SYNTHESIS, NMR STUDIES AND CRYSTAL STRUCTURES OF 1,3-DIHYDRO-2δ⁴-BENZOTELLUROLE-2, 2-DIYL DIACETATE, $C_8H_8Te(OAc)_2$ AND 1,3-DIHYDRO-2δ⁴-BENZOTELLUROLE-2,2-DIYL DIETHYLDITHIOCARBAMATE DIETHYLDITHIO-PHOSPHATE, $C_8H_8Te(Et_2NCS_2)[(EtO)_2PS_2]$

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PLEASE SCROLL DOWN FOR ARTICLE

SYNTHESIS, NMR STUDIES AND CRYSTAL STRUCTURES OF 1,3-DIHYDRO-2λ⁴-BENZOTELLUROLE-2, 2-DIYL DIACETATE, $C_8H_8Te(OAc)_2$ AND 1,3-DIHYDRO-2λ⁴-BENZOTELLUROLE-2,2-DIYL DIETHYLDITHIOCARBAMATE DIETHYLDITHIO-PHOSPHATE, $C_8H_8Te(Et_2NCS_2)[(EtO)_2PS_2]$

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The crystal and molecular structures of $C_8H_8Te(OAc)_2$, **1**, and $C_8H_8Te(Et_2NCS_2)[(EtO)_2PS_2]$, **2**, have been determined. The crystals of **1** are monoclinic with a = 10.632(1), b = 9.200(1), c = 13.589(1) Å, β = 101.330(6)°, Z = 4 and space group $P2_1/a$; the crystals of **2** are orthorhombic with a = 6.653(1), b = 9.876(2), c = 36.347(6) Å, Z = 4 and space group $P2_12_12_1$. In both compounds, the lone pair of electrons of tellurium is stereochemically active. In **1**, tellurium is coordinated by the benzylic carbon atoms and by the four oxygens of the two anisobidentate acetate ligands. In addition, the molecules are joined into chains by weak intermolecular Te. . .O bonds. This results in seven-coordination for the tellurium atom. **2** consists of monomeric molecules where tellurium is bonded to the two benzylic carbons and to the four sulfur atoms of the two anisobidentate dithio ligands. Here, tellurium is six-coordinate. The structures may be described as distorted pseudo dodecahedral (**1**) and pseudo penta-gonal bipyramidal (**2**) when the lone pair of electrons is included in the coordination sphere. Tellurium-125 NMR data indicate that rates of intermolecular ligand exchange are slow on the NMR time-scale.

Key words: Tellurium(IV) compounds with two Te—C bonds; $C_8H_8Te(Et_2NCS_2)[(EtO)_2PS_2]$ and $C_8H_8Te(OAc)_2$; X-ray structure; NMR.

INTRODUCTION

It has been shown that tellurium can have a maximum coordination number of 8.[1] Compounds where Te(IV) forms eight bonds are limited to dialkyldithiocarbamate complexes of the type TeL_4, where L is a bidentate dialkyldithiocarbamate ligand. If one of these ligands is replaced by a monodentate ligand (an aromatic group, or a halogen or pseudohalogen) the maximum coordination number is reduced to 7. With other bidentate dithio ligands such complexes disproportionate: $Te^{IV}L_4 = Te^{II}L_2 + L_2$, where L_2 is the oxidation product of two ligands (a disulphide).[1,2]

With an organic dinegative bidentate ligand such as *o*-xylene-α,α-diyl bonded to Te(IV), the latter can add two more bidentate ligands of various types.

An important feature of the stereochemistry of Te(IV) is its lone pair of electrons. At coordination numbers 6 or higher, it is sometimes stereochemically inert, in violation of the VSEPR theory.[1,3]

In recent years, a series of highly coordinated tellurium complexes with thio, halogen and hydrocarbon ligands have been prepared and several of their structures

solved. In most complexes with one or more hydrocarbon ligands the lone pair is stereochemically active.[1]

Recently, mixed dithiolate ligand complexes of both Te(II) and Te(IV) have been studied.[2,4,5] Such studies give an indication of relative ligand donor strength. It is also found that in Te(IV) complexes, ligands with weak donor strength result in formation of secondary bonds between a tellurium atom of one complex molecule and a halogen or chalcogen ligand on a neighboring molecule (Te coordinatively unsaturated). To further study these effects we decided to prepare and solve the structures of the two tellurium complexes $C_8H_8Te(OAc)_2$, **1** and $C_8H_8Te(Et_2NCS_2)[(EtO)_2PS_2]$, **2**.

RESULTS AND DISCUSSION

The structures of the two compounds are shown in Figures 1 and 2. From the figures it is seen that tellurium is seven-coordinate in **1** if the weak, intermolecular bond involving tellurium is included, and six-coordinate in **2**.

Bond lengths are shown in Tables III and IV. For comparison, the structures of **1** and **2** are compared to those of some related compounds,[6] $C_8H_8TeL_2$, with L = $Et_2NCS_2^-$, $(EtO)_2PS_2^-$ and $EtOCS_2^-$ (Table VI). Molecular packing in the unit cells of **1** and **2** are shown in Figures 3 and 4. From the figures, it may be seen that the molecules of **1** are knit together into zig-zag chains by means of weak secondary Te···O bonds while the molecules of **2** are monomeric.

Structure. The structure of $C_8H_8Te(OAc)_2$, **1**, is similar to those of $C_8H_8Te[(EtO)_2PS_2]_2$, **4** and $C_8H_8Te(EtOCS_2)_2$, **5**.[6] It may be described as distorted pentagonal bipyramidal with C8 and O2' in axial positions and C1, O1, O2, O3, O4 in equatorial positions. The lone pair is probably stereochemically active, and positioned in the eight position of a distorted pseudododecahedral structure. This position is probably near the plane defined by Te, C1, C8 and O2', but below the
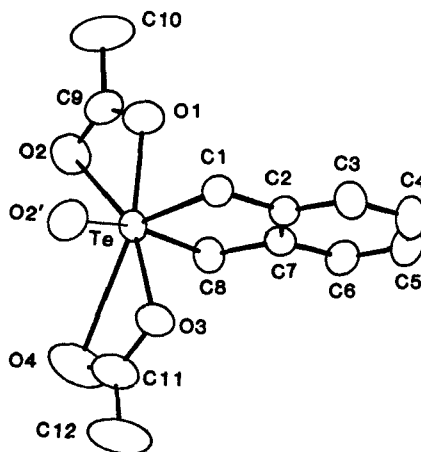
FIGURE 1   The structure of $C_8H_8Te(OAc)_2$, **1**. 02′ represents an atom in a neighboring molecule related to the original one by the transformation 1/2 + *x*, 1/2 − *y*, *z*.
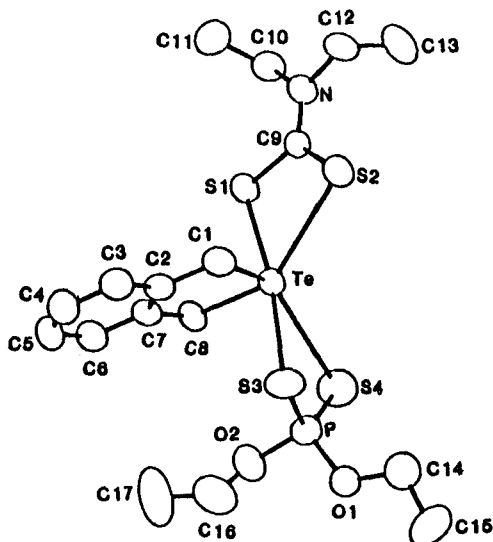
FIGURE 2   The structure of $C_8H_8Te(Et_2NCS_2)[(EtO)_2PS_2]$, **2**.

TABLE I

Crystal data on $C_8H_8Te(OAc)_2$ and $C_8H_8Te(Et_2NCS_2)[(EtO)_2PS_2]$

	1	**2**
Compound	$C_8H_8Te(OAc)_2$	$C_8H_8Te(Et_2NCS_2)[(EtO)_2PS_2]$
Diffractometer	Enraf-Nonius CAD-4	
Radiation	MoK_α (graphite monochromator)	
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/a$	$P2_12_12_1$
a/Å	10.632(1)	6.653(1)
b/Å	9.200(1)	9.876(2)
c/Å	13.589(1)	36.347(6)
$\beta/^0$	101.330(6)	
V/Å^3	1303.3(2)	2388.0(6)
Z	4	4
d_{calc}/gcm^{-3}	1.783	1.639
$\mu(MoK\alpha)/cm^{-1}$	22.85	16.65
Cryst.size/mm	0.16x0.34x0.23	0.39x0.31x0.11
Scan-mode/max.$\theta/^0$	ω-scan, 28^0	
Scale factor	0.960	2.124
No. indep. refl. (295 ^{0}K)	3134	3290
No. with $I>2\sigma(I)$	2763[a]	2730
Transm. factors (min/max)	0.59/0.83	0.76/0.84
$R=\Sigma\|F_o-F_c/\Sigma F_o$	0.036	0.029
$Rw=[\Sigma w(F_o-F_c)^2/\Sigma wF^2]^{1/2}$	0.043	0.030
$S=[\Sigma w(\Delta F)^2/(N-n)]^{1/2}$	1.099	1.420

[a] 91 "bad" reflections with $\sin\theta/\lambda<0.2$ were further deleted in the final refinements.

TABLE II

Positional parameters with estimated standard deviations

$C_8H_8Te(OAc)_2$, **1**					$C_8H_8Te(Et_2NCS_2)[(EtO)_2PS_2]$, **2**			
Atom	x	y	z	B(Å²)	Atom	x	y	z	B(Å²)
Te	0.02791(2)	0.11702(3)	-0.26197(2)	2.424(4)	Te	0.20195(5)	0.80518(3)	0.14396(1)	3.148(5)
O1	-0.1249(3)	0.1012(4)	-0.3983(2)	3.77(6)	S1	-0.0077(2)	0.6438(1)	0.18157(4)	3.63(3)
O2	-0.2334(3)	0.2490(4)	-0.3169(3)	4.22(7)	S2	0.4338(2)	0.6130(2)	0.19648(4)	4.30(3)
O3	0.1853(3)	0.0667(4)	-0.1475(2)	3.44(6)	S3	0.4031(3)	0.9647(2)	0.09439(4)	4.68(3)
O4	0.1006(4)	0.2222(6)	-0.0573(3)	7.2(1)	S4	0.1633(3)	1.1462(2)	0.15847(5)	5.73(4)
C1	0.1026(4)	-0.0560(4)	-0.3340(3)	2.49(6)	P	0.2743(2)	1.1422(2)	0.10952(4)	3.97(3)
C2	0.0526(3)	-0.1935(4)	-0.2948(3)	2.28(6)	O1	0.4300(6)	1.2586(4)	0.0998(1)	5.16(9)
C3	0.0929(4)	-0.3294(5)	-0.3218(3)	3.12(8)	O2	0.0994(6)	1.1749(4)	0.0814(1)	5.7(1)
C4	0.0466(5)	-0.4548(5)	-0.2871(4)	3.75(9)	N	0.1415(6)	0.4932(4)	0.2346(1)	3.55(9)
C5	-0.0422(4)	-0.4478(5)	-0.2253(4)	3.67(9)	C1	0.2746(9)	0.6482(5)	0.1056(1)	4.0(1)
C6	-0.0819(4)	-0.3150(5)	-0.1969(3)	2.99(7)	C2	0.1171(8)	0.6528(5)	0.0757(1)	3.4(1)
C7	-0.0349(3)	-0.1865(4)	-0.2308(3)	2.41(6)	C3	0.132(1)	0.5687(6)	0.0451(1)	4.4(1)
C8	-0.0763(4)	-0.0412(4)	-0.1979(3)	2.83(7)	C4	-0.006(1)	0.5736(6)	0.0178(2)	5.0(1)
C9	-0.2225(4)	0.1835(5)	-0.3931(3)	3.30(8)	C5	-0.167(1)	0.6611(6)	0.0196(1)	5.2(1)
C10	-0.3243(5)	0.191(1)	-0.4856(4)	6.2(2)	C6	-0.188(1)	0.7449(6)	0.0504(1)	4.2(1)
C11	0.1899(5)	0.1457(7)	-0.0675(4)	4.4(1)	C7	-0.0459(8)	0.7403(5)	0.0784(1)	3.4(1)
C12	0.3113(6)	0.133(1)	0.0085(5)	6.7(2)	C8	-0.0658(8)	0.8342(5)	0.1114(1)	3.6(1)
					C9	0.1935(8)	0.5750(5)	0.2071(1)	3.05(9)
					C10	-0.0690(8)	0.4661(6)	0.2449(1)	4.1(1)
					C11	-0.1469(9)	0.3391(6)	0.2253(2)	5.1(1)
					C12	0.293(1)	0.4209(6)	0.2564(2)	4.8(1)
					C13	0.354(1)	0.4935(7)	0.2904(2)	6.7(2)
					C14	0.613(1)	1.2735(8)	0.1215(2)	6.9(2)
					C15	0.721(1)	1.3945(7)	0.1091(2)	7.0(2)
					C16	0.126(1)	1.1719(8)	0.0438(2)	8.1(2)
					C17	-0.051(2)	1.136(1)	0.0240(2)	13.2(3)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

$$\frac{4}{3}[a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$$

TABLE III

Bond lengths/Å and angles/° with estimated standard deviations for $C_8H_8Te(OAc)_2$

Te–C1	2.104(4)	C11–C12	1.490(7)
Te–C8	2.117(4)	C1–C2	1.509(6)
Te–O1	2.216(3)	C2–C3	1.394(6)
Te–O2	2.989(3)	C3–C4	1.373(6)
Te–O3	2.100(3)	C4–C5	1.384(8)
Te–O4	2.903(5)	C5–C6	1.372(7)
O1–C9	1.297(6)	C6–C7	1.396(6)
O2–C9	1.223(6)	C7–C8	1.503(6)
C9–C10	1.490(7)	C7–C2	1.394(6)
O3–C11	1.301(6)	Te···O2′	3.044(4)
O4–C11	1.211(8)		
C1–Te–C8	87.0(2)	O2–Te–O2′	123.6(1)
C1–Te–O1	81.0(1)	O3–Te–O4	48.7(1)
C1–Te–O2	127.5(1)	O3–Te–O2′	71.9(1)
C1–Te–O3	81.9(1)	O4–Te–O2′	91.3(1)
C1–Te–O4	130.1(1)	Te–C1–C2	106.2(3)
C1–Te–O2′	77.5(1)	Te–C8–C7	106.3(3)
C8–Te–O1	86.6(1)	Te–O1–C9	112.3(3)
C8–Te–O2	81.1(1)	Te–O2–C9	76.9(2)
C8–Te–O3	87.1(1)	O1–C9–O2	122.9(4)
C8–Te–O4	84.1(2)	O1–C9–C10	115.8(5)
C8–Te–O2′	155.3(1)	O2–C9–C10	121.3(5)
O1–Te–O2	47.5(1)	Te–O3–C11	112.9(3)
O1–Te–O3	162.0(1)	Te–O4–C11	76.3(3)
O1–Te–O4	146.8(1)	O3–C11–O4	121.3(4)
O1–Te–O2′	109.4(1)	O3–C11–C12	114.9(5)
O2–Te–O3	147.2(1)	O4–C11–C12	123.8(6)
O2–Te–O4	99.4(1)	C–C–C(Ph,ave)	120.0(8)

TABLE IV

Bond lengths/Å and angles/° with estimated standard
deviations for $C_8H_8Te(Et_2NCS_2)[(EtO)_2PS_2]$

Te–C1	2.139(5)	C12–C13	1.488(9)
Te–C8	2.158(5)	S3–P	2.027(2)
Te–S1	2.521(1)	S4–P	1.927(2)
Te–S2	3.103(2)	P–O1	1.587(4)
Te–S3	2.742(2)	O1–C14	1.456(8)
Te–S4	3.438(2)	C14–C15	1.47(1)
S1–C9	1.765(5)	P–O2	1.581(4)
S2–C9	1.687(5)	O2–C16	1.380(8)
C9–N	1.330(6)	C16–C17	1.43(1)
N–C10	1.477(7)	C1–C2	1.512(7)

N-C12	1.466(7)	C7-C8	1.521(7) ·
C10-C11	1.516(8)	C-C (Ph,ave)	1.384(15)
C1-Te-C8	85.7(2)	C9-N-C10	123.7(4)
C1-Te-S1	91.1(1)	C9-N-C12	121.5(4)
C1-Te-S2	81.1(1)	C10-N-C12	114.7(4)
C1-Te-S3	83.0(1)	N-C10-C11	111.3(4)
C1-Te-S4	146.2(1)	N-C12-C13	113.8(5)
C8-Te-S1	85.7(1)	Te-S3-P	96.46(7)
C8-Te-S2	146.0(1)	Te-S4-P	78.44(7)
C8-Te-S3	88.0(1)	S3-P-S4	116.0(1)
C8-Te-S4	83.8(1)	S3-P-O1	106.9(2)
S1-Te-S2	63.54(4)	S3-P-O2	108.2(2)
S1-Te-S3	171.75(5)	S4-P-O1	115.7(2)
S1-Te-S4	119.89(4)	S4-P-O2	107.9(2)
S2-Te-S3	120.88(4)	O1-P-O2	100.9(2)
S2-Te-S4	123.06(4)	P-O1-C14	119.9(4)
S3-Te-S4	64.60(4)	O1-C14-C15	109.0(6)
Te-C1-C2	106.9(3)	P-O2-C16	122.8(5)
Te-C8-C7	106.2(3)	O2-C16-C17	113.5(7)
Te-S1-C9	96.3(2)	C1-C2-C7	120.6(4)
Te-S2-C9	78.8(2)	C8-C7-C2	120.2(4)
S1-C9-S2	120.8(3)	C1-C2-C3	120.5(5)
S1-C9-N	115.5(4)	C8-C7-C6	119.9(5)
S2-C9-N	123.6(4)	C-C-C (Ph,ave)	120.0(8)

TABLE V

Molecular planes

No. of plane		Atoms in plane	Δ^a	Dist.to other atoms/Å	Interplanar angles /°	
<u>1</u>	1	C1-C8	-0.024	Te,0.140	1-2	94.9(2)
	2	O1,O2,C9,C10	0.009	Te,0.221	1-3	87.4(2)
	3	O3,O4,C11,C12	0.001	Te,0.355	2-3	8.0(1.4)
	4	Te,C1,O1,O2,		C8,-1.941;	1-4	92.2(1)
		O3,O4	0.169	O2´,2.905	2-4	4.7(1.7)
					3-4	4.9(1.9)
<u>2</u>	1	C1-C8	0.014	Te, 0.190	1-2	104.1(1)
	2	S1,S2,C9,N,			1-3	121.6(1)
		C10,C12	0.000	Te,-0.314	2-3	62.5(1)
	3	S3,S4,P	0	Te, 1.039	1-4	94.9(1)
	4	Te,C1,S1,		S2,-2.702;	2-4	73.6(1)
		S3,S4	-0.160	C8, 1.995	3-4	27.8(1)

^{a}Represents the maximum deviation from planarity.

TABLE VI

Structural parameters of related compounds, $C_8H_8TeL_1L_2$. Bond lengths in Å, angles in °

|	**1** $L_1=L_2=OAC^-$	**2** $L_1=Et_2NCS_2^-$ $L_2=(EtO)_2PS_2^-$	**3** $L_1=L_2=EtOCS_2^-$	**4** $L_1=L_2=(EtO)_2PS_2^-$	**5** $L_1=L_2=Et_2NCS_2^-$
Ref.	Present work		6	6	6
Te-C1	2.104(4)	2.139(5)	2.125(2)	2.133(11)	2.150(4)
Te-C8	2.117(4)	2.158(5)	2.143(2)	2.109(9)	2.143(4)
Te-S1/O1	2.216(3)	2.521(1)	2.6142(7)	2.627(4)	2.599(1)
Te-S2/O2	2.989(3)	3.103(2)	3.3220(7)	3.493(4)	3.220(1)
Te-S3/O3	2.100(3)	2.742(2)	2.6410(5)	2.621(3)	2.622(1)
Te-S4/O4	2.903(5)	3.438(2)	3.2720(6)	3.447(4)	3.270(1)
Te-S2'/O2'	3.044(5)	-	3.4796(7)	3.729(4)	-
S1/O1-Te-S3/O3	162.0(1)	171.75(5)	164.63(2)	163.6(1)	168.55(4)
C8-Te-S2/O2	81.1(1)	146.0(1)	85.83(5)	83.9(3)	140.6(1)
C8-Te-S2'/O2'	155.3(1)	-	166.65(7)	151.3(3)	-
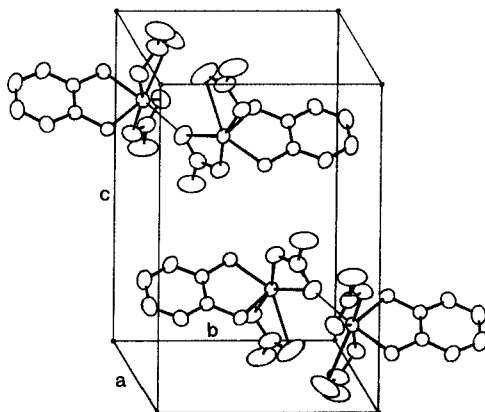
FIGURE 3   Molecular packing of $C_8H_8Te(OAc)_2$, **1** in the unit cell. Weak intermolecular Te. . .O bonds are indicated by thin lines.
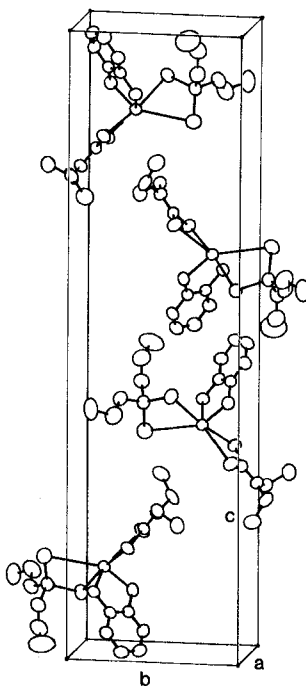

FIGURE 4   Molecular packing of $C_8H_8Te(Et_2NCS_2)[EtO)_2PS_2]$, **2**, in the unit cell.

latter atom when looking at Figure 1. It is also interesting to compare the structure of **1** to that of the similar $(p\text{-MeOC}_6H_4)_2Te(OAc)_2$, **6**.[7] In the latter, two anisyl groups replace $C_8H_8^{2-}$ and as the bidentate ligand with a relatively small C-C bite is replaced by two monodentate ligands, the C-Te-C angle increases from 87.0 to 99.0°. Also the C8-Te-O2' angle increases from 155.3 to 176.6° for the corresponding angle in **6**. Thus the geometrical distortion is less in **6** when compared to **1**.
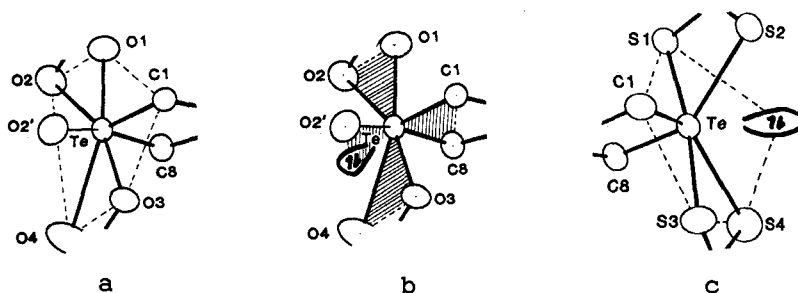
FIGURE 5   a) The pentagonal bipyramidal coordination sphere of Te in **1**. b) The alternate ψ-dodeca-hedral coordination sphere in **1**. c) The ψ-pentagonal bipyramidal coordination sphere of Te in **2**.

However, the structures are different also in another respect. In **1**, the acetate planes are roughly coplanar, this is not the case in **6**.

The structure of $C_8H_8Te(Et_2NCS_2)[(EtO)_2PS_2]$, **2**, is somewhat different from that of **1**. First, there are no intermolecular, secondary bonds in **2**, resulting in a coordination number of 6 compared to 7 in **1**. This is in agreement with the stronger donor properties of $EtNCS_2^-$. Second, whereas the central parts of the bidentate acetate ligands are nearly coplanar in **1**, (dihedral angle ca. 8.0°) the corresponding dihedral angle between the dithiolate ligands is ca. 62.50° in **2**. However the structure of **2** is analogous to that of $C_8H_8Te(Et_2NCS_2)_2$, **3**,[6] which also lacks inter-molecular secondary bonds. The atoms C1, S1, S3, S4 and Te are nearly coplanar with S2 above and C8 below the plane. Thus the structure may be considered strongly distorted pseudo pentagonal bipyramidal with the lone pair of electrons together with C1, S1, S3 and S4 being equatorial. The greatest distortion is represented by the axial C8-Te-S2 angle of 146.0(1)°. The C_8H_8 group is approximately planar and at nearly right angles to the acetate ligand planes in **1**. The corresponding angles in **2** are ca. 104 and 121.5° for the central parts of the $Et_2NCS_2^-$ and the $(EtO)_2PS_2^-$ ligands, respectively (Table V).

Bonding.   The $C_8H_8^{2-}$ ligand is isobidentate in both **1** and **2** with average Te—C bond lengths of 2.111 Å for **1** and 2.149 Å for **2**. These values are somewhat different, but both lie within the normal range for such bonds.[1] The other ligands are strongly anisobidentate. In **1** the average short Te—O bonds are 2.158 Å while the long ones are 2.946 Å. The average of these values is close to that of **6**, but there the asymmetry is a little smaller. The above bond lengths may be compared to the sum of the covalent radii of Te and O of 2.03 Å. The corresponding van der Waals radial sum is 3.58 Å.[1]

In **2**, there is a significant difference between the Te—S bond lengths of the two ligands. For $Et_2NCS_2^-$ they are 2.521(1) and 3.103(2) Å, for $(EtO)_2PS_2^-$ they are 2.742(2) and 3.438(2) Å. This clearly shows that $Et_2NCS_2^-$ has better donor prop-erties than $(EtO)_2PS_2^-$. From Table VI, it can be seen that in compounds of the type $C_8H_8TeL_2$ where L is a dithiolate ligand, the Te—S bond length variation is $Et_2NCS_2^- < EtOCS_2^- < (EtO)_2PS_2^-$ indicating that the ligand donor strength varies in the opposite manner. Structures of Ph_2TeL_2 (L = alkyl or aryl dithiocarbamates also show similar, strong Te—S bonding).[8] It can also be seen that $Et_2NCS_2^-$ forms stronger bonds to tellurium in **2** as compared to **5**. In **2**, the increased bond strength

is realized at the expense of the $(EtO)_2PS_2^-$ ligand which is more weakly bonded in **2** as compared to **4**. The same trend is observed when comparing $PhTe(Et_2NCS_2)_2$ $[(EtO)_2PS_2]$[4] and $PhTe(Et_2NCS_2)_3$.[9] Here the structures may be described as distorted pentagonal bipyramidal with Ph axial; two $Et_2NCS_2^-$ ligands are isobidentate and equatorial and the last ligand axial—equatorial and strongly anisobidentate. The average Te—S bond lengths involving the isobidentate $Et_2NCS_2^-$ ligands are 2.690 and 2.743 Å, respectively, taking the mixed ligand compound first. The corresponding averages for the anisobidentate $(EtO)_2PS_2^{2-}$ and $Et_2NCS_2^-$ ligands are 3.072 and 2.917 Å, respectively. Also the Te—C bonding from the $C_8H_8^{2-}$ ligand seems to be influenced by the relative donor strength of the dithiolate ligands in these compounds.

The Te—S bond length in **2** varies between 2.521 and 3.438 Å. Such wide variations are normal (Table VI),[1] and these bond lengths may be compared to 2.41 and 3.86 Å which are the sums of the respective covalent and van der Waals radii.[1] The structures of $Ph_2Te(R_2NCS_2)_2$, R = Me, Et and Bu, and $Ph_2Te[(RO)_2PS_2]_2$, R = Me and Et, are similar to that of **2**.[8,10-12] Average Te—S bond lengths in the dialkyl dithiocarbamates are similar to that found for **5**, 2.904, 2.883 and 2.909 compared to 2.928 Å.

However it is a bit surprising to find that whereas the diethyldithiophosphate $C_8H_8Te[EtO)_2PS_2]_2$ has a structure similar to **1** with a weak intermolecular bond, the $Ph_2Te[(RO)_2PS_2]_2$ structures are similar to that of **2**, a structure characteristic of strong donors such as dialkyldithiocarbamates. They also lack short intermolecular contacts, but the average Te—S bond lengths are 2.997 and 2.988 Å significantly shorter than 3.047 Å found in $C_8H_8Te[(EtO)_2PS_2]_2$, **4**.[6] This difference in structure has been explained in terms of the greater stability of the reduced species Ph_2Te.[2,11]

NMR studies. Earlier NMR investigations have shown that mixed ligand species such as $C_8H_8Te(Et_2NCS_2)(EtOCS_2)$ and $C_8H_8Te(EtOCS_2)[(EtO)_2PS_2]$ are formed in solution when the appropriate starting materials $C_8H_8Te(L)_2$ and $C_8H_8Te(L')_2$ are mixed.[6] In each of these cases the ^{125}Te spectrum of equimolar mixtures shows resonances for the starting materials $C_8H_8Te(L)_2$ and $C_8H_8Te(L')_2$ as well as for the mixed ligand species $C_8H_8Te(L')(L)$. The simultaneous observation of all three species indicates not only the formation of the mixed ligand species but also that the rate of intermolecular ligand exchange of (L) or (L') is slow on the NMR timescale.

However, the ^{125}Te NMR spectrum of a dichloromethane solution formed by addition of equimolar quantities of $C_8H_8Te(Et_2NCS_2)_2$ and $C_8H_8Te[(EtO)_2PS_2]_2$ shows a single resonance $[\delta(^{125}Te)\text{-}1060 \text{ ppm}]$. The same single resonance is observed for a dichloromethane solution in which an isolated sample of **2** has been dissolved. As the temperature is lowered to $-60°C$ the resonance becomes a doublet due to coupling to phosphorus $[^2J(\text{Te-P})29 \text{ Hz}]$. These NMR data imply either that the equilibrium $C_8H_8Te(Et_2NCS_2)_2 + C_8H_8Te[(EtO)_2PS_2]_2 \rightleftharpoons 2C_8H_8Te(Et_2NCS_2[(EtO)_2PS_2]$ lies substantively towards formation of the mixed ligand species or that appreciable intermolecular dithiolate exchange occurs such that an equilibrium exchanged averaged position is observed in the ^{125}Te spectrum. The crystal structure of **2** supports the notion that in solution this compound undergoes negligible dissociation to $C_8H_8Te(Et_2NCS_2)_2$ and $C_8H_8Te[(EtO)_2PS_2]_2$.

Reaction of 1 mol equivalent of $NaEt_2NCS_2$ with **1** in dichloromethane solution at room temperature shows resonances for **1** $[\delta(^{125}Te)$-674 ppm] as well as the mixed ligand species $C_8H_8Te(OAc)(Et_2NCS_2)[\delta(^{125}Te)$-924 ppm] and $C_8H_8Te(Et_2NCS_2)_2$ $[\delta(^{125}Te)$-1105 ppm]. These ^{125}Te resonances appear in an approximately statistical distribution. Intermolecular ligand exchange is slow for this system. Attempts at isolation of solid $C_8H_8Te(OAc)(Et_2NCS_2)$ were not successful.

EXPERIMENTAL

Preparation of **1**.   First $C_8H_8TeI_2$ was prepared according to Ziolo and Günther.[14] To the iodide (4 mmol) suspended in benzene was added $Ag(OAc)$ (8 mmol), the solution warmed to 50°C whilst maintaining stirring. Stirring was continued until the solution became colorless (about 3h). The AgI was removed by filtration and the solvent removed at reduced pressure. The residual solid material was recrystallized from benzene to give colorless crystals suitable for X-ray study, mp 135°C (darkens), 165–168°C (melts).

Attempts to isolate $C_8H_8TeI(OAc)$, using the appropriate ratios of reactants, were not successful.

Preparation of **2**.   First $C_8H_8Te(Et_2NCS_2)I$ was prepared: To $C_8H_8TeI_2$ (4 mmol) suspended in dichloromethane (200 cm³) was added $NaEt_2NCS_2$ (4 mmol). The solution was stirred for 3 hours, or until no orange $C_8H_8TeI_2$ crystals remained. The solution was filtered and evaporated to dryness. The crude product was recrystallized from CS_2/ether to give quantitative yields of the yellow crystalline $C_8H_8Te(Et_2NCS_2)I$ (mp 141–143°C decomp.).

$C_8H_8Te(Et_2NCS_2)I$ (4 mmol) was dissolved in dichloromethane (200 cm³) with stirring. To this was added an excess of $K(EtO)_2PS_2$ (5 mmol), and the solution stirred for 1 hour. The solution was filtered to remove unreacted $K(EtO)_2PS_2$ and KI precipitates, and then taken to dryness. The yellow product (often an oil) was dissolved in a minimum of boiling methanol, filtered and left to stand. Pale yellow needles of $C_8H_8Te(Et_2NCS_2)[(EtO)_2PS_2]$ were obtained (mp 109–110°C).

Crystals for X-ray studies were obtained by slow evaporation from a solvent mixture of dichloromethane and hexane.

Instrumentation.   NMR spectra were recorded on a JEOL GX 270 spectrometer. Tellurium-125 spectra were recorded at 85.3 MHz and referenced against 0.7 M K_2TeO_3 in water. Temperatures were maintained using a JEOL GTV3 control system. High frequency positive convention is used.

Crystal Data.   Crystallographic data and structural refinement parameters are listed in Table I. Three standard reflections were remeasured every 2 h for scaling purposes. There was no significant decrease in intensity for **1**, for **2** a small correction was applied (Max 2.5%). The intensity data were corrected for Lorentz, polarization and absorption effects.

Structure Determination.   Accurate cell dimensions were obtained from setting angles of 25 carefully centered reflections, using a least squares procedure. The structures were solved by standard Patterson and Fourier methods. Hydrogen atoms were positioned and constrained at their estimated geometrical positions at a fixed C—H bond length of 0.95 Å. The structures were refined by a full-matrix least-squares procedure. During refinement, the function minimized was $\Sigma w(\Delta F)^2$. The diethyldithiophosphate ligand in **2** (C16,C17) had very high temperature parameters. Attempts to solve the apparent disorder did not succeed. Since the space group of **2** was acentric, both enantiomers were refined. The selected enantiomer (Table II) was chosen on basis of Hamiltons R test.

During refinement of **1**, it became obvious that ΔF values were very high for several low-angle reflections. The 91 reflections with $\sin\Theta/\lambda \leqslant 0.2$ were therefore eliminated from the intensity data. When the parameter shifts were less than 1% of the associated standard deviations, the refinements were ended. Final difference maps showed no maxima above 0.6 $e^-/Å^3$ for **1**. For **2**, maxima of ca. $2e^-/Å^3$ were found close to the tellurium position. Computer programs were supplied by Enraf-Nonius.[11]

SUPPLEMENTARY MATERIAL

Further details of the crystal structure work is deposited with the Cambridge Crystallographic Data Centre, U.K.

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