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SYNTHESIS AND CHARACTERIZATION OF *BIS*-(*P*-METHOXYPHENYL)TELLURIUM DICHLORIDE: $(P\text{-MEOC}_6\text{H}_4)_2\text{TECL}_2$

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ABSTRACT

In the current research we tried to isolate unsymmetrical Schiff base bearing *bis*-aryl tellurium dichloride by the treatment of 1-(thiophen-2-yl)-N-(*p*-tolyl)methanimine with anisyltellurium trichloride in carbon tetrachloride solvent at 80°C. However, we are unable to isolate our desired compounds due to decomposition takes place along with tellurium separation. From the reaction mixture, we are able to isolate only yellow coloured needle shaped crystal of *bis*-(*p*-methoxyphenyl)tellurium dichloride: $(p\text{-MeOC}_6\text{H}_4)_2\text{TeCl}_2$. The crystal was characterized by several spectroscopic techniques along with single crystal x-ray studies. The crystal are triclinic with $a = 10.1853(12)$, $b = 12.3771(16)$, $c = 13.4842(17)$ Å, $\alpha = 109.235(5)°$, $\beta = 99.519(5)°$, $\gamma = 102.705(5)°$, Z = 4 and the space group is *P*-1. The structure has been determined by single crystal x-ray studies at 100(2) K and the final R value calculated from 11485 reflections was 0.0497.

Keywords: Crystal Structure, Schiff base, Tellurium, Anisyltellurium trichloride, Secondary bonding Interaction.

1. INTRODUCTION

The first organotellurium compound, diethyltelluride was developed by Wöhler in 1840 [1]. Organotellurium chemistry is paying attention of several research groups in academia and industry throughout the world. These derivatives have been widely employed in the field of organic chemistry [2, 3], semiconducting materials [4, 5] and biochemistry [6]. Several well characterized *bis*-aryltelluriumdihalides have been widely reported in the literature [7]. The geometry around the tellurium atom in *bis*-aryltelluriumdihalides is ***Ψ***-trigonal bipyramidal. The *bis*-aryltelluriumdihalides employed four valence electrons to form four sigma bonds (two sigma bonds with Te-Carbon and two with Te-halogen in organotellurium(IV) halides) along with a lone pair electrons situated on equatorial position. These bonding utilized five valence shell orbitals of tellurium atom (5s, 5p and one 5d orbital) through the sp^3d hybridization to give rise a pseudo-trigonal bipyramidal geometry. In these molecules, a stereochemically active lone pair is situated on equatorial position. In literature, several well characterized *bis*-organotelluriumdichlorides are reported, some representative molecules (1-13) are shown in Fig. 1 [8-16]. These *bis*-organotellurium-dichlorides can be prepared through the oxidative addition reactions, electrophilic substitution reactions and transmetallation reactions. Recently Chauhan and co-workers have reported the synthesis of $[2\text{-}(4,4'\text{-NO}_2\text{C}_6\text{H}_4\text{CHNC}_6\text{H}_3\text{Me}]p\text{-MeOC}_6\text{H}_5\text{TeCl}_2$ (4) by the transmetallation of *para*-methoxyphenyltellurium trichloride with [{2-(4-nitrobenzylideneamino)-5-methyl}phenyl]mercurychloride, R'HgCl (R' = $2\text{-}(4,4'\text{-NO}_2\text{C}_6\text{H}_4\text{CHNC}_6\text{H}_3\text{Me})$ in chloroform solvent [11]. Same group have also reported carbonyl functionalized unsymmetrical *bis*-organotellurium dichloride (5-11) through the electrophilic substitution reaction of aryl tellurium trichlorides with respective ketones at room temperature in excellent yields [12-15]. Thereafter Chauhan and coworkers have developed a new type of unsymmetrical *bis*-organotellurium dichlorides (12-13) bearing vinyl groups through the insertion of terminal acetylenes RC≡CH (R = C_6H_5, *t*-Bu) across a Tellurium-Chlorine bond of aryltellurium trichlorides, ArTeCl_3 (Ar = 1-napthyl and 1-mesityl) in excellent yields [16].

On the basis of these observations, we plan to develop a new unsymmetrical *bis*-organotellurium dichlorides bearing schiff base ligand through the electrophilic substitution reaction. However, from the reaction mixture, we are able to isolate only *bis*(*p*-methoxyphenyl) tellurium dichloride in quantitative yield. The same molecule can also be prepared in good yield by the treatment of anisole with tellurium tetrachloride [17].

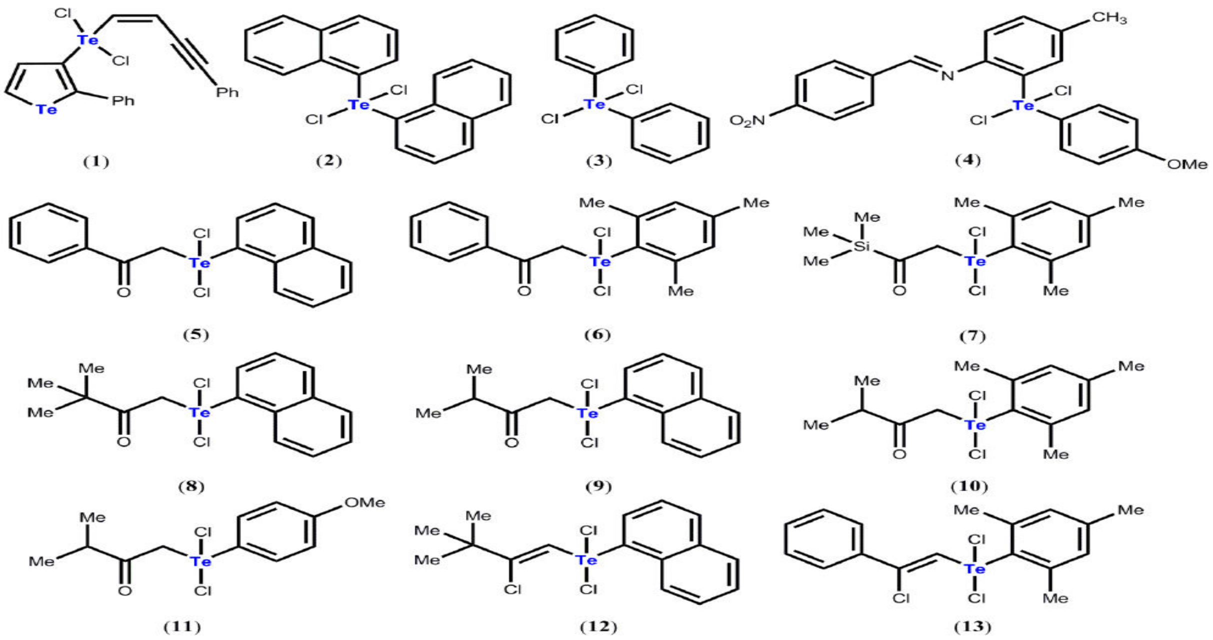


Fig. 1: Representatives of bis(organo)tellurium(IV)dichloride

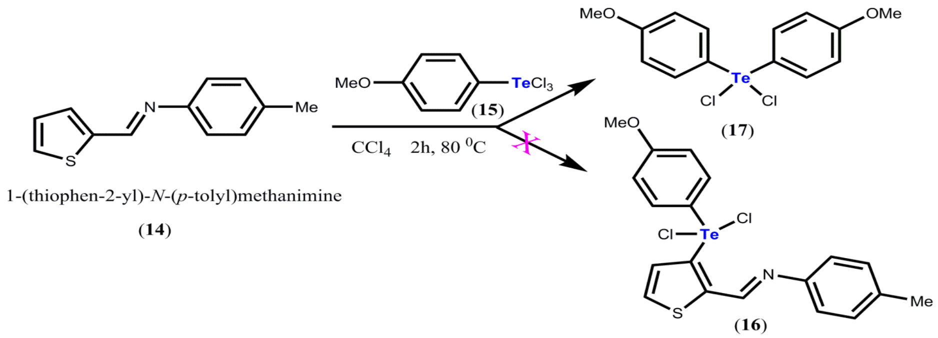
2. MATERIAL AND METHODS

2.1. Chemicals and experimental methodology employed

Solvents employed in this experiment were freshly distilled and used. Anisole, tellurium tetrachloride, 2-carboxyldehydethiophene and *p*-toluidine was purchased from Sigma Aldrich and Merck. Elemental analysis of the molecule was carried out on Perkin-Elmer 2400 elemental instrument.

2.2. Synthesis of bis(p-methoxyphenyl) tellurium dichloride (17)

A solution of 1-(thiophen-2-yl)-N-(*p*-tolyl)methanimine (2.01 g, 10.0 mmol) with anisyltellurium trichloride (3.41 g, 10.0 mmol) in 50 ml carbon tetrachloride solvent at 80°C was allowed to reflux for two hours. After two hours, a black colour tellurium powder separation took place in the reaction mixture. Heating was stopped and allowed to attain room temperature. A black coloured residue was filtered off. A yellow coloured filtrate was obtained which was put for slow evaporation at room temperature. After 24 h, yellow coloured needle shaped crystal was obtained for molecule 17 along with some black coloured residue. Crystal was separated by hand picking process. Yield: 0.53 g (26 %), m.p. 182°C (lit 182-183°C) [17]. Anal. Calcd. For $C_{14}H_{14}OTeCl_2$: C, 40.74; H, 3.42. Found: C, 40.60, H 3.49. ^{1}H NMR (400 MHz, $CDCl_3$) 3.85 6H, s, 2OMe), 7.06 (4H, d, *J* = 9 Hz, *o*-aryl) and 8.10 (4H, d, *J* = 9 Hz, *m*-aryl).



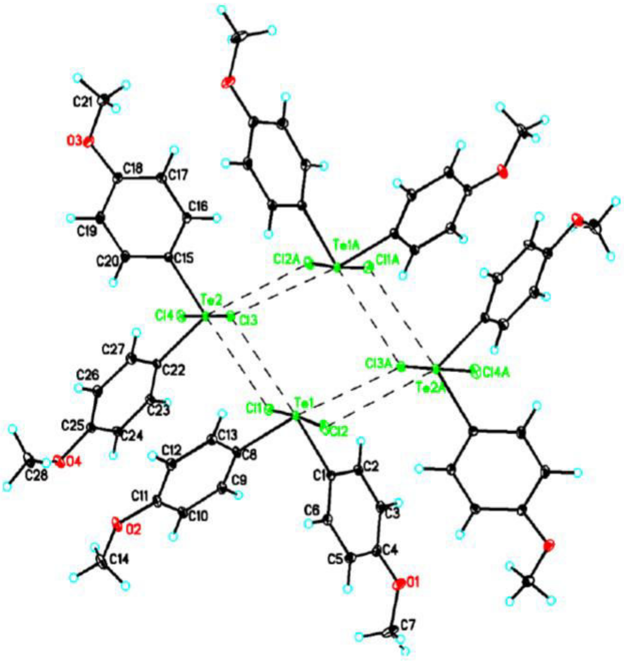
Scheme 1: Synthesis of *bis*-(*p*-methoxyphenyl) tellurium dichloride

3. RESULTS AND DISCUSSION

We tried to isolate unsymmetrical Schiff base bearing *bis*-aryl tellurium dichloride (**16**) by the treatment of 1-(thiophen-2-yl)-N-(*p*-tolyl)methanimine (**14**) with anisyltellurium trichloride (**15**) in carbon tetrachloride solvent at 80°C. However, we are unable to isolate our desired compounds due to decomposition takes place along with tellurium separation. From the reaction mixture, we were able to isolate only yellow coloured needle shaped crystal of *bis*(*p*-methoxyphenyl)tellurium dichloride (**17**): (p-$MeOC_6H_4)_2TeCl_2$ in quantitative yield in carbontetrachloride solvent at 80°C. The *bis*-(*p*-methoxyphenyl) tellurium dichloride has been characterized by ^{1}H NMR, elemental analysis and melting point. Molecular structure was further confirmed by single-crystal X-ray studies (*vide infra*). The ^{1}H NMR, elemental analysis and melting point of the molecule was obtained as reported in the earlier literature.

3.1. Molecular Structures of bis-(p-methoxyphenyl)tellurium dichloride

Single crystal x-ray data and structure refinement details for molecule are given in Table 1. ORTEP observation of the molecular structure is depicted in Fig. 2 and captioned with the geometrical parameters relevant to the primary geometry. Molecule **17** crystallizes in a triclinic crystal system with the *P-1* space group. In crystal packing diagram, each unit cell contains four molecules. Each molecule is interconnected through Te---Cl secondary bonding interactions to give rise a tetrameric structure (Fig.2). In this report we are able to observe better refinement data than the earlier reported value. However, observed R value (4.97) is higher than the previous reported value (0.28) [18]. Asymmetric unit of this molecule consists of four formula units and therefore, there are two sets crystallographically unique (but chemically similar). The geometry around the tellurium atom in the molecules is trigonal bipyramidal. If we consider the secondary bonding interaction, geometry around tellurium atom will be octahedral in which a lone pair and two carbon atoms are located at equatorial position and the chlorine atoms are situated at the axial site. It should be well-known that the C-Te-C bond angles are 95.89(12)° & 95.86(12)° for molecule 1, and molecule 2 respectively. Similarly observed, Cl-Te-Cl bond angles in both molecule are 176.99(3)° & 178.25(2)°. Packing diagram of Molecule **17**, (Fig. 2) is similar to $(C_6H_5)(p\text{-}BrC_6H_4)TeCI_2$ [19], and $C_{12}H_8OTeCI_2$ [20]. All the three molecules give rise discrete tetramers through Te---C1 secondary bonding interactions with the Te_4CI_6 unit acquiring the step-like structure and a similar geometry was observed around each tellurium atom. However, a critical observation about the structure shows some interesting features. The Te-C bonds, are situated always at the equatorial positions along with a stereochemically active lone pairs in all three molecules. The Te-C1 bonds which occupy the axial positions along with the number of Te---CI secondary bonding interactions.



Selected bond distances (A°) and angles (°): Molecule 1: Te1-C1 = 2.102(3), Te1-C8 = 2.103(3), Te1-Cl1 = 2.5203(8), Te1-Cl2 = 2.5161(8), Te1···Cl3 = 3.4480(9); Te1···Cl3A = 3.5167(8); C1-Te1-C8 = 95.89(12), Cl1-Te1-Cl2 = 176.99(3). Molecule 2: Te2-C15 = 2.109(3), Te2-C22 = 2.115(3), Te2-Cl3 = 2.5692(8), Te2-Cl4 = 2.4757(8), Te2···Cl1 = 3.4090(9); Te2···Cl2A = 3.6318(9); C15-Te2-C22 = 95.86(12), Cl3-Te2-Cl4 = 178.25(2).

Fig. 2: ORTEP diagram of *bis*-(*p*-methoxyphenyl)tellurium dichloride exhibiting 50% probability dislodgment ellipsoids with the atom numbering method

3.2. Single Crystal X-ray Crystallographic Studies

The collected crystal data and structure refinement for *bis*-(*p*-methoxyphenyl) tellurium dichloride are exhibited in Table 1. Atomic coordinates of the molecule are shown in Table 2. Suitable size of single crystal was selected under an optical microscope and attached on the top of a glass fiber for data collection. Intensity data of the molecule was recorded by the use of MoKα (λ=0.71073 Å) radiation on a Bruker SMART APEX diffractometer operational with CCD area detector at 100(2)K. The data was integrated with SAINT software [21]. An experimental absorption modification was engaged to the collected reflections with SADABS [22]. The structure was confirmed by direct methods using SHELXTL and was refined on F2 by the full-matrix least-squares procedure using the program SHELXL-2018 [23, 24]. All non-hydrogen atoms were refined with anisotropic dislocation parameters. All hydrogen atoms were positioned geometrically and refined with relative isotropic dislocation parameters.

Table 1: Single crystal X-ray data and structure refinement for *bis*-(*p*-methoxyphenyl)tellurium dichloride

Empirical formula	$C_{14}H_{14}Cl_2O_2Te$	Crystal size	0.23 x 0.18 x 0.09 mm^3
Formula weight	412.75	Theta range for data collection	2.122 to 33.168°.
Temperature	100(2) K	Reflections collected	11485
Wavelength	0.71073 Å	Independent reflections	11485 [R(int) = ?]
Crystal system	Triclinic	Completeness to θ = 25.242°	99.7 %
Space group	P -1	Absorption correction	Semi-empirical from equivalents
Unit cell dimensions	a = 10.1853(12) Å α = 109.235(5)°	Max. and min. transmission	0.5524 and 0.0931
	b = 12.3771(16) Å β = 99.519(5)°	Refinement method	Full-matrix least-squares on F^2
	c = 13.4842(17) Å γ = 102.705(5)°	Data/restraints/parameters	11485/0/348
Volume	1512.6(3) Å^3	Goodness-of-fit on F^2	1.024
Z	4	Final R indices [I>2sigma(I)]	R1 = 0.0497, wR2 = 0.1022
Density (calculated)	1.812 Mg/m^3	R indices (all data)	R1 = 0.0899, wR2 = 0.1163
Absorption coefficient	2.314 mm^{-1}	Extinction coefficient	0.0043(5)
F(000)	800	Largest diff. peak and hole	2.374 and -2.056 e.Å^{-3}

Table 2: Atomic coordinates (x 10^4) and corresponding isotropic dislodgment data (Å^{2}x 10^3) for *bis*-(*p*-methoxyphenyl) tellurium dichloride

	x	y	z	U(eq)
Te(1)	8849(1)	3983(1)	5806(1)	16(1)
Te(2)	7569(1)	2417(1)	2115(1)	16(1)
Cl(1)	8847(1)	2023(1)	4431(1)	21(1)
Cl(2)	8797(1)	5878(1)	7235(1)	25(1)
Cl(3)	7594(1)	4440(1)	3488(1)	18(1)
Cl(4)	7469(1)	455(1)	767(1)	23(1)
O(1)	11251(3)	2159(2)	9292(2)	33(1)
O(2)	2548(2)	1888(2)	5379(2)	27(1)
O(3)	5030(2)	3832(2)	-1651(2)	27(1)
O(4)	1820(2)	46(2)	2693(2)	26(1)
C(1)	9604(3)	3404(3)	7028(2)	16(1)
C(2)	10815(3)	3054(3)	7001(3)	20(1)
C(3)	11336(3)	2668(3)	7786(3)	24(1)
C(4)	10666(3)	2591(3)	8586(3)	23(1)
C(5)	9473(3)	2964(3)	8627(3)	24(1)
C(6)	8955(3)	3377(3)	7849(3)	21(1)
C(7)	10468(5)	1856(4)	10003(3)	40(1)

C(8)	6726(3)	3239(3)	5657(3)	17(1)
C(9)	6256(3)	2110(3)	5674(3)	20(1)
C(10)	4853(3)	1616(3)	5578(3)	21(1)
C(11)	3932(3)	2271(3)	5460(3)	20(1)
C(12)	4402(3)	3395(3)	5426(3)	21(1)
C(13)	5800(3)	3893(3)	5529(3)	21(1)
C(14)	2005(3)	734(3)	5406(3)	31(1)
C(15)	6774(3)	2927(3)	848(2)	17(1)
C(16)	7432(3)	4001(3)	807(3)	21(1)
C(17)	6898(3)	4342(3)	-30(3)	20(1)
C(18)	5679(3)	3586(3)	-815(2)	20(1)
C(19)	5020(3)	2498(3)	-767(3)	25(1)
C(20)	5558(3)	2158(3)	48(3)	22(1)
C(21)	5558(4)	4990(3)	-1671(3)	26(1)
C(22)	5609(3)	1642(3)	2310(2)	16(1)
C(23)	5347(3)	548(3)	2413(3)	18(1)
C(24)	4064(3)	30(3)	2538(3)	21(1)
C(25)	3050(3)	630(3)	2569(3)	19(1)
C(26)	3320(3)	1729(3)	2476(3)	21(1)
C(27)	4607(3)	2241(3)	2352(3)	23(1)
C(28)	737(3)	622(3)	2722(3)	30(1)

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

4. CONCLUSION

In conclusion, we have reported synthesis and single crystal x-ray studies of *bis*(*p*-methoxyphenyl)tellurium dichloride, in quantitative yield. Our new single crystal x-ray studies provide triclinic crystal system, space group P-1 with cell dimensions a = 10.1853(12) Å, b = 12.3771(16) Å, c = 13.4842(17) Å and α= 109.235(5)°, β = 99.519(5)°, γ = 102.705(5)°. The geometry about the central tellurium atoms adopt octahedral geometry through the Te···Cl secondary bonding interactions in which a lone pair, two carbon atoms and two Te···Cl secondary bonding interactions are located at equatorial position and both chlorine atoms are situated at the axial site. The crystal packing of the molecule, reveal each unit cell contain four molecules and each molecule are interconnected through C-H···Cl intermolecular hydrogen bonding and Te···Cl secondary bonding interactions. In future, the role of secondary bonding interactions and hydrogen bonding interactions can give better understanding ideas to explore a new dimension of supramolecular chemistry.

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Conflict of interest

The authors declare no conflict of interest.

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