6762 *J. Am. Chem. Soc.* **1988**, *110*, 6762–6768

Synthesis, NMR Study, and Crystal Structures of Bis(diethyldithiocarbamato)-(*O*,*O*′-diethyl dithiophosphato)phenyltellurium(IV), $PhTe(S_2CNEt_2)_2[S_2P(OEt)_2]$, and Bis(diethyldithiocarbamato)iodomethyltellurium(IV), $MeTe(I)(S_2CNEt_2)_2$

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Abstract: Reactions of $PhTeCl_3$ with the dithiolate ligands $(S_2CNEt_2)^-$, $(S_2P(OEt)_2)^-$, and $(S_2COEt)^-$ in solution were studied by variable-temperature ^{125}Te, ^{31}P, and ^{13}C NMR spectroscopy, which show the formation of a variety of mixed-ligand species, some of which were subsequently isolated. $MeTe(I)(S_2CNEt_2)_2$, formed by oxidative addition of MeI to $Te(S_2CNEt_2)_2$, also provides a useful pathway to the synthesis of mixed-ligand species, but in general the products are less stable than the phenyl analogues. Solvent-dependent intramolecular exchange processes were observed for the alkyl and aryl series. The crystal and molecular structures of the mixed-ligand complexes bis(diethyldithiocarbamato)(*O*,*O*′-diethyl dithiophosphato)phenyltellurium(IV), $PhTe(S_2CNEt_2)_2[S_2P(OEt)_2]$ (**1**), and bis(diethyldithiocarbamato)iodomethyltellurium(IV), $MeTe(I)[S_2CNEt_2]_2$ (**2**), have been determined; crystals of **1** are triclinic, $P\bar{1}$, $a = 9.078$ (2) Å, $b = 11.823$ (2) Å, $c = 14.941$ (2) Å, and $\alpha = 69.28$ (1)°, $\beta = 88.29$ (1)°, $\gamma = 89.40$ (1)°, $Z = 4$. **1** is monomeric with five sulfur atoms, approximately equidistant from tellurium [Te–S range 2.674 (4) to 2.708 (4) Å], forming a pentagonal plane. The axial position above the pentagonal plane is occupied by the phenyl ring [Te–C = 2.138 (13) Å]. There is a further, secondary, interaction with the remaining sulfur [3.44 (1) Å] below the plane. Crystals of **2** are orthorhombic, *Pbca*, with $a = 11.999(1)$ Å, $b = 18.219$ (2) Å, $c = 18.411$ (2) Å, $Z = 8$. **2** is monomeric with four sulfur atoms and the iodine forming a pentagonal plane about tellurium [Te–S range 2.618 (1) to 2.725 (1) Å, Te–I = 3.117 (1) Å] with the methyl group perpendicular to the plane [Te–C = 2.115 (5) Å]. Both **1** and **2** show evidence of stereochemically active lone pairs at tellurium producing eight- and seven-coordinated geometries, respectively. Compounds **1** and **2** appear to be the first examples of a main group element containing symmetrically coordinated dithiocarbamate ligands.

Although dithiocarbamate complexes of the type $Te(S_2CNR_2)_4$ (R = ethyl, morpholino) are well-known[3,4] the analogous dithiophosphate and xanthate complexes have not yet been prepared, probably because such complexes are unstable with respect to reduction to tellurium(II) complexes and the disulfide of the dithiolate. Introduction of alkyl or aryl groups seems to stabilize the tellurium(IV) complexes, to the extent that complexes of the type $C_8H_8Te(S–S)_2$[5] and $Ph_2Te(S–S)_2$[6] (S–S = S_2CNR_2, $S_2P(OR)_2$, S_2COR) containing two tellurium–carbon bonds can be synthesized. The stability within each series increases in the order $S_2COR < S_2P(OR)_2 < S_2CNR_2$, with the $C_8H_8Te(S–S)_2$ series overall being more stable than the $Ph_2Te(S–S)_2$ series. The products of decomposition are the disulfide and the dialkyl or diaryl tellurium(II) compound. Futhermore, the electron lone pair at the tellurium atom in the complexes $Te(S_2CNR_2)_4$ appears inert in the solid state[7–9] whereas the lone pair is clearly stereochemically active in the complexes $C_8H_8Te(S–S)_2$[5] and $Ph_2Te(S–S)_2$.[6]

Complexes of the type $R'Te(S–S)_3$ (R′ = Ph, Me), which contain only one tellurium–carbon bond, should provide an interesting series for study since their stability could be expected to be intermediate to that of their $R_2Te(S–S)_2$ analogues and $Te(S–S)_4$ complexes. Apart from $PhTe(Etdtc)_3$[10] the only other monoaryl tellurium(IV) complexes for which solid-state structures have been reported are those of $PhTeX_3$(X = Cl, Br, I)[11–13], *p*-$PhOC_6H_4TeCl_3$,[14] (*p*-$EtOC_6H_4$)$TeCl_3$,[15] and $C_{12}H_9TeI_3$.[16,17] To date the solution chemistry of organotellurium(IV) trichlorides has been limited to the formation of ionic tetrahaloaryltellurate(IV) complexes[18–20] and molecular adducts of alkyl tellurium(IV) trihalides.[21,22]

In continuation of our investigations of the stereochemistry and bonding in hypervalent tellurium compounds in the solid state and in solution, we now report the synthesis and solution NMR study of $PhTe(Etdtc)_nCl_{3-n}$ (n = 1,2). The synthesis of $PhTeCl(Etdtc)_2$ and the subsequent observation in solution by tellurium-125 NMR spectroscopy of the mixed-ligand complexes $PhTe(Etdtc)_2(Etxan)$ and $PhTe(Etdtc)_2(Etdtp)$ (Etdtc = S_2CNEt_2, Etdtp = $S_2P(OEt)_2$, Etxan = S_2COR) are described. The methyl analogues were

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investigated by using oxidative addition of MeI to $Te(Etdtc)_2$ as an alternative synthesis for $R'Te(dtc)_2X$ complexes. The X-ray crystal-structure determinations of $PhTe(Etdtc)_2(Etdtp)$ and $MeTe(I)(Etdtc)_2$ are presented and compared with other, related, structures.

Experimental Section

Preparation of $PhTe(Cl)(Etdtc)_2$. To a suspension of $PhTeCl_3$[23] (4 mmol) in dichloromethane was added NaEtdtc (8 mmol). Reaction is rapid, the solution becoming bright yellow. The solution was taken to dryness, yielding the crude yellow compound $PhTe(Cl)(Etdtc)_2$. The crude material was recrystallized from benzene/ether to give crystalline $PhTe(Cl)(Etdtc)_2$ (mp 172–174 °C). Anal. Calcd for $PhTe(Cl)(Etdtc)_2$; ($C_{16}H_{25}ClN_2S_4Te$): C, 35.80; H, 4.70. Found: C, 36.2; H, 4.7.

Analyses were performed by Australian Microanalytical Service (Amdel).

Preparation of $PhTe(Etdtc)_2(Etdtp)$ (1). To a solution of PhTe(Cl)$(Etdtc)_2$ (4 mmol) in dichloromethane was added KEtdtp (4 mmol). The reaction mixture was stirred for 2 h, filtered, and taken to dryness, giving a yellow solid. Pale yellow crystals suitable for X-ray crystallography were obtained by slow evaporation of a dilute solution of $PhTe(Etdtc)_2(Etdtp)$ in dichloromethane/hexane (mp 149–151 °C dec).

Preparation of $MeTe(I)(Etdtc)_2$ (2). To a solution of $Te(Etdtc)_2$[24] in dichloromethane was added an excess of MeI. Reaction is not rapid, as judged by the slow color change from red (i.e., $Te(Etdtc)_2$) to yellow (i.e., $MeTe(I)(Etdtc)_2$ that takes place over the period of several hours. The solution was taken to dryness to give the crude yellow compound $MeTe(I)(Etdtc)_2$. Recrystallization from CS_2/ether gives yellow needles of $MeTe(I)(Etdtc)_2$ (mp 132 °C dec).

NMR spectra were recorded with broad band decoupling on a JEOL FX 100 spectrometer. Temperatures were maintained by a NM 5471 controller calibrated with a platinum resistance thermometer. Carbon-13 spectra were generally recorded in CH_2Cl_2 at 25.0 MHz and measured against internal Me_4Si; tellurium-125 spectra were recorded at 31.4 MHz with an external ^7Li lock and referenced against external aqueous 0.7 M K_2TeO_3. Phosphorus-31 spectra were measured at 40.26 MHz and referenced against 85% H_3PO_4. High-frequency positive convention is used.

Structure Determination and Refinement. Intensity data for both structures were collected on an Enraf-Nonius CAD-4F single-crystal, automatic diffractometer. Accurate cell dimensions were obtained from the setting angles of 25 reflections, measured with Mo Kα (graphite monochromatized) radiation ($\lambda = 0.71069$ Å) by a least-squares procedure. Crystals of **1** showed no symmetry other than that required by Freidel's law and hence are triclinic; the space group proved to be $P\bar{1}$. Crystals of **2** are orthorhombic, exhibiting systematic absences uniquely consistent with the space group *Pbca*.

Details of the data collection refer to **1**, with the corresponding details for **2** in brackets. Intensity data were collected by using the ω:2θ scan method. Four reference reflections, which were monitored every 1800 (4000) s of X-ray exposure time, indicated that there was no significant (3%) decrease in intensity. For the latter compound the data were corrected in accordance with this variation. The data for both crystals were corrected for Lorentz and polarization effects[25a] but not for extinction. The crystal data and remaining details of data collection are given in Table I.

Table I. Summary of Crystal Data, Intensity Collection, and Structural Refinement for $PhTe(Etdtc)_2(Etdtp)$ (**1**) and $MeTe(I)(Etdtc)_2$ (**2**)

	1	**2**
formula	$C_{20}H_{35}N_2O_2PS_6Te$	$C_{11}H_{23}IN_2S_4Te$
M_r	686.45	566.05
cryst system	triclinic	orthorhombic
space group	$P\bar{1}$ (C_i^1; No. 2)	*Pbca* (D_{2h}^{15}; No. 61)
a, Å	9.078 (2)	11.999 (1)
b, Å	11.823 (2)	18.219 (2)
c, Å	14.941 (2)	18.411 (2)
α, deg	69.28 (1)	
β, deg	88.29 (1)	
γ, deg	89.40 (1)	
Z	2	8
vol, Å^3	1499.2 (7)	4025 (1)
ρ(calcd), g cm^{-3}	1.52	1.87
ρ(measd), g cm^{-3}	1.51	1.87
cryst dimen (dist in mm from centroid)	±$(10\bar{1})$ 0.140 ±$(10\bar{1})$ 0.0565 ±(011) 0.0333	±(011) 0.073, $(0\bar{1}1)$ 0.067 $(\bar{1}11)$ 0.253, $(\bar{1}\bar{1}\bar{1})$ 0.253 (100) 0.293, $(\bar{1}00)$ 0.333 $(\bar{1}\bar{1}1)$ 0.233, $(\bar{1}1\bar{1})$ 0.233
temp, K	295 (1)	
radiation, Å	Mo Kα (graphite monochromator) ($\lambda = 0.71069$)	
F(000)	696	2176
μ, cm^{-1}	14.67	33.91
transmission factors	max 0.9151 min 0.8395	max 0.6604 min 0.5934
2θ limits	$2° \leq 2\theta \leq 53°$	$2° \leq 2\theta \leq 56°$
no. of reflcns collected	8088	12753
no. of unique reflcns	6112	4839
no. of unique reflctns used in refinement ($I > 2\sigma(I)$)	2566	3227
no. of variables	289	196
R_{amal}[a]	0.029	0.024
R[b]	0.054	0.034
R_w[b]	0.050	0.030
hkl range	$-2 \leq h \leq 10$ $-14 \leq k \leq 14$ $-17 \leq l \leq 17$	$-1 \leq h \leq 15$ $-24 \leq k \leq 24$ $-2 \leq l \leq 24$

[a] See ref 26. [b] See ref 27.

For **1** the position of the tellurium atom was determined from a three-dimensional Patterson synthesis, while the other non-hydrogen atoms were located from subsequent difference maps. The structure was refined by using a full-matrix least-squares refinement procedure,[27] with anisotropic temperature factors assigned to all atoms, the refinement converging with $R = 0.054$. Inspection of the model at this stage showed that the carbon atoms of the ethyl groups had very high thermal parameters, as well as some anomalous bond lengths, suggesting that these atoms were disordered. A full difference map with these atoms removed ($R = 0.159$) showed broad peaks that could not be resolved, so that no account of the possible disorder was included in the model. The positions of 26 of the 35 possible hydrogen atoms could be located from the difference maps. All hydrogen atoms, including those not located, were included in the model, at their geometrically estimated positions with a C–H bond length of 1.08 Å. Refinement was continued with a weighting scheme of the type $w = k/(\sigma^2(F) + gF^2)$, where *k* and *g* were varied in the refinement procedure. The refinement converged with $k = 1.43$, $g = 0.0006$, $R = 0.054$, and $R_w = 0.050$. Analysis of variance showed that an appropriate weighting scheme was used. After the final refinement cycle, the greatest residual electron density peak was 0.75 e Å^{-3}, which is in the proximity of the tellurium atom and is most likely due to disorder associated with this molecule.

For **2** the positions of the tellurium and iodine atoms were determined from an *E*-map. All other non-hydrogen atoms were determined from subsequent difference maps. The structure was refined by using a full-matrix least-squares refinement procedure,[27] with anisotropic temperature factors assigned to all atoms, the refinement converging with $R = 0.040$. All hydrogen atoms, which were located from the subsequent difference map, were included in the model at their geometrically estimated positions, with a C–H bond length of 1.08 Å. The refinement of **2** converged with $k = 2.032$, $g = 0.00015$, $R = 0.034$, and $R_w = 0.030$. The final difference map showed that the greatest residual electron density peak, 1.73 e Å^{-3}, is in close proximity to the Te and C(1) atoms. There were also several peaks, of heights 0.5–0.8 e Å^{-3}, close to the tellurium and iodine atoms. All other peaks in the map had heights of less than 0.5 e Å^{-3}. The analysis of variance showed no unusual features.

The scattering factors used for atomic C, H, O, P, and S were those collected by Sheldrick[28] while the scattering factors and anomalous dispersion terms for atomic tellurium were those given in ref 25b and 25c.

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(26) $R_{amal} = [\sum(N\sum(w(F_{mean} - F)^2))/\sum((N-1)\sum(wF^2))]^{1/2}$ where the inner summations are over *N* equivalent reflections averaged to give F_{mean}, the outer summations are over all unique reflections, and the weight, *w*, is taken as $(\sigma(F))^{1/2}$.

(27) The function minimized was $\sum w(|F_o| - |F_c|)^2$. The unweighted and weighted residuals were defined as $R = (\sum|F_o| - |F_c|)/\sum|F_o|$ and $R_w = \sum w^{1/2}(|F_o| - |F_c|)/\sum w^{1/2}|F_o|$.

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Table II. Final Fractional Atomic Coordinates for $PhTe(Etdtc)_2(Etdtp)$ (**1**)[a]

	x	*y*	*z*
Te	0.3038 (1)	0.1755 (1)	0.2156 (1)
C(1)	0.4993 (13)	0.1014 (11)	0.1748 (9)
C(2)	0.6061 (22)	0.0545 (15)	0.2357 (13)
C(3)	0.7395 (20)	0.0108 (15)	0.2047 (19)
C(4)	0.7594 (20)	0.0138 (15)	0.1161 (14)
C(5)	0.6536 (26)	0.0498 (21)	0.0646 (15)
C(6)	0.5228 (21)	0.0942 (17)	0.0909 (13)
S(1)	0.3373 (4)	0.0379 (3)	0.4006 (2)
S(2)	0.1711 (3)	−0.0422 (3)	0.2688 (2)
C(7)	0.2185 (11)	−0.0662 (9)	0.3848 (7)
C(8)	0.0594 (15)	−0.2441 (11)	0.4446 (9)
C(9)	0.1389 (18)	−0.3549 (12)	0.4402 (11)
C(10)	0.2094 (14)	−0.1772 (11)	0.5558 (8)
C(11)	0.1063 (16)	−0.1143 (12)	0.6038 (8)
N(1)	0.1679 (10)	−0.1580 (8)	0.4573 (6)
S(3)	0.1582 (3)	0.1750 (3)	0.0608 (2)
S(4)	0.3461 (4)	0.3743 (3)	0.0606 (2)
C(12)	0.2170 (12)	0.3210 (10)	0.0042 (7)
C(13)	0.0425 (16)	0.3476 (13)	−0.1246 (9)
C(14)	0.0994 (18)	0.3123 (13)	−0.2015 (10)
C(15)	0.2157 (15)	0.5147 (11)	−0.1287 (8)
C(16)	0.1266 (18)	0.6077 (12)	−0.1026 (11)
N(2)	0.1616 (12)	0.3899 (9)	−0.0785 (7)
S(5)	0.4897 (4)	0.3081 (3)	0.2775 (2)
S(6)	0.1489 (5)	0.3793 (4)	0.3072 (3)
P(1)	0.3422 (5)	0.4029 (3)	0.3231 (2)
O(1)	0.3838 (20)	0.3847 (11)	0.4308 (8)
O(2)	0.3925 (17)	0.5402 (8)	0.2814 (8)
C(17)	0.3873 (28)	0.3047 (24)	0.5076 (14)
C(18)	0.3886 (29)	0.2950 (23)	0.5891 (13)
C(19)	0.3899 (23)	0.6147 (15)	0.1902 (12)
C(20)	0.4309 (30)	0.7292 (15)	0.1734 (15)

[a] Standard deviations are in parentheses.

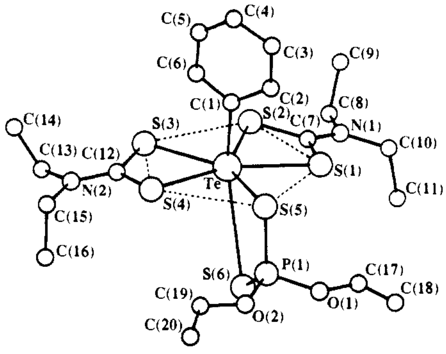

Figure 1. ORTEP of $PhTe(Etdtc)_2(Etdtp)$. Because of disorder, isotropic thermal parameters have been assigned to the atoms.

Structure determination and refinement was performed by using the programs SHELX-76,[28] ORTEP,[29] DISTAN,[30] and MEAN PLANES[31] and the University of Melbourne Cyber 170-730 and VAX 11/780 computer systems. The fractional atomic coordinates together with their estimated standard deviations are given in Tables II and III.

Results and Discussion

Description of the Structure of $PhTe(Etdtc)_2(Etdtp)$. The structure of $PhTe(Etdtc)_2(Etdtp)$ is monomeric with no significant interactions with adjacent molecules. Figure 1 shows the ORTEP diagram with the atomic numbering scheme. The coordination to the tellurium atom is from six sulfur atoms and a phenylic carbon. The four sulfur atoms from the dithiocarbamate ligands and one of the sulfur atoms of the dithiophosphate ligand are arranged in a pentagonal plane about the tellurium atom at distances ranging from 2.674 (3) to 2.708 (4) Å. The axial tellurium–carbon bond [Te–C(1) = 2.14 (1) Å] is perpendicular to the pentagonal sulfur plane. The sixth sulfur interaction from the dithiophosphate ligand [Te–S(6) = 3.436 (5) Å] is below the plane at a distance considerably less than the sum of the van der Waals radii 3.86 Å.[32] The eighth coordination position, on the same side of the pentagonal plane as the long tellurium–sulfur interaction, is apparently occupied by a stereochemically active lone pair. The presence of this lone pair is presumably responsible for the C(1)–Te–S(6) angle [i.e., 148.0 (4)°] deviating considerably from linearity. Selected bond lengths and angles are given in Tables IV and V.

Table III. Final Fractional Atomic Coordinates for $MeTe(I)(Etdtc)_2$ (**2**)

	x	*y*	*z*
C(1)	−0.1046 (4)	0.0540 (3)	0.0723 (3)
Te	0.00849 (2)	0.11618 (2)	0.13536 (2)
I	−0.19417 (3)	0.14463 (2)	0.23742 (2)
S(1)	−0.09090 (11)	0.23723 (7)	0.07742 (7)
S(2)	0.10048 (11)	0.1611 (7)	0.01255 (7)
C(2)	0.0042 (4)	0.23130 (2)	0.0079 (3)
N(1)	0.0051 (3)	0.2778 (2)	−0.0472 (2)
C(3)	0.0860 (4)	0.2718 (3)	−0.1067 (3)
C(4)	0.0445 (5)	0.2236 (3)	−0.1673 (3)
C(5)	−0.0774 (4)	0.3377 (2)	−0.0533 (3)
C(6)	−0.0320 (6)	0.4091 (3)	−0.0263 (4)
S(3)	0.16444 (11)	0.02000 (7)	0.10644 (7)
S(4)	0.01429 (11)	0.00499 (7)	0.23148 (7)
C(7)	0.1308 (4)	−0.0255 (2)	0.1856 (2)
N(2)	0.1903 (3)	−0.0815 (2)	0.2087 (2)
C(8)	0.2908 (4)	−0.1055 (3)	0.1708 (3)
C(9)	0.2679 (6)	−0.1677 (3)	0.1175 (4)
C(10)	0.1634 (5)	−0.1204 (3)	0.2763 (3)
C(11)	0.2157 (5)	−0.0836 (3)	0.3412 (3)

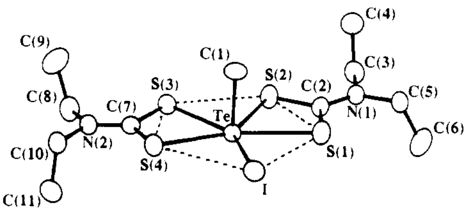

Figure 2. ORTEP of $MeTe(I)(Etdtc)_2$.

According to the VSEPR theory, the most favorable arrangement for eight electron pair about the central tellurium atom is a dodecahedron.[33] The regularity of a dodecahedron can be measured by considering it to be composed of two interpenetrating trapezia, the dihedral angle between the two trapezia being 90° for the ideal case. Thus in $PhTe(Etdtc)_2(Etdtp)$ the dihedral angle between the two planes formed by S(1), S(2), S(3), S(4) and C(1), S(5), S(6) and the lone pair (the lone pair assigned as being in the center of a triangle formed by S(2), S(4), S(6) and at a distance of 2.0 Å from the tellurium atom) is 88.9°, which is close to that of 90° required for a regular dodecahedron. In fact, the dodecahedral description seems even more appropriate here than was the case for $C_8H_8Te(Etdtp)_2$,[5] where the analogous interplanar angle was 88.1°.

Description of the Structure of $MeTe(I)(Etdtc)_2$. Coordination to the tellurium atom in **2** is from four sulfur atoms, one methyl carbon, and an iodine atom. An ORTEP diagram of $MeTe(I)(Etdtc)_2$ is shown in Figure 2. Selected interatomic bond distances and angles are given in Table VI and VII. The four sulfur atoms [Te–S(1) = 2.723 (1) Å, Te–S(2) = 2.646 (1) Å, Te–S(3) = 2.618 (1) Å, Te–S(4) = 2.691 (1) Å] and the iodine atom [Te–I = 3.117 (1) Å] are arranged in a pentagonal plane about the tellurium atom. The methyl group perpendicular to the plane [Te–C(1) = 2.115 (5) Å] and a sterically active lone electron pair, on the opposite side of the plane, impart an overall seven-coordinate

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Table IV. Interatomic Distances (Å) for $PhTe(Etdtc)_2(Etdtp)$ (**1**)[a]

Te–C(1)	2.138 (13)	Te–S(2)	2.696 (4)	Te–S(1)	2.690 (3)
Te–S(6)	3.436 (5)	Te–S(5)	2.708 (4)	Te–S(4)	2.674 (4)
Te–S(3)	2.700 (3)	S(1)–C(7)	1.727 (11)	S(2)–C(7)	1.722 (10)
C(7)–N(1)	1.308 (14)	C(8)–N(1)	1.49 (2)	C(9)–C(8)	1.51 (2)
C(1)–N(1)	1.468 (14)	C(11)–C(10)	1.51 (2)	S(3)–C(12)	1.714 (12)
S(4)–C(12)	1.712 (12)	C(12)–N(2)	1.327 (14)	C(13)–N(2)	1.48 (2)
C(14)–C(13)	1.44 (2)	C(15)–N(2)	1.48 (2)	C(16)–C(15)	1.51 (2)
S(5)–P(1)	1.992 (5)	S(6)–P(1)	1.815 (6)	O(1)–P(1)	1.602 (12)
O(2)–P(1)	1.586 (12)	C(17)–O(1)	1.20 (2)	C(18)–C(17)	1.18 (3)
C(19)–O(2)	1.34 (2)	C(20)–C(19)	1.34 (3)		

[a] Phenyl ring C–C bonds range from 1.23 (4) to 1.44 (3) Å.

Table V. Selected Bond Angles (deg) for $PhTe(Etdtc)_2(Etdtp)$ (**1**)[a]

Te–C(1)–C(6)	124 (1)	Te–C(1)–C(2)	122 (1)
Te–S(2)–C(7)	88.4 (4)	Te–S(1)–C(7)	88.5 (3)
Te–S(3)–C(12)	87.5 (4)	Te–S(4)–C(12)	88.4 (4)
Te–S(5)–P(1)	99.3 (2)	Te–S(6)–P(1)	80.5 (2)
C(1)–Te–S(3)	93.0 (3)	C(1)–Te–S(4)	88.4 (4)
C(1)–Te–S(5)	85.4 (4)	C(1)–Te–S(6)	148.0 (4)
C(1)–Te–S(1)	91.2 (3)	C(1)–Te–S(2)	90.3 (4)
S(1)–Te–S(3)	140.0 (1)	S(1)–Te–S(4)	154.0 (1)
S(1)–Te–S(5)	77.0 (1)	S(1)–C(7)–S(2)	116.3 (6)
S(1)–C(7)–N(1)	121.5 (8)	S(2)–C(7)–N(1)	122.2 (8)
S(1)–Te–S(2)	65.9 (1)	S(3)–Te–S(4)	65.9 (1)
S(5)–Te–S(6)	62.7 (1)	C(7)–N(1)–C(8)	121.7 (9)
C(7)–N(1)–C(10)	121.5 (9)	N(1)–C(10)–C(11)	112 (1)
S(3)–Te–S(5)	143.0 (1)	S(3)–C(12)–S(4)	117.1 (6)
S(3)–C(12)–N(2)	121.0 (9)	S(4)–C(12)–N(2)	121.9 (9)
C(12)–N(2)–C(13)	122 (1)	C(12)–N(2)–C(15)	121 (1)
N(2)–C(13)–C(14)	111 (1)	N(2)–C(15)–C(16)	113 (1)

[a] Phenyl ring angles range from 115 (2) to 125 (2)°.

pseudo-pentagonal-bipyramidal environment about the tellurium atom. This structure differs significantly from that of $C_8H_8Te(Etdtc)_2$[5] in which the pentagonal bipyramidal geometry about the tellurium atom is much more distorted. Futhermore, the dithiocarbamate ligands are ansiobidentically chelated in $C_8H_8Te(Etdtc)_2$, whereas the $MeTe(I)(Etdtc)_2$ all tellurium–sulfur bonds are close to equivalent. Compound **2** appears to be the first example of a dithiocarbamate complex of a main group element in which the dithiocarbamate ligand is symmetrically chelated.

It is interesting to note that changing the donor set about the tellurium atom from S_4C_2 in $C_8H_8Te(Etdtc)_2$ to S_4IC in $MeTeI(Etdtc)_2$ causes the dithiocarbamate ligands to coordinate symmetrically in the latter case. This in turn, implies that the asymmetry observed in the former is not a result of steric strain within the four-membered (TeS_2C) rings. It is also interesting to compare these two structures with those of several other related compounds.

The structure of $PhTe(Etdtc)_3$[10] also shows a distorted pentagonal bipyramid about the tellurium atom with five sulfur atoms arranged in the pentagonal plane (all atoms within 0.13 Å of the plane) and with the axial carbon–tellurium–sulfur angle 144.6 (2)°. In this case the distortion was thought to result from geometrical constraints of the narrow bite of the dithiocarbamate ligand and from a large trans effect of the phenyl group. In contrast, the structure of $ClTe(HOEtdtc)_3{\cdot}2H_2O$,[34] also pentagonal bipyramidal about the tellurium center, shows an almost linear axial carbon–tellurium–sulfur angle (176.4°). However, there is a distortion within the pentagonal plane, with one sulfur atom being displaced from the plane toward the axial sulfur by approximately 18°, which implies that geometrical constraints alone do not satisfactorily explain the axial distortions observed in $PhTe(Etdtc)_3$. In steric repulsion terms a lower energy would be required to distort the pentagonal plane than to distort the axial bonds.[35,36] Therefore the distortion observed in $PhTe(Etdtc)_3$ probably arises from the presence of a stereochemically active lone pair located near the position occupied by the axial sulfur. Furthermore, the axial tellurium–sulfur distance of 3.228 (4) Å is fairly long and is also consistent with the presence of a lone electron pair on that side of the pentagonal plane.

Solution NMR Study of $PhTeCl_3$. Reactions with Sodium Diethyldithiocarbamate. The compound $PhTeCl_3$ in a variety of solvents and at different temperatures gives a single tellurium-125 resonance (Table VIII), but the solutions are unstable with time and decompose to give unidentified products. Addition of an equimolar proportion of NaEtdtc to a solution of $PhTeCl_3$ in thf results in no tellurium-125 resonances being observed at room temperature, which indicates that the system is undergoing ligand exchange at a rate that approximates the NMR time scale. Lowering the temperature to −40 °C results in the observation of three sharp tellurium-125 resonances [$\delta(^{125}Te)$ −539, −1098, −1643 ppm] of approximate relative intensity 1:2:1.5. The signal at −539 ppm is due to $PhTeCl_3$ with the signals at −1098 and −1643 ppm being assigned to the species $PhTeCl_2(Etdtc)$ and $PhTeCl(Etdtc)_2$, respectively. The compound $PhTeCl_2(Etdtc)$ could not be isolated; however, the species $PhTeCl(Etdtc)_2$ was isolated and recrystallized from benzene/ether to give yellow needles of satisfactory elemental analysis. A pure sample of $PhTeCl(Etdtc)_2$ in thf at −40 °C gives a single sharp tellurium-125 resonance at −1647 ppm, which indicates that the above spectral assignment is correct.

Reaction of $PhTeCl_3$ with 2 molar equiv of NaEtdtc in a variety of solvents and differing temperatures results in a single tellurium-125 resonance due to $PhTeCl(Etdtc)_2$ (Table VIII). Whereas reaction of $PhTeCl_3$ with 1 molar equiv of NaEtdtc results in a labile system due to exchange between $PhTeCl_2(Etdtc)$ and $PhTeCl(Etdtc)_2$, reaction with 2 molar equiv of NaEtdtc gives a system that is static on the NMR time scale, even at 80 °C. The tellurium-125 resonance of $PhTeCl(Etdtc)_2$, in thf shifts to lower frequency as the temperature is lowered (Table VIII). The carbon-13 spectrum of a solution of $PhTeCl(Etdtc)_2$ in thf at −80 °C shows four resonances from the two apparently equivalent dithiocarbamate ligands (Table IX). The carbon-13 spectrum at −100 °C shows all signals slightly broadened, with the methylene dithiocarbamate resonance [$\delta(^{13}C)$ 51.2 ppm] showing indications of splitting. Further cooling of the solution results in precipitation.

The variable-temperature study on $PhTeCl(Etdtc)_2$ was repeated in dcm, where it is more soluble. The simplicity of the carbon-13 spectrum of $PhTeCl(Etdtc)_2$ in dcm at room temperature indicates that, as in thf solvent, the complex is subject to rapid intramolecular processes. Four phenyl resonances are observed with the remaining three resonances due to the dithio (i.e., S_2C–), methylene, and methyl carbons. There are no significant changes in spectra on cooling the solution down to −80 °C at which point the methylene carbon-13 resonance is slightly broadened. At −100 °C only the methylene carbon-13 resonance separates into two signals [$\delta(^{13}C)$ 50.5, 49.4 ppm], indicating nonequivalent dithiocarbamate ligands at this temperature. Nonequivalent methylene carbon-13 resonances have been observed previously in related compounds,[5] and this nonequivalence is attributed to intramolecular monodentate–bidentate dithiocarbamate exchange slowing on the NMR time scale which, in turn, results in the ethyl groups of each dithiocarbamate ligand residing in different magnetic environments (i.e., anisochronous). Of all the seven coordinate geometries that are possible, only a pentagonal bipy-

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Table VI. Interatomic distances (Å) in MeTe(I)(Etdtc)$_2$ (**2**)

C(1)–Te	2.115 (5)	Te–I	3.1165 (5)	Te–S(1)	2.7247 (13)
Te–S(2)	2.6458 (13)	Te–S(4)	2.6908 (13)	Te–S(3)	2.6183 (13)
S(1)–C(2)	1.718 (5)	S(2)–C(2)	1.730 (4)	C(2)–N(1)	1.318 (6)
N(1)–C(3)	1.468 (6)	N(1)–C(5)	1.478 (6)	C(3)–C(4)	1.505 (8)
C(5)–C(6)	1.495 (7)	S(3)–C(7)	1.725 (4)	S(4)–C(7)	1.725 (5)
C(7)–N(2)	1.316 (5)	N(2)–C(8)	1.460 (6)	N(2)–C(10)	1.468 (7)
C(8)–C(9)	1.524 (8)	C(10)–C(11)	1.507 (8)		
S(1)···S(2)	2.937 (2)	S(3)···S(4)	2.936 (2)		
I···S(1)	3.6138 (13)	I···S(4)	3.5694 (13)		
S(2)···S(3)	3.192 (2)				

Table VII. Bond Angles (deg) for MeTe(I)(Etdtc)$_2$ (**2**)

C(1)–Te–I	85.38 (14)	C(1)–Te–S(1)	86.43 (15)
C(1)–Te–S(2)	87.95 (15)	C(1)–Te–S(3)	89.34 (14)
C(1)–Te–S(4)	88.53 (15)	I–Te–S(1)	76.11 (3)
I–Te–S(2)	142.12 (3)	I–Te–S(3)	142.33 (3)
I–Te–S(4)	75.46 (3)	S(1)–Te–S(2)	66.28 (4)
S(1)–Te–S(3)	140.80 (4)	S(1)–Te–S(4)	151.42 (4)
S(2)–Te–S(3)	74.64 (4)	S(2)–Te–S(4)	141.64 (4)
S(3)–Te–Si(4)	67.13 (4)	Te–S(1)–C(2)	87.28 (15)
Te–S(2)–C(2)	89.62 (18)	S(1)–C(2)–S(2)	116.8 (3)
S(1)–C(2)–N(1)	122.7 (3)	S(2)–C(2)–N(1)	120.4 (4)
C(2)–N(1)–C(3)	122.2 (4)	C(2)–N(1)–C(5)	121.6 (4)
C(3)–N(1)–C(5)	116.2 (4)	N(1)–C(3)–C(4)	112.2 (4)
N(1)–C(5)–C(6)	111.9 (4)	Te–S(3)–C(7)	89.00 (15)
Te–S(4)–C(7)	86.64 (13)	S(4)–C(7)–S(3)	116.66 (2)
S(4)–C(7)–N(2)	122.1 (3)	S(3)–C(7)–N(2)	121.3 (3)
C(7)–N(2)–C(8)	121.7 (4)	C(7)–N(2)–C(10)	121.9 (4)
C(8)–N(2)–C(10)	116.2 (4)	N(2)–C(8)–C(9)	112.4 (4)
N(2)–C(10)–C(11)	111.5 (4)		

Table VIII. Tellurium-125 and Phosphorus-31 NMR Data for Various Te(IV) Complexes

compd	solvent	temp (°C)	$\delta(^{125}Te)$	$\delta(^{31}P)$
PhTeCl$_3$	dmso	30	−503	
	dmf	−40	−524	
	thf	−80	−532	
PhTe(Cl)$_2$(Etdtc)	thf	−40	−1098	
PhTe(Cl)(Etdtc)$_2$	thf	30	−1622	
	thf	−40	−1647	
	thf	−80	−1660	
	thf	−100	−1666	
	dmf	−40	−1667	
	dcm	−20	−1667	
	dcm	−100	−1687	
	tce	80	−1617	
PhTe(Etdtc)$_3$	thf	30	−1455	
	thf	−80	−1497	
	dcm	30	−1472	
	dcm	−80	−1526	
	dcm	−100	−1537	
PhTe(Etdtc)$_2$(Etdtp)	dcm	30	−1563	94.6
	dcm	−40	−1596	95.6
	dcm	−80	−1612	95.4
PhTe(Etdtc)$_2$(Etxan)	dcm	30	−1510	
MeTe(I)(Etdtc)$_2$	dcm	30	−1892	
MeTe(Etxan)(Etdtc)$_2$	dcm	30	−1722	
	dcm	−80	−1764	
MeTe(Etdtp)(Etdtc)$_2$	dcm	30	−1768	98.1
	dcm	−80	−1796	97.7
MeTe(Etdtc)$_3$	dcm	30	−1673	
	dcm	−80	−1711	
	dcm	−100	−1722	

ramidal geometry can account for the ^{13}C spectra observed at low temperature. Other seven-coordinate geometries require the dithiocarbamate ligands to be nonequivalent (i.e., the observation of two dithio, S_2C–, carbon-13 resonances) whereas only a pentagonal bipyramidal geometry, with the phenyl group and the lone electron pair in the axial positions, and the two isobidentate dithiocarbamate ligands together with the chlorine atom in the equatorial plane will give a single dithio (i.e., S_2C–) carbon-13 resonance.

Table IX. Carbon-13 Data for Selected Te(IV) Complexes in Dichloromethane Solution at 30 °C

	$\delta(^{13}C)$			
species	$-CH_3$	$-CH_2$	$-CS_2$	$-C_6H_5$ (or $-CH_3$)
PhTeCl(Etdtc)$_2$	12.5	50.8	199.0	141.4, 133.7, 130.8, 129.8
PhTe(Etdtc)$_3$	12.7	50.1	199.9^a	138.9, 135.4, 130.3, 129.9
PhTe(Etdtc)$_2$(Etdtp)	12.6	50.9	199.4	139.8, 134.7, 130.6, 130.0
	16.6^b	63.6^c		
MeTe(I)(Etdtc)$_2$	12.7	51.2	201.4	38.2
MeTe(Etxan)(Etdtc)$_2$	12.6	50.6^d	200.9	30.4
	14.4	71.0	219.9	
MeTe(Etdtp)(Etdtc)$_2$	12.5	50.7^e	199.7	33.1
	16.5^b	63.4^c		
MeTe(Etdtc)$_3$	12.6	50.1	200.1^f	27.4

^{a}Splits at −100 °C, in thf solution; 201.4, 195.7 ppm. ^{b} $^3J_{C-P} = 8$ Hz. ^{c} $^3J_{C-P} = 6$ Hz. ^{d}Splits at −100 °C; 50.1, 49.3 ppm. ^{e}Splits at −100 °C; 50.4, 49.7 ppm. ^{f}Splits at −100 °C; 198.0, 193.9 ppm.

The reaction of PhTeCl$_3$ with 3 molar equiv of NaEtdtc in thf at room temperature results in a single tellurium-125 resonance that shifts progressively to lower frequency as the temperature is lowered (Table VIII). In order to confirm that the observed tellurium-125 resonances assigned to PhTe(Etdtc)$_3$ and PhTeCl(Etdtc)$_2$ are not actually time averaged signals, equimolar mixtures of the two compounds in thf (and dcm) were examined. Only two resonances are observed in the temperature range 25 to −80 °C, corresponding to the tellurium-125 shifts for the isolated compounds. At room temperature, however, both resonances are somewhat broad, indicating that the rate of ligand exchange was approaching the NMR time scale.

The ^{13}C spectrum of PhTe(Etdtc)$_3$ in thf at −80 °C shows only three resonances for the phenyl carbons. Only three resonances due to the dithiocarbamate ligands are observed (Table IX), indicating that all three dithiocarbamate ligands are equivalent. The simplicity of the spectrum indicates that the complex PhTe(Etdtc)$_3$ is subject to rapid intramolecular exchange processes although the dithio carbon (i.e., S_2C–) resonance [$\delta(^{13}C)$ 199.8 ppm] is very broad with respect to the other signals. The carbon-13 spectrum at −100 °C still shows only three phenyl resonances; however, the dithio (i.e. S_2C–) carbon-13 resonance has now split into two broad resonances [$\delta(^{13}C)$ 201.4, 195.7 ppm] of relative intensity 2:1, indicating that the dithiocarbamate ligands themselves are no longer equivalent (i.e., two dithiocarbamate ligands are the same and different from the third). The methylene carbon resonance [$\delta(^{13}C)$ 49.8 ppm] is extremely broad as is the methyl resonance. At −100 °C a single tellurium-125 resonance [$\delta(^{125}Te)$ −1503 ppm, $w_{1/2} = 80$ Hz] is observed. The complex PhTe(Etdtc)$_3$ has limited solubility in thf, and at −100 °C, considerable precipitation occurs which probably contributes to line broadening in the spectra. The complex is more soluble in dcm and subsequent variable temperature NMR experiments were conducted in this solvent.

An isolated sample of PhTe(Etdtc)$_3$ dissolved in dichloromethane solution gives a single tellurium-125 resonance from room temperature to −80 °C (Table VIII). The carbon-13 spectrum at room-temperature is identical with that observed in thf, except that now all four phenyl resonances are observed (Table IX). The three dithiocarbamate ligands are equivalent with only three sharp resonances being observed. There are no significant changes in the carbon-13 spectrum down to −100 °C. At −100 °C the dithio (i.e., S_2C–) carbon-13 resonance [$\delta(^{13}C)$ 197.9 ppm] is very broad as is the methylene carbon resonance [δ(^{13}C) 49.2 ppm] of the dithiocarbamate ligand. The tellurium-125 spectrum at −100 °C consists of a single resonance [δ(^{125}Te) −1537, $w_{1/2}$ = 75 Hz]. The data suggest that in dcm solution the compound PhTe(Etdtc)$_3$ is subject to intramolecular exchange processes even at −100 °C, whereas in thf solution, nonequivalent dithiocarbamate ligands are observed at −100 °C.

Two possible solution geometries at −100 °C are consistent with the above NMR data in thf: (i) The first is a pentagonal-bipyramidal geometry with the phenyl group and the lone pair in axial positions. The pentagonal plane is occupied by two isobidentically chelated dithiocarbamate ligands and one monodentate dithiocarbamate ligand. (ii) The second is a dodecahedral geometry, derived from the above structure by the monodentate dithiocarbamate ligand isobidentically chelated to the tellurium atom. This proposed geometry is very similar to that observed in the solid state.[37] The two structures postulated both result in nonequivalent ethyl groups, and the structures can be easily interconverted by the chelation of the monodentate dithiocarbamate ligand in the pentagonal bipyramid structure. Because of the similarity of the two geometries they are indistinguishable by solution NMR techniques. However, due to the increased degrees of freedom available in solution, possibility (i) is discounted since it is improbable that two dithiocarbamate ligands would be bidentate while a third remains statically monodentate. Support for this is also found in our earlier data for which slow intramolecular monodentate–bidentate dithiocarbamate ligand exchange at low temperature was observed for analogous C$_8$H$_8$Te(Etdtc)$_2$ compounds.[5]

Solution NMR Studies of PhTe(Etdtc)$_2$(Etxan) and PhTe(Etdtc)$_2$(Etdtp). The ^{125}Te spectrum of an isolated sample of PhTe(Etdtc)$_2$(Etdtp) freshly dissolved in dcm contains only one broad resonance at −1563 ppm ($w_{1/2}$ = 240 Hz) and the ^{31}P spectrum contains a single resonance at 94.6 ppm with no indication of Te–P coupling. The carbon-13 spectrum at room temperature shows four sharp phenyl resonances (Table IX). The three carbon-13 resonances at δ(^{13}C) 199.4, 50.9, and 12.6 ppm indicate equivalent dithiocarbamate ligands, and the chemical shifts are almost identical with those observed for the compound PhTe(Etdtc)$_3$. The remaining two carbon-13 resonances are both doublets due to tellurium–phosphorus coupling and are assigned to the methyl and methylene carbons respectively of the dithiophosphate ligand.

The carbon-13 spectrum is somewhat broadened at −80 °C but otherwise unchanged. At −100 °C the most noticeable difference in the carbon-13 spectrum is that the methylene carbon-13 resonance of the dithiocarbamate ligand begins to separate into two resonances [δ(^{13}C) 49.9, 50.5 ppm]. The dithio (i.e., S$_2$*C*–) carbon resonance is still sharp and is indicative of two equivalent dithiocarbamate ligands. The multiplicity of the methylene carbon-13 resonance is suggestive of two magnetically nonequivalent ethyl groups on each dithiocarbamate ligand. This nonequivalence is due to slowing of intramolecular monodentate–bidentate exchange of the dithiocarbamate ligand. However, the absence of tellurium–phosphorus coupling may indicate that the dithiophosphate ligand is still subject to monodentate–bidentate exchange processes. The NMR data are consistent with a dodecahedral geometry similar to that observed in the solid state (Figure 1). At −40 °C, the tellurium-125 resonance is considerably sharpened [δ(^{125}Te) −1596 ppm] while the corresponding phosphorus-31 spectrum shows the resonance attributed to PhTe(Etdtc)$_2$(Etdtp) to be shifted slightly [δ(^{31}P) 95.6 ppm]. The tellurium-125 spectrum at −80 °C gives a single resonance [δ(^{125}Te) −1612 ppm, $w_{1/2}$ = 140 Hz] while the phosphorus-31 resonance at δ(^{31}P) 95.4 ppm is sharp. Further lowering of the temperature to −100 °C has little effect on the line width of the tellurium-125 resonance [δ(^{125}Te) −1621 ppm, $w_{1/2}$ = 150 Hz].

The ^{125}Te spectrum of an equimolar solution of PhTeCl(Etdtc)$_2$ and KEtxan in dcm consists of a single resonance that is assigned to PhTe(Etdtc)$_2$(Etxan) (Table VIII). This solution is unstable with time and the ^{125}Te spectrum recorded 1 h after mixing contains two resonances [δ(^{125}Te) −1510, −1471 ppm]. The corresponding carbon-13 spectrum contains broad resonances at room temperature. Lowering the temperature to −80 °C causes resolution into several new resonances. The observation of at least five dithio (i.e., S$_2$*C*–) carbon-13 resonances is supportive of decomposition to unidentified products, although the possibility of redistribution reactions giving the species, PhTe(Etxan)$_n$(Etdtc)$_{3-n}$ (n = 1, 2, 3 with n = 1, 2 being the most favored statistically) cannot be discounted. We have thus far been unable to isolate the complex PhTe(Etdtc)$_2$(Etxan).

The reaction of PhTeCl$_3$ with 3 molar equiv of KEtxan or KEtdtp in dcm did not result in the formation of either PhTe(Etxan)$_3$ or PhTe(Etdtp)$_3$. In both cases decomposition occurred and the tellurium-125 spectrum of each solution contained only one resonance at δ(^{125}Te) −715 ppm, which could not be assigned to any particular species.

Solution NMR Study of MeTe(I)(Etdtc)$_2$. Reaction with Sodium Diethyldithiocarbamate, Potassium Diethyldithiophosphate, and Potassium Ethylxanthate. Several attempts were made to extend the range of tellurium(IV) complexes containing dithiolate ligands by using oxidative addition of alkyl and aryl halides to the tellurium(II) complexes Te(S–S)$_2$. Oxidative addition of MeI to the compounds Te(Etxan)$_2$ and Te(Etdtp)$_2$ was not successful as a useful synthetic route and in both cases decomposition occurred to the extent that a tellurium mirror formed inside the reaction vessel. However, when Te(Etdtc)$_2$ was dissolved in dcm, to which an excess of methyl iodide was added, and the solution stirred for several hours, a color change occurred and the initially deep red solution became yellow. Evaporation of the solvent led to isolation of a yellow powder which was recrystallized from CS$_2$/ether to give yellow needles of MeTe(I)(Etdtc)$_2$. No reaction could be induced between Te(Etdtc)$_2$ and phenyl iodide, despite using a variety of reaction conditions including UV irradiation.

The tellurium-125 spectrum at room temperature of MeTe(I)(Etdtc)$_2$ in dcm shows a single tellurium-125 resonance (Table VIII), the position of which is considerably shifted from that of the tellurium-125 resonance of the parent compound, Te(Etdtc)$_2$[δ(^{125}Te) −930 ppm]. The corresponding carbon-13 spectrum consists of four resonances, three of which [δ(^{13}C) 12.7, 51.2, 201.4 ppm] are attributed to the two equivalent dithiocarbamate ligands. The remaining carbon-13 resonance [δ(^{13}C) 38.2 ppm] is attributed to the methyl group attached to the tellurium atom. Cooling the solution to −100 °C causes no significant change in the tellurium-125 or carbon-13 spectra. Taking signal intensities into account, the NMR data are consistent with the compound being formulated as MeTe(I)(Etdtc)$_2$. Although the geometry of MeTe(I)(Etdtc)$_2$ has a pentagonal bipyramidal geometry in the solid state, deductions about the stereochemistry adopted in solution are made difficult by the apparent lability of this system in solution even at low temperatures. This lability may arise due to the greater relative electron donating ability of the methyl group compared with the phenyl group in PhTe(Cl)(Etdtc)$_2$ and the *o*-xylene-α,α'-diyl group in C$_8$H$_8$Te(I)(Etdtc).[6]

A tellurium-125 spectrum of equimolar amounts of MeTe(I)(Etdtc)$_2$ and NaEtdtc in dcm at room temperature consists of a single resonance (Table VIII) attributed to the species MeTe(Etdtc)$_3$. The room temperature carbon-13 spectrum indicates that the three dithiocarbamate ligands are equivalent [δ(^{13}C) 12.6, 50.1, 200.1 ppm]. The methyl group bonded to the tellurium atom gives a single carbon-13 resonance at δ(^{13}C) 27.4 ppm. At −80 °C, the tellurium-125 spectrum consists of a single broad resonance [δ(^{125}Te) −1711 ppm; $w_{1/2}$ = 160 Hz] (Table VIII). The corresponding carbon-13 spectrum contains broad resonances for the dithio (i.e., S$_2$*C*–) and methylene carbons. The remaining carbon-13 resonances, due to the methyl group at the tellurium atom and the methyl groups of the dithiocarbamate ligands, are sharp. At −100 °C, the tellurium-125 resonance has sharpened considerably [δ(^{125}Te) −1722 ppm; $w_{1/2}$ = 60 Hz]. The carbon-13 spectrum at the same temperature now contains two well-separated resonances for the dithio (i.e., S$_2$*C*–) carbons. The integrated

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[37] Esperas, S.; Husebye, S. *Acta Chem. Scand.* **1972**, *26*, 3293.

intensities of approximately 2:1 indicate that two dithiocarbamate ligands are equivalent and are in a different environment to the third dithiocarbamate ligand. The remaining carbon-13 resonances, although broadened, are at similar chemical shift positions to those observed in the carbon-13 spectrum recorded at -80 °C. In this compound, the ratio and multiplicity of the dithio (i.e., S_2C–) carbon resonances are consistent with the geometry postulated earlier for the compound PhTe(Etdtc)$_3$ (i.e., a dodecahedral geometry). The compound MeTe(Etdtc)$_3$ was not isolated.

The reaction of MeTe(I)(Etdtc)$_2$ with an equimolar amount of KEtdp in dcm at room temperature results in a single tellurium-125 resonance, $w_{1/2}$ = 100 Hz (Table VIII), attributed to formation of the species MeTe(Etdtp)(Etdtc)$_2$. The phosphorus-31 spectrum consists of a single resonance [$\delta(^{31}P)$ 98.1 ppm] with no evidence for P–Te coupling. The carbon-13 spectrum contains three characteristic resonances indicative of two equivalent dithiocarbamate ligands while the presence of the dithiophosphate ligand gives rise to two doublets, due to coupling with phosphorus (Table IX). At -80 °C, the solution gives sharp tellurium-125 and phosphorus-31 resonances. The carbon-13 spectrum of -80 °C shows a single sharp ditho (i.e., S_2C–) resonance indicating equivalent dithiocarbamate ligands. However, the methylene carbons of the dithiocarbamate ligand are nonequivalent [$\delta(^{13}C)$ 49.7, 50.4 ppm]. Reducing the temperature to -100 °C does not cause any further significant change in the NMR spectra. The complex MeTe(Etdtp)(Etdtc)$_2$ could not be isolated; however, a structure similar to that proposed for PhTe(Etdtc)$_2$(Etdtp) can be postulated in solution at low temperature.

Reaction of MeTe(I)(Etdtc)$_2$ with an equimolar amount of KEtxan in dcm at room temperature results in a single tellurium-125 resonance (Table VIII) that is attributed to the formation of the species MeTe(Etxan)(Etdtc)$_2$. The corresponding carbon-13 spectrum contains three resonances arising from the two equivalent dithiocarbamate ligands. The methyl group attached to the tellurium atom gives a single carbon-13 resonance [$\delta(^{13}C)$ 30.4 ppm] with the remaining three carbon-13 resonances due to the xanthate ligand. At -80 °C, the tellurium-125 spectrum consists of a single resonance [$\delta(^{125}Te)$ -1764 ppm, $w_{1/2}$ = 100 Hz] and there is no significant change in the carbon-13 spectrum. At -100 °C, the tellurium-125 resonance is slightly sharper [$\delta(^{125}Te)$ -1773 ppm; $w_{1/2}$ = 80 Hz] while the carbon-13 spectrum is unchanged apart from the resonance due to the methylene carbons of the dithiocarbamate ligand which is now split into two signals [$\delta(^{13}C)$ 49.3, 50.1 ppm] indicating that there are now two types of methylene carbons. However, only one dithio (i.e., S_2C–) carbon-13 [$\delta(^{13}C)$ 197.1 ppm] is observed, which suggests that the two dithiocarbamate ligands themselves are in identical environments. Therefore the splitting of the methylene resonances probably arises from a slowing of intramolecular monodentate–bidentate dithiocarbamate ligand exchange which results in magnetic nonequivalence of the two methylene carbons on each dithiocarbamate ligand. By analogy with the discussion of PhTe(Etdtc)$_2$(Etdtp), it is likely that the xanthate ligand is still subject to monodentate–bidentate exchange. Similarly, a dodecahedral geometry is postulated for MeTe(Etxan)(Etdtc)$_2$ in solution at low temperature.

Conclusions

In general most compounds discussed in this work display magnetically nonequivalent methylene carbon atoms and in some cases nonequivalent dithio carbons (i.e., S_2C–) at low temperature. These spectral changes can be explained in terms of seven or eight coordinate geometries that are based on pentagonal-bipyramidal or dodecahedral geometries. Although NMR data cannot distinguish between the two possibilities, it is likely that there is a small energy barrier between these two geometries in solution and it may well be that these molecules are fluxional in solution. Nevertheless the NMR data for PhTe(Etdtc)$_2$(Etdtp) in solution at low temperature are consistent with the geometry determined directly for the solid state.

Acknowledgment. We are grateful for the award of a Commonwealth of Australia Postgraduate Research Award (to R. D.) and for financial assistance from the Australian Research Grants Scheme (A.R.G.S.).

Supplementary Material Available: Tables S-I–S-VIII listing anisotropic temperature factors, hydrogen atom coordinates and their isotropic temperature factors, and mean planes (12 pages); listing of structure factor tables (29 pages). Ordering information is given on any current masthead page.