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Reactions of Tellurium(IV) Chloride, Aryl-, Diaryl-, and Triaryl Tellurium(IV) Chlorides with Pyrimidine-2-thiols

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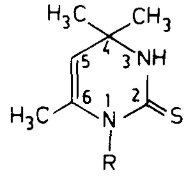
ABSTRACT

1-Substituted 4,4,6-trimethyl-1H, 4H-pyrimidine-2-thiol(L), whose substituents are C_6H_5 (**1**), p-$CH_3OC_6H_4$ (**2**), p-$O_2NC_6H_4$ (**3**), n-C_4H_9 (**4**), *and* NH_2 (**5**), *react with* $TeCl_4$, $ArTeCl_3$ *(Ar =* C_6H_5, 4-$CH_3OC_6H_4$, *or* 4-$C_2H_5OC_6H_4$*),* Ph_2TeCl_2, *and* Ph_3TeCl, *resulting in* $TeCl_3(L{-}H)$, $ArTeCl_2(L{-}H)$, $Ph_2TeCl_2.L$, *and* $Ph_3TeCl.L$ *types of compounds. Elemental analyses, molecular weights, conductances in solutions, IR, and* ^1H *and* ^{13}C *NMR spectral data of these compounds suggest that, in all of them, the pyrimidine-2-thiols ligate through sulfur only. In the first two types of derivatives, the thiol form of L reacts with tellurium moieties, resulting in the liberation of HCl. On the basis of these data* $TeCl_3(L{-}H)$ *appears to exist as a dimer in which two Te atoms are probably 5-coordinated and are bridged by two Cl. Tellurium in* $ArTeCl_2(L{-}H)$, $Ph_2TeCl_2.L$, *and* $Ph_3TeCl.L$ *also appears to be 5-coordinated. IR data suggest that the Te–S bond in* $Ph_2TeCl_2.L$ *is weak and, therefore, because of partial dissociation, the molecular complexes exhibit lower molecular weights in* CH_3CN. $Ph_3TeCl.L$ *in acetonitrile behaves as a 1:1 electrolyte. Attempts to synthesize N-, S-, and Te-containing heterocycle ring compounds from* $TeCl_3$(**1**/**2**–*H) and ArTe*(**1**/**2**–*H)*Cl_2 *did not succeed.*

INTRODUCTION

The interest in the Te(II and IV)-sulfur donor complexes is mainly a result of their unique structural features [1–2] and the promise shown by them for rubber and polymer strengthening [3]. Consequently, the ligation of tellurium moieties with sulfur donors has received much attention. Thioureas and thiosemicarbazones ligate with Te(II) only through their thiocarbonyl sulfur even when other donor sites in appropriate conformations are available [1–2,11,15]. Pyrimidine-2-thiol exists significantly in the thione form in which a $\rangle C{=}S$ group is located between two N atoms (part of the pyrimidine ring) as in a thiourea. It is reasonable to expect that such a structural system would behave like a thiourea toward a tellurium-containing species; that is, pyrimidine-2-thiol would interact with tellurium(II and IV) in the thione form, exhibiting a ligation behavior parallel to that of thiourea. However, surprisingly, we have observed that $TeCl_4$ and $ArTeCl_3$ react with pyrimidine-2-thiols (1–5), not in the thione form, but in the thiol form via deprotonation of the –SH group.



R = C_6H_5 (**1**)
p-$CH_3OC_6H_4$ (**2**)
p-$O_2NC_6H_4$ (**3**)
n-C_4H_9 (**4**)
NH_2 (**5**)

However, with Ph_2TeCl_2 and Ph_3TeCl, the thione form of **1–5** reacts, resulting in $Ph_2TeCl_2.L$ and $Ph_3TeCl.L$ types of molecular addition complexes, respectively. The results of these investigations are

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described in the present article. Such reactions may be important to understand the behavior of tellurium species in biologically important systems, as the pyrimidine skeletons having substituents such as NH_2, SH, and OH groups are either constituents of biomolecules or are important biologically. The main reasons for choosing pyrimidine-2-thiols **1–5** are the ease with which they can be synthesized and the possibility of cyclization/coordination through R. The cyclization, if successful, would have resulted in a novel heterocycle containing N, S, and Te as hetero atoms. Unfortunately, our all attempts to carry out cyclizations have failed so far.

EXPERIMENTAL

Carbon, hydrogen, and nitrogen analyses were carried out on a Perkin-Elmer elemental analyzer 240 C. Tellurium [4] and chloride [5] contents were determined by standard methods. Metrohm conductometer 660 and Knauer vapor pressure osmometers were used to determine (at 0.1–1 mM concentration levels) conductances and molecular weights, respectively. IR spectra in the range 4000–200 cm^{-1} of KBr/CsI discs or Nujol mulls between CsI windows were recorded on a Nicolet 5DX FT-IR spectrometer. A Perkin-Elmer 1700X far FT-infrared spectrometer was used to record the IR spectra in the range 700–30 cm^{-1} with polyethylene pellets. The ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-100 FT-NMR spectrometer at 99.55 and 25 MHz, respectively.

Published methods were used to synthesize $TeCl_4$ [6], $PhTeCl_3$ [7a], $4\text{-}CH_3OC_6H_4TeCl_3$ [7b], $4\text{-}C_2H_5OC_6H_4TeCl_3$ [8], and pyrimidine-2-thiols [9]. Solvents were employed after purification by standard methods [10].

Synthesis of Te(L–H)Cl₃ (where L = **1** *to* **5***)*

Tellurium(IV) chloride (1 mmol) dissolved in 30 cm^3 benzene was added to solutions/slurries of pyrimidine 2-thiols (**1** to **5**; 1 mmol) made up in 10 cm^3 of chloroform. The mixture was stirred and refluxed for 5–6 h under a dinitrogen atmosphere. The yellow solution was concentrated to 5 cm^3 under reduced pressure and mixed with hexane (10–15 cm^3). The precipitated yellow compound was filtered off, washed with hexane, and dried in vacuo. Yield 60–65%. The results of elemental analyses and mp's of the compounds are given in Table 1.

Synthesis of PhTe(L–H)Cl₂ (where L = **1** *to* **5***)*

A solution of $PhTeCl_3$ (1 mmol) in 10 cm^3 methanol was added to the respective ligand (**1** to **5**; 1 mmol) solution/slurry in chloroform (30 cm^3). The mixture was stirred and refluxed for 3–4 h. The solvent was removed thereafter under reduced pressure and the residue extracted with chloroform. Petroleum ether (40–60°C) was added to the chloroform extract and the compound that precipitated was filtered off, washed with petroleum ether, and dried in vacuo. Yield 70–78%. The results of elemental analyses and mp's of the compounds are given in Table 1.

Synthesis of 4-CH₃OC₆H₄Te(L–H)Cl₂ and 4-C₂H₅OC₆H₄Te(L–H)Cl₂ (L = **1** *to* **5***)*

To synthesize these derivatives, the reactions of $ArTeCl_3$ (Ar = $4\text{-}CH_3OC_6H_4$ or $4\text{-}C_2H_5OC_6H_4$) with **1** to **5** were carried out in a manner described for the synthesis of $PhTe(L\text{–}H)Cl_2$. Yield 80–90%. The results of elemental analyses and mp's of some representative compounds of these two types are given in Table 1.

Synthesis of Ph₂TeCl₂.L (L = **1** *to* **5***)*

Ph_2TeCl_2 (1 mmol) dissolved in chloroform (30 cm^3) was mixed with a solution of each ligand (**1** to **5**; 1 mmol) in chloroform (20 cm^3). The mixture was refluxed with stirring for 5 h and thereafter concentrated to 5 cm^3 under reduced pressure. A 20 cm^3 portion of petroleum ether (40–60°C) was added to this concentrate. The precipitated compound was filtered off, washed with petroleum ether, and dried in vacuo. Yield 65–75%. The results of elemental analyses and melting points of these compounds are recorded in Table 1.

Synthesis of Ph₃TeCl.L

A mixture of Ph_3TeCl (1 mmol) dissolved in dry methanol (20 cm^3) and a solution of each ligand (**1** to **5**; 1 mmol) in chloroform (20 cm^3) was refluxed with stirring for 8–10 h. After cooling, the mixture was filtered and the filtrate evaporated to dryness under reduced pressure. The residue was extracted with 5–10 cm^3 of chloroform and petroleum ether (40–60°C) was added to this extract. The compound that separated out was filtered off, washed with petroleum ether (40–60°C), and dried in vacuo. The yield was 62–65%. The mp's and results of elemental analyses are given in Table 1.

RESULTS AND DISCUSSION

Pyrimidine-2-thiols (L = **1** to **5**) react with $TeCl_4$, $ArTeCl_3$, Ph_2TeCl_2, and Ph_3TeCl according to Equations 1 to 4, respectively.

$$TeCl_4 + L \longrightarrow Te(L\text{–}H)Cl_3 + HCl \qquad (1)$$

$$ArTeCl_3 + L \longrightarrow ArTe(L\text{–}H)Cl_2 + HCl \qquad (2)$$

$$Ph_2TeCl_2 + L \longrightarrow Ph_2TeCl_2.L \qquad (3)$$

$$Ph_3TeCl + L \longrightarrow Ph_3TeCl.L \qquad (4)$$

The compounds of all the four types are more soluble in polar organic solvents than in nonpolar ones. However, their DMSO solutions have poor stability as the deposition of elemental tellurium is observed

TABLE 1 Analytical Data and Physical Properties of Te Complexes of **1–5**

Compounds	*Mol. Formula*	*Yield* (%)	*MP °C*	*Mol. Wt. Found* (*Calcd.*)	*Found* (*Calcd.*), (%)				
					C	*H*	*N*	*Te*	*Cl*
1. Te(**1**–H)Cl$_3$	$C_{13}H_{15}N_2STeCl_3$	65	148(d)	714	33.03	3.32	6.21	27.23	22.70
				(465)	(33.54)	(3.22)	(6.02)	(27.43)	(22.90)
2. Te(**2**–H)Cl$_3$	$C_{14}H_{17}ON_2STeCl_3$	62	120	725	33.63	3.23	5.41	25.57	21.21
				(495)	(33.93)	(3.43)	(5.66)	(25.77)	(21.51)
3. Te(**3**–H)Cl$_3$	$C_{13}H_{14}N_3O_2STeCl_3$	64	115	879	30.20	2.55	8.01	25.20	20.76
				(510)	(30.58)	(2.74)	(8.23)	(25.01)	(20.88)
4. Te(**4**–H)Cl$_3$	$C_{11}H_{19}N_2STeCl_3$	60	65	704	29.41	4.01	6.01	28.41	23.73
				(445)	(29.65)	(4.21)	(6.24)	(28.66)	(23.92)
5. Te(**5**–H)Cl$_3$	$C_7H_{12}N_3STeCl_3$	60	150	660	20.51	2.62	10.03	31.04	26.05
				(404)	(20.79)	(2.97)	(10.39)	(31.58)	(26.35)
6. PhTe(**1**–H)Cl$_2$	$C_{19}H_{20}N_2STeCl_2$	76	130	526	44.81	3.75	5.31	24.91	13.70
				(507)	(45.0)	(3.75)	(5.31)	(25.12)	(14.01)
7. PhTe(**2**–H)Cl$_2$	$C_{20}H_{22}ON_2STeCl_2$	72	85	561	44.51	3.62	5.02	23.52	12.91
				(536)	(44.80)	(3.92)	(5.22)	(23.82)	(13.26)
8. PhTe(**3**–H)Cl$_2$	$C_{19}H_{19}N_3O_2STeCl_2$	74	146	571	41.01	3.02	7.52	22.63	12.51
				(552)	(41.33)	(3.44)	(7.61)	(23.13)	(12.87)
9. PhTe(**4**–H)Cl$_2$	$C_{17}H_{24}N_2STeCl_2$	78	76	505	41.69	4.72	5.54	25.92	14.01
				(487)	(41.92)	(4.93)	(5.75)	(26.22)	(14.59)
10. PhTe(**5**–H)Cl$_2$	$C_{13}H_{17}N_3STeCl_2$	70	80	458	34.73	3.61	9.03	28.32	15.63
				(446)	(35.01)	(3.82)	(9.42)	(28.64)	(15.93)
11. 4-CH$_3$OC$_6$H$_4$Te(**1**–H)Cl$_2$	$C_{20}H_{22}N_2OSTe$ Cl_2	81	100	537	45.72	3.92	4.89	24.05	13.13
				(521)	(46.10)	(4.22)	(5.38)	(24.51)	(13.63)
12. 4-CH$_3$OC$_6$H$_4$Te(**2**–H)Cl$_2$	$C_{21}H_{22}N_2$ O_2STeCl_2	85	110	580	44.05	3.92	4.63	22.05	12.14
				(567)	(44.47)	(4.24)	(4.94)	(22.52)	(12.53)
13. 4-CH$_3$OC$_6$H$_4$Te(**3**–H)Cl$_2$	$C_{20}H_{21}N_3O_3$ $STeCl_2$	87	140	598	40.96	3.15	7.01	21.75	12.01
				(582)	(41.26)	(3.61)	(7.22)	(21.94)	(12.21)
14. 4-CH$_3$OC$_6$H$_4$Te(**4**–H)Cl$_2$	$C_{18}H_{26}N_2OSTe$ Cl_2	88	105	527	41.65	4.75	5.03	24.35	13.45
				(517)	(41.81)	(5.03)	(5.42)	(24.70)	(13.74)
15. 4-C$_2$H$_5$OC$_6$H$_4$Te(**5**–H)Cl$_2$	$C_{15}H_{21}N_3OSTe$ Cl_2	96	85	506	36.50	3.99	8.05	25.75	14.01
				(496)	(36.76)	(4.29)	(8.58)	(26.06)	(14.50)
16. Ph$_2$TeCl$_2$.**1**	$C_{25}H_{26}N_2STeCl_2$	72	140	311	51.42	4.31	4.51	21.91	11.90
				(585)	(51.32)	(4.45)	(4.79)	(21.82)	(12.14)
17. Ph$_2$TeCl$_2$.**2**	$C_{26}H_{28}ON_2STeCl_2$	76	128	322	50.53	4.25	4.31	20.56	11.25
				(615)	(50.76)	(4.56)	(4.56)	(20.76)	(11.55)
18. Ph$_2$TeCl$_2$.**3**	$C_{25}H_{25}N_3O_2STeCl_2$	75	134	354	47.51	3.72	6.42	20.15	11.05
				(629)	(47.72)	(3.98)	(6.68)	(20.30)	(11.29)
19. Ph$_2$TeCl$_2$.**4**	$C_{23}H_{30}ON_2STeCl_2$	70	148	398	48.53	5.16	4.75	22.45	12.34
				(565)	(48.88)	(5.31)	(4.95)	(22.60)	(12.58)
20. Ph$_2$TeCl$_2$.**5**	$C_{19}H_{23}N_3STeCl_2$	65	142	334	43.50	4.23	7.95	24.25	13.39
				(523)	(43.63)	(4.40)	(8.04)	(24.42)	(13.58)
21. Ph$_3$TeCl.**1**	$C_{31}H_{31}N_2STeCl$	68	60	358	59.90	4.62	4.21	20.54	5.98
				(626)	(59.42)	(4.95)	(4.47)	(20.38)	(5.67)
22. Ph$_3$TeCl.**2**	$C_{32}H_{33}N_2OSTeCl$	62	70	350	58.75	5.43	4.52	19.95	5.72
				(656)	(58.53)	(5.03)	(4.27)	(19.45)	(5.41)
23. Ph$_3$TeCl.**3**	$C_{31}H_{30}N_3O_2STeCl$	65	72	390	55.84	4.32	6.01	19.54	5.42
				(670)	(55.44)	(4.47)	(6.26)	(19.02)	(5.30)
24. Ph$_3$TeCl.**4**	$C_{29}H_{35}N_2STeCl$	63	85	335	57.68	5.92	4.89	21.46	6.02
				(606)	(57.42)	(5.78)	(4.62)	(21.06)	(5.85)
25. Ph$_3$TeCl.**5**	$C_{25}H_{26}N_3STeCl$	62	80	322	53.50	4.52	7.92	22.94	6.58
				(566)	(53.10)	(4.96)	(7.43)	(22.58)	(6.28)

after 15 minutes of the dissolution. These complexes, when stored as solids for several months, do not show any sign of decomposition.

In nitrobenzene, the Te(L–H)Cl$_3$ types of compounds exhibit molar conductances around 14–15 ohm^{-1} cm^2 mol^{-1}, indicating their non-ionic nature. However, their Δ_M values in acetonitrile at concentration levels <0.5 mM have been found to be in the range of 100–200 ohm^{-1} cm^2 mol^{-1}, suggesting that they behave at least as 1 : 1 electrolytes. Most probably the solvolysis of these compounds is responsible for their conducting nature in acetonitrile. The molecular weights of $Te(L-H)Cl_3$ types of molecules in chloroform have been found significantly higher than the formula weights, suggesting that most probably there exists strong molecular associations, resulting in dimers.

The $ArTe(L-H)Cl_2$ types of compounds have been found to be invariably non-ionic in acetonitrile ($\Lambda_M < 75$ ohm^{-1} cm^2 mol^{-1}) at concentration levels up to 0.5 mM. However, at still lower concentrations Λ_M increases but becomes nearly equal to that of a 1:1 electrolyte (100 ohm^{-1} cm^2 mol^{-1}) in the cases of $4\text{-}CH_3OC_6H_3Te(\mathbf{2/3}-H)Cl_2$ and $PhTe(\mathbf{5}-H)Cl_2$ only. The molecular weights of this class of compounds have been found to be very close to their formula weights, suggesting their monomeric nature. The compounds of the type $Ph_2TeCl_2.L$ exhibit very low conductances in acetonitrile (Λ_M = 3.6–8.8 ohm^{-1} cm^2 mol^{-1}) as well as molecular weights (little more than half of the formula weights). These observations suggest that they are partially dissociated into Ph_2TeCl_2 and L in acetronitrile solution, as observed for several other molecular complexes

TABLE 2 Chemical Shift in ^1H NMR Spectra of Pyrimidine-2-thiols **1–5** and their Te Complexes at 25°C

	Chemical Shift (δ, ppm)								
Compound	*$\rangle C(CH_3)_2$*	*$-CH_3$*	*$-OCH_3$*	*$-OC_2H_5$*	*$-CH$*	*$-SH$*	*$-NH$*	*Phenyl*	*$-NH_2$*
1. **1**	1.35	1.48	—	—	4.79	merged with phenyl	merged with phenyl	7.30	—
2. $Te(\mathbf{1}-H)Cl_3$	1.30	1.50	—	—	4.90	—	—	7.40	—
3. $PhTe(\mathbf{1}-H)Cl_2$	1.39	1.51	—	—	4.87	—	—	7.30	—
4. $4\text{-}CH_3OC_6H_4Te(\mathbf{1}-H)Cl_2$	1.38	1.50	3.80	—	4.81	—	—	7.30	—
5. $4\text{-}C_2H_5OC_6H_4Te(\mathbf{1}-H)Cl_2$	1.39	1.52	—	1.33, 4.10	4.90	—	—	6.80–8.30	—
6. $Ph_2teCl_2.\mathbf{1}$	1.30	1.50	—	—	4.80	—	6.70	6.80–8.10	—
7. $Ph_3TeCl.\mathbf{1}$	1.30	1.50	—	—	4.80	—	6.80	6.90–8.40	—
8. **2**	1.35	1.48	3.82	—	4.79	merged with phenyl	merged with phenyl	6.80–7.20	—
9. $Te(\mathbf{2}-H)Cl_3$	1.35	1.50	3.85	—	4.93	—	—	7.20	—
10. $PhTe(\mathbf{2}-H)Cl_2$	1.30	1.50	3.80	—	4.80	—	—	6.80–7.30	—
11. $4\text{-}CH_3OC_6H_4Te(\mathbf{2}-H)Cl_2$	1.38	1.53	3.80	—	4.80	—	—	6.80–8.35	—
12. $4\text{-}C_2H_5OC_6H_4Te(\mathbf{2}-H)Cl_2$	1.38	1.46	3.82	1.33, 4.10	4.87	—	—	6.80–8.30	—
13. $Ph_2TeCl_2.\mathbf{2}$	1.30	1.50	3.80	—	4.80	—	6.80	6.90–8.10	—
14. $Ph_3TeCl.\mathbf{2}$	1.30	1.50	3.80	—	4.80	—	6.80	6.90–8.40	—
15. **3**	1.38	1.49	—	—	4.90	7.01	6.80	7.39–8.33	—
16. $Te(\mathbf{3}-H)Cl_3$	1.37	1.50	—	—	4.92	—	—	7.4–7.5, 8.1–8.2	—
17. $PhTe(\mathbf{3}-H)Cl_2$	1.40	1.52	—	—	4.90	—	—	7.3–7.4, 8.2–8.3	—
18. $4\text{-}CH_3OC_6H_4Te(\mathbf{3}-H)Cl_2$	1.40	1.53	3.82	—	4.95	—	—	6.8–6.9, 7.3–7.4	—
19. $4\text{-}C_2H_5OC_6H_4Te(\mathbf{3}-H)Cl_2$	1.40	1.50	—	1.33, 4.10	4.90	—	—	6.8–6.9, 8.3–8.4	—
20. $Ph_2TeCl_2.\mathbf{3}$	1.30	1.50	—	—	4.90	—	6.90	7.2–8.3	—
21. $Ph_3TeCl.\mathbf{3}$	1.30	1.50	—	—	4.90	—	6.90	7.2–8.3	—
22. **4**	1.60	1.95	—	—	4.74	6.79	6.90	—	—
23. $Te(\mathbf{4}-H)Cl_3$	1.60	1.92	—	—	4.80	—	—	—	—
24. $PhTe(\mathbf{4}-H)Cl_2$	1.62	1.93	—	—	4.80	—	—	—	—
25. $4\text{-}CH_3OC_6H_4Te(\mathbf{4}-H)Cl_2$	1.62	1.94	3.80	—	4.80	—	—	—	—
26. $4\text{-}C_2H_5OC_6H_4Te(\mathbf{4}-H)Cl_2$	1.61	1.95	—	1.33, 4.10	4.80	—	—	—	—
27. $Ph_2TeCl_2.\mathbf{4}$	1.60	1.95	—	—	4.80	—	6.80	—	—
28. $Ph_3TeCl.\mathbf{4}$	1.61	1.95	—	—	4.80	—	6.80	—	—
29. **5**	1.35	1.48	—	—	4.79	6.92	7.00	—	8.79
30. $Te(\mathbf{5}-H)Cl_3$	1.37	1.51	—	—	4.72	—	—	—	—
31. $PhTe(\mathbf{5}-H)Cl_2$	1.38	1.51	—	—	4.82	—	—	7.4	8.5
32. $4\text{-}CH_3OC_6H_4Te(\mathbf{5}-H)Cl_2$	1.34	1.42	3.83	—	4.85	—	—	6.90, 8.30	merged with phenyl
33. $4\text{-}C_2H_5OC_6H_4Te(\mathbf{5}-H)Cl_2$	1.33	1.47	—	1.33, 4.10	4.86	—	—	6.91, 8.30	8.50
34. $Ph_2TeCl_2.\mathbf{5}$	1.30	1.50	—	—	4.80	—	6.80	6.90–7.30	8.10
35. $Ph_3TeCl.\mathbf{5}$	1.30	1.50	—	—	4.80	—	6.80	6.90–7.30	8.20

[11], but they are essentially non-ionic in nature. The molar conductance of $Ph_3TeCl.L$ types of compounds (concentration $\leq$1.5 mM) in acetonitrile have been found to be in the range 52–111 ohm^{-1} cm^2 mol^{-1}, whereas the molecular weights in the same solvent have been observed as half of the formula weights. This suggests the ionic nature of $Ph_3TeCl.L$ and the existence of moderate to strong association between the heavy cation and Cl^- ion even in the dilute solutions.

The ^{1}H NMR spectral data of pyrimidine thiols **1–5** are recorded in Table 2. The presence of an NH signal but not of SH (except in the ^{1}H NMR of **3**) suggests that **1–5** exist predominently in the thione form in solution. The ^{1}H NMR spectra of $Te(L-H)Cl_3$ and $ArTe(L-H)Cl_2$ types of derivatives authenticate the structures, as the various signals expected of **1–5** appear in the spectra of these tellurium derivatives with small variances owing to shielding/deshielding effects, except for the NH signals, which disappear as the thione form of the ligands is converted into the thiol form before the reaction (Equations 1 and 2) and finally results in the loss of a proton. Additional characteristic signals resulting from the ring (around δ, 7 ppm) and OCH_3/OC_2H_5 protons (around δ, 3.81/1.33, 4.0 ppm) of the aryl groups linked to Te were also observed in the spectra of $ArTe(L-H)Cl_2$ types of compounds, further supporting their formation. The ^{1}H NMR spectra of $Ph_2TeCl_2.L$ and $Ph_3TeCl.L$ are similar to those of the ligands except that the phenyl groups linked to Te give additional signals that complicate the aromatic region in the spectrum, and the signals originating from the ligands exhibit minor shielding or deshielding (<0.3 ppm) effects. Since NH proton appears in the spectra of all of these molecular complexes around δ, 6.8 ppm, it is reasonable to presume that the thione form of these pyrimidine-2 thiols ligates with tellurium through the sulfur of the $\rangle C{=}S$ group.

The ^{13}C NMR spectral data of **1** to **5** are recorded along with the assignments of the various signals

TABLE 3 Chemical Shift in ^{13}C NMR Spectra of Pyrimidine-2-thiols **1–5** and their Te Complexes in $CDCl_3$

	Chemical Shift (δ, ppm)							
Compound	*$-CH_3$(at C_6)*	*$-CH_3$(at C_4)*	*C_5*	*C_6*	*C_4*	*C_2*	*Phenyl*	*N–C*
1. **1**	20.5	31.3	97.0	110.0	132.4	177.8	128–130	141.5
2. $Te(\mathbf{1}-H)Cl_3$	20.5	31.3	97.0	110.0	132.4	177.8	128–130	141.5
3. $PhTe(\mathbf{1}-H)Cl_2$	20.8	31.2	97.5	110.0	132.4	177.8	128–130	141.6
4. $4\text{-}CH_3OC_6H_4Te(\mathbf{1}-H)Cl_2$	20.9	31.2	98.9	110.2	132.2	175.5	128–130	140.6
5. $4\text{-}C_2H_5OC_6H_4Te(\mathbf{1}-H)Cl_2$	19.9	31.0	98.9	111.7	132.1	175.5	128–130	140.6
6. $Ph_2TeCl_2.\mathbf{1}$	20.8	31.2	98.9	111.5	132.0	178.0	128–130	140.6
7. $Ph_3TeCl.\mathbf{1}$	20.8	31.2	97.5	110.0	132.4	178.0	128–130	140.6
8. **2**	19.6	31.2	98.8	111.5	132.0	172.3	128–131	144.0
9. $Te(\mathbf{2}-H)Cl_3$	19.6	31.2	98.8	111.5	132.0	172.3	128–131	144.1
10. $PhTe(\mathbf{2}-H)Cl_2$	19.7	31.2	98.8	111.8	132.0	172.3	128–131	144.0
11. $4\text{-}CH_3OC_6H_4Te(\mathbf{2}-H)Cl_2$	19.7	31.2	98.8	112.4	132.1	172.3	128–131	144.2
12. $4\text{-}C_2H_5OC_6H_4Te(\mathbf{2}-H)Cl_2$	19.6	31.2	98.8	112.1	132.6	172.3	128–131	144.0
13. $Ph_2TeCl_2.\mathbf{2}$	19.6	31.3	98.8	111.8	132.0	172.3	128–131	144.0
14. $Ph_3TeCl.\mathbf{2}$	19.7	31.3	98.8	111.8	132.0	172.3	128–131	144.0
15. **3**	20.1	31.3	98.0	112.3	135.9	168.4	124–131	143.4
16. $Te(\mathbf{3}-H)Cl_3$	20.1	31.3	98.0	112.3	135.9	168.4	124–131	143.4
17. $PhTe(\mathbf{3}-H)Cl_2$	20.1	31.3	98.0	112.3	135.9	168.4	124–131	143.5
18. $4\text{-}CH_3OC_6H_4Te(\mathbf{3}-H)Cl_2$	20.1	31.3	98.0	112.3	135.9	168.4	124–131	143.3
19. $4\text{-}C_2H_5OC_6H_4Te(\mathbf{3}-H)Cl_2$	20.1	31.3	98.0	112.3	135.9	168.4	124–131	143.4
20. $Ph_2TeCl_2.\mathbf{3}$	20.1	31.3	98.0	112.3	135.9	168.4	124–131	143.4
21. $Ph_3TeCl.\mathbf{3}$	20.1	31.3	98.0	112.3	135.9	168.4	124–131	143.5
22. **4**	19.9	31.1	97.6	110.3	131.5	172.0	—	31.1
23. $Te(\mathbf{4}-H)Cl_3$	19.9	31.1	97.6	110.3	131.5	172.0	—	31.1
24. $PhTe(\mathbf{4}-H)Cl_2$	20.6	31.1	97.6	110.3	131.5	172.0	114,166	31.1
25. $4\text{-}CH_3OC_6H_4Te(\mathbf{4}-H)Cl_2$	20.6	31.1	97.6	111.8	131.5	172.0	111,166	31.1
26. $4\text{-}C_2H_5OC_6H_4Te(\mathbf{4}-H)Cl_2$	19.7	31.1	97.6	111.8	131.8	172.0	117,166	31.1
27. $Ph_2TeCl_2.\mathbf{4}$	20.1	31.1	97.6	110.3	131.5	172.0	117,166	31.1
28. $Ph_3TeCl.\mathbf{4}$	20.1	31.1	97.6	111.8	131.5	172.0	—	31.1
29. **5**	16.5	31.5	97.5	110.0	133.7	177.8	—	—
30. $Te(\mathbf{5}-H)Cl_3$	16.5	31.5	97.5	110.0	133.7	177.8	114,161	—
31. $PhTe(\mathbf{5}-H)Cl_2$	16.5	31.5	97.5	110.0	133.7	177.8	114,161	—
32. $4\text{-}CH_3OC_6H_4Te(\mathbf{5}-H)Cl_2$	16.5	31.5	97.5	110.0	135.9	177.8	114,161	—
33. $4\text{-}C_2H_5OC_6H_4Te(\mathbf{5}-H)Cl_2$	16.5	31.5	97.5	110.0	135.8	177.8	114,161	—
34. $Ph_2TeCl_2.\mathbf{5}$	16.5	31.5	97.5	110.0	133.7	177.8	114,161	—
35. $Ph_3TeCl.\mathbf{5}$	16.5	31.5	97.5	110.0	133.5	177.8	114,161	—

in Table 3. Based on the earlier studies [11–12], the position of C_2 signals in ^{13}C NMR spectra of **1–5** suggests that the pyrimidine-2-thiols exist in solution predominently in the thione form, as inferred by the ^1H NMR spectra. The ^{13}C NMR spectra of the compounds Te(L–H)Cl_3 and ArTe(L–H)Cl_2 exhibit all the signals of **1** to **5**, almost at similar positions; additional signals are the result of the carbon atoms of the Ar group. The small shielding/deshielding (1–3 ppm) of C_2 suggests that the present S donors do not ligate in the thione form in Te(L–H)Cl_3 and ArTe(L–H)Cl_2; otherwise a deshielding of the order of 10–15 ppm might have been expected as noticed in the ^{13}C NMR spectra of Ph_2TeCl_2.L and earlier for the ⟩C=S group ligated to Te [11]. In the ^{13}C NMR spectra of Ph_3TeCl.L the various carbon signals of **1–5** appear almost unchanged, except for that of C_2, which undergoes small deshielding ≤ 4 ppm. The carbon atoms of the phenyl groups of Ph_3Te^+ appear around 103–115 (C linked to Te) and 129–132 ppm (other C atoms). These observations authenticate the derivatives and suggest that pyrimidine-2-thiols **1–5** ligate in the thione form via sulfur of the ⟩C=S group only.

The main IR spectral bands of the ligands **1–5** and their Te complexes are given in Table 4 along with their assignments. The presence of ν(N–H) (strong), ν(SH) (weak) and ν(C–S) (strong) vibrations in the regions around 3200, 2200, and 860 cm^{-1}, respectively, in the IR spectra of **1–5**, suggests that they predominently exist in the thione form even in the solid state. On the formation of the complexes of the types $TeCl_3$(L–H) and Ar$TeCl_2$(L–H), the ν(N–H) and ν(SH) bands vanish and new ones appear between 260–295, 215–240, and 249–250 (only in the case of Ar$TeCl_2$(L–H)), which may be assigned to ν(Te–Cl) [14], ν(Te–S) [15] and ν(Te–C) [14], respectively. These observations authenticate the formation of the complexes and suggest that the thiol form of **1–5** ligates with Te after deprotonation. In the IR spectra of Ph_2TeCl_2.L and Ph_3TeCl.L types of complexes, the ν(NH) appears around 3400 cm^{-1}, exhibiting a blue shift, and ν(SH) vanishes. This suggests that the ligands **1–5** coordinate with tel-

TABLE 4 IR Spectral Data of **1–5** and their Te Complexes in cm^{-1}

Compound	ν_{NH}	ν_{SH}	ν_{C-S}	$\nu_{C=S}$	ν_{Te-Cl}	ν_{Te-S}	ν_{Te-C}
1. **1**	3200	2200	—	875	—	—	—
2. Te(**1**–H)Cl_3	—	—	865	—	266	216	245
3. PhTe(**1**–H)Cl_2	—	—	870	—	268	228	249
4. 4-$CH_3OC_6H_4$Te(**1**–H)Cl_2	—	—	870	—	280	230	249
5. 4-$C_2H_5OC_6H_4$Te(**1**–H)Cl_2	—	—	865	—	260	240	250
6. Ph_2TeCl_2.**1**	3400	—	—	865	260	220	250
7. Ph_3TeCl.**1**	3400	—	—	865	270	216	245
8. **2**	3210	2160	—	860	—	—	—
9. Te(**2**–H)Cl_3	—	—	870	—	260	220	248
10. PhTe(**2**–H)Cl_2	—	—	865	—	265	231	242
11. 4-$CH_3OC_6H_4$Te(**2**–H)Cl_2	—	—	870	—	256	234	250
12. 4-$C_2H_5OC_6H_4$Te(**2**–H)Cl_2	—	—	860	—	270	244	248
13. Ph_2TeCl_2.**2**	3400	—	—	850	275	220	252
14. Ph_3TeCl.**2**	3400	—	—	850	280	225	250
15. **3**	3220	2368	—	870	—	—	—
16. Te(**3**–H)Cl_3	—	—	870	—	267	225	250
17. PhTe(**3**–H)Cl_2	—	—	875	—	262	225	252
18. 4-$CH_3OC_6H_4$Te(**3**–H)Cl_2	—	—	875	—	273	239	245
19. 4-$C_2H_5OC_6H_4$Te(**3**–H)Cl_2	—	—	880	—	260	218	248
20. Ph_2TeCl_2.**3**	3400	—	—	860	275	225	252
21. Ph_3TeCl.**3**	3400	—	—	860	275	225	252
22. **4**	3200	2360	—	875	—	—	—
23. Te(**4**–H)Cl_3	—	—	875	—	266	222	250
24. PhTe(**4**–H)Cl_2	—	—	870	—	260	220	252
25. 4-$CH_3OC_6H_4$Te(**4**–H)Cl_2	—	—	880	—	290	225	249
26. 4-$C_2H_5OC_6H_4$Te(**4**–H)Cl_2	—	—	875	—	295	240	249
27. Ph_2TeCl_2.**4**	3400	—	—	865	290	242	252
28. Ph_3TeCl.**4**	3400	—	—	865	290	242	250
29. **5**	3210	2380	—	870	—	—	—
30. Te(**5**–H)Cl_3	—	—	875	—	270	230	252
31. PhTe(**5**–H)Cl_2	—	—	870	—	264	225	250
32. 4-$CH_3OC_6H_4$Te(**5**–H)Cl_2	—	—	880	—	273	239	249
33. 4-$C_2H_5OC_6H_4$Te(**5**–H)Cl_2	—	—	870	—	266	230	250
34. Ph_2TeCl_2.**5**	3410	—	—	860	300	230	240
35. Ph_3TeCl.**5**	3410	—	—	860	300	235	250

lurium in the thione form. The ν(C=S) undergoes a red shift of $\approx 10\ cm^{-1}$, suggesting the weak nature of the Te–S interaction. Probably because of the weakness of this bond, Ph_2TeCl_2.L and Ph_3TeCl.L partially dissociate in CH_3CN and exhibit lower molecular weights. In the IR spectra of Ph_2TeCl_2.L and Ph_3TeCl.L, the ν(Te–Cl), ν(Te–S), and ν(Te–C) bands also appear around 260–300, 215–245, and 240–255 cm^{-1}, respectively.

On considering the molecular weights and ν(Te–Cl) ($\approx$260–270 cm^{-1}) frequencies of $TeCl_3$(L–H) types of complexes relative to those observed for other Te–Cl bond-containing compounds [14], dimeric structures appear to be the most reasonable for them. In $ArTeCl_2$(L–H) types of derivatives, Te seems to be four-coordinated (trigonal bipyramidal structure with lone pair on one corner) as it agrees well with all the spectral and molecular weight data. In the solid state, these derivatives appear to acquire five coordination, either by Te···Cl or Te···N (pyrimidine ring) secondary interactions, but this would be confirmed only after single crystal structure determinations of some $ArTeCl_2$(L–H) type of compounds have been carried out. These determinations could not be carried out because of our inability to grow their suitable crystals. However, the crystal structure of $PhTeCl_3$ [15–16] supports our presumption about the five coordination number of Te in solid state. The structure of Ph_2TeCl_2.L types of compounds may be presumed to be derived from the structure of Ph_2TeCl_2 [15–16], in which Cl···Te secondary interactions with the neighboring molecule are replaced by Te–S interactions. Most probably, Ph_3TeCl.L in solution exists as $[Ph_3TeL]^+Cl^-$ in which Te is four coordinated. In the solid state, Te may acquire five coordination, as is the case for many other triphenyl telluronium salts [17]. However, it could not be confirmed for the compounds under present discussion by X-ray diffraction because they did not give suitable crystals for such studies. The refluxing of $TeCl_3$(**1**/**2**–H) and $ArTeCl_2$(**1**/**2**–H) with and without $AlCl_3$ in several solvents ($CHCl_3$, CCl_4, benzene, and toluene) was carried out in an attempt to synthesize novel heterocyclic ring compounds containing N, S, and Te atoms, but the original Te species were recovered. On taking *m*-$CH_3OC_6H_4$ as a substituent at position '1' of these pyrimidine-2-thiols, the course of this reaction could not be changed. The decomposition temperature of polypropylene (183.3°C) revealed by the TGA values of 12.12-mg samples shifts to higher values by adding $TeCl_3$(**1**–H) in incremental amounts. When the Te complex is 5%, the temperature of decomposition becomes 362.7°C. This preliminary investigation suggests the possible use of some of the present Te–S donors complexes as polypropylene stabilizers.

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