Polyhedron 29 (2010) 2202–2212

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Mono- and bis(dialkyl/aryl dithiocarbamato) complexes of 1,1,2,3,4,5,6-heptahydro-1,1-dihalido telluranes: Synthesis, spectroscopy, structures and cleavage reaction

Prakash C. Srivastava [a,*], Shrinkhala Dwivedi [a], Vikas Singh [a], Ray J. Butcher [b]

[a] Department of Chemistry, Lucknow University, Lucknow 226007, India
[b] Department of Chemistry, Howard University, Washington, DC 20059, USA

ARTICLE INFO

Article history:
Received 18 March 2010
Accepted 13 April 2010
Available online 29 April 2010

Keywords:
Self assembly
Organotellurium(IV)
Dithiocarbamate
Cleavage reaction
Crystal structure

ABSTRACT

Reactions of 1,1,2,3,4,5,6-heptahydro-1,1-dihalido telluranes [($C_5H_{10}TeX_2$), X = Cl, Br, I] with sodium/ammonium (dialkyl/aryl dithiocarbamates) viz. $NaS_2CN(C_2H_5)_2$, $NH_4S_2CNC_4H_8O$, $NH_4S_2CNC_5H_{10}$, $NH_4S_2CNHC_6H_5$ yield new [$C_5H_{10}TeI\{S_2CN(C_2H_5)_2\}$ (**1**), $C_5H_{10}TeI(S_2CNC_4H_8O)$ (**2**), $C_5H_{10}TeI(S_2CNC_5H_{10})$ (**3**), $C_5H_{10}TeBr\{S_2CN(C_2H_5)_2\}$ (**4**), $C_5H_{10}TeBr(S_2CNC_4H_8O)$ (**5**), $C_5H_{10}TeBr(S_2CNC_5H_{10})$ (**6**), $C_5H_{10}TeCl\{S_2CN(C_2H_5)_2\}$ (**7**), $C_5H_{10}TeCl(S_2CNC_4H_8O)$ (**8**), $C_5H_{10}TeCl(S_2CNC_5H_{10})$ (**9**), $C_5H_{10}TeCl(S_2CNHC_6H_5)$ (**10**), $C_5H_{10}Te\{S_2CN(C_2H_5)_2\}_2$ (**12**), $C_5H_{10}Te(S_2CNC_4H_8O)_2$ (**13**), $C_5H_{10}Te(S_2CNC_5H_{10})_2$ (**14**)] complexes. The substitution reaction of $C_5H_{10}TeCl_2$ with $NH_4S_2CNHC_6H_5$ yields complex (**10**) along with the cleaved product $SC(NHC_6H_5)_2$ (**11**). In such type of substitution reaction, the formation of $SC(NHC_6H_5)_2$ ($H_5C_6HN{-}\overset{\overset{S}{\|}}{C}{-}NHC_6H_5$) (**11**) is uncommon. The probable pathway for obtaining the cleaved product has been postulated on the basis of a comparative account with other similar type of cleavage reactions. The intermolecular Te···S secondary bonds and/or C–H···X (X = O, Cl, I) hydrogen bonds lead to the formation of (stairs, zig-zag ribbons), trimeric, tetrameric, hexameric and decameric supramolecular assemblies. The complexes have been characterized by elemental analysis, IR and (^1H, ^{13}C, ^{125}Te) NMR spectroscopy and single crystal X-ray crystallography of **1**, **2**, **4**, **7**, **8**, **9** and **11**.

1. Introduction

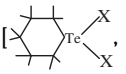
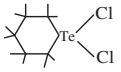
Dithiocarbamates have been widely used as versatile ligands in Tellurium/organotellurium coordination chemistry [1] and in most of the cases the *N,N*-dialkyldithiocarbamates behave as dithio ligands [2–6], whereas, to our knowledge, the reports related to halido derivatives of the type Me_2TeXL (X = Cl, Br, I) (L = dialkyldithiocarbamates) and $C_4H_8TeI(S_2CNEt_2)$ are restricted to two reports only [3d,5] apart from the mention of $C_5H_{10}TeI(S_2CNC_4H_8O)$ characterized through single crystal X-ray diffraction data only in our earlier report [6] where dithiocarbamate groups act as monothio ligands. The dithiocarbamate ligands lead to the interesting supramolecular arrays and the use of optical and analytical properties of dithiocarbamate complexes in constructing sensor for guest molecules and their capability of introducing functionality has been reported [7]. The chemotherapeutic use of *cis*-diamine dichloro platinum(II) and related drugs consists of some negative side effects including nephrotoxicity [8] because of the inactivation of enzymes by coordination of Pt(II) to thiol groups and diethyldithiocarbamate ions $(Et_2NCS_2)^-$ [9–11] containing soft sulfur atoms have been used as "rescue agents" for the protection of these thiols.

On the other hand, there is considerable interest in organotellurium compounds because of their utility in organic synthesis, nuclear medicine, conductive materials and precursors for metal organic chemical vapour deposition (MOCVD) [6]. In addition to these potential utilities, there has been a significant interest in exploiting remarkable structure plasticity of organotelluriums [2,6,12] possibly because of the interest in the usefulness of supramolecular associations of organometallic compounds in non-linear optics, solid state electrical conductivity and molecular sieves [6]. Apart from specific intermolecular non-covalent interactions [13–16], the hydrogen bonds with well characterized geometry and robustness are also frequently used in designing supramolecular arrays [17–20] and amongst hydrogen bonds, C–H···X (X = O or Cl or I) hydrogen bonds play a dominant role in the stability and possibly even in the activity of biological macromolecules, organometallic crystals and molecular recognition processes [21].

In view of the usefulness of C–H···X (X = O, Cl, I) hydrogen bonds; the remarkable utilities of dialkyl/aryl dithiocarbamate

* Corresponding author. Tel.: +91 522 2358473.
E-mail address: pcsrivastava31@rediffmail.com (P.C. Srivastava).

0277-5387/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2010.04.020

groups coupled with their coordination characteristics and the potentials, organotelluriums, have exhibited; we in the present investigation report the supramolecular associations of hitherto unknown mono- and bis(dialkyl/diaryl dithiocarbamates) of 1,1,2,3,4,5,6-heptahydro-1,1-dihalido tellurane [ , (X = Cl, Br, I)] built up through intermolecular Te···S secondary bonds and/or C–H···X (X = O, Cl, I) hydrogen bonds. They have been characterized through (^{1}H, ^{13}C, ^{125}Te) NMR spectroscopy and/or single crystal diffraction studies. On the basis of a comparative account of the cleavage reactions, the possible pathway for the cleaved product (**11**) obtained in the reaction of  with $NH_4S_2CNHC_6H_5$ is postulated.

2. Experimental

1,1,2,3,4,5,6-Heptahydro-1,1-diiodo tellurane [$C_5H_{10}TeI_2$] [22,23], 1,1,2,3,4,5,6-heptahydro-1,1-dibromo tellurane [$C_5H_{10}TeBr_2$] [24] and 1,1,2,3,4,5,6-heptahydro-1,1-dichloro tellurane [$C_5H_{10}TeCl_2$] [25], were prepared by literature method. Tellurium, 1,5-pentanediol, potassium iodide, *o*-phosphoric acid, P_2O_5 and silver nitrate were commercially obtained from Aldrich and used as received. Diethylamine, morpholine, piperidine, aniline and carbon disulfide (Aldrich) were distilled before use. Acetone, ethanol, solvent ether, petroleum ether, were dried by standard procedures and freshly distilled before use. Sodium/ammonium salts of diethyl-, morpholine-, piperidine- and aniline dithiocarbamates were freshly prepared. Melting points were recorded in capillary tubes and are uncorrected. Elemental analyses for C, H and N were carried on an Elemental Analyser Heraeus Carlo Erba 1108. Tellurium content was determined volumetrically in the laboratory [26]. IR spectra were recorded using a Shimadzu 8210 PC FT-IR spectrometer in the frequency range 4000–350 cm^{-1} with the samples in KBr discs. ^{1}H, ^{13}C and ^{125}Te NMR spectra were recorded at 300.13 MHz in $CDCl_3$ solutions containing tetramethyl silane as internal standard on a Bruker DRX 300 or Varian VXR 3005 spectrometer.

2.1. Synthesis of $C_5H_{10}TeL_2$, $C_5H_{10}TeXL$ and $SC(NHC_6H_5)_2$ [X = Cl, Br, I; L = $S_2CN(C_2H_5)_2$, $S_2CNC_4H_8O$, $S_2CNC_5H_{10}$, $S_2CNHC_6H_5$]

1,1,2,3,4,5,6-Heptahydro-1-iodo-1-(diethyldithiocarbamato) tellurane $C_5H_{10}TeI\{S_2CN(C_2H_5)_2\}$ (**1**), 1,1,2,3,4,5,6-heptahydro-1-iodo-1-(morpholine dithiocarbamato) tellurane $C_5H_{10}TeI(S_2CNC_4H_8O)$ (**2**), 1,1,2,3,4,5,6-heptahydro-1-iodo-1-(piperidine dithiocarbamato) tellurane $C_5H_{10}TeI(S_2CNC_5H_{10})$ (**3**), 1,1,2,3,4,5,6-heptahydro-1-bromo-1-(diethyldithiocarbamato) tellurane $C_5H_{10}TeBr\{S_2CN(C_2H_5)_2\}$ (**4**), 1,1,2,3,4,5,6-heptahydro-1-bromo-1-(morpholine dithiocarbamato) tellurane $C_5H_{10}TeBr(S_2CNC_4H_8O)$ (**5**), 1,1,2,3,4,5,6-heptahydro-1-bromo-1-(piperidine dithiocarbamato) tellurane $C_5H_{10}Te\text{-}Br(S_2CNC_5H_{10})$ (**6**), 1,1,2,3,4,5,6-heptahydro-1-chloro-1-(diethyldithiocarbamato) tellurane $C_5H_{10}TeCl\text{-}\{S_2CN(C_2H_5)_2\}$ (**7**), 1,1,2,3,4,5,6-heptahydro-1-chloro-1-(morpholine dithiocarbamato) tellurane $C_5H_{10}TeCl(S_2CNC_4H_8O)$ (**8**), 1,1,2,3,4,5,6-heptahydro-1-chloro-1-(piperidine dithiocarbamato) tellurane $C_5H_{10}TeCl(S_2CNC_5H_{10})$ (**9**), 1,1,2,3,4,5,6-heptahydro-1-chloro-1-(aniline dithiocarbamato) tellurane $C_5H_{10}TeCl(S_2CNHC_6H_5)$ (**10**), 1,1,2,3,4,5,6-heptahydro-1,1-(diethyldithiocarbamato) tellurane $C_5H_{10}Te\{S_2CN(C_2H_5)_2\}_2$ (**12**), 1,1,2,3,4,5,6-heptahydro-1,1-bis(morpholine dithiocarbamato) tellurane $C_5H_{10}Te(S_2CNC_4H_8O)_2$ (**13**), 1,1,2,3,4,5,6-heptahydro-1,1-(piperidine dithiocarbamato) tellurane $C_5H_{10}Te(S_2CNC_5H_{10})_2$ (**14**) were prepared by stirring 1,1,2,3,4,5,6-heptahydro-1,1-dihalido telluranes with freshly prepared sodium/ammonium salts of diethyl-, morpholine-, piperidine- and aniline dithiocarbamates in 1:1 and 1:2 M ratio in acetone (Scheme 1).

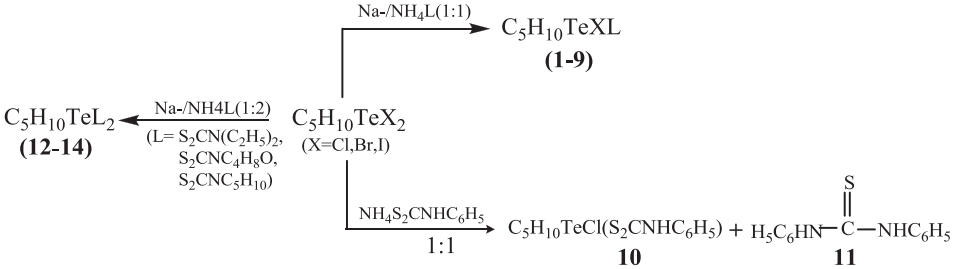
Complex (**1**) was prepared by stirring $C_5H_{10}TeI_2$ (2.00 g, 4.43 mmol) in acetone (~25 ml) with freshly prepared sodium salt of diethyldithiocarbamate (0.99 g, 4.43 mmol) in 1:1 M ratio at room temperature (25 °C). After ~4 h the reaction mixture was filtered to eliminate the unidentified material. The filtrate was concentrated to ~10 ml under reduced pressure and kept overnight. Yellow crystals were obtained and they were analysed through elemental analysis, FT-IR, ^{1}H NMR and single crystal X-ray diffraction studies. These yellow crystals corresponded to $C_5H_{10}TeI\{S_2CN(C_2H_5)_2\}$ (**1**). Complexes **2–14** were obtained by the reaction of $C_5H_{10}TeX_2$ (X = Cl, Br, I) and corresponding dithiocarbamates following the same procedure as in (**1**).

The complexes **2**, **4**, **7**, **8** and **9** also yield their crystals which were analysed through single crystal X-ray diffraction studies. The reaction of $C_5H_{10}TeCl_2$ with $NH_4S_2CNC_6H_5$ gives yellow colour solid complex (**10**) with few transparent crystals. These transparent crystals were analysed through single crystal X-ray diffraction studies only and corresponded to the cleaved product (**11**) (Fig. 13 and Table 1) indicating cleavage of Te–C, Te–Cl and Te–S bonds and, probably, some sort of rearrangement.

The analytical and spectroscopic data for the complexes **1–14** are given as follows:

*1,1,2,3,4,5,6-Heptahydro-1-iodo-1-(diethyldithiocarbamato)tellurane $C_5H_{10}TeI\{S_2CN(C_2H_5)_2\}$ (**1**):* yield: 1.00 g (48%), m.p. 110 °C. *Anal.* Calc. for $C_{10}H_{20}INS_2Te$: C, 25.39; H, 4.23; N, 2.96; Te, 26.9. Found: C, 25.38; H, 4.20; N, 2.94; Te, 26.9%. FT-IR (KBr, cm^{-1}): 1494 vs 1424 s (νCN); 995 s (νCS); 500 s (νTeCH$_2$). ^{1}H NMR ($CDCl_3$) δ ppm: 3.37 [t, 4H, Te(CH$_2$)$_2$], 2.31 [m, 4H and 2H, TeCCH$_2$ and TeCCH$_2$CH$_2$], 3.71 [m, 4H, (–CH$_2$)$_2$N], 1.28 [m, 6H, (–CH$_3$)C].

*1,1,2,3,4,5,6-Heptahydro-1-iodo-1-(morpholine dithiocarbamato) tellurane $C_5H_{10}TeI(S_2CNC_4H_8O)$ (**2**):* yield: 1.90 g (88%), m.p. 186 °C. *Anal.* Calc. for $C_{10}H_{18}INOS_2Te$: C, 24.66; H, 3.69; N, 2.87; Te, 26.2. Found: C, 24.63; H, 3.67; N, 2.86; Te, 26.2%. FT-IR (KBr, cm^{-1}): 1428 m, 1381 m (νCN); 1038 s (νCS); 585 s (νTeCH$_2$); ^{1}H NMR ($CDCl_3$) δ ppm: 3.66 [t, 4H, (CH$_2$)$_2$Te], 2.33 [m, 4H and 2H, TeCCH$_2$ and TeCCH$_2$CH$_2$], 4.14 [t, 4H, (–CH$_2$)$_2$N], 3.87 [t, 4H, (–CH$_2$)$_2$O].



Scheme 1. Method of preparation of complexes **1–14**.

Table 1
Crystal data and structure parameters for complexes **1**, **2**, **4**, **7**, **8**, **9** and **11**.

	1	**2**	**4**	**7**	**8**	**9**	**11**
Empirical formula	$C_{10}H_{20}INS_2Te$	$C_{10}H_{18}INOS_2Te$	$C_{10}H_{19}BrNS_2Te$	$C_{10}H_{20}ClNS_2Te$	$C_{10}H_{18}ClNOS_2Te$	$C_{11}H_{20}ClNS_2Te$	$C_{13}H_{12}N_2S$
Formula weight	472.89	486.87	424.89	381.44	395.42	393.45	228.31
T (K)	103(2)	293(2)	200(2)	200(2)	296(2)	110(2)	200(2)
Wave length (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	orthorhombic	orthorhombic	triclinic	monoclinic	orthorhombic
Space group	*P*212121	*P*2(1)/*n*	*P*212121	*Pbca*	*P*1	*P*121/*c*1	*Pnma*
Unit cell dimension							
a (Å)	6.6612(8)	11.0450(5)	6.6031(3)	12.1485(3)	6.8744(4)	6.53301(17)	7.8552(6)
b (Å)	10.2132(13)	11.4427(5)	10.1476(4)	10.6964(3)	9.4989(5)	19.7309(5)	25.5231(8)
c (Å)	22.665(3)	12.4484(5)	22.2337(9)	22.4477(6)	11.8929(7)	11.2816(3)	5.6920(5)
α (°)	90	90	90	90	87.142(5)	90	90
β (°)	90	90	90	90	73.531(5)	96.494(3)	90
γ (°)	90	90	90	90	81.320(5)	90	90
Volume (Å^3)	1542.0(3)	1561.41(12)	1489.78(11)	2916.97(13)	736.19(7)	1444.88(7)	1141.18(14)
Z	4	4	4	8	2	4	4
Calculated density (mg/m^3)	2.037	2.071	1.894	1.737	1.784	1.809	1.329
Absorption coefficient (mm^{-1})	4.177	4.133	4.932	2.482	2.467	2.508	0.255
F(0 0 0)	896	920	820	1504	388	776	480
Crystal size (mm^3)	0.40 × 0.45 × 0.65	0.20 × 0.44 × 0.72	0.53 × 0.38 × 0.22	0.46 × 0.25 × 0.22	0.52 × 0.37 × 0.12	0.47 × 0.35 × 0.12	0.53 × 0.38 × 0.19
θ Range for data collection (°)	1.80–28.28	2.33–28.32	4.79–32.54	4.68–32.47	4.68–32.47	4.78–32.71	4.70–32.44
Reflection collected/ unique (R_{int})	11 605	11 984	10 219	17 111	6254	10 566	8782
Completeness to θ_{max} (%)	97.3	98.6	98.7	99.0	85.1	99.2	99.4
Maximum and minimum transmission	0.894386 and 0.609696	0.928068 and 0.650419	1.00000 and 0.19244	1.00000 and 0.54887	1.00000 and 0.39785	1.00000 and 0.53811	1.00000 and 0.81722
Refinement method	full-matrix least squares on F^2						
Data/restraints/ parameters	3723/0/139	3837/0/145	4731/0/134	4844/0/147	3911/0/145	4757/0/145	1971/0/76
Goodness-of-fit (GOF) on F^2	1.243	1.066	1.052	0.934	1.020	0.999	1.086
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0227, wR_2 = 0.0567	R_1 = 0.0302, wR_2 = 0.0799	R_1 = 0.0484, wR_2 = 0.1169	R_1 = 0.0272, wR_2 = 0.0525	R_1 = 0.0732, wR_2 = 0.2085	R_1 = 0.0283, wR_2 = 0.0583	R_1 = 0.0419, wR_2 = 0.1128
R indices (all data)	R_1 = 0.0230, wR_2 = 0.0568	R_1 = 0.0393, wR_2 = 0.0828	R_1 = 0.0611, wR_2 = 0.1240	R_1 = 0.0651, wR_2 = 0.0596	R_1 = 0.0972, wR_2 = 0.2238	R_1 = 0.0397, wR_2 = 0.0606	R_1 = 0.0631, wR_2 = 0.1195
Largest difference peak and hole (e Å^{-3})	1.299 and −0.785	0.962 and −0.728	1.790 and −1.744	1.367 and −0.706	3.946 and −1.114	1.242 and −0.688	0.385 and −0.207

*1,1,2,3,4,5,6-Heptahydro-1-iodo-1-(piperidine dithiocarbamato) tellurane $C_5H_{10}TeI(S_2CNC_5H_{10})$ (**3**):* yield: 0.50 g (23%), m.p. 150 °C. *Anal.* Calc. for $C_{11}H_{20}INS_2Te$: C, 29.23; H, 3.24; N, 2.84; Te, 25.9. Found: C, 29.21; H, 3.22; N, 2.83; Te, 25.8%. FT-IR (KBr, cm^{-1}): 1439 m, 1354 m; (νCN); 1010 m (νCS); 616 w (νTeCH$_2$). ^{1}H NMR ($CDCl_3$) δ ppm: 3.64 [t, 4H, –$(CH_2)_2$Te], 2.32 [m, 4H and 2H, TeCCH$_2$ and TeCCH$_2$CH$_2$], 3.86 [s,4H, $(-CH_2)_2$N], 1.95,1.80 [m, 4H, $(-CH_2)_2$C].

*1,1,2,3,4,5,6-Heptahydro-1-bromo-1-(diethyldithiocarbamato) tellurane $C_5H_{10}TeBr\{S_2CN(C_2H_5)_2\}$ (**4**):* yield: 1.10 g (92%), m.p. 115 °C. *Anal.* Calc. for $C_{10}H_{20}BrNS_2Te$: C, 28.19; H, 4.69; N, 3.29; Te, 30.0. Found: C, 28.15; H, 4.64; N, 3.27; Te, 29.9%. FT-IR (KBr, cm^{-1}): 1499 m, 1428 s (νCN); 1011 m, 960 s (νCS); 501 m (νTeCH$_2$). ^{1}H NMR ($CDCl_3$) δ ppm: 3.44 [m, 4H, –$(CH_2)_2$Te], 2.20 [m, 4H TeCCH$_2$], 1.84 [m, 2H, TeCCH$_2$CH$_2$], 3.88 [q, 4H, $(-CH_2)_2$N], 1.28 [t, 6H, $(-CH_3)_2$C]. ^{13}C{^{1}H} NMR ($CDCl_3$) δ ppm: 31.70 (TeCH$_2$), 21.97 (TeCCH$_2$), 26.22 (TeCCH$_2$CH$_2$), 49.26 (NCH$_2$), 12.09 (NCCH$_3$), 193.13 (S_2CN).

*1,1,2,3,4,5,6-Heptahydro-1-bromo-1-(morpholine dithiocarbamato) tellurane $C_5H_{10}TeBr(S_2CNC_4H_8O)$ (**5**):* yield: 0.75 g (61%), m.p. 155 °C. *Anal.* Calc. for $C_{10}H_{18}BrNOS_2Te$: C, 27.30; H, 4.10; N, 3.18; Te, 29.0. Found: C, 27.28; H, 4.10; N, 3.17; Te, 29.0%. FT-IR (KBr, cm^{-1}): 1463 m, 1425 s; (νCN); 1024 s, 988 s (νCS); 540 s (νTeCH$_2$). ^{1}H NMR ($CDCl_3$) δ ppm: 3.40 [t, 4H, $(-CH_2)_2$Te], 2.16 [m, 4H and 2H, TeCCH$_2$ and TeCCH$_2$CH$_2$], 4.17 [t, 4H, $(-CH_2)_2$N], 3.70 [m, 4H, $(-CH_2)_2$O].

1,1,2,3,4,5,6-Heptahydro-1-bromo-1-(piperidine dithiocarbamato) tellurane $C_5H_{10}TeBr(S_2CNC_5H_{10})$ (**6**): yield: 0.23 g (19%), m.p. 170 °C. *Anal.* Calc. for $C_{11}H_{20}BrNS_2Te$: C, 30.02; H, 4.55; N, 3.18; Te, 29.0. Found: C, 30.01; H, 4.52; N, 3.15; Te, 29.0%. FT-IR (KBr, cm^{-1}): 1459 s, 1432 s (νCN); 1029 s, 999 m (νCS); 513 m (νTeCH$_2$); ^{1}H NMR ($CDCl_3$) δ ppm: 3.19 [t, 4H, $(-CH_2)_2$Te], 1.96 [m, 4H and 2H, TeCCH$_2$ and TeCCH$_2$CH$_2$], 4.09 [m, 4H, $(-CH_2)_2$N], 1.70 [d, 4H, –CH$_2$(a) and –CH$_2$(b)].

*1,1,2,3,4,5,6-Heptahydro-1-chloro-1-(diethyldithiocarbamato)tellurane $C_5H_{10}TeCl\{S_2CN(C_2H_5)_2\}$ (**7**)*: yield: 0.70 g (49%), m.p. 145 °C. *Anal.* Calc. for $C_{10}H_{20}ClNS_2Te$: C, 31.48; H, 5.24; N, 3.67; Te, 33.0. Found: C, 31.45; H, 5.22; N, 3.66; Te, 33.0%. FT-IR (KBr, cm^{-1}): 1494 s, 1423 s (νCN); 1010 w, 985 m (νCS); 562 w (νTeCH$_2$). ^{1}H NMR ($CDCl_3$) δ ppm: 3.40 [q, 4H, –$(CH_2)_2$Te], 1.76–2.42 [m, 4H and 2H, TeCCH$_2$ and TeCCH$_2$CH$_2$], 3.88 [q, 4H, $(-CH_2)_2$N], 1.30 [t, 6H, $(-CH_3)$C]. ^{13}C{^{1}H} NMR ($CDCl_3$) δ ppm: 33.04 (TeCH$_2$), 26.34 (TeCCH$_2$), 21.75 (TeCCH$_2$CH$_2$), 48.96 (NCH$_2$), 11.98 (NCCH$_3$), 193.32 (S_2CN). ^{125}Te NMR ($CDCl_3$, 25 °C) δ ppm: 592.0.

*1,1,2,3,4,5,6-Heptahydro-1-chloro-1-(morpholine dithiocarbamato) tellurane $C_5H_{10}TeCl(S_2CNC_4H_8O)$ (**8**)*: yield: 1.90 g (72%), m.p. 140 °C. *Anal.* Calc. for $C_{10}H_{18}ClNOS_2Te$: C, 30.37; H, 4.55; N, 3.54; Te, 32.0. Found: C, 30.35; H, 4.54; N, 3.51; Te, 32.0%. FT-IR (KBr, cm^{-1}): 1459 s, 1428 m (νCN); 1026 s, 990 s (νCS); 547 s (νTeCH$_2$); ^{1}H NMR ($CDCl_3$) δ ppm: 3.30–3.60 [m, 4H, $(CH_2)_2$Te], 1.70–2.44 [m, 4H and 2H, TeCCH$_2$ and TeCCH$_2$CH$_2$], 4.16 [t, 4H, $(-CH_2)_2$N], 3.76 [t, 4H, $(-CH_2)_2$O].

Table 2
Bond lengths and bond angles for complexes $C_5H_{10}TeI[S_2CN(C_2H_5)_2]$ (**1**), $C_5H_{10}TeI[S_2CNC_4H_8O]$ (**2**), $C_5H_{10}TeBr[S_2CN(C_2H_5)_2]$ (**4**), $C_5H_{10}TeCl[S_2CN(C_2H_5)_2]$ (**7**), $C_5H_{10}TeCl[S_2CNC_4H_8O]$ (**8**) and $C_5H_{10}TeCl[S_2CNC_5H_{10}]$ (**9**).

Bond lengths and angles	1	2	4	7	8	9
Te–C	2.182(5)	2.144(4)	2.152(7)	2.151(2)	2.118(6)	2.154(2)
	2.169(5)	2.151(4)	2.170(7)	2.142(2)	2.158(8)	2.158(4)
Te–S	2.522(1)	2.520(10)	2.5057(17)	2.5329(7)	2.541(2)	2.5037(6)
Te–I	3.094(5)	3.0418(4)				
Te–Br			2.9324(8)			
Te–Cl				2.6031(4)	2.662(2)	2.6863(5)
∠I–Te–S	175.48(3)	171.92(2)				
∠Br–Te–S			175.34(5)			
∠Cl–Te–S				169.58(2)	171.24(2)	171.475(19)
∠C–Te–C	93.10	97.82	93.40	97.58	99.40	95.28
∠Te–C(1)–C(2)/∠Te–C(11)–C(12)*	115.4(3)	116.5(3)*	115.5(5)	115.17(17)	115.17(17)*	115.97(15)*
∠C(1)–C(2)–C(3)/∠C(11)–C(12)–C(13)*	116.8(4)	119.1(5)*	117.2(6)	116.1(2)	116.1(2)*	115.89(19)*
∠C(2)–C(3)–C(4)/∠C(12)–C(13)–C(14)*	113.5(4)	116.8(5)*	114.2(7)	114.6(2)	114.6(2)*	114.09(18)*
∠C(3)–C(4)–C(5)/∠C(13)–C(14)–C(15)*	113.6(4)	118.5(4)*	115.7(6)	115.1(2)	115.1(2)*	114.7(2)*
∠C(4)–C(5)–Te/∠C(14)–C(15)–Te*	115.5(3)	115.6(3)*	114.6(5)	114.96(16)	114.96(16)*	114.84(15)*
C–S	1.788(5)	1.751(3)	1.776(7)	1.765(3)	1.765(3)	1.773(2)
C=S	1.644(5)	1.685(3)	1.699(7)	1.688(3)	1.688(3)	1.694(2)
C–N	1.343(6)	1.316(4)	1.306(9)	1.318(3)	1.318(3)	1.329(3)
S–C–S	121.9(3)	120.7(2)	120.4(4)	120.18(16)	120.18(16)	120.56(12)
S–C–N	114.4(4)	115.5(2)	116.0(5)	115.2(2)	115.2(2)	115.59(16)
N–C–S	123.7(4)	123.7(3)	123.7(6)	124.6(2)	124.6(2)	123.84(16)

*1,1,2,3,4,5,6-Heptahydro-1-chloro-1-(piperidine dithiocarbamato) tellurane $C_5H_{10}TeCl(S_2CNC_5H_{10})$ (**9**):* yield: 1.40 g (43%), m.p. 120 °C (dec.). *Anal.* Calc. for $C_{11}H_{20}ClNS_2Te$: C, 33.58; H, 5.09; N, 3.56; Te, 32.0. Found: C, 33.55; H, 5.08; N, 3.54; Te, 32.0%. FT-IR (KBr, cm^{-1}): 1475 m, 1433 s; (*ν*CN); 1006 s, 971 s (*ν*CS); 507 m (*ν*$TeCH_2$). ^1H NMR ($CDCl_3$) *δ* ppm: 3.18 [t, 4H, $-(CH_2)_2Te$], 2.38 [m, 4H and 2H, $TeCCH_2$ and $TeCCH_2CH_2$], 1.94 [m, 4H and 2H, $NCCH_2$ and $NCCCH_2$], 4.10 [s, 4H, $(-CH_2)_2N$].

*1,1,2,3,4,5,6-Heptahydro-1-chloro-1-(aniline dithiocarbamato) tellurane $C_5H_{10}TeCl(S_2CNHC_6H_5)$ (**10**):* yield: 1.00 g (67%), m.p. 115 °C. *Anal.* Calc. for $C_{12}H_{16}ClNS_2Te$: C, 35.90; H, 3.99; N, 3.49; Te, 31.8. Found: C, 35.88; H, 3.95; N, 3.46; Te, 31.7%. FT-IR (KBr, cm^{-1}): 1525 m, 1454 m; (*ν*CN); 1031 m, 1000 w (*ν*CS); 527 m (*ν*$TeCH_2$). ^1H NMR ($CDCl_3$) *δ* ppm: 3.54 [t, 4H, $-(CH_2)_2Te$], 2.14 [m, 4H, $TeCCH_2$], 1.88 [m, 2H, $TeCCH_2CH_2$], 7.25–7.47 [m, 5H, $-C_6H_5$].

*1,1,2,3,4,5,6-Heptahydro-1,1-(diethyldithiocarbamato) tellurane $C_5H_{10}Te\{S_2CN(C_2H_5)_2\}_2$ (**12**):* yield: 0.59 g (27%), m.p. 118 °C. *Anal.* Calc. for $C_{15}H_{30}N_2S_4Te$: C, 36.46; H, 6.08; N, 5.67; Te, 25.8. Found: C, 36.43; H, 6.05; N, 5.66; Te, 25.8%. FT-IR (KBr, cm^{-1}): 1483 s., 1445 s (*ν*CN); 976 s (*ν*CS); 563 s (*ν*$TeCH_2$). ^1H NMR ($CDCl_3$) *δ* ppm: 3.20 [t, 4H, $-(CH_2)_2Te$], 2.13 [m, 4H, $TeCCH_2$], 1.75 [m, 2H, $TeCCH_2CH_2$], 3.94 [q, 8H, $(-CH_2)_2N$], 1.28 [t, 12H, $(-CH_3)C$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$) *δ* ppm: 40.25 ($TeCH_2$), 27.17 ($TeCCH_2$), 30.55 ($TeCCH_2CH_2$), 48.39 (NCH_2), 23.25 ($NCCH_3$), 198.73 (S_2CN). ^{125}Te NMR ($CDCl_3$, 25 °C) *δ* ppm: 526.0.

*1,1,2,3,4,5,6-Heptahydro-1,1-bis(morpholine dithiocarbamato)tellurane $C_5H_{10}Te(S_2CNC_4H_8O)_2$ (**13**)*: yield: 1.22 g (56%), m.p. 170 °C. *Anal.* Calc. for $C_{15}H_{26}N_2O_2S_4Te$: C, 34.50; H, 4.98; N, 5.37; Te, 24.5. Found: C, 34.48; H, 4.94; N, 5.36; Te, 24.4%. FT-IR (KBr, cm^{-1}): 1465 s, 1427 s (*ν*CN); 984 m (*ν*CS); 539 s (*ν*$TeCH_2$); ^1H NMR ($CDCl_3$) *δ* ppm: 3.77 [t, 4H, $(CH_2)_2Te$], 2.17 [m, 4H, $TeCCH_2$], 4.13 [t, 4H, $(-CH_2)_2N$], 3.84 [t, 8H, $(-CH_2)_2O$].

1,1,2,3,4,5,6-Heptahydro-1,1-(piperidine dithiocarbamato) tellurane $C_5H_{10}Te(S_2CNC_5H_{10})_2$ (**14**): yield: 0.50 g (22%), m.p. 120 °C. *Anal.* Calc. for $C_{17}H_{30}N_2S_4Te$: C, 39.41; H, 5.79; N, 5.40; Te, 24.6. Found: C, 39.40; H, 5.77; N, 5.37; Te, 24.6%. FT-IR (KBr, cm^{-1}): 1475 vs 1431 vs; (*ν*CN); 967 s (*ν*CS); 510 m (*ν*$TeCH_2$). ^1H NMR ($CDCl_3$) *δ* ppm: 3.33 [t, 4H, $-(CH_2)_2Te$], 2.07 [m, 4H, $TeCCH_2$], 4.04 [s, 8H, $(-CH_2)_2N$], 1.96,1.59 [m, 8H, $(-CH_2)_2C$] $^{13}C\{^1H\}$ NMR ($CDCl_3$) *δ* ppm: 40.42 ($TeCH_2$), 25.90 ($TeCCH_2$), 29.74 ($TeCCH_2CH_2$), 53.38 (NCH_2), 20.54 ($NCCH_2$), 145.31 (S_2CN).

2.2. X-ray measurements

A summary of the crystal data and refinement parameters for $C_5H_{10}TeI\{S_2CN(C_2H_5)_2\}$ (**1**), $C_5H_{10}TeI(S_2CNC_4H_8O)$ (**2**), $C_5H_{10}TeBr\{S_2CN(C_2H_5)_2\}$ (**4**), $C_5H_{10}TeCl\{S_2CN(C_2H_5)_2\}$ (**7**), $C_5H_{10}TeCl(S_2CNC_4H_8O)$ (**8**), $C_5H_{10}TeCl(S_2CNC_5H_{10})$ (**9**) and $SC(NHC_6H_5)_2$ (**11**) are given in Table 1. The crystals of **1**, **2** were mounted on a Bruker P4S and of **4**, **7**, **8**, **9** and **11** on an Oxford Diffraction Gemini diffractometer using graphite-monochromatic Mo Kα radiation (*λ* = 0.71073 Å). The structures of **1** and **4** were solved in space group *P*212121, **2** in space group *P*2(1)/*n*, **7** in space group *Pbca*, **8** in space group *P*1, **9** in space group *P*121/*c*1 and **11** in space group *Pnma*. The data were corrected for Lorentz, polarization and absorption effects. The structures were solved by routine heavy atom and Fourier methods (SHELXS-97 [27]). Non-hydrogen atoms were refined anisotropically by full-matrix least squares

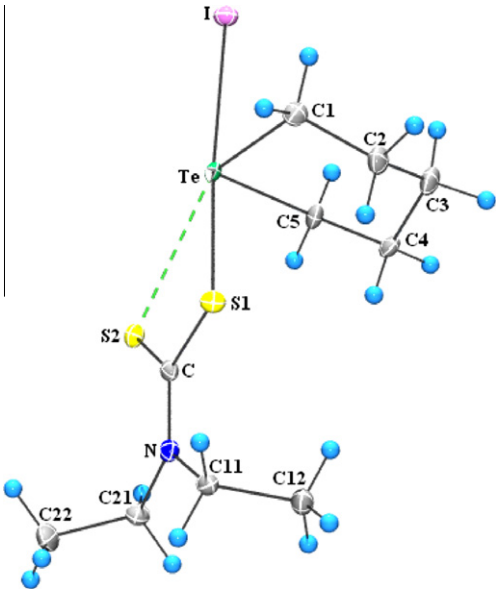


Fig. 1. Crystal structure of $C_5H_{10}TeI\{S_2CN(C_2H_5)_2\}$ (**1**).

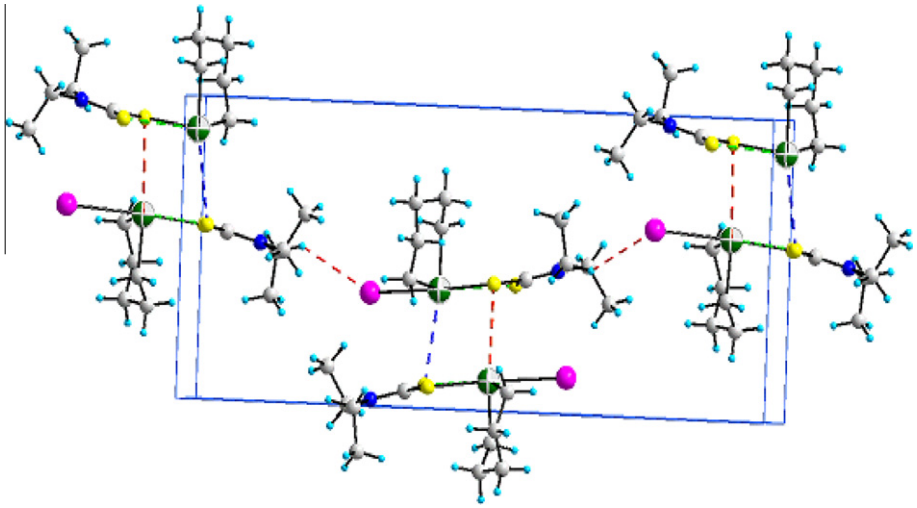


Fig. 2. Stair type supramolecular association of $C_5H_{10}TeI\{S_2CN(C_2H_5)_2$ (**1**).

using the SHELXL-97 program [27] with hydrogen atoms in idealized positions (Table 1). Selected bond lengths and bond angles for **1**, **2**, **4, 7**, **8**, and **9** are listed in Table 2.

3. Results and discussion

3.1. X-ray structures of complexes *1*, *2*, *4*, *7*, *8* and *9*

The X-ray structures of complexes **1**, **2**, **4**, **7**, **8** and **9** show that these complexes contain the monomeric unit of $C_5H_{10}TeX(S_2CNR)$ (X = Cl, Br, or I; R = $(C_2H_5)_2$, C_4H_8O, C_5H_{10}, C_6H_5NH). In complexes (**1**, **2**, **4**, **7**, 8 and **9**), there is telluracyclohexane ring and the ring has chair conformation due to staggered situation of C–H bonds on neighbouring carbon atoms. The tellurium atom is bonded through one of the sulfur of alkyl/aryl dithiocarbamate group (S_2CNR) and one halogen atom (X) by two axial bonds approximately perpendicular to the C–Te–C plane (Table 2) which deviates from linearity with a sulfur and halogen atom pushed away from the equatorial electron lone pair in agreement with the earlier observations [5,6]. Tellurium atom forms two normal bonds with the two neighbouring carbon atoms (average ∠C–Te–C = 96.25 ± 3.15) (Table 2). The four closest atoms S,C,C,X and steriochemically active electron lone pair provide a distorted trigonal bipyramidal geometry around tellurium atom. The other three atoms makes an angle (average ∠C(2)–C(3)–C(4)/C(12)–C(13)–C(14) = 115.15 ± 1.65) (Table 2). The ring has chair confirmation in which part of the ring is flattened and a part is considerably puckered.

The S_2CNR group is bonded to tellurium through one of the sulfur which is connected to carbon through single bond and the other sulfur of C=S (CS_2 group) is attached to tellurium through intramolecular Te···S secondary bonds in complexes **1**, **2**, **4**, **7**, **8** and **9** (Figs. 1, 3, 5, 7, 9 and 11 and Table 3). In complexes **1**, **2**, **4**, **7** and **9** this sulfur atom also enters into the formation of intermolecular Te···S secondary bonds (Table 3).

In complexes **1, 2** and **4**, the supramolecular association is formed only through Te–S secondary bonds whereas in the case of complexes **7**, **8** and **9**, the supramolecular association is achieved through Te···S secondary bonds, C–H···O/C–H···Cl hydrogen bonds (Table 3). These supramolecular associations have been discussed as follows.

3.2. Supramolecular association of $C_5H_{10}TeI\{S_2CN(C_2H_5)_2\}$ (*1*)

In the unit cell, molecules of $C_5H_{10}TeI\{S_2CN(C_2H_5)_2\}$ (**1**) are interconnected through intermolecular Te···S secondary bonds (3.574, 3.915 Å) resulting in the formation of a dimer. The sulfur atoms involved in the formation of Te···S secondary bonds are those of $>CS_2$ group (a) free sulfur (b) sulfur covalently bonded to tellurium.

The former sulfur atom of $>CS_2$ group also enters into the formation of intramolecular Te···S secondary bonds (3.253 Å) [28,29]. These dimers are further connected through C–H···I hydrogen bonds (Table 3) in which hydrogen of $>CH_2$ of diethyl dithiocarbamate group forms hydrogen bond with free iodine atom of (**1**). The binding of dimers through C–H···I interactions results in the formation of stair like supramolecular association (Fig. 2).

3.3. Supramolecular association of $C_5H_{10}TeI(S_2CNC_4H_8O)$ (*2*)

In the same way as discussed above for the supramolecular association of (**1**), the two molecules of $C_5H_{10}TeI(S_2CNC_4H_8O)$ (**2**) are interconnected through intermolecular Te···S secondary bonds (3.618 Å) (sulfur atom involved is free sulfur atom of CS_2 group) resulting in the formation of dimer. This sulfur atom also enter into the formation of intramolecular Te···S secondary bond (3.196 Å). Another dimer is formed through $C(sp^3)H\cdots O$ hydrogen bonds

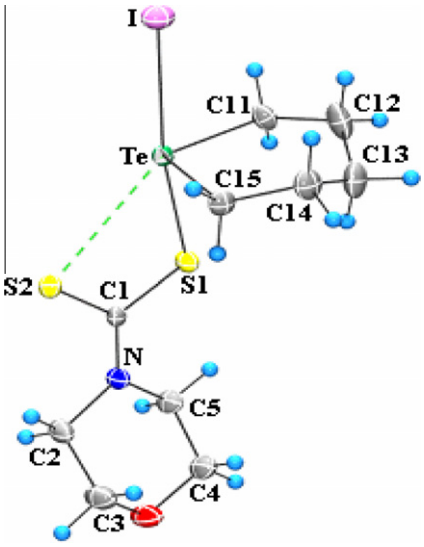


Fig. 3. Crystal structure of $C_5H_{10}TeI(S_2CNC_4H_8O)$ (**2**).

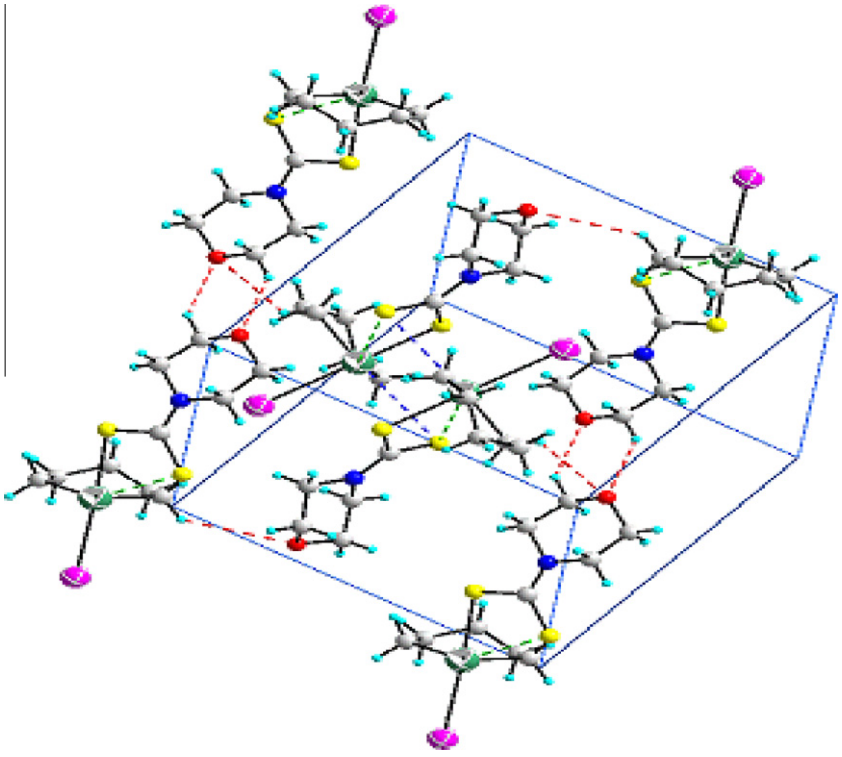


Fig. 4. Hexameric supramolecular association of $C_5H_{10}TeI(S_2CNC_4H_8O)$ (**2**).

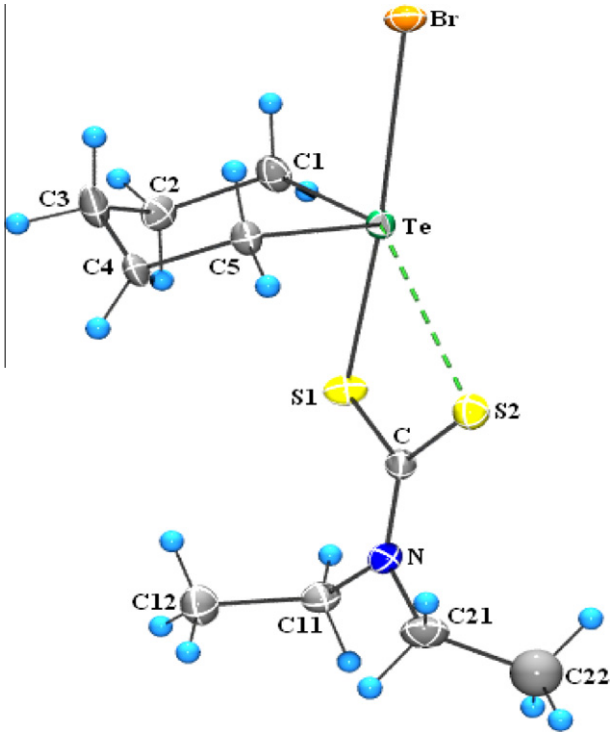


Fig. 5. Crystal structure of $C_5H_{10}TeBr\{S_2CN(C_2H_5)_2\}$ (**4**).

(hydrogen is of $>CH_2$ group of the ligand C_4H_8O group and oxygen is of C_4H_8O group of another molecule).

These two different type of dimers (one formed through intermolecular Te···S secondary bonds and the other formed through C–H···O hydrogen bonds) are further connected through $C(sp^3)H\cdots O$ hydrogen bonds [hydrogen is of $>CH_2$ group of $C_5H_{10}Te$ heterocycle and O is of the ligand C_4H_8O] resulting in the formation of hexameric supramolecular association for (**2**) (Fig. 4).

3.4. Supramolecular association of $C_5H_{10}TeBr\{S_2CN(C_2H_5)_2\}$ (**4**)

In the unit cell, molecules of $C_5H_{10}TeBr[S_2CN(C_2H_5)_2]$ (**4**) are interconnected through intermolecular Te···S secondary bonds [30] resulting in the formation of dimers. In the dimers sulfur of first monomeric unit (sulfur covalently bonded to Te atom) is bonded to Te of second monomeric unit through intermolecular Te···S secondary bonds while the sulfur of second monomeric unit (free sulfur of CS_2 group) is bound to Te atom of first monomeric unit.

The free sulfur of CS_2 group also forms intramolecular Te···S secondary bonds [3.228 Å]. These dimers are interconnected through intermolecular Te···S secondary bonds (Te···S(2)#1 = 3.5789(18) Å, Te···S(1)#2 = 3.8876(18) Å) resulting in hexameric supramolecular association (zig-zag ribbon) (Fig. 6).

The hexameric supramolecular association formed in complex (**4**) is different from the hexameric supramolecular association present in (**1**) and (**2**) in the respect that in complex (**4**) the dimers are interconnected through Te···S secondary bonds. Whereas in complex (**4**) the dimers are interconnected through C–H–I hydrogen bonds and in complex (**2**) the dimers are interconnected through $C(sp^3)H\cdots O$ hydrogen bonds.

3.5. Supramolecular association of $C_5H_{10}TeCl\{S_2CN(C_2H_5)_2\}$ (**7**)

As discussed above for the complexes (**1**) and (**4**) in the unit cell of complex (**7**), in the unit cell, molecules of $C_5H_{10}TeCl[S_2CN(C_2H_5)_2]$ are connected through intermolecular Te···S secondary bonds [3.5760(7) Å] [2] resulting in the formation of dimers.

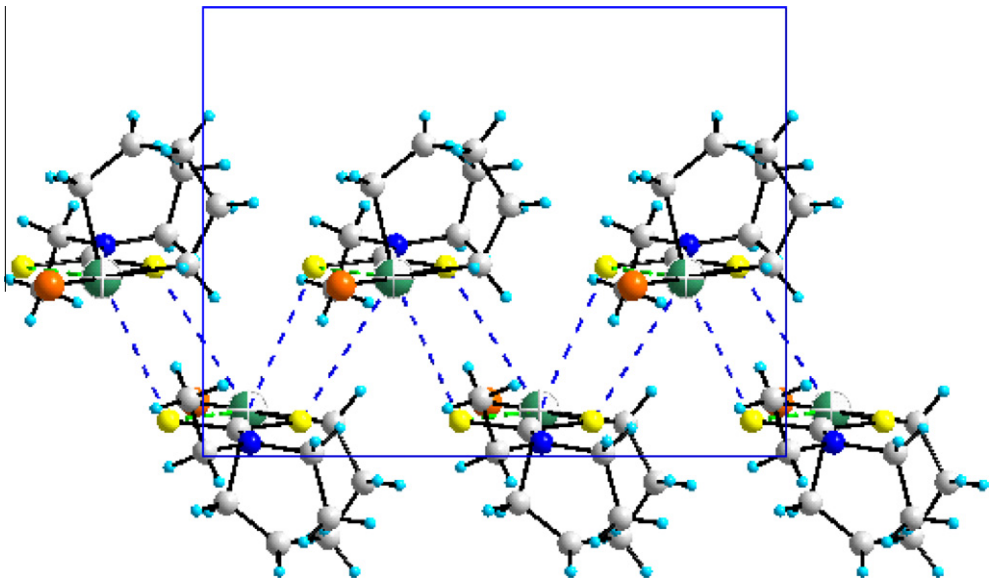


Fig. 6. Hexameric supramolecular association (zig-zag ribbon) of $C_5H_{10}TeBr\{S_2CN(C_2H_5)_2\}$ (**4**).

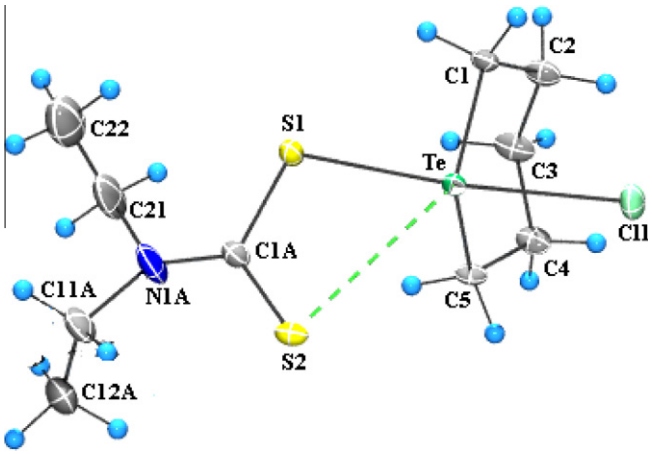


Fig. 7. Crystal structure of $C_5H_{10}TeCl\{S_2CN(C_2H_5)_2\}$ (**7**).

These dimers are further interconnected through C(sp^3)–H···Cl hydrogen bonds (Table 3) to form stair type supramolecular association (Fig. 8) as is present in complex (**1**). Apart from these intermolecular Te···S secondary bonds, intramolecular Te···S secondary bonds [3.2468(7) Å] is also present.

A comparative account of supramolecular association present in the complexes $C_5H_{10}TeI\{S_2CN(C_2H_5)_2\}$ (**1**), $C_5H_{10}TeBr\{S_2CN(C_2H_5)_2\}$ (**4**) and $C_5H_{10}TeCl\{S_2CN\text{-}(C_2H_5)_2\}$ (**7**) reveals that complexes (**1**) and (**7**) possess stair type supramolecular associations whereas the complex (**4**) possess different (zig-zag ribbon) type supramolecular association.

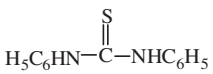
3.6. Supramolecular association of $C_5H_{10}TeCl(S_2CNC_4H_8O)$ (*8*)

In the unit cell, molecules of $C_5H_{10}TeCl(S_2CNC_4H_8O)$ are connected through C(sp^3)–H···O hydrogen bonds to form dimers. These dimers are interconnected through C(sp^3)–H···Cl hydrogen bonds to form tetrameric supramolecular association (Fig. 10 and Table 3).

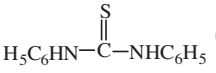
A comparative account of supramolecular association present in complexes (**2**) and (**8**) reveals that with the change of I atom with Cl the nuclearity of the supramolecular association is reduced from hexameric to tetrameric supramolecular association.

3.7. Supramolecular association of $C_5H_{10}TeCl(S_2CNC_5H_{10})$ (*9*)

In the unit cell, molecules of $C_5H_{10}TeCl(S_2CNC_5H_{10})$ form dimers through cooperative participation of intermolecular Te···S secondary bonds (3.557 Å) [2] and C–H···Cl hydrogen bonds. The C(sp^3)–H···Cl hydrogen bonds (Table 3) involve C–H group of piperidine ring and Cl of the same molecule. These dimers are joined through C(sp^3)–H···Cl hydrogen bond resulting in the formation of decameric supramolecular association (Fig. 12), having the highest nuclearity in the supramolecular associations in the present investigation. The C(sp^3)–H···Cl hydrogen bonds involve C–H groups of telluracyclohexane ring and Cl of other molecules (Table 3).

3.8. The X-ray structure and supramolecular association of the cleaved product $SC(NHC_6H_5)_2$  (*11*)

The X-ray structure analysis data at 200(2) K of the cleaved product [obtained in the substitution reaction of $C_5H_{10}TeCl_2$ and $NH_4S_2CNHC_6H_5$ in 1:1 M ratio] reveals that the carbon atom of C=S of CS_2 group is bonded to two C_6H_5NH groups (Fig. 13) with the bond distances and bond angles S–C(1) = 1.6930(18) Å, C(1)–N = 1.3462(13) Å, N–C(2) = 1.4295(14) Å, ∠S–C(1)–N = 122.73(8)°, ∠C(1)–N–C(2) = 124.71(10)°, ∠N–C(2)–C(3) = 120.31(12)°. The C–C bond lengths and ∠C–C–C bond angles of C_6H_5 rings are in the usual range 1.3795–1.3925 Å and 119.31–120.53°, respectively.

In the unit cell, the molecules of  (**11**) are interconnected through N–H···S hydrogen bonds resulting in the formation of trimeric supramolecular associations having distorted hexagonal cavities (Fig. 14). Such type of supramolecular associations with cavities might be, probably, suitable for the binding of guest molecules [31]. The parameters related to N–H(0A)···S hydrogen bonds are: N···S#2 = 3.4917(11) Å, H(0A)···S#2 = 2.65 Å and ∠N–H(0A)···S#2 = 160.2°.

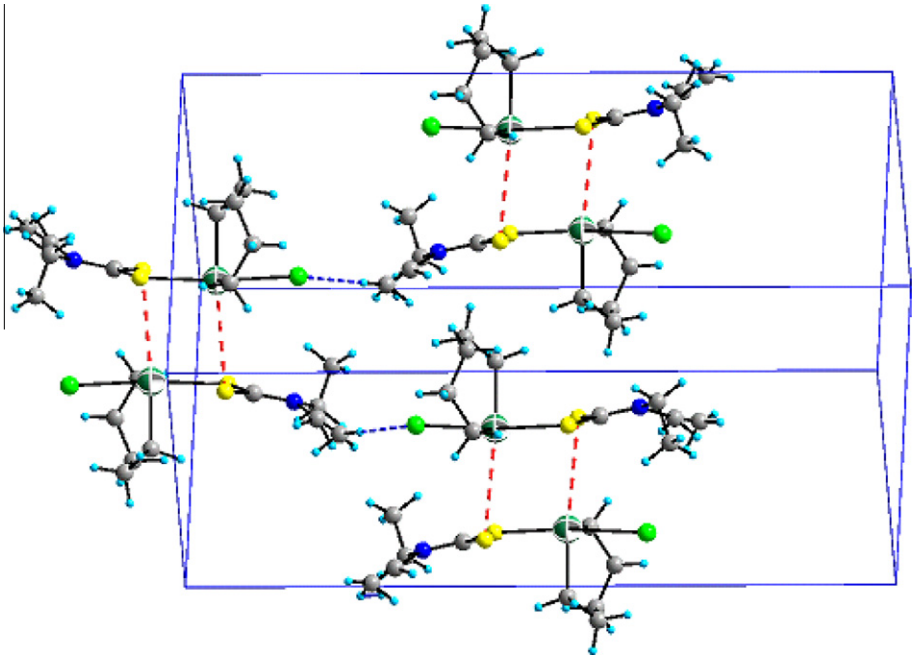


Fig. 8. Hexameric supramolecular association of $C_5H_{10}TeCl\{S_2CN(C_2H_5)_2\}$ (**7**).

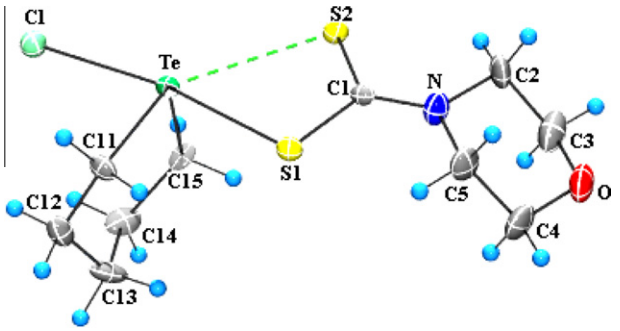


Fig. 9. Crystal structure of $C_5H_{10}TeCl(S_2CNC_4H_8O)$ (**8**).

The above cleaved product $H_5C_6HN{-}\overset{\overset{S}{\|}}{C}{-}NHC_6H_5$ (**11**) obtained in the substitution reaction of $C_5H_{10}TeCl_2$ (heterocyclic organotellurium complex) with $NH_4S_2CNHC_6H_5$ (Reaction 1) is when compared to our earlier report [6] on the cleaved product $Te(S_2CNC_5H_{10})_2$ (**15**) obtained in the substitution reaction of $C_8H_8TeI_2$ (heterocyclic organotellurium complex) with $NH_4S_2CNC_5H_{10}$ (Reaction 2) (supported by QC calculations) indicates that in the former reaction, from the product obtained after substitution(exchange) reaction with dithiocarbamate ligand, all the bonds associated with Te viz. Te–C, Te–Cl, Te–S are cleaved and, probably, some rearrangement takes place whereas in the latter reaction after substitution (exchange) reaction with dithiocarbamate ligand the cleavage of only Te–C bonds takes place (Table 4).

Such type of cleavage reactions are also comparable with our next report on dialkyltellurium dithiocarbamates viz. the reaction of $(C_2H_5)_2TeI_2$ with $NH_4S_2CNC_5H_{10}$ (Reaction 3) and $NH_4S_2CNC_4H_8O$ (Reaction 4) resulting in the formation of the cleaved products $Te(S_2CNC_5H_{10})_2$ (**15**) and $TeOC_4H_8N\begin{smallmatrix}H\\H\end{smallmatrix}$ (**16**), respectively. Here, in the former case after substitution (exchange) reaction of dithiocarbamate group Te–C bonds are broken as was in the above sited case with $C_8H_8TeI_2$ as precursor [6] while in the

Table 3
Secondary bonds (Te···S) and C–H···X (X = O, Cl) hydrogen bond parameters for complexes **1**, **2**, **4**, **7**, **8** and **9**.

Bond lengths and angles	1	2	4	7	8	9
Te···S (intramolecular)	3.253	3.196	3.228	3.2468(7)	3.218	3.226
Te···S (intermolecular)	3.574 3.915	3.618	3.5789(18) 3.8876(18)	3.5760(7)		3.557
C···I (d)	4.149					
C···Cl (d)				3.866(10)	3.860	3.527(2) 3.668(2)
C···O (d)					3.465	
H···I (d)	3.169					
H···Cl (d)				2.89	2.89	2.81 2.74
H···O (d)					2.49	
C–H···I (θ)	134.88					
C–H···Cl (θ)				177.2	162.9	129.4 155.4
C–H···O (θ)					147.8	

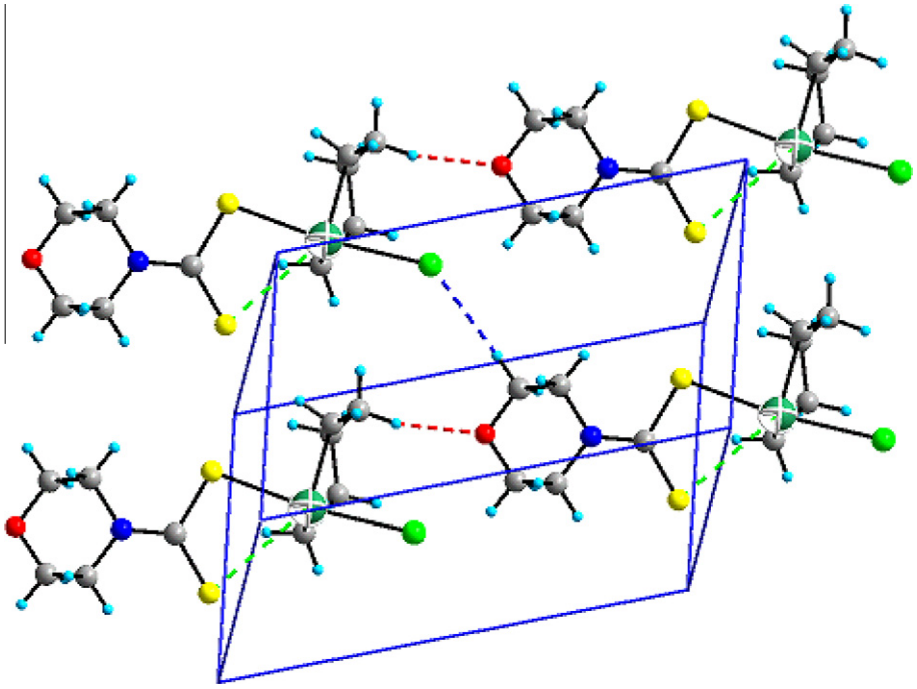


Fig. 10. Tetrameric supramolecular association of $C_5H_{10}TeCl(S_2CNC_4H_8O)$ (**8**).

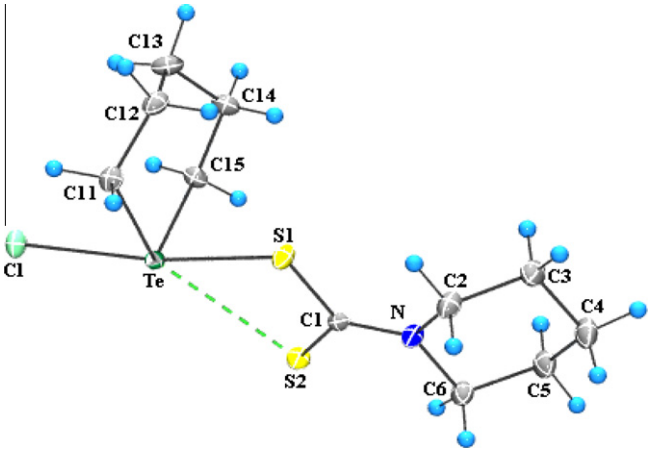


Fig. 11. Crystal structure of $C_5H_{10}TeCl(S_2CNC_5H_{10})$ (**9**).

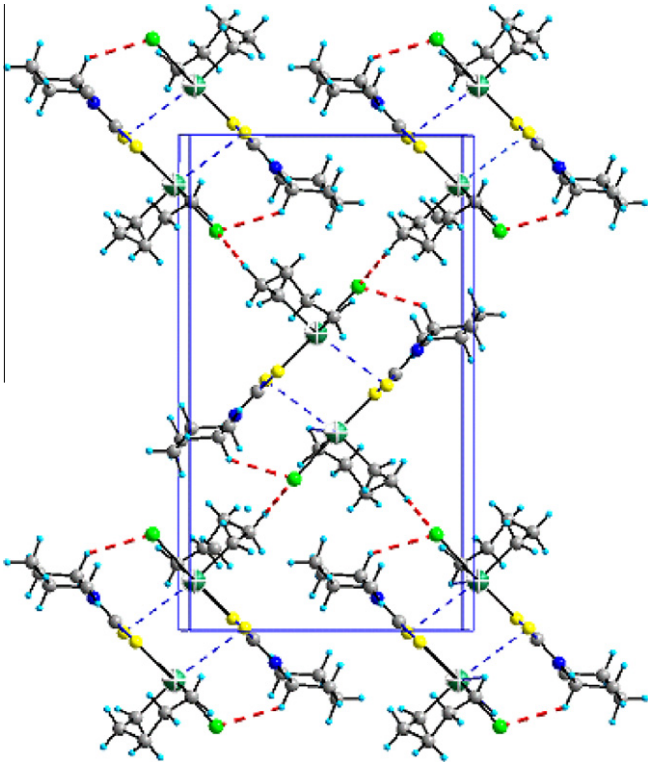


Fig. 12. Decameric supramolecular association of $C_5H_{10}TeCl(S_2CNC_5H_{10})$ (**9**).

latter case the cleaved product $TeOC_4H_8N\begin{matrix}H\\H\end{matrix}$ is, probably, due to (a) the evolution of CS_2 and (b) breaking of Te–C bonds and then some sort of rearrangement (Table 4).

Thus in nut-shell in the first place, in the present investigation; in the absence of QC calculations on the cleaved product $H_5C_6HN-\overset{\overset{S}{\|}}{C}-NHC_6H_5$ (**11**) it is actually difficult to define the pathway through which the cleaved product has been obtained. On the basis of our earlier QC calculations on the cleaved product $Te(S_2CNC_5H_{10})_2$ [6], the postulated pathways involve (a) first ligand (dtc) substitution/exchange reaction occurs which is followed by (b) cleavage reaction. In the second place, the Te–C (alkyl) bonds are, in general, very stable for example we [32] have observed that even the reaction of Me_2TeI_2 [containing Te–C (alkyl) bond] with fuming nitric acid is not able to break Te–C (alkyl) bonds instead it results in the formation of $(Me_2TeNO_3)_2O$ whereas in contrast to this, in all the above discussed cleavage reactions carried out in our research group, Te–C (alkyl) bonds have been scissioned (Table 4).

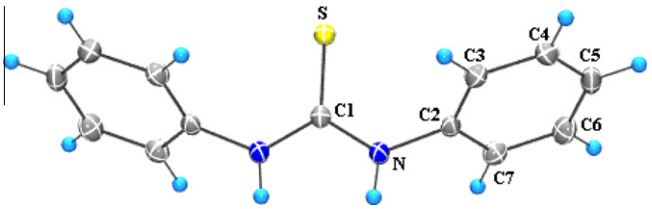


Fig. 13. Crystal structure of $SC(NHC_6H_5)_2$ (**11**).

4. Conclusions

Among organo (heterocyclic) tellurium(IV) dialky/aryl dithiocarbamates there is no report on supramolecular assemblies of $C_5H_{10}Te$ dialky/aryl dithiocarbamates where dithiocarbamate groups behave as unidentate ligands. The supramolecular associations, reported in the present investigation, have been built up through intermolecular Te···S secondary bonds and/or C–H···X (X = O, Cl, I) hydrogen bonds. The postulated pathway for obtaining

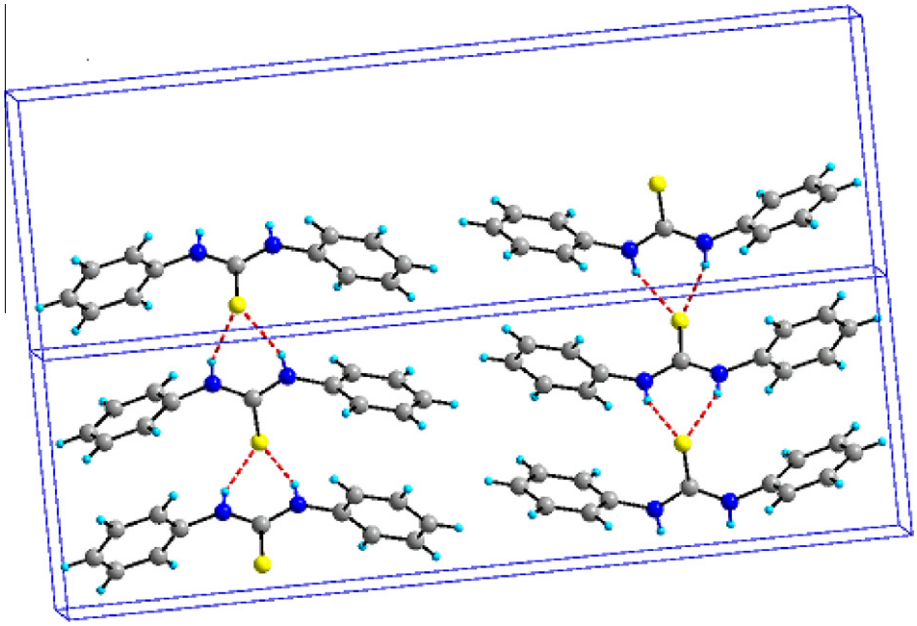
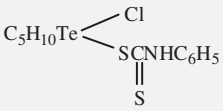
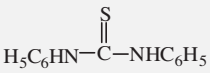
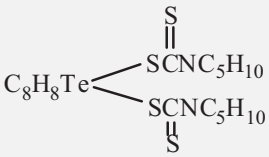
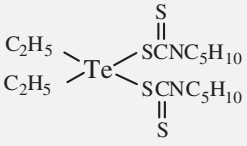
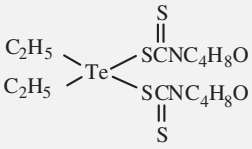
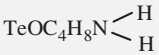


Fig. 14. Trimeric supramolecular association of $SC(NHC_6H_5)_2$ (**11**).

Table 4
Description of the cleavage reactions.

Reaction	Molar ratio	Postulated intermediate product obtained by substitution/exchange of the ligand (dithiocarbamate group)	Cleaved product	Characterization mode of the cleaved product	Reference
1. $C_5H_{10}TeCl_2$ + $NH_4S_2CNHC_6H_5$	1:1			single crystal X-ray diffraction data	[present Investigation]
2. $C_8H_8TeI_2$ + $NH_4S_2CNC_5H_{10}$	1:2		$H_{10}C_5NCS_2TeS_2CNC_5H_{10}$	single crystal X-ray diffraction data	[6]
3. $(C_2H_5)_2TeI_2$ + $NH_4S_2CNC_5H_{10}$	1:2		$H_{10}C_5NCS_2TeS_2CNC_5H_{10}$	single crystal X-ray diffraction data	[to be published]
4. $(C_2H_5)_2TeI_2$ + $NH_4S_2CNC_4H_8O$	1:2			single crystal X-ray diffraction data	[to be published]

the cleaved product is based on the comparative account with other similar type of cleavage reactions.

5. Supplementary data

CCDC 660999, 654231, 763397, 763398, 763399, 763400 and 763401 contain the supplementary crystallographic data for **1**, **2**, **4**, **7**, **8**, **9** and **11**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

P.C.S. is thankful to Department of Science and Technology (DST), Government of India and Council of Scientific and Industrial Research (CSIR), New Delhi for financial support.

References

[1] O. Foss, Acta Chem. Scand. 7 (1953) 227.
[2] I. Haiduc, R.B. King, M.G. Newton, Chem. Rev. 94 (1994) 301. and references therein.
[3] (a) J.E. Drake, L.N. Khasrou, A.G. Mislankar, R. Ratnani, Inorg. Chem. 38 (1999) 3994;
(b) J.E. Drake, J. Yang, Inorg. Chem. 36 (1997) 1890;
(c) J.E. Drake, R.J. Drake, L.N. Khasrou, R. Ratnani, Inorg. Chem. 35 (1996) 2831;
(d) J.H.E. Bailey, J.E. Drake, Can. J. Chem. 71 (1993) 42.
[4] V.G. Montalvo, R.A. Toscano, A.B. Delgado, R. Cea-Olivares, Polyhedron 20 (2001) 203.
[5] V.G. Montalvo, A.M. Polo, R. Montoya, R.A. Toscano, S.H. Ortega, R. Cea-Olivares, J. Organomet. Chem. 623 (2001) 74.
[6] P.C. Srivastava, S. Bajpai, R. Lath, R. Kumar, V. Singh, S. Dwivedi, R.J. Butcher, S. Hayashi, W. Nakanishi, Polyhedron 27 (2008) 835. and references therein.
[7] (a) P.D. Beer, N. Berry, M.G.B. Drew, O.D. Fox, M.E.P. Tosta, S. Patell, Chem. Commun. (2001) 199;
(b) O.D. Fox, M.G.B. Drew, E.J.S. Wilkinson, P.D. Beer, Chem. Commun. (2000) 391;
(c) O.D. Fox, M.G.B. Drew, P.D. Beer, Angew. Chem., Int. Ed. 39 (2000) 136.
[8] J.E. Huheey, E.A. Keiter, R.L. Keiter, Inorganic Chemistry: Principles of Structure and Reactivity, Pearson Education, Inc., 2000. pp. 929, 958.
[9] E.L.M. Lempers, J. Reedjik, Adv. Inorg. Chem. 37 (1991) 175.
[10] R.C. Vallari, R. Pietruszko, Science 216 (1982) 637.
[11] M.S. Wysor, L.A. Zwelling, J.E. Sanders, M.M. Grenan, Science 217 (1982) 454.
[12] (a) I. Haiduc, F.T. Edelmann, Supramolecular Chemistry, Wiley VCH, Weinheim, NY, 1999;
(b) I. Haiduc, J. Zukerman-Schpector, Phosphorus, Sulfur Silicon 171 (2001) 171.
[13] (a) J.-M. Lehn, Angew. Chem., Int. Ed. Engl. 27 (1988) 89;
(b) J.-M. Lehn, Supramolecular Chemistry, VCH, Weinheim, 1995.
[14] E. Weber, J. Mol. Graphics 7 (1989) 12.
[15] F. Vögtle, Supramolecular Chemistry, Wiley, Chichester, 1991.
[16] (a) G.R. Desiraju, Angew. Chem., Int. Ed. Engl. 34 (1995) 2311;
(b) P.J.M.W.L. Birker, H.C. Freeman, Chem. Commun. (1976) 312.
[17] G.M. Whitesides, E.C. Simanek, J.P. Mathias, C.T. Seto, D.N. Chin, M. Mammen, D.M. Gordon, Acc. Chem. Res. 28 (1995) 37.
[18] J. Bernstein, M.C. Etter, L. Leiserowitz, in: H.B. Burgi, J.D. Dunitz (Eds.), Structure Correlation, vol. 2, VCH, Weinheim, 1994, pp. 431–507.
[19] G.R. Desiraju, in: Crystal Engineering: The Design of Organic Solids, Elsevier, New York, 1989.
[20] (a) M.C. Etter, Acc. Chem. Res. 23 (1990) 120;
(b) M.C. Etter, J. Phys. Chem. 95 (1991) 4601.
[21] P.C. Srivastava, S. Bajpai, R. Lath, C. Ram, Sm. Bajpai, R.J. Butcher, M. Zimmer, M. Veith, J. Organomet. Chem. 649 (2002) 70.
[22] W.V. Farrar, J.M. Gulland, J. Chem. Soc. (1945) 11.
[23] F. Einstein, J. Trotter, C. Williston, J. Chem. Soc. A (1967) 2018.
[24] P.C. Srivastava, S. Bajpai, R. Lath, Sm. Bajpai, R. Kumar, R.J. Butcher, Polyhedron 23 (2004) 1629.
[25] P.C. Srivastava, Sm. Bajpai, S. Bajpai, R. Kumar, R.J. Butcher, Indian J. Chem. 43A (2004) 2558.
[26] A.I. Vogel, Quantitative Inorganic Analysis, Longman, London, 1975. p. 267.
[27] G.M. Sheldrick, SHELXS 86, SHELXS 97 and SHELXL 97, University of Göttingen, 1987 and 1997.
[28] A. Panda, G. Mugaesh, H.B. Singh, R.J. Butcher, Organometallics 18 (1999) 1986.
[29] N. Sudha, H.B. Singh, Coord. Chem. Rev. 135/136 (1994) 469.
[30] N.W. Alcock, Adv. Inorg. Chem. RadioChem. 15 (1972) 1.
[31] D.M. Roundhill, Prog. Inorg. Chem. 43 (1995) 533.
[32] P.C. Srivastava, S. Bajpai, C. Ram, R. Kumar, R.J. Butcher, J. Organomet. Chem. 692 (2007) 2482.