond distances Te(1)-Cl(1A)=2.48(3)Å, Te(1)-Cl(2A)=2.49(3)Å forming bond angle Cl(1A)-Te(1)-Cl(2A)=174.8(1)° in molecule A, Te(2)-

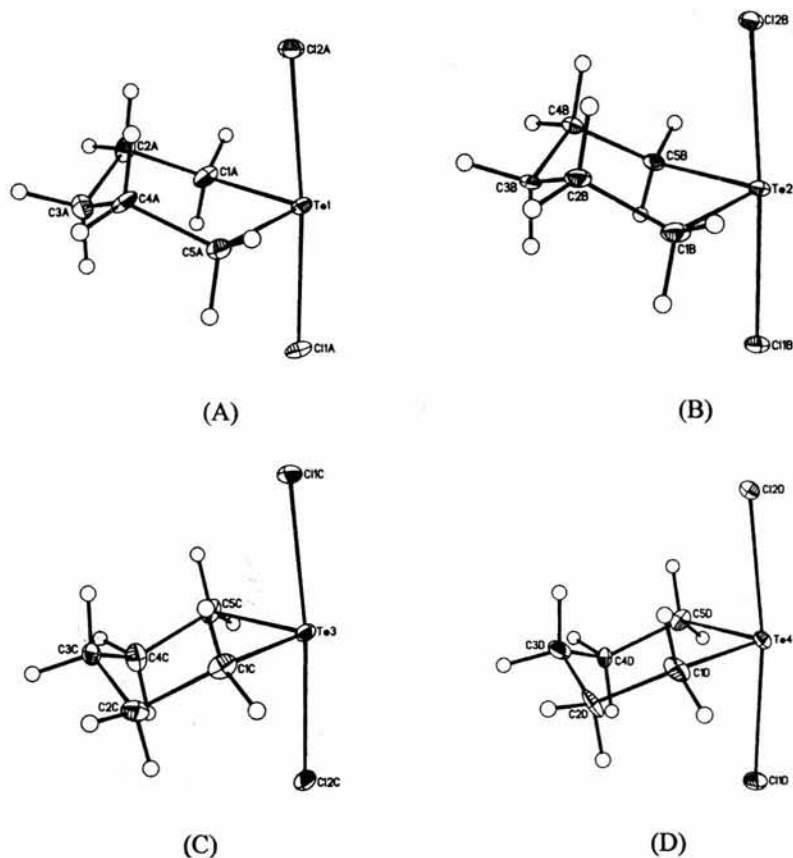
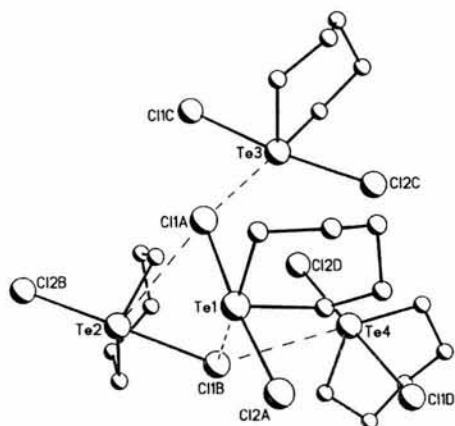
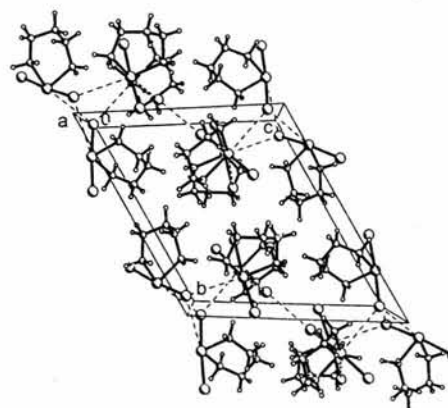
Table 2 — Selected bond angles (°) for C₅H₁₀TeCl₂

C(5A)-Te(1)-C(1A)	97.3(6)	C(2A)-C(1A)-Te(1)	114.6(1)
C(5A)-Te(1)-Cl(1A)	88.2(4)	C(1A)-C(2A)-C(3A)	115.1(1)
C(1A)-Te(1)-Cl(1A)	89.3(4)	C(4A)-C(3A)-C(2A)	113.0(1)
C(5A)-Te(1)-Cl(2A)	87.5(4)	C(3A)-C(4A)-C(5A)	114.5(1)
C(1A)-Te(1)-Cl(2A)	88.3(4)	C(4A)-C(5A)-Te(1)	115.1(1)
Cl(1A)-Te(1)-Cl(2A)	174.8(1)	C(2B)-C(1B)-Te(2)	114.7(9)
Cl(1B)---Te(1)-C(1A)	129.8	C(3B)-C(2B)-C(1B)	113.0(1)
C(5B)-Te(2)-C(1B)	96.1(5)	C(2B)-C(3B)-C(4B)	116.1(1)
C(1B)-Te(2)-Cl(2B)	88.2(4)	C(5B)-C(4B)-C(3B)	112.8(1)
C(5B)-Te(2)-Cl(1B)	89.8(4)	C(4B)-C(5B)-Te(2)	115.7(1)
C(1B)-Te(2)-Cl(1B)	87.8(4)	C(2C)-C(1C)-Te(3)	114.5(1)
Cl(2B)-Te(2)-Cl(1B)	175.5(1)	C(1C)-C(2C)-C(3C)	112.0(1)
Cl(1A)---Te(2)-C(1B)	130.7	C(4C)-C(3C)-C(2C)	113.6(1)
C(1C)-Te(3)-C(5C)	96.9(6)	C(5C)-C(4C)-C(3C)	114.8(1)
C(1C)-Te(3)-Cl(2C)	89.1(4)	C(4C)-C(5C)-Te(3)	114.9(1)
C(5C)-Te(3)-Cl(2C)	89.2(4)	C(2D)-C(1D)-Te(4)	116.9(1)
C(1C)-Te(3)-Cl(1C)	86.2(4)	C(1D)-C(2D)-C(3D)	112.9(1)
C(5C)-Te(3)-Cl(1C)	87.8(4)	C(4D)-C(3D)-C(2D)	113.8(1)
Cl(2C)-Te(3)-Cl(1C)	174.0(1)	C(3D)-C(4D)-C(5D)	116.8(1)
Cl(1A)---Te(3)-C(1C)	132.8	C(4D)-C(5D)-Te(4)	113.7(1)
C(1D)-Te(4)-C(5D)	98.3(6)		
C(1D)-Te(4)-Cl(2D)	88.1(4)		
C(5D)-Te(4)-Cl(2D)	87.8(4)		
C(1D)-Te(4)-Cl(1D)	87.3(4)		
C(5D)-Te(4)-Cl(1D)	87.0(4)		
Cl(2D)-Te(4)-Cl(1D)	172.5(1)		
Cl(1B)---Te(4)-C(1D)	131.8		

Cl(1B)=2.49(3) Å, Te(2)-Cl(2B)=2.49(3) Å forming bond angle Cl(1B)-Te(2)-Cl(2B)=175.5(1)° in molecule B, Te(3)-Cl(1C)=2.52(4) Å, Te(3)-Cl(2C)=2.49(4) Å forming bond angle Cl(1C)-Te(3)-Cl(2C)=174.0(1)° in molecule C and Te(4)-Cl(1D)=2.50(3) Å, Te(4)-Cl(2D)=2.50(3) Å forming bond angle Cl(1D)-Te(4)-Cl(2D)=172.5(1)° in molecule D. The configuration around tellurium atom in all four molecules approximates a distorted trigonal

bipyramid (TBP) with C(1A), C(5A) and an unshared lone pair of electrons in equatorial position and Cl(1A) and Cl(2A) in axial position in molecule A; C(1B), C(5B) and an unshared lone pair of electrons in equatorial position and Cl(1B) and Cl(2B) in axial position in molecule B; C(1C), C(5C) and an unshared lone pair of electrons in equatorial position and Cl(1C) and Cl(2C) in axial position in molecule C and C(1D), C(5D) and an unshared lone pair of electrons in equatorial position and Cl(1D) and Cl(2D) in axial position in molecule D. The Cl-Te-Cl angles (as quoted above) in A, B, C and D molecules deviate from linearity with the chlorine atoms pushed away from the equatorial electron lone pair^{12-18,28-30}. The average C-C-C angles are 114.20°, 113.97°, 113.47° and 114.50°, respectively, in molecule A, B, C and D. The carbon atoms at the other end of C₅H₁₀TeCl₂ cyclohexane ring make an angle C(2A)-C(3A)-C(4A)=113.0° in molecule A, C(4B)-C(3B)-C(2B)=116.1° in molecule B, C(4C)-C(3C)-C(2C)=113.6° in molecule C and C(4D)-C(3D)-C(2D)=113.8° in molecule D. The C₅H₁₀TeCl₂ has chair conformation in which part of the ring is flattened and a part is considerably puckered. A similar chair conformation has previously been qualitatively predicted for 1,2,3,4,5,6,7-heptahydro-1,1-dibromotellurane (C₅H₁₀TeBr₂) by Lambert *et al.*²¹ through $R = J_{trans}/J_{cis}$ values (1.5, 3.6) in NMR spectrum of its solution. We have confirmed similar chair conformation in C₅H₁₀TeBr₂²² and C₅H₁₀TeI₂¹² through single crystal X-ray diffraction studies.

The Te---Cl and Cl---Cl intermolecular interactions are presented in Figs 2 and 3. All the four molecules (A, B, C & D) are connected through Te---Cl [Te(1)---Cl(1B)=3.602 Å, Te(2)---Cl(1A)=3.816 Å, Te(3)---Cl(1A)=3.543 Å, Te(4)---Cl(1B)=3.505 Å] secondary bonds to form the tetramer (Fig. 2). With the Te---Cl secondary bonds, each tellurium atom is hexa coordinated with an unshared electron pair at the vertex situated *trans* to one of the CH₂ group attached to tellurium. The angle Cl(1B)---Te(1)-C(1A) is 129.8° in molecule A; Cl(1A)---Te(2)-C(1B) is 130.7° in molecule B; Cl(1A)---Te(3)-C(1C) is 132.8° in molecule C and Cl(1B)---Te(4)-C(1D) is 131.8° in molecule D. The Te---Cl distances (as quoted above) are shorter than the sum of van der Waals radii (4.00 Å)³¹ and longer than the sum of covalent radii (2.36 Å)³² and therefore correspond to secondary bonds. These tetramers are asymmetrically interlinked through Cl---Cl (3.315, 3.362 Å) long contacts

Fig. 1 — Crystal structure of $C_5H_{10}TeCl_2$ Fig. 2 — Tetrameric molecular aggregate of $C_5H_{10}TeCl_2$ linked by Te---Cl secondary bonds.Fig. 3 — Octameric molecular aggregates of $C_5H_{10}TeCl_2$ linked by Te---Cl secondary bonds and long Cl---Cl contacts.

resulting in octameric molecular aggregates (Fig. 3). The Cl---Cl distances are shorter than the sum of van der Waals radii ($3.60 \text{ \AA}$)³¹ and longer than the sum of covalent radii ($1.98 \text{ \AA}$)³². The value of Cl---Cl contacts is comparable to Cl---Cl contacts ($3.28 \text{ \AA}$) in

$[Ph_3P-Cl---Cl---Cl-PPh_3]Cl$ ³³ and the distances are although long but correspond to significant interaction in the solid state³⁴.

A comparative account of supramolecular associations in $C_5H_{10}TeCl_2$ (present investigation),

$C_5H_{10}TeBr_2^{22}$ and $C_5H_{10}TeI_2^{12}$ reveals that in each case the primary geometry around tellurium is distorted trigonal bipyramidal (ψ TBP) with two $-CH_2-$ groups and stereochemically active electron lone pair in equatorial plane with halogens (Cl, Br, I) occupying the axial positions. In each case $C_5H_{10}Te$ cycle has chair conformation in which part of the ring is flattened and a part is considerably puckered.

We conclude that through change of halogen from Cl to Br to I in $C_5H_{10}TeX_2$ ($X = Cl, Br, I$) the nature of conformation of $C_5H_{10}Te$ cycle remains the same and primary geometry around tellurium is ψ TBP. The trimeric molecular aggregates exist in $C_5H_{10}TeI_2^{12}$ through $Te---I$ and $I---I$ secondary bonds and in $C_5H_{10}TeBr_2^{22}$ through $Te---Br$ secondary bonds whereas octameric molecular aggregates exist in $C_5H_{10}TeCl_2$ through $Te---Cl$ secondary bonds and long $Cl---Cl$ contacts. The $Te---Cl$ secondary bonds act as crystal structure directors whereas $Cl---Cl$ contacts increase the aggregation of the species.

Supplementary Data

Tables containing listing of positional parameters, thermal parameters, all distances and angles for $C_5H_{10}TeCl_2$ are available from the authors.

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