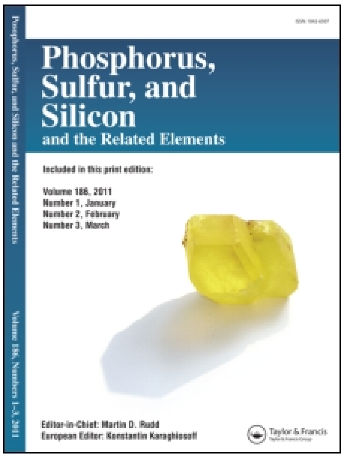

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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Martin D. Rudd[a]; Angela Defferding[a]; Kevin K. Klausmeyer[b]
[a] Department of Chemistry, University of Wisconsin-Fox Valley, Menasha, Wisconsin, USA [b] Department of Chemistry and Biochemistry, Baylor University, Waco, Texas, USA

To cite this Article Rudd, Martin D. , Defferding, Angela and Klausmeyer, Kevin K.(2008) 'Reactions of Naphthyl Tellurium Trihalides with Some Dithiocarbamates and Xanthates: X-Ray Structure of “T-Shaped” Naphthyl Tellurium 1-Pyrrolidinecarbodithioate', Phosphorus, Sulfur, and Silicon and the Related Elements, 183: 10, 2361 — 2372

To link to this Article: DOI: 10.1080/10426500802202063

URL: http://dx.doi.org/10.1080/10426500802202063

Phosphorus, Sulfur, and Silicon, 183:2361–2372, 2008
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802202063

Reactions of Naphthyl Tellurium Trihalides with Some Dithiocarbamates and Xanthates: X-Ray Structure of "T-Shaped" Naphthyl Tellurium 1-Pyrrolidinecarbodithioate

Martin D. Rudd,[1] Angela Defferding,[1]
and Kevin K. Klausmeyer[2]
[1]Department of Chemistry, University of Wisconsin–Fox Valley,
Menasha, Wisconsin, USA; [2]Department of Chemistry and
Biochemistry, Baylor University, Waco, Texas, USA

*The reaction of naphthyl tellurium trihalides, $ArTeX_3$ (X = Br, Cl; Ar = naphthyl) with several salts of dithiocarbamate and xanthate ligands (L) have been investigated by metathesis in tetrahydrofuran. The products (**1–3**) were characterized by multinuclear NMR spectroscopy and elemental analysis. Crystals of ArTeL (L = 1-pyrrolidine-carbodithioate, **1**) were obtained from the reaction of $ArTeCl_3$ and 3 equivalents of $NH_4[S_2CNC_4H_8]$. The structure shows a three-coordinate T-shaped tellurium(II) geometry with one "short" and one "long" Te-S bond: the two independent molecules in the unit cell have Te-S distances of 2.444(3) Å, 2.494(3) Å and 3.271(5) Å, 3.042(5) Å respectively, the latter two distances being intermolecular. The intermolecular interactions and the NMR spectra are discussed, together with a structural comparison of related Te(II) complexes.*

Keywords Coordination; dithiocarbamate; tellurium; X-ray structure

INTRODUCTION

As part of our investigation into the coordination chemistry of Te(II) and Te(IV), we have used a naphthyl group in some of our studies of new complexes with sulfur and selenium containing ligands. In a recent article, we described the T-shaped structures of two thiourea complexes of Te(II), namely [(naphthyl)TeBr(thiourea)] and

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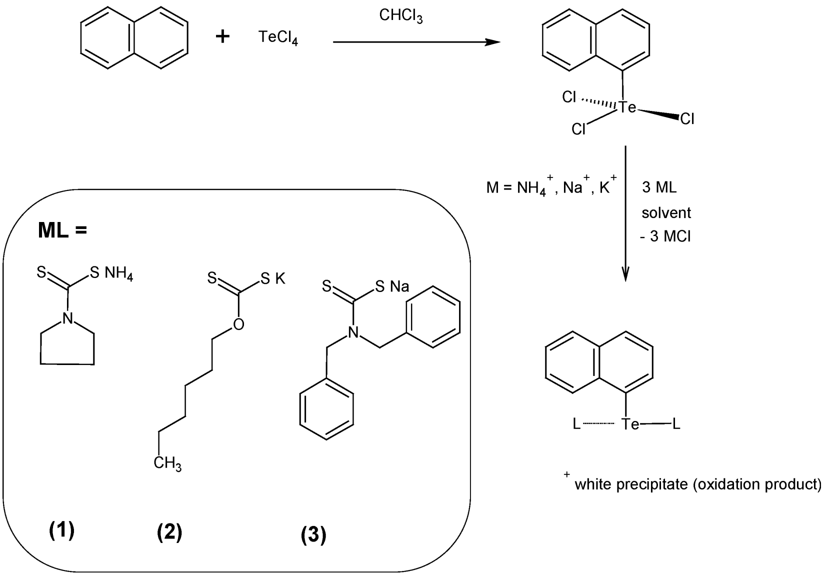
Received 18 March 2008; accepted 14 May 2008.

M.D.R. would like to thank the Professional Development Committee at the University of Wisconsin–Fox Valley for generous funding of this undergraduate research and for travel funds. We would also like to acknowledge Dr. Jerry Lokensgard (Lawrence University, Appleton) for assistance with the NMR spectra.

Address correspondence to Martin D. Rudd, Department of Chemistry, University of Wisconsin–Fox Valley, Menasha, WI 54952, USA. E-mail: martin.rudd@uwc.edu

[(naphthyl)TeBr(tetramethylthiourea)],[1] and we indicated that there is a strong *trans* influence from the aromatic ligand, which leads to the formation of three-coordinate, rather than four-coordinate structures. In the literature, there have been some comprehensive reviews of the structural chemistry of both selenium and tellurium with sulfur (and selenium) containing ligands: in much of the "organo-coordination" chemistry of Te(II), the phenyl group or closely related groups have been employed, presumably because of the availability (or more straightforward synthesis) of diphenyl ditelluride. In these reviews,[2–4] several complexes of the type [PhTe(L)X] are described, where L = sulfur or selenium monodentate ligand and X = halide with the central tellurium atoms showing an approximate T-shaped, three-coordinate geometry. Weak interactions with a fourth "square planar" positioned ligand are noted in several cases. Interestingly, this structural variation continues into a range of bidentate ligands, which were first noted by Husebye et al. in their presentation of xanthates and dithiophosphates as examples.[3–7]

In continuation of our investigation of the coordination chemisty of Te(II), with bulky aromatic ligands, we have prepared a series of naphthyl tellurium complexes with dithiocarbamate and xanthate ligands.



SCHEME 1 Synthesis of Te(II) complexes.

RESULTS AND DISCUSSION

Synthesis

The aromatic tellurium trihalides used here reacted cleanly with three equivalents of dithiocarbamate or xanthate salts in a variety of organic solvents forming a precipitate of insoluble halides and the corresponding naphthyl tellurium dithiocarbamate or xanthate complex in fair to good yields. The structures of the new complexes are shown in Scheme 1. A reduction from Te(IV) to Te(II) has taken place in the course of the reaction, presumably with a concomitant oxidation of two molecules of the ligand (resulting in a white precipitate, not isolated) to form S—S bonded species. This has been reported previously for two related tellurium examples.[2,4]

Molecular Structure

The structure of one of the two independent molecules of **1** is shown in Figure 1. The crystals are built up from naphthyl tellurium(II) 1-pyrrolidinecarbodithioate molecules connected through weak intermolecular Te$\cdots$S bonds forming a three-coordinate T-shaped molecule. Table I shows a list of selected bond lengths and angles. Firstly, the bond angle C(6)-Te(1)-S(1) of 85.1(2)° is considerably smaller than in related angular tellurium(II) structures; for instance in the structure of 4-$CH_3OC_6H_4TeSC(S)OCH_3$ (4-methoxyphenyl tellurium(II) methylxanthate) reported by Husebye an angle of 97.24(8)° is observed.[5]

Tellurium Ligand Bonding

Table II compares some of the structural features from related molecules and the present work. There are notable features that can

TABLE I Selected Bond Lengths (Å) and Angles (°) for Compound 1

Te(1)-C(6)	2.140(9)	C(6)-Te(1)-S(1)	85.1(2)
Te(1)-S(1)	2.444(3)	C(21)-Te(2)-S(3)	84.2(2)
Te(2)-C(21)	2.139(8)	C(1)-S(1)-Te(1)	100.6(3)
Te(2)-S(3)	2.494(3)	C(16)-S(3)-Te(2)	99.4(3)
S(1)-C(1)	1.749(8)	C(1)-N(1)-C(5)	124.4(7)
S(2)-C(1)	1.700(8)	C(1)-N(1)-C(2)	123.6(7)
S(3)-C(16)	1.749(8)	C(5)-N(1)-C(2)	112.0(7)
S(4)-C(16)	1.693(8)	C(16)-N(2)-C(17)	125.4(7)
Te(2)-S(2)	3.042(5)	C(16)-N(2)-C(20)	122.6(7)
Te(1)-S(3)	3.271(5)	S(2)-C(1)-S(2)	121.3(5)

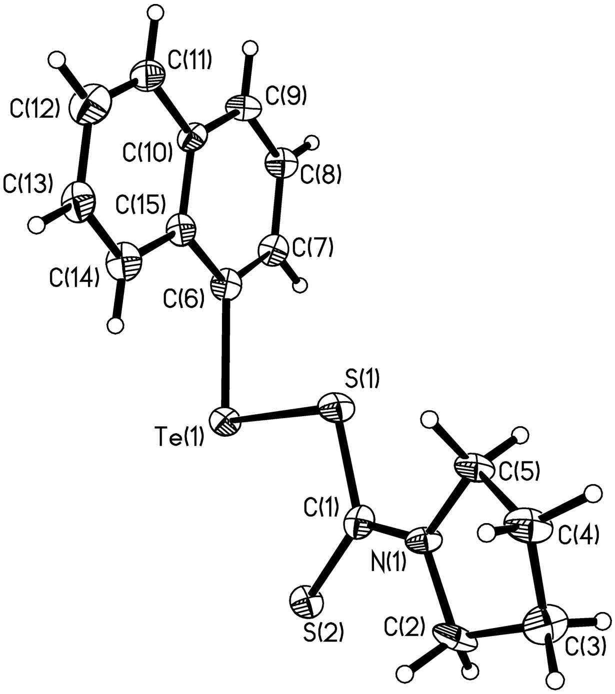


FIGURE 1 Molecular structure of one of the independent molecules of **1** in the crystal. Displacement ellipsoids are shown at the 30% probability level.

be determined from the data and the literature. The two examples in Table II of coordinated dimethyldithiophosphate ligands to Te(II) both exhibit a three-coordinate T-shaped type of geometry at the tellurium atom, that is also seen in **1**. In all cases, there is a short (*ca*. 2.4 Å) Te-S bond and an additional long (more than 3.0 Å) Te-S interaction with STeS angles of approximately 170°. These compounds can be thought of as 3c-4e models. Examples of methylxanthate ligands coordinated to Te(II) are also displayed but these show a rather different type of geometry. In addition to a coordinated sulfur atom with a Te-S distance of around 2.4 Å, there are two longer interactions to other xanthate ligands forming a distorted square planar geometry at the tellurium atom——in the two molecules presented here, the Te$\cdots$S bonds lay between *ca* 3.4–3.7 Å. Furthermore, another two examples from the literature reveal that Te(II) coordination to a methylthiosulfate ligand gives a two-coordinate (angular) geometry at tellurium, in which there is no structural evidence of a third weak interaction with a distant ligand. Interestingly, the Te—S bond distances in these three different geometric structures are close to 2.4 Å. In compound **1**, the two independent molecules exhibit a three-coordinate T-shaped geometry at the tellurium atom, similar to that described with the dimethyldithiophosphate ligands. The Te–S bonds of 2.444(3) and 2.494(3) Å are slightly longer than many of the examples presented here, but these are well within the usual range found in the literature; the two longer interactions are at 3.271(5) and 3.042(5) Å, respectively. In the second of these independent molecules, the sum of the Te-S distances is only 5.536 Å and thus, considerably shorter than 5.871 Å seen in a related literature example.[5] Figure 2 shows the intramolecular interactions of the pairs of independent molecules. As can be seen, a single sulfur atom from a dithiocarbamate ligand forms two links to two adjacent Te atoms ("short" and "long"). The distance Te(2)· · ·S(2) at 3.042(5) Å ("shorter") lies opposite the "longer" Te(2)-S(3) [2.494(3) Å] interaction at a bond angle of *ca.* 167°. Conversely, the distance Te(1)-S(3) measures 3.271(5) Å ("longer") and is found ca. 170° from the related "shorter" Te(1)-S(1) distance at 2.444(3) Å. Thus, a twelve-membered linkage of Te, S, and C atoms is assembled from the independent molecules.

Within the ligand itself, there are the expected differences in C–S bond lengths that are reflected in the coordination of sulfur;[5] in fact, three different coordination environments are observed for sulfur. The sulfur atoms bonded to Te [either S(1) or S(3)] in the "short bonds" exhibit the greatest elongation of their carbon-sulfur length to 1.749(8) Å (in both cases, and consistent with previous bonding examples), whereas the sulfur atom [S(2)], that is "more C=S in nature," shows a bond length of 1.700(8) Å, well within the ranges typically seen.[2] The "uncoordinated" C=S bonds [C(16)-S(4) 1.693(8) Å] are the strongest of the three types exhibited in the molecular structure. It should be noted that one dithiocarbamate ligand has both its sulfur atoms [S(1) and S(2)] coordinated to two different Te atoms whereas the other ligand coordinates to two tellurium atoms via a single sulfur atom, S(3). The sums of the two Te-S-C-(S)-Te bridges are 8.935 Å [Te(1)-S(1)-C(1)-S(2)-Te(2)] and 9.207 Å [Te(2)-S(3)-C(16)-S(4)-Te(1)], and this is reflected in the two very dissimilar Te-Te distances in the assembly via the S(1)-S(2) linkage the Te(1)-Te(2) distance is 5.098 Å, but through the doubly coordinated S(3) atom, the Te(1)-Te(2) distance is only 4.358 Å. With the current literature in this area, it is not possible to compare **1** with corresponding three-coordinate T-shaped molecules as these examples here represent the first T-shaped molecules containing dithiocarbamate ligands. Table II indicates that with dimethyldithiophosphate ligands typically this type of structure is found. Figure 3 shows the basic structural types of divalent Te(II) complexes discussed in this section.

TABLE II Comparison of Structurally Related Divalent Tellurium Complexes

Molecule	Ref.	Te-S (Å)	Te-S' (Å)	ΣS-Te-S (Å)	C-Te-S (°)	S-Te-S' (°)	Notes
NaphTe{dtcpyr}	This work	2.444(3)	3.271(5)	5.715	85.1(2)	170.65(11)	3-Coordinate T-shaped. Two independent molecules
NaphTe{dtcpyr}	This work	2.494(3)	3.042(5)	5.536	84.2(2)	167.23(11)	3-Coordinate T-shaped. Two independent molecules
$MeOC_6H_4Te$\{dmdtp\}	[8]	2.4435(8)	3.262(1)	5.710	94.89(8)	172.84(3)	3-Coordinate T-shaped
$EtOC_6H_4Te$\{dmdtp\}	[9]	2.4391(8)	3.309(1)	5.748	94.75(8)	172.41(3)	3-Coordinate T-shaped
$MeOC_6H_4Te$\{Mexan\}	[5]	2.4040(9)	3.4668(8)	5.871	97.24(8)	167.84(3)	Distorted square planar. Additional Te-S" at 3.622(1)Å
$EtOC_6H_4Te$\{Mexan\}	[9]	2.4040(9)	3.451(1)	5.855	96.53(9)	170.43(3)	Distorted square planar. Additional Te-S" at 3.707(1)Å
$MeOC_6H_4Te$\{Mts\}	[6]	2.387(1)	—	—	96.77(9)	—	Angular 2-Coordinate.
$EtOC_6H_4Te$\{Mts\}	[7]	2.400(1)	—	—	97.98(9)	—	Angular 2-Coordinate.

dtcpyr = dithiocarbamatopyrrolidine; dmdtp = dimethyldithiophosphate; Mexan = methylxanthate; and Mts = methylthiosulfonate.

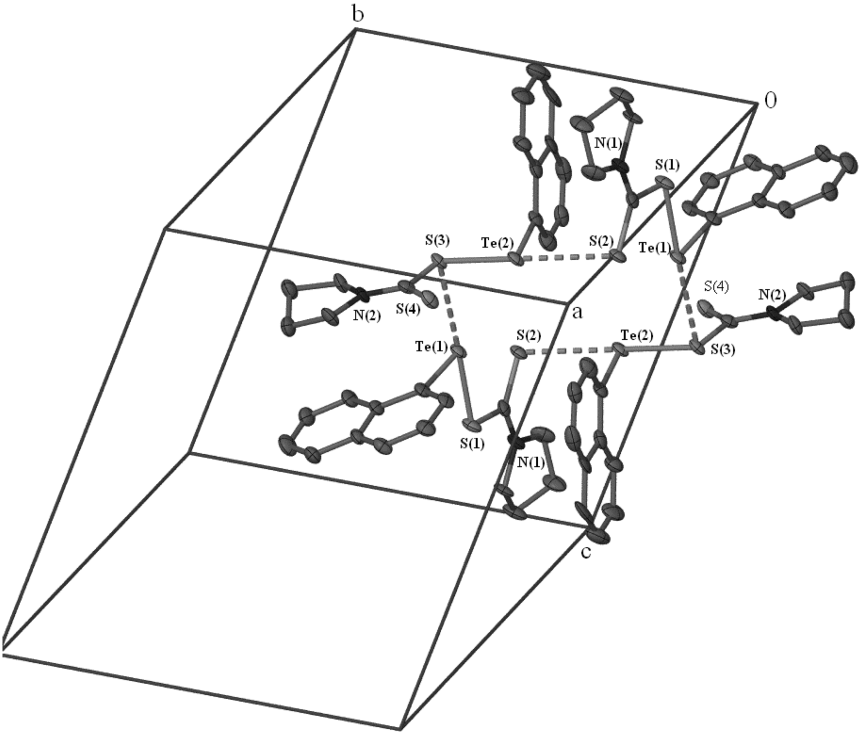
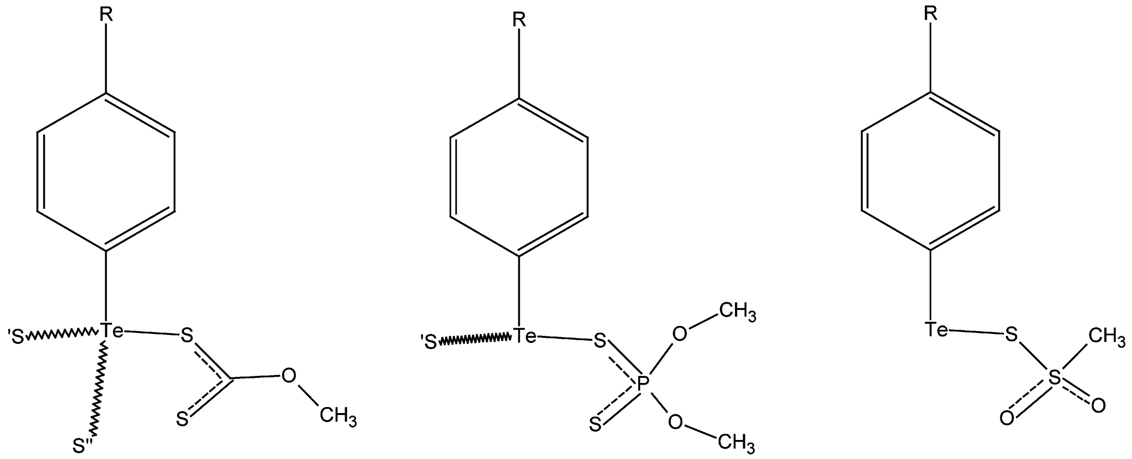


FIGURE 2 Packing diagram for **1** showing the T-shaped three-coordinate geometry of the tellurium atom.

NMR Spectroscopy

The ^{1}H and ^{13}C NMR spectra for the newly synthesized compounds show the expected signals from both the coordinated sulfur ligands, and the aromatic naphthyl group coordinated to the tellurium atom. For instance in **1**, the signals of the 1-pyrrolidine-carbodithioate protons are located at 2.10 and 3.61 ppm as multiplets. The corresponding NMR signals of the carbon atoms appear at 25 ppm and 52 ppm. The signal of the dithiocarbamato carbon atom appears well downfield at *ca.* 190 ppm, which is typical of coordination in such complexes. The other compounds display similar characteristics; in compound **2**, there are a large number of aromatic signals from the two phenyl rings of the dithiocarbamate and the naphthyl group together with a signal at 5.09 ppm resulting from the benzyl methylene hydrogen atoms. In compound **3**, the ^{13}C NMR signal of the coordinated xanthate ligand is well downfield at *ca.* 210 ppm. For all previously reported two-coordinate



R = OCH_3, OCH_2CH_3 R = OCH_3, OCH_2CH_3, $(CH)_4$ R = OCH_3, OCH_2CH_3

Distorted Square Planar (Xanthates) Three Coordinate T- Shaped (Phosphates, this work) Two Coordinate Angular (Thiosulfonates)

FIGURE 3 Structures of related molecules with two, three, and four-coordinate tellurium.

angular, "T," and distorted square planar complexes containing this type of "anionic" ligand no NMR studies were conducted. The chemical shifts are however in agreement with those reported for similar complexes with neutral thio- or selenoureas coordinated to Te(II).[1,6] The relative simplicity of the spectra and the elemental analyses confirm the 1:1 ratio of the naphthyl tellurium (ligand) formulation.

EXPERIMENTAL

General

All experiments were performed on a Schlenk line equipped with a supply of dried argon gas and a vacuum pump. Melting points were recorded on a Meltemp 4000 and are uncorrected. NMR spectra were recorded on a Bruker AMX 250 in $CDCl_3$ with TMS as internal standard unless otherwise indicated. The operating frequency of the instrument was 250 MHz for ^1H and 62.8 MHz for ^{13}C. All solvents were of commercial grade and were used as received from Fisher Chemical Co. Naphthyl tellurium trichloride was prepared according to a literature method;[7] naphthyl tellurium tribromide and the dithiocarbamate/xanthate salts were purchased from Aldrich Chemical Co. Elemental analyses were performed by Atlantic Microlab Inc. (Norcross, GA).

Synthesis of [$(C_{10}H_7)Te(S_2CNC_4H_8)$] (1)

This product can be prepared from either naphthyl tellurium trichloride or naphthyl tellurium tribromide. One of the reactions is shown here as an example. To a solution of naphthyl tellurium trichloride (0.100 g, 0.27 mmol) in tetrahydrofuran (10 mL) was added a solution of ammonium 1-pyrrolidinecarbodithioate (0.136 g, 0.83 mmol) in the same solvent (10 mL). The reaction mixture was vigorously stirred for 10 min during which time a white precipitate formed in the orange solution. After filtration, the solvent was removed in vacuo, and the orange-red oil was dissolved in methylene chloride (3 mL). Upon cooling at −20°C a crop of red crystals formed together with an insoluble white precipitate. Yield: 0.125 g, (71%); m.p.: 105–107°C. Calcd. (found) for $C_{31}H_{32}Cl_2N_2S_4Te_2$: C 42.0 (42.0); H 3.64 (3.71); N 3.16 (3.33). ^1H NMR: 2.10 [m, 4H, $N(CH_2)_2(CH_2)_2$]; 3.61 [m, 4H, $N(CH_2)_2(CH_2)_2$], 7.29–8.12 [m, 7H, arom-H]; ^{13}C NMR: 25.0 [s, $N(CH_2)_2(CH_2)_2$], 51.2 [s, $N(CH_2)_2(CH_2)_2$], 119.2, 121.6, 125.1, 126.9, 127.7, 129.3, 132.1, 136.0, 189.7 [s, CS_2-pyrrol].

Synthesis of [($C_{10}H_7$)Te($S_2COC_6H_{13}$)] (2)

To a solution of naphthyl tellurium trichloride (0.100 g, 0.27 mmol) in methanol was added a suspension of potassium hexylxanthate (0.147 g, 0.83 mmol) in the same solvent (20 mL). The reaction was warmed to 50°C for 1 h and filtered at 30°C. The solvent was removed in vacuo and the residue dissolved in methylene chloride (10 mL). Addition of *n*-hexane afforded a pale yellow microcrystalline solid. Yield: 0.105 g, 65%; m.p.: 145–147°C. Calcd. (found) for $C_{17}H_{20}OS_2Te$: C 47.3 (47.2); H 4.66 (4.70). ^{1}H NMR: 0.88 [t, $J = 6.0$ Hz, 3H, CH_3], 1.50 [m, 4H, $(CH_2)_2$], 1.88 [m, 4H, $(CH_2)_2$], 4.68 [t, $J = 6.0$ Hz, 2H, O-CH_2], 7.31–8.38 (m, 7H, naphthyl); ^{13}C NMR: 14.1 [s, CH_3], 24.5 [s, $CH_3 - CH_2$], 25.6 [s, CH_2-CH_2], 29.2 [s, $CH_2 - CH_2$], 33.0 [s, CH_2CH_2-O], 74.4 [s, O-CH_2], 122.7, 125.5, 126.2, 127.7, 129.0, 130.3, 134.2, 134.7, 210.7 [CS_2-O$(CH_2)_5CH_3$].

Synthesis of [($C_{10}H_7$)$TeS_2CN(CH_2C_6H_5)_2$] (3)

Naphthyl tellurium tribromide (0.060 g, 0.16 mmol) was dissolved in methylene chloride (20 mL). To this solution, with vigorous stirring, was added a solution of sodium dibenzyldithiocarbamate (0.135 g, 0.50 mmol) in methylene chloride (5 mL). The solution immediately became dark orange and after stirring for 1 h, a fine white precipitate was filtered out. The solution was concentrated to *ca.* 2 mL and layered with *n*-hexane. After 2 days, a microcrystalline yellow solid was collected by filtration. Yield: 0.099 g, 61%; m.p.: 188–192°C. Calcd. (found) for $C_{25}H_{21}NS_2Te$: C 57.0 (57.1); H 4.01 (4.09); N 2.66 (2.73). ^{1}H NMR: 5.09 [s, 4H, CH_2-Ph], 7.20–8.36 [m, 17H, Ph and naphthyl]; ^{13}C NMR: 55.1 [s, CH_2-Ph], 122.6, 124.6, 126.6, 127.2, 127.7, 127.9, 128.5, 129.7, 130.3, 134.1, 139.8, 195.7 [s, CS_2].

X-Ray Structure Determination

Crystal data and structure refinement parameters are shown in Table III. During recrystallization, compound **1** picked up a molecule of methylene chloride solvent (reflected in elemental analysis). Crystallographic data for **1** was collected on a crystal with dimensions 0.185 × 0.105 × 0.105 mm. Data were collected at 110 K on a Bruker X8 Apex diffractometer using MoKα radiation ($\lambda = 0.71073$ Å). The structure was solved by Direct Methods after absorption correction of the data using SADABS.[8] All of the data were processed using the Bruker AXS SHELXTL software, version 6.10.[9] Unless otherwise noted, all

TABLE III Crystal Structure and Data Refinement Parameters for Compound 1

Empirical formula	$C_{31}H_{32}Cl_2N_2S_4Te_2$
Formula weight	886.93
Crystal system / space group	Triclinic/P-1
a/Å	11.595(8)
b/Å	11.974(8)
c/Å	13.888(10)
$\alpha/^\circ$	77.809(14)
$\beta/^\circ$	65.851(18)
$\gamma/^\circ$	72.678(16)
V/Å^3	1671(2)
Z	2
D_{calc} (g/cm^3)	1.763
μ(mm^{-1})	2.181
Crystal size (mm)	$0.185 \times 0.105 \times 0.105$
Color/shape	Red/block
Temp (K)	110(2)
Theta range for collection	2.29 to 26.88
Reflections collected	23387
Independent reflections	6834
Data/restraints/parameters	6834/0/370
Goodness of fit on F^2	1.011
Final R indices [I > 2σ(I)]	$R1 = 0.0652$ w$R2 = 0.1519$
R indices (all data)	$R1 = 0.1054$ w$R2 = 0.1733$
Largest difference peak/hole	1.845/−2.356 e/A^3

non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions.

SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis of compound **1** has been deposited at the Cambridge Crystallographic Data Center (CCDC number 620510). Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223-336033; email: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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