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Synthesis and Characterization of Novel Chiral Ortho-Tellurated Complexes Derived from [(*S*)-1-(Dimethylamino)ethyl]benzene: Crystal and Molecular Structure of {2-[(*S*)-1-(Dimethylamino)ethyl]phenyl}tellurium Trichloride

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Received May 6, 1991

Novel chiral ortho-tellurated compounds of the types $ArTeX_3$, ArTeX, and $ArMeTeX_2$ (X = Cl, Br, diethyldithiocarbamate) in which the Ar group is (*S*)-2-$Me_2NCH(Me)C_6H_4$, have been synthesized by the organolithium route. The derivatives were characterized by ^1H NMR, ^{13}C NMR, IR, specific rotation, and MS techniques. The room-temperature and variable-temperature NMR (^1H and ^{13}C) studies indicate that a strong intramolecular Te···N coordination renders the tellurium atom in $ArTeX_3$ and $ArMeTeX_2$ pentacoordinate and in ArTeX tricoordinate. The optical purity of the complexes has been determined with the use of a chiral shift reagent. The crystal structure of [(*S*)-2-$Me_2NCH(Me)C_6H_4]TeCl_3$ (**6**) has been determined. The crystals form in the trigonal space group $P3_2$ with $a = 11.814$ (2) Å, $c = 8.532$ (10) Å, and $Z = 3$; $R = 2.12\%$ for 847 observed reflections. The complex is monomeric with weak association between Te and a neighboring chlorine.

Introduction

Organotellurium compounds have attracted considerable current interest in the fields of (1) organic synthesis,[1,2] (2) ligand chemistry,[3,4] (3) organic superconductors,[5,6] (4) photoimaging agents,[7] and (5) semiconductors.[8] Organoselenium reagents, in particular arylselenenyl halides, have become commonplace in organic synthesis.[9] The tellurium analogues, i.e. simple aryltellurenyl halides, are thermally unstable and polymeric in nature. However, recently some monomeric tellurenyl halides stabilized by intramolecular coordination have been isolated and structurally characterized. The built-in donor groups include carbonyl,[10,11] nitro,[12] azo,[13] azomethine,[14-16] and substituted pyridines.[17,18]

In addition, the ortho-telluration reactions, used to synthesize intramolecularly coordinated compounds, also provide a convenient method for the synthesis of hybrid bidentate and multidentate ligands containing both "hard" and "soft" donor atoms. Despite their importance in organic synthesis and ligand chemistry, examples of such organotellurium derivatives are scarce.[18] This is especially true for the optically active analogues where, to the best of our knowledge, no examples bearing a chiral carbon have been reported.

In recent years, the coordination behavior of organometallic compounds containing the potentially bidentate ligand 2-$Me_2NCH(Me)C_6H_5$ has been the subject of extensive studies.[19-22] In particular, dimeric ortho-palladated complexes derived from the amine are used for the optical resolution of racemic phosphines.[23] Rhodium complexes of the chiral phosphines and arsines have found applications in asymmetric hydrosilylation of a series of prochiral ketones.[24,25]

Recently we reported the synthesis and structure of ortho-tellurated derivatives of *N,N*-dimethylbenzylamine.[26] In this work, we report the first examples of a novel chiral tellurenyl halide and bidentate ligand derived from [(*S*)-1-(dimethylamino)ethyl]benzene. The X-ray crystal structure determination of [(*S*)-2-$Me_2NCH(Me)C_6H_4]TeCl_3$ (**6**) is presented and compared with other related structures.

Experimental Section

General Procedures. Air-sensitive reagents were manipulated in a prepurified argon atmosphere. All chemicals were of reagent grade and were used as received. Solvents were purified and dried by standard methods. [(*S*)-1-(Dimethylamino)ethyl]benzene and the shift reagents tris[3-((heptafluoropropyl)hydroxymethylene)-(+)-camphorato]europium(III) and tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium(III), $Eu(fod)_3$, were obtained from Aldrich.

The melting points are uncorrected and were determined using Ketan's melting point apparatus. UV–vis spectra in solution (methanol) were recorded on a Shimadzu UV-260 spectrophotometer. ^1H NMR and ^{13}C NMR spectra were obtained by the use of Varian VXR 300S and Bruker 500 spectrometers with chemical shifts reported in parts per million

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0020-1669/92/1331-1431$03.00/0

(ppm) downfield from a TMS internal standard. ^1H NMR spectra of the solutions containing complex **5** and the chiral shift reagent Eu(fod)$_3$ were recorded using 0.25:1–1.5:1 molar ratios of the shift reagent to the tellurium complex. IR spectra were obtained by use of a Perkin-Elmer 681 spectrometer. The solid samples were examined as KBr pellets. Mass spectra were obtained by means of a Varian MAT 1125 mass spectrometer at 70 eV and are reported as m/e (ion percent relative intensity). In the case of isotope patterns, the value given is for the most intense peak. Elemental analyses were performed on a Carbo Erba Model 1106 elemental analyzer. Optical rotations were measured by a JASCO Model DIP 370 digital polarimeter.

Synthesis. All the reactions of lithium arenetellurolate were carried out in a three-necked 100-mL flask fitted with a rubber septum, a glass stopper, and a reflux condenser connected to an argon/vacuum line. A commercial solution of *n*-butyllithium (EMERK) was syringed into the solution of the amine in dry ether. Elemental tellurium (Fluka) was finely ground with a mortar and pestle and introduced under a brisk stream of argon to avoid any introduction of air/moisture.

Attempted Synthesis of Bis{2-[(*S*)-1-(dimethylamino)ethyl]phenyl} Ditelluride (3). A 1.6 M solution of *n*-BuLi in hexane (2.5 mL, 4.0 mmol) was added over a 0.5-h period to a solution of (*S*)-Me$_2$NCH(Me)C$_6$H$_5$ (0.5 mL, 3.35 mmol) in dry ether (20 mL) at room temperature. The suspension was stirred for 24 h, and then elemental tellurium (0.42 g, 3.35 mmol) was added rapidly. After 3 h of stirring, all the tellurium dissolved. The yellowish red solution of lithium arenetellurolate was slowly added to cold water in beaker and left overnight to effect complete oxidation. The resulting organic layer and the dichloromethane extracts from the aqueous layer were combined, washed with ice water, dried over anhydrous magnesium sulfate, and concentrated in vacuo to afford a yellowish semisolid (**4**). Recrystallization from chloroform gave solid **4**.

{2-[(*S*)-1-(Dimethylamino)ethyl]phenyl}tellurium(IV) Tribromide (5). A solution of bromide (0.04 mL, 0.94 mmol) in chloroform was added dropwise to a stirred solution of **4** (0.15 g) in a mixture of chloroform (15 mL) and hexane (10 mL) at room temperature. The yellowish orange compound that precipitated completely in 1 h was filtered off and washed with hexane to give **5**: yield 60%; mp 165 °C. Anal. Calcd for $C_{10}H_{14}NBr_3Te$: C, 23.7; H, 2.7; N, 2.7. Found: C, 23.7; H, 2.9; N, 2.8. $[\alpha]^{27}{}_D = -56.32°$ (c = 1, DMSO). MS: m/e 357 ($M^+ - Br$, 30), 275 ($M^+ - Br_3$, 54), 232 ($M^+ - BrNMe_2$, 24), 148 ($M^+ - TeBr_3$, 100), 105 ($M^+ - NMe_2TeBr_3$, 100).

{2-[(*S*)-1-(Dimethylamino)ethyl]phenyl}tellurium(II) Bromide (7). In a 100-mL two-necked flask fitted with a dropping funnel, **5** (0.2 g, 0.38 mmol) was suspended in methanol (15 mL). To the suspension was added dropwise hydrazine hydrate in methanol with vigorous stirring till the solution became clear. The reaction mixture was stirred for an additional 0.5 h and filtered to remove the precipitated tellurium. The filtrate was concentrateed and the resulting orange solid recrystallized from chloroform: yield 54%; mp 120 °C. Anal. Calcd for $C_{10}H_{14}NBrTe$: C, 33.7; H, 3.6; N, 3.9. Found: C, 32.7; H, 3.3; N, 3.6. MS: m/e 357 (M^+, 65), 275 ($M^+ - Br$, 100).

{2-[(*S*)-1-(Diethylamino)ethyl]phenyl}tellurium(IV) Trichloride (6). Compound **4** (0.15 g) was dissolved in a mixture of chloroform (15 mL) and hexane (15 mL). Addition of excess thionyl chloride at 0 °C caused immediate precipitation. The light yellow precipitate was washed with ether and recrystallized from ethanol to give the desired product: yield 62% mp 170 °C dec. Anal. Calcd for $C_{10}H_{14}NCl_3Te$: C, 31.4; H, 3.6; N, 3.6. Found: C, 30.9; H, 3.6; N, 3.4. $[\alpha]^{27}{}_D = -90.97°$ (c = 1, DMSO). MS: m/e 348 ($M^+ - Cl$, 10), 313 ($M^+ - Cl_2$, 60), 277 ($M^+ - Cl_3$, 100), 232 ($M^+ - Cl_3NMe_2$, 20).

Tris(diethyldithiocarbamato){2-[(*S*)-1-(dimethylamino)ethyl]phenyl}tellurium(IV) (8). A solution of sodium diethyldithiocarbamate (0.27 g, 1.2 mmol) in methanol (10 mL) was added to a stirred solution of **6** (0.14 g, 0.366 mmol) in acetone (20 mL) from a dropping funnel at room temperature. The reaction mixture was stirred for 1 h and then filtered. Concentration of the filtrate followed by recrystallization from acetone gave a yellow crystalline solid: yield 57%; mp 105 °C. Anal. Calcd for $C_{25}H_{44}N_4S_6Te$: C, 41.6; H, 6.1; N, 7.7. Found: C, 42.1; H, 6.2; N, 7.7. $[\alpha]^{27}{}_D = -85.10°$ (c = 1, DMSO).

Methyl{2-[(*S*)-1-(dimethylamino)ethyl]phenyl}tellurium(IV) Dibromide (10). [(*S*)-2-Me$_2$NCH(Me)C$_6$H$_4$]TeLi was obtained from (*S*)-Me$_2$NCH(CH$_3$)C$_6$H$_5$ (0.55 mL, 3.35 mmol), *n*-butyllithium (2.5 mL, 1.6 M, 4.0 mmol), and tellurium powder (0.42 g, 3.35 mmol) in a manner similar to that described for **4**. Then iodomethane (0.2 mL, 3.35 mmol) was syringed into the flask. The reaction mixture was stirred for 0.5 h. The solution was slowly added to an aqueous sodium chloride solution. The organic phase was removed and the aqueous phase extracted with ether. The combined ether extract was dried over anhydrous sodium sulfate, filtered, and concentrated. The crude telluride (**9**) was converted to the solid dibromide (**10**) by addition of bromide to a solution of the telluride in a mixture of ether (15 mL) and hexane (10 mL). The desired product was recrystallized from hexane: yield 30%; mp 155 °C dec. Anal. Calcd for $C_{11}H_{17}NBr_2Te$: C, 29.3; H, 3.7; N, 3.1. Found: C, 29.9; H, 3.5; N, 3.5. $[\alpha]^{27}{}_D = -57.59°$ (c = 1, DMSO). MS: m/e 357 ($M^+ - CH_3Br$, 30).

Table I. Structure Determination Summary

	Crystal Data
empirical formula	$C_{10}H_{14}Cl_3NTe$
color and habit	transparent needle
crystal size	0.50 × 0.25 × 0.20 mm^3
crystal system	trigonal
space group	$P3_2$
unit cell dimens	a = 11.814 (2) Å c = 8.5320 (10) Å
volume	1031.3 (3) Å^3
Z	3
fw	382.2
density (calcd)	1.844 Mg/m^3
abs coeff	2.714 mm^{-1}
F(000)	552
	Data Collection
diffractometer used	Siemens R3m/V
radiation	Mo Kα (λ = 0.71069 Å)
temperature	296 K
monochromator	highly oriented graphite crystal
2θ range	4.0–55.0°
scan type	Wyckoff
scan speed	variable; 5.00–15.00°/min in ω
scan range (ω)	1.00°
bkgd measurement	stationary crystal and stationary counter at beginning and end of scan, each for 50.0% of total scan time
stdard reflns	4 measured every 96 reflections
index ranges	$-15 \le h \le 7, 0 \le k \le 12, -10 \le l \le 11$
no. of reflns collected	993
no. of indep reflns	993 (R_{int} = 0.00%)
no. of obsd reflns	847 ($F > 3.0\sigma(F)$)
abs cor	N/A
	Solution and Refinement
system used	Siemens SHELXTL PLUS (VMS)
solution	direct methods
refinement method	full-matrix least-squares
quantity minimized	$\sum w(F_o - F_c)^2$
absolute structure	η = 1.07 (9)
extinction cor	χ = −0.00022 (10), where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
hydrogen atoms	riding model, fixed isotropic U
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0010F^2$
no. of params refined	137
final R indices (obsd data)	R = 2.12%, R_w = 2.19%
R indices (all data)	R = 2.39%, R_w = 2.24%
goodness-of-fit	0.37
largest and mean Δ/σ	2.209, 0.019
data-to-parameter ratio	6.2:1
largest diff peak	0.37 e Å^{-3}
largest diff hole	−0.35 e Å^{-3}

Structure Determination and Refinement of [(*S*)-2-Me$_2$NCH(Me)C$_6$H$_4$]TeCl$_3$ (6). A transparent needle-shaped crystal of the title compound was mounted on a glass fiber and a data set collected on a Siemens R3m/v diffractometer. Crystal data and numerical details of the data collection and refinement are given in Table I. During data collection, the intensities of four monitor reflections showed no significant decay effects.

The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement, based on 847 observed reflections [$F > 3.0\sigma(R)$] and 137 variable parameters, converged with unweighted and weighted agreement factors of R = 2.12% and R_w = 2.19%. The maximum and minimum peaks on the final difference Fourier map correspond to 0.37 and −0.35 e Å^{-3}, respectively. Neutral-atom scattering factors were taken from

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Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$)

	x	*y*	*z*	*U*(eq)[a]
Te	7282 (1)	1191 (1)	964	38 (1)
Cl(1)	5414 (3)	1552 (3)	1749 (3)	60 (2)
Cl(2)	8977 (3)	650 (3)	243 (4)	62 (2)
Cl(3)	5833 (3)	−445 (3)	−936 (3)	67 (2)
C(2)	7463 (9)	136 (9)	4075 (11)	36 (5)
N	8659 (8)	2368 (8)	3148 (10)	49 (5)
C(1)	6665 (11)	−167 (10)	2773 (11)	37 (6)
C(4)	5834 (13)	−1862 (12)	5283 (14)	69 (8)
C(3)	7028 (12)	−748 (11)	5321 (12)	59 (8)
C(8)	8017 (11)	2970 (11)	4043 (13)	63 (7)
C(7)	8794 (10)	1358 (11)	4051 (12)	49 (6)
C(5)	5090 (12)	−2133 (11)	4014 (14)	68 (6)
C(7)	9418 (11)	1855 (12)	5654 (13)	65 (7)
C(6)	5453 (11)	−1336 (11)	2720 (14)	58 (6)
C(9)	9960 (11)	3427 (12)	2528 (13)	79 (7)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III

Bond Lengths (Å)			
Te–Cl(1)	2.538 (4)	Te–Cl(2)	2.465 (4)
Te–Cl(3)	2.447 (3)	Te–N	2.406 (8)
Te–C(1)	2.078 (10)	C(2)–C(1)	1.384 (14)
C(2)–C(3)	1.395 (14)	C(2)–C(7)	1.512 (12)
N–C(8)	1.485 (18)	N–C(7)	1.495 (17)
N–C(9)	1.511 (12)	C(1)–C(6)	1.408 (13)
C(4)–C(3)	1.367 (14)	C(4)–C(5)	1.328 (18)
C(7)–C(7)	1.526 (14)	C(5)–C(6)	1.373 (17)
Bond Angles (deg)			
Cl(1)–Te–Cl(2)	175.4 (1)	Cl(1)–Te–Cl(3)	89.1 (1)
Cl(2)–Te–Cl(3)	88.2 (1)	Cl(1)–Te–N	95.3 (3)
Cl(2)–Te–N	86.6 (3)	Cl(3)–Te–N	166.8 (2)
Cl(1)–Te–C(1)	86.3 (4)	Cl(2)–Te–C(1)	90.1 (4)
Cl(3)–Te–C(1)	92.6 (3)	N–Te–C(1)	75.3 (3)
C(1)–C(2)–C(3)	118.0 (8)	C(1)–C(2)–C(7)	119.0 (8)
C(3)–C(2)–C(7)	122.9 (9)	Te–N–C(8)	108.4 (7)
Te–N–C(7)	104.4 (5)	C(8)–N–C(7)	113.7 (8)
Te–N–C(9)	108.8 (6)	C(8)–N–C(9)	109.6 (9)
C(7)–N–C(9)	111.8 (10)	Te–C(1)–C(2)	117.8 (6)
Te–C(1)–C(6)	121.7 (8)	C(2)–C(1)–C(6)	120.5 (9)
C(3)–C(4)–C(5)	119.4 (11)	C(2)–C(3)–C(4)	121.3 (11)
C(2)–C(7)–N	107.1 (9)	C(2)–C(7)–C(7)	115.3 (8)
N–C(7)–C(7)	112.3 (10)	C(4)–C(5)–C(6)	123.3 (10)
C(1)–C(6)–C(5)	117.5 (10)		

Cromer and Waber.[27] All calculations were performed using the Siemens programs SHELXTL PLUS,[28] PLUTO,[29] and ORTEP.[30] The atomic coordinates and isotropic thermal parameters are collected in Table II. Selected bond lengths and bond angles are given in Table III.

Results and Discussion

The optically active ortho-tellurated compounds were readily obtained via the organolithium route. The chiral lithiated starting material, [(*S*)-2-$Me_2NCH(Me)C_6H_4$]Li[19] (**1**), was prepared by the reaction of (*S*)-$Me_2NCH(Me)C_6H_5$ with *n*-butyllithium at room temperature. Addition of elemental tellurium to **1** resulted in a facile insertion to yield the corresponding lithium arenetellurolate, [(*S*)-2-$Me_2NCH(Me)C_6H_4$]TeLi (**2**). Aqueous oxidative workup of the resulting mixture afforded a yellowish solid (**4**) which was shown to be a oxygenated tellurium compound, a "tellurenic anhydride", and not the expected ditelluride [(*S*)-2-$Me_2NCH(Me)C_6H_4]_2Te_2$ (**3**). The ill-characterized compound **4** showed a broad IR band around 650 cm^{-1}, suggesting the presence of a Te–O bond. However, the UV–vis spectrum in methanol exhibited a shoulder at ~400 nm, which is characteristic of the Te–Te chromophore. This suggests that partial oxidation of the ditelluride (**3**) has occurred. Analytical values observed for the tellurenic anhydride fluctuated over a few percent from preparation to preparation.

Compound **4** underwent facile halogenolysis with bromine and thionyl chloride, providing the novel ortho-tellurated aryltellurium trihalides **5** and **6**, respectively. Reduction of the tribromide (**5**) with hydrazine hydrate afforded the crystalline arenetellurenyl bromide **7**, which is stabilized by coordination with the tertiary amine nitrogen atom. The trichloride (**6**) was found to undergo metathesis with 3.3 equiv of sodium diethyldithiocarbamate to give the tris(diethyldithiocarbamate) derivative **8**.

The "hybrid" bidentate chiral ligand **9** incorporating both tellurium and nitrogen donor atoms was obtained when **2** was treated with iodomethane at ambient temperature. The oily viscous telluride was characterized as its dibromide derivative **10**. It was assumed that the integrity of the chiral carbon atom of the (*S*)-amine is unaffected by the reaction with *n*-BuLi and that the ortho-lithiated amine gave optically pure complexes (vide infra).

The new compounds were identified by their elemental analysis and mass spectral data. Compounds **5** and **10** failed to show the molecular ion M^+, the ion $\{[(S)\text{-}2\text{-}Me_2NCH(Me)C_6H_4Te]Br\}^+$ (*m*/*e* = 357, ^{130}Te) appearing as the highest mass in the spectra. However, the aryltellurium(II) bromide **7** was found to show the molecular ion cluster centered at *m*/*e* 357. The fragmentation patterns of all the derivatives suggest monomeric structures.

The ^1H NMR data (Table IV) of the chiral tellurated complexes show some interesting features. The fact that telluration has taken place in a position ortho to the functional group, $-CH(Me)NMe_2$, is confirmed by the considerable downfield shift of the resonances of the NMe_2, α-CH, and α-CH_3 groups compared to those in the free amine. The downfield shift of the NMe_2 resonances also suggests that a shielding effect is caused by the coordination of the nitrogen to tellurium.

The existence of M–N coordination (where M = Hg, Sn, Si, and In) with built-in donor groups has been established by dynamic ^1H and ^{13}C NMR studies.[19–22] Intramolecular Te···N interaction in the ortho-tellurated complexes would not only result in five-membered chelate rings but also give nitrogen a stable tetrahedral coordination. In such a situation, the Me groups would be diastereotopic, leading to anisochronous resonances. The fact that such an interaction exists in all these complexes at ambient temperature is apparent from the observation of two singlets for the NMe_2 protons. In the case of complex **5**, when the temperature is raised, the singlets do not coalesce at temperatures as high as 140 °C, indicating a strong Te···N interaction. It is worth mentioning here that, for the analogous derivatives of *N*,*N*-dimethylbenzylamine, in particular, (*N*,*N*-dimethyl-2-benzylaminato-*C*,*N*)tellurium tribromide, which shows a strong Te···N interaction in the solid state, no anisochronous resonances for the NMe_2 group were observed.[26] The Te···N distance of 2.422 (14) Å is considerably less than the sum of van der Waals radii.

This coalescence, for example in (*S*)-ArHgX[19] [Ar = (*S*)-2-$NMe_2CH(Me)C_6H_4$], is observed at −60 °C but becomes labile at ambient temperature. Stabled M–N interactions at high temperature (cf. this study) have been observed in the following cases. The arylindium compound (*S*)-$ArInMe_2$[21] shows diastereotopic NMe_2 groups up to 100 °C. Interestingly, no coalescence could be observed up to 120 °C for the NMe_2 group of the ligand in the palladium complex.[31]

The ^{13}C chemical shifts are gathered in Table V. The downfield shifts of the ipso carbon atoms, i.e. the carbons bonded to tellurium, range from 17.3 to 5.6 ppm relative to that of the free amine. Consistent with the ^1H NMR data, two singlets were observed for the NMe_2 carbons at ambient temperature. A variable-temperature ^{13}C NMR study of **5** was carried out in acetone-d_6 over

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Table IV. ^{1}H NMR Data for the Chiral Tellurated Compounds at Ambient Temperature[a]

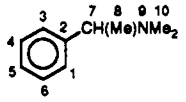
compound	$N(CH_3)_2$	α-CH	α-CH_3	aryl protons	others
(*S*)-$Me_2NCH(Me)C_6H_5$	2.17 (s)	3.20 (q)	1.33 (d)	7.25 (m)	
[(*S*)-2-$Me_2NCH(Me)C_6H_4$]$TeBr_3$ (**5**)	3.15 (s)	4.84 (q)	1.55 (d)	7.43–7.72 (m)	
	2.66 (s)				
[(*S*)-2-$Me_2NCH(Me)C_6H_4$]TeBr (**7**)	2.91 (s)	4.0 (q)	1.36 (d)	7.21–7.32 (m)	
	2.58 (s)				
[(*S*)-2-$Me_2NCH(Me)C_6H_4$]$TeCl_3$ (**6**)	3.08 (s)	4.81 (q)	1.56 (d)	7.47–7.73 (m)	
	2.53 (s)				
[(*S*)-2-$Me_2NCH(Me)C_6H_4$]Te(detc)$_3$ (**8**)	2.67 (s)	3.78 (q)	1.34 (d)	7.17–7.61 (m)	3.96 (q), 1.19 (t) [NCH_2CH_3]
	2.32 (s)				
[(*S*)-2-$Me_2NCH(Me)C_6H_4$]$Te(CH_3)Br_2$ (**10**)	3.17 (s)	4.86 (q)	1.58 (d)	7.46–7.73 (m)	2.9 (s) [$TeCH_3$]
	2.69 (s)				

[a] Chemical shifts δ (ppm) relative to TMS; recorded in DMSO-d_6.

Table V. ^{13}C Chemical Shifts of the Chiral Tellurated Derivatives[a–c]

				aryl carbons						
compound	$N(CH_3)_2$	α-CH	α-CH_3	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	others
(*S*)-$Me_2NCH(Me)C_6H_5$	43.0	65.6	20.4	127.9	143.2	127.9	127.1	126.7	127.1	
[(*S*)-2-$Me_2NCH(Me)C_6H_4$]$TeBr_3$ (**5**)	44.0	64.3	9.7	138.4	143.6	130.5	132.1	127.2	133.4	
	43.2	(−1.3)	(−10.7)	(10.5)	(0.4)	(2.6)	(5.0)	(0.5)	(6.3)	
[(*S*)-2-$Me_2NCH(Me)C_6H_4$]TeBr (**7**)	46.0	68.1	11.9	133.5	143.0	126.3	127.3	122.1	128.7	
	41.0	(2.5)	(−8.4)	(5.6)	(−0.2)	(−1.6)	(0.2)	(−4.6)	(1.6)	
[(*S*)-2-$Me_2NCH(Me)C_6H_4$]$TeCl_3$ (**6**)	43.1	63.4	9.9	145.2	142.9	130.1	130.7	127.1	131.9	
	40.9	(−2.2)	(−10.5)	(17.3)	(−0.3)	(2.2)	(3.6)	(0.4)	(4.8)	
[(*S*)-2-$Me_2NCH(Me)C_6H_4$]Te(detc)$_3$ (**8**)	48.3	65.6	11.1	134.3	144.2	126.6	127.0	126.5	128.0	51.4, 13.2 [NCH_2CH_3]
	47.4	(0)	(−9.3)	(6.4)	(1.0)	(−1.3)	(−0.1)	(−0.2)	(0.9)	190.8 (C═S)

[a] Chemical shifts δ (ppm) relative to TMS. [b] Difference in shifts relative to (*S*)-$Me_2NCH(Me)C_6H_5$ in parentheses. [c] Numbering scheme:



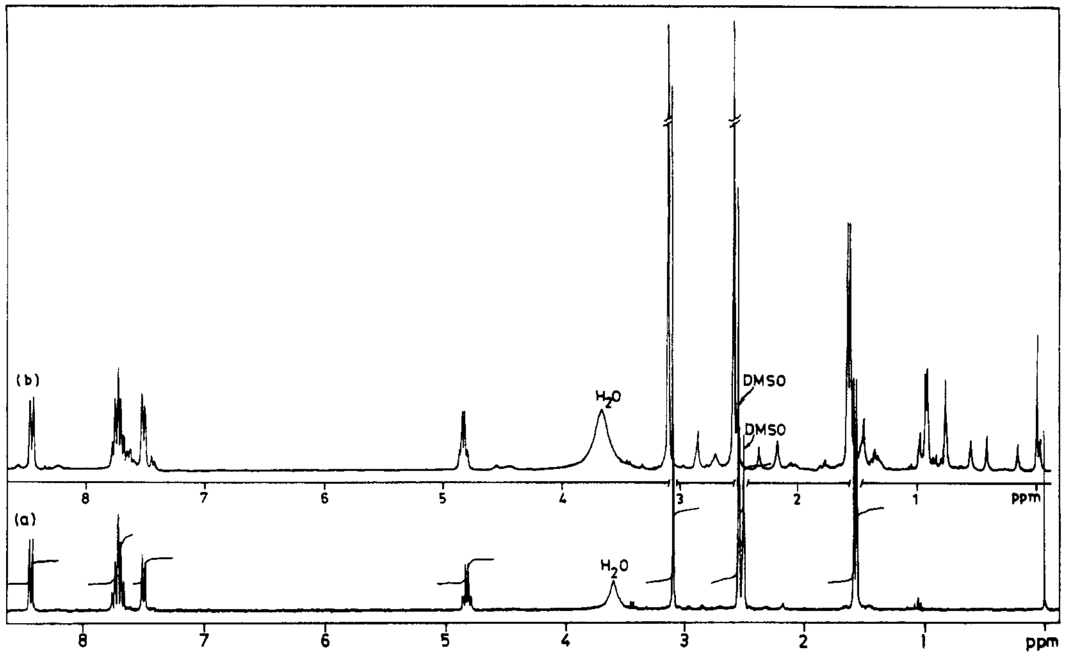


Figure 1. (a) Proton NMR spectrum (300 MHz) of complex **5** at room temperature. (b) Proton NMR spectrum (300 MHz) of complex **5** in the presence of the chiral shift reagent.

the temperature range +40 to −50 °C. Again, anisochronous resonances were observed for the NMe_2 carbons up to +40 °C, thus providing further evidence for a strong Te···N coordination.

Optical rotations are given with the analytical data. Optical purity of the compounds was determined by recording the ^{1}H NMR spectra in the presence of different mole ratios of the chiral shift reagent[32] in solvent DMSO-d_6. It was observed that, in all cases, there was no change in the resonances of the compounds except slight changes in the aromatic region (Figure 1). The NMe_2, α-CH, and α-CH_3 peaks remain unaffected, indicating the enantiomeric purity of the compounds. Similar observations were made when ^{1}H NMR spectra of the chiral compounds in the presence of the simple shift reagent Eu(fod)$_3$ were recorded.

The structure of **6** is shown in Figure 2. The coordination about tellurium can be considered as essentially pseudooctahedral, with a lone pair of electrons occupying the fourth equatorial site. The distortion of the coordination geometry from ideal octahedral angles, N–Te–Cl(3) [166.8 (2)°], can be explained in terms of a lone pair of electrons occupying an equatorial position. The small

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(32) Whitesides, G. M.; Lewis, D. W. *J. Am. Chem. Soc.* **1970**, *92*, 6979.

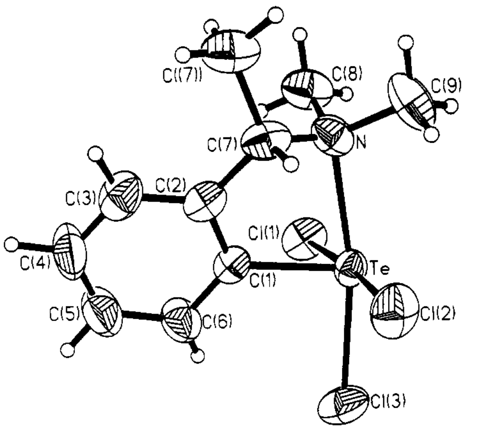

Figure 2. ORTEP diagram for [(*S*)-2-$Me_2NCH(Me)C_6H_4$]$TeCl_3$ (**6**).

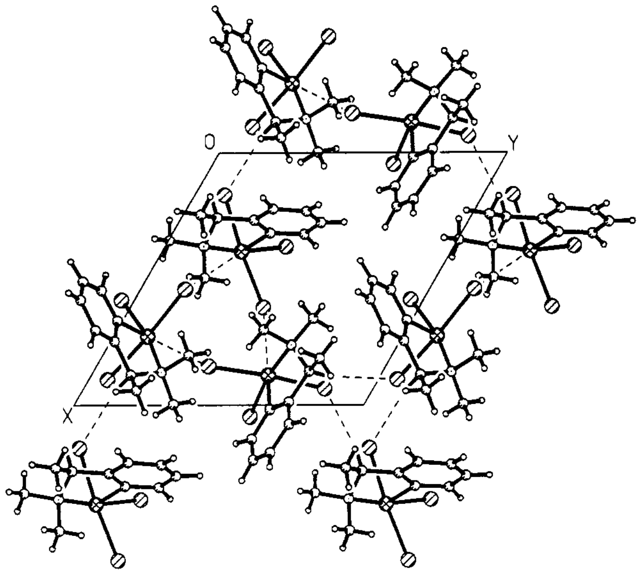

Figure 3. Packing diagram for **6**.

value of the angle N–Te–C(1) [75.3 (3)°] is due to the constraint of the five-membered ring. The axial atoms are slightly displaced away from the lone-pair electrons, reducing the Cl(2)–Te–Cl(1) angle to 175.4 (1)° from an ideal angle of 180 °C.

The Te–C(1) distance [2.078 (10) Å] is less than the sum of the Pauling single-bond covalent radii[33] (1.37 Å) and sp^2-hybridized carbon (0.74 Å) and differs from the values in the crystal structures of the related compounds (2-$Me_2NCH_2C_6H_4$)$TeBr_3$,[26] ($C_{11}H_8N$)$TeBr_3$,[18] and ($C_{12}H_9N_2$)$TeCl_3$.[34] The axial Te–Cl bond lengths [2.538 (4) Å] and [2.465 (4) Å] span the value for the sum of the Pauling covalent radii [axial Te–Cl (2.36 Å)]. The Te–N bond distance [2.406 (8) Å] is much larger than the sum of covalent radii, 2.07 Å, but is close to the values in the crystal structures of ($C_9H_8NO_2$)$TeCl_3$[17] and $C_{12}H_9N_2$)$TeCl_3$.[34] The five-member hetero ring is not planar. The nitrogen atom is −0.716 (8) Å from the plane of the rest of the atoms.

The title compound is monomeric; however, it is linked to neighboring molecules by weak Te···Cl intermolecular interactions. Examination of the intermolecular distances shows that the shortest distance between the Te and Cl atoms, Te··Cl(1)^{i} (i = $1 + x - y$, $1 - x$, $^1/_3 + z$), is 3.498 (4) Å (Figure 2), which is approximately trans to the Te–C(sp^2) bond. This distance, 3.498 (4) Å, is larger than the sum of covalent radii, 2.36 Å; however, very much shorter than the sum of van der Waals radii, 4.00 Å. Perhaps the most interesting feature of the structure is the occurrence of H···Cl intermolecular interaction Cl(2)···H(7)^{ii} (ii = $1 - y$, $1 + x$, $^5/_3 + z$). Such interactions have not been observed in any of the intramolecularly coordinated tellurium complexes.

Of the two possible space groups $P3_1$ and $P3_2$, the structure has been refined on the basis of space group $P3_2$. An absolute configuration test has been performed according to Rogers[35] and a value of $\eta = 1.07$ (9) obtained. This is an excellent confirmation of the correctness of the absolute configuration. Application of the Cahn, Ingold, and Prelog rule[36] confirms the presence of the (*S*)-enantiomorph.

Acknowledgment. H.B.S. is grateful to the CSIR, New Delhi, for financial assistance.

Registry No. **3**, 139494-96-5; **5**, 139494-98-7; **6**, 139494-99-8; **7**, 139495-00-4; **8**, 139495-01-5; **10**, 139495-03-7; (*S*)-$Me_2NCH(Me)C_6H_5$, 17279-31-1; Te, 13494-80-9; [(*S*)-2-$Me_2NCH(Me)C_6H_4$]TeLi, 139494-97-6; [(*S*)-2-$Me_2NCH(Me)C_6H_4$]TeMe, 139495-02-6.

Supplementary Material Available: Tables of anisotropic displacement coefficients, hydrogen coordinates, nonbonded distances, and torsion angles (3 pages); a listing of structure factors (4 pages). Ordering information is given on any current masthead page.

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