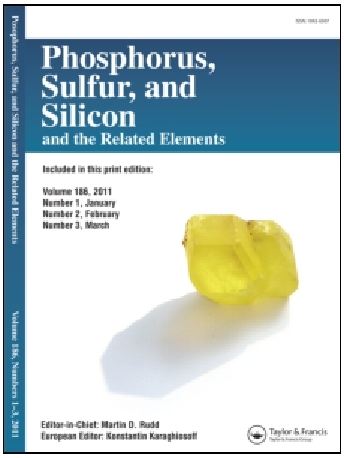

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Synthesis and Characterization of Complexes of Te(IV) with Sulfur and Selenium Containing Ligands: Crystal and Molecular Structure of Trichloro(4-methoxyphenyl)tellurium(IV)· N -methylbenzothiazole-2-(3H)-thione

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SYNTHESIS AND CHARACTERIZATION OF COMPLEXES OF TE(IV) WITH SULFUR AND SELENIUM CONTAINING LIGANDS: CRYSTAL AND MOLECULAR STRUCTURE OF TRICHLORO(4-METHOXYPHENYL)-TELLURIUM(IV)·*N*-METHYLBENZOTHIAZOLE-2-(*3H*)-THIONE

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We report the synthesis and characterization of two new complexes of trichloro(4-methoxyphenyl)tellurium(IV) with N-*methylbenzothiazole-2-(*3H*)-thione (**1**) and* N-*methylbenzothiazole-2-(*3H*)-selone (**2**). Both are obtained as air-stable complexes by the addition of a 1:1 molar ratio of the substituted tellurium(IV) trichloride with the appropriate ligand in tetrahydrofuran under an atmosphere of dry nitrogen. Both (**1**) and (**2**) have been characterized by ^1H and ^{13}C NMR spectroscopy, elemental analysis, and, in the case of (**1**), by a single crystal x-ray diffraction study. The molecular structure of (**1**) shows an approximately square-based pyramidal structure with one short Te—Cl bond [2.388(2)Å]* trans *to a very long Te—S linkage [2.883(2)Å]. A comparison with the related structures of some heavy main group elements is included.*

Keywords: Selone; tellurium (IV) complex; thione; *trans* influence; x-ray structure

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INTRODUCTION

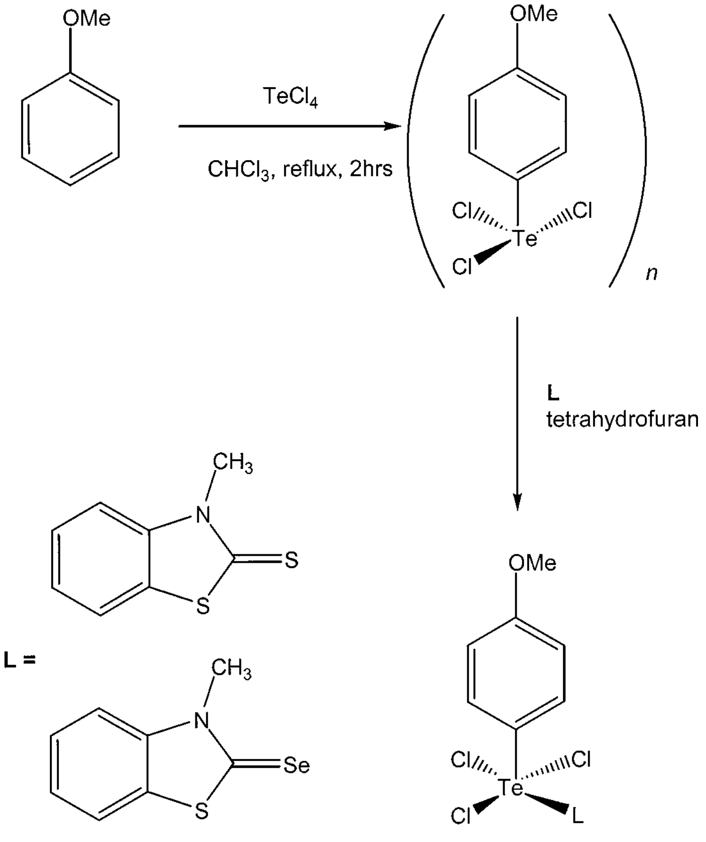
There are several reports of the synthesis and characterization of five coordinate complexes of the type $ArTeX_3(L)^{1-3}$ (where Ar = aryl group, X = halogen, L = Se/S coordinated ligand) but only a few of these have been studied by X-ray diffraction to establish their geometries and bonding characteristics.[4,5] We wanted to investigate how two little studied ligands would react with an aryl tellurium(IV) chloride derivative. Trichloro(4-methoxyphenyl)tellurium(IV) is relatively straightforward to prepare and has a good NMR handle for characterization of its complexes.

We have shown in previous studies that *N*-methylbenzothiazole-2-(*3H*)-selone (*L*) forms a stable complex with tellurium(II), in the compound PhTeBr(*L*) whose structure was established by x-ray crystallography to be "T-shaped."[6] Work by DeVillanova et al.[7,8] and Pritchard et al.[9,10] with these, and closely related ligands has revealed that the heteroatom of the C=S/Se linkage can be reacted with halogens to form an extensive and interesting series of charge transfer complexes. There are only two reports in the literature of these, or related ligands being coordinated to tellurium however. In both papers, 2:1 ligand:tellurium tetrachloride adducts were formed, with an octahedral geometry and the ligands occupying the *trans* positions.[11,12] Mandak et al. report that the reaction of tellurium tetrachloride with two equivalents of a large variety of thiones in dioxane or tetrahydrofuran form $TeCl_4L_2$ complexes in moderate to high yields (50–90%).[11] They structurally characterized two such molecules, *trans*-$TeCl_4L_2$ (L = benzothiazolethione)[12] and *cis*-$TeCl_4L_2$ (L = benzimidazolethione).[13]

The structural chemistry of complexes of tellurium (IV) with sulfur and selenium containing ligands has been well reviewed in recent years[14,15] but to our knowledge, there are no structural reports of molecules of the type $RTeCl_3{\cdot}L$ (L = S donor ligand; R = 4-CH_3OPh). There are two reports of thiocyanate ions being involved in weak secondary bonding to Ph_3Te, namely in the structures of $[Ph_3Te(SCN)]$ and $[\{Ph_2Te(SCN)\}_2O]$.[16,17] There have been several published papers over the past 10 years that have dealt with the addition of trichloro(4-methoxyphenyl)tellurium(IV) to various substituted alkynes[18] because vinylic tellurides are becoming more important as versatile synthetic reagents.[19,20] It should be noted that the usual products of a reaction between $RTeX_3$ and a thiourea ($S{=}C(NR_2)_2$ (R=H or alkyl) are RTe(tu)X, a three coordinate, Te(II) derivative.[21] However, when the thioureas used are cyclic (e.g., benzimidazolethione[12]) then there is a tendency for the Te(IV) oxidation state to remain stable.[22]

EXPERIMENTAL

Trichloro(4-methoxyphenyl)tellurium(IV) was prepared according to the literature method by refluxing tellurium tetrachloride with anisole in dry chloroform.[23] *N*-methylbenzothiazole-2-(*3H*)-thione and *N*-methylbenzothiazole-2-(*3H*)-selone were purchased from Aldrich Chemical Co. and recrystallized from methylene chloride prior to use. Anisole and tellurium (IV) chloride were purchased from Acros and used as supplied. All solvents were dried over the appropriate drying agents and distilled from an atmosphere of nitrogen prior to use. Elemental analyses were performed by Atlantic Microlab. Inc. (Norcross, GA). ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR400 spectrometer running at 400 MHz (^{1}H) and 100 MHz (^{13}C) at Iowa State University and are referenced to tetramethylsilane at 0 ppm. Scheme 1 outlines the general reaction that was used. Melting points are uncorrected.



SCHEME 1 Outline of the synthesis of $CH_3OPhTeCl_3{\cdot}L$.

Synthesis of (1). To a solution of trichloro(4-methoxyphenyl)-tellurium(IV) (0.30 g, 0.88 mmol) dissolved in tetrahydrofuran (20 mL) was added a solution of *N*-methylbenzothiazole-2-(*3H*)-thione (0.159 g, 0.88 mmol) in the same solvent (10 mL). The reaction was allowed to stir at room temperature for 1 h under an atmosphere of nitrogen during which time a yellow precipitate formed. The solvent was removed in vacuo and the solid was dissolved in hot tetrahydrofuran and filtered. A yellow microcrystalline solid formed (0.40 g, 87% yield).

Elemental Analysis: Required for $C_{15}H_{14}Cl_3N_1O_1S_2Te_1$: C 34.49%; H 2.70%; Found: C 34.56%; H 2.68%. ^{1}H NMR (400 MHz, CD_2Cl_2): 3.89 (s, O—CH_3), 4.02 (s, N—CH_3), 7.07 (d, $J = 8.8$ Hz, 2H) 7.54–7.79 (m, 4H), 8.48 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): 186.8 (*C*=S), 162.6 (*C*1), 145.1, 142.3, 135.6, 127.4, 126.8, 124.7, 121.0, 116.1, 112.6, 56.1 (O—*C*H_3), 34.8 (N—*C*H_3). m.p.: 96–98°C.

Crystals suitable for single crystal x-ray diffraction studies were grown by layering a CH_2Cl_2 solution of (**1**) with *n*-hexane and storing for 1 week at −20°C.

Synthesis of (2). To a solution of *N*-methylbenzothiazole-2-(*3H*)-selone (0.10 g, 0.44 mmol) dissolved in tetrahydrofuran (10 mL) was added a solution of trichloro(4-methoxyphenyl)tellurium(IV) (0.15 g, 0.44 mmol) in tetrahydrofuran (10 mL). The reaction was stirred overnight at room temperature under an atmosphere of nitrogen in the dark. A deep red precipitate formed during this time. The precipitate was filtered off and washed with *n*-hexane (2 × 10 mL).

Elemental Analysis: Required for $C_{15}H_{14}Cl_3N_1O_1S_1Se_1Te_1$: C 31.65%; H 2.48%; Found: C 31.78%; H 2.56%. ^{1}H NMR (400 MHz, CD_2Cl_2): 3.86 (s, O—*C*H_3), 3.99 (s, N—CH_3), 7.11 (d, $J = 8.8$ Hz, 2H), 7.56–7.77 (m, 4H), 8.45 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2) 184.9 (C=Se), 162.6 (C1), 145.3, 142.5, 135.9, 128.1, 127.0, 124.8, 121.1, 116.1, 112.4, 56.3 (O—*C*H_3), 33.7 (N—*C*H_3). Recrystallization from warm tetrahydrofuran yielded 0.16 g (64%) of orange-red microcrystals of (**2**). m.p.: 60–62°C.

Structure Determination: Crystal data are given in Table I, together with some data collection and refinement details. Diffracted intensities were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα x-radiation. Final unit cell dimensions were determined from the setting angles of 25 accurately centered reflections. The data were corrected for Lorentz, polarization, and x-ray absorption effects, the latter using a numerical method based on the measurements of crystal faces.[24] The structure was solved by direct methods and successive difference Fourier syntheses were used to locate all non-hydrogen atoms using SHELXTL version 5.03.[24]

TABLE I Crystal Data and Structure Refinement Parameters for (**1**)

Empirical formula	$C_{15}H_{14}Cl_3NOS_2Te$
M	522.34
Crystal system	Triclinic
Space group	P-1
Crystal habit	Yellow blocks
a/Å	8.9132(8)
b/Å	9.2340(4)
c/Å	12.547(2)
α/°	71.007(8)
β/°	83.001(10)
γ/°	70.005(6)
T/K	293(2)
V/$Å^3$	917.5(2)
Z	2
D_c Mg/m^3	1.891
μ/mm^{-1}	2.287
F(000)	508
θ range/°	1.72–25.07
hkl ranges	0/10, −10/10, −14/14
Total no. reflections	3601
Independent reflections $I > 2\sigma(I)$	2423
Data (all)/parameters	3237/208
Final R indices	
R_1 (obs/all data)	0.0484/0.0748
wR_2 (obs/all data)	0.0975/0.1063
Largest peak and hole/e A^{-3}	1.268/−1.109
Goodness of Fit on F^2	1.095

Refinements were made by full-matrix least squares on all F^2 data using SHELXL-97.[25] Anisotropic thermal parameters were included for all non-hydrogen atoms. All hydrogen atoms were included in calculated positions and allowed to ride on their parent carbon atoms with fixed isotropic thermal parameters [$U_{iso}(H) = 1.2U_{iso}(C)$ or $U_{iso}(H) = 1.5U_{iso}(C)$ for methyl protons]. The methyl group corresponding to C(15) was refined with an ideally disordered model, that is, with two sets of hydrogen atoms rotated from each other by 60 degrees. The occupation factors for both sets of hydrogens were fixed at 0.5. Final electron density maps indicated a small residual peak (1.27 $e^-Å^{-3}$) in the vicinity of the Te atom, most likely due to an inability to completely correct the effects of x-ray absorption. All calculations were carried out on Dell PC computers.

Some selected bond lengths and angles for complex (**1**) are listed in Table II. The molecular structure of (**1**) is shown in Figure 1 and the

TABLE II Selected Bond Lengths (Å) and Angles (°) for (**1**)

Te—C(1)	2.122(6)	S(1)—C(8)	1.683(8)
Te—Cl(2)	2.388(2)	S(2)—C(8)	1.719(8)
TeCl(3)	2.471(2)	C(8)—N	1.345(9)
Te—Cl(4)	2.534(2)	N—C(15)	1.468(9)
Te—S(1)	2.883(2)	C(9)—C(14)	1.387(10)
C(1)—Te—Cl(2)	92.5(2)	Cl(3)—Te—S(1)	78.11(6)
C(1)—Te—Cl(3)	89.6(2)	Cl(1)—Te—S(1)	102.82(6)
C(1)—Te—Cl(1)	88.3(2)	C(8)—S(1)—Te	116.8(3)
Cl(2)—Te—S(1)	167.10(6)	C(1)—Te—S(1)	85.1(2)
Cl(1)—Te—Cl(3)	177.64(8)	N—C(8)—S(2)	111.3(6)

crystal packing is shown in Figure 2. Supplementary data including a full set of bond lengths, angles, and atomic coordinates are available from the Cambridge Crystallographic Data Center (12 Union Road, Cambridge, CB2 1EZ) upon request.

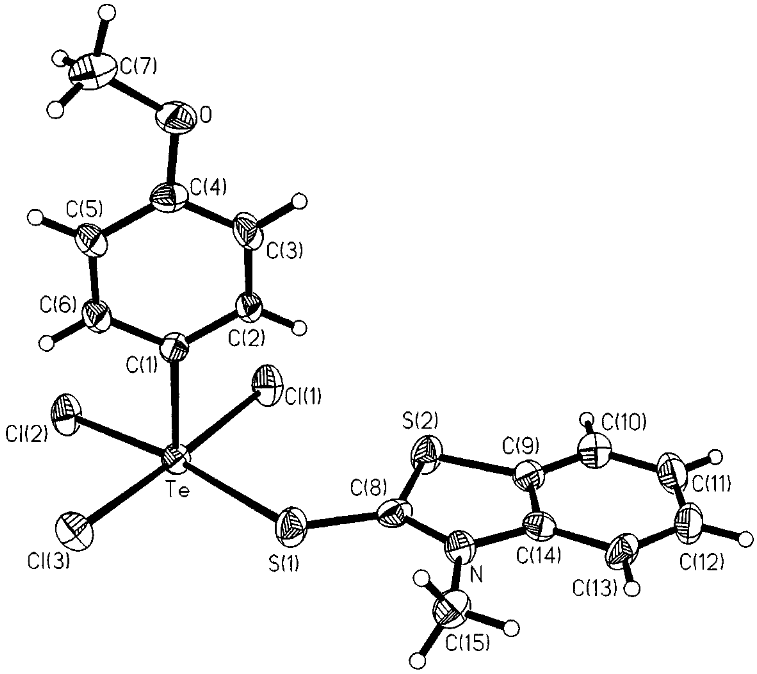


FIGURE 1 Perspective projection of the molecule (**1**). The thermal displacement ellipsoids are given at the 40% level.

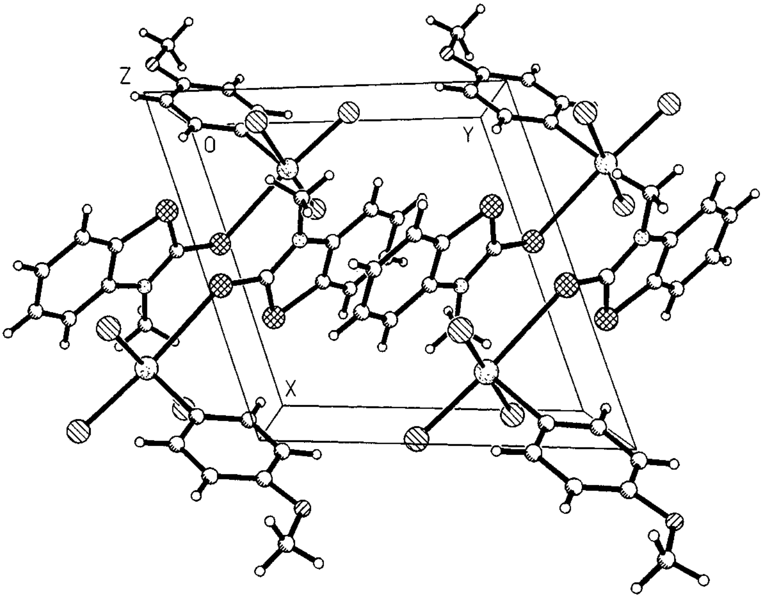


FIGURE 2 Perspective packing of the crystal structure of (**1**).

RESULTS AND DISCUSSION

Addition of a molar equivalent of the fused-ring heterocycles, *N*-methylbenzothiazole-2-(*3H*)-selone and *N*-methylbenzothiazole-2-(*3H*)-thione to a solution of trichloro(4-methoxyphenyl)tellurium(IV) yields two new adducts in high yield.

The molecular formulae of these complexes have been confirmed by elemental analysis and nuclear magnetic resonance spectroscopy.

The ^{1}H and ^{13}C NMR spectra feature signals for the methoxyphenyl group on the tellurium atom and the ligands themselves. The changes in chemical shift of the free ligands in both the ^{1}H and ^{13}C spectra[26] upon complexation are slight as might be expected from the formation of these relatively weakly bonded adducts. This was noted in the ^{1}H and ^{13}C spectra of PhTeBr(*L*) (*L* = *N*-methylbenzothiazole-2-(*3H*)-selone).[6] It appears that in the ^{13}C NMR spectra of (**1**) and (**2**), only the *C*=X (X=S, Se) carbon changes chemical shift to any significant degree (approx. 3–4 ppm).

Molecular Structure: The molecular structure of (**1**) reveals an approximately square based pyramidal geometry around the central tellurium atom with a seemingly inactive lone pair of electrons. The sixth coordination position is apparently occupied by a long range interaction in the direction of the ligand's benzene π electron system from a neighboring molecule. The Cl—Te—Cl bond angles are close to 90 degrees as are those in the two recently reported [(4-MeOPhTeCl$_3$)$_2$(L)] structures (L = μ-Ph$_2$P(S)CH$_2$CH$_2$P(S)Ph$_2^4$, μ-^{i}PrP(S)-Fc-P(S)^{i}Pr$_2$).[5]

There is some deviation away from linearity across the Cl(2)—Te—S(1) linkage (167.10(6)°) presumably as a result of steric interaction of the ligand with the planar TeCl$_3$ moiety. The long Te—S(1) bond (2.883(2)Å) is *trans* to a short Te—Cl(2) bond (2.388(2)Å) with the Te—S bond being considerably longer than, and the *trans* Te—Cl bond being considerably shorter than, those previously reported in CH$_3$OPhTeCl$_3$(S) complexes. In the bis(diphenylphosphino)ethane disulfide structure the average Te—S length is 2.797Å and the corresponding average *trans* Te—Cl bond is 2.432Å. In the ferrocenyl bridged complex, again the average Te—S distance is 2.723Å and the average *trans* Te—Cl distance is 2.419Å. The weak *trans* influence of the thione ligand, which is clearly a relatively weak electron donor, especially when compared to thioureas,[14,15] causes the short distance observed for Te—Cl(2). Inspection of the Te—C(1) distance in the aryl ring reveals a distance of 2.122(6)Å, close to the norm for such bonds.[27] The C=S bond length of the *N*-methylbenzothiazole-2-(*3H*)-thione ligand is 1.683(8)Å, considerably longer than that reported for the free ligand at 1.63Å. It should be pointed out, however, that the early nature (two-dimensional x-ray diffraction) of this crystallographic investigation does cast some uncertainty on the exact C=S bond length.[28] As expected, upon coordination to the ArTeCl$_3$ molecule, there is an increase in the C=S bond length and a subsequent shortening of the N—C(=S)—S bonds of the pentaatomic ring. This is also observed in the x-ray structures of *N*-methylbenzothiazole-2-(*3H*)-thione with halogens. For instance, in the bis(*N*-methylbenzothiazole-2-(*3H*)-thione)iodinium cation reported by Devillanova,[7,8] a C=S bond length of 1.694(7)Å is observed, close to the value in this present study. In the related adducts of tellurium tetrachloride,[12,13] the structure of *trans*-TeCl$_4$L$_2$ (L = benzothiazolethione) reveals an octahedral geometry with, of course, no *trans* effect visible on the Te—Cl bond lengths. The Te—S distance is 2.704(2)Å and the C=S distance is 1.711(7)Å, somewhat longer than in complex (**1**). This is indicative of the stronger Te—S bonding present.

Crystal Packing and Molecular Interactions

The crystal packing is shown in Figure 2 and the projection of the dimers of (**1**) is shown in Figure 3.

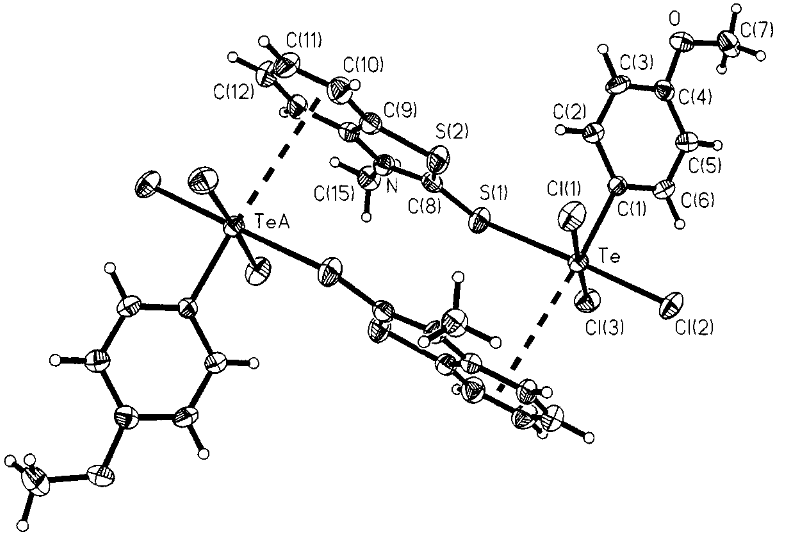


FIGURE 3 Perspective projections of the dimers of (**1**) by an inversion center. Close contacts Te· · ·C are shown by dashed lines.

Molecules of (**1**) are joined together in the crystals into centrosymmetric dimers in an unusual manner [symmetry transformation $(1 - x)$, $-y$, $(1 - z)$].

The additional coordination occurs as an η-coordination from the 6 membered planar ring of the *N*-methylbenzothiazole-2-(*3H*)-thione ligand. The distance between the Te atom and the centroid of [C(9)-C(10)-C(11)-C(12)-C(13)-C(14)] is 3.518Å with a C(1)-Te-(Centroid) angle of 172.9°. This is considerably shorter than the closest interaction found in one of the independent molecules of PhTeBr(*L*) ($L =$ *N*-methylbenzothiazole-2-(*3H*)-selone).[6] The angles between Cl/S—Te-(Centroid) range from 87.0–95.2°.

This type of secondary coordination in tellurium complexes was also noted in the crystal structure of bromobis(dimethyldithiocarbamato-*S,S′*)(4-methoxyphenyl)tellurium(IV)[29] where a the π system of a dithiocarbamate group of an neighboring molecule coordinates to an empty position in the Te(IV) coordination sphere *trans* to the aryl ligand (C· · ·Te· · ·C 170.2(1)° and Te· · ·C 3.688Å) in much the same way as seen in this work.

REFERENCES

[1] K. K. Verma, *Phosphorus, Sulfur, Silicon*, **148,** 227 (1999).
[2] T. N. Srivastava, R. C. Srivastava, and M. Srivastava, *Ind. J. Chem.*, **21,** 539 (1982).

[3] K. J. Wynne and P. S. Pearson, *Inorg. Chem.*, **10,** 2735 (1971).

[4] J. Novosad, K. W. Törnroos, M. Necas, A. M. Z. Slawin, J. D. Woolins, and S. Husebye, *Polyhedron*, **18,** 2861 (1999).

[5] S. Husebye, J. Novosad, and M. Necas, *J. Organomet. Chem.*, **623,** 124 (2001).

[6] M. D. Rudd, S. Husebye, and S. V. Lindeman, *Acta Chem. Scand.*, **50,** 759 (1996).

[7] F. Demartin, P. Deplano, F. A. Devillanova, F. Isaia, V. Lippolis, and G. Verani, *Inorg. Chem.*, **32,** 3694 (1993).

[8] M. Arca, F. Demartin, F. A. Devillanova, A. Garau, F. Isaia, V. Lippolis, S. Pidula, and G. Verani, *Polyhedron*, **17,** 3111 (1998).

[9] P. D. Boyle, W. I. Cross, S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard, and S. J. Teat, *J. Chem. Soc., Dalton Trans.*, 2845 (1999).

[10] P. D. Boyle, S. M. Godfrey, and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 4245 (1999).

[11] D. Mandak, W. Schnabel, and G. Klar, *J. Chem. Res. Synop.*, **3,** 74 (1984).

[12] K. von Deuten, W. Schnabel, and G. Klar, *Cryst. Struct. Commun.*, **8,** 221 (1979).

[13] K. von Deuten, W. Schnabel, and G. Klar, *Cryst. Struct. Commun.*, **8,** 679 (1979).

[14] S. Husebye, in *Proceedings of the Fourth International Conference on the Organic Chemistry of Selenium and Tellurium* (The University of Aston, Birmingham, UK, 1983), p. 298.

[15] S. Husebye, *Phosphorus and Sulfur*, **38,** 271 (1988).

[16] J.-S. Lee, D. D. Titus, and R. F. Ziolo, *Inorg. Chem.*, **16,** 2487 (1977).

[17] C. S. Mancinelli, D. D. Titus, and R. F. Ziolo, *J. Organomet. Chem.*, **140,** 113 (1977).

[18] G. Zeni, A. Chieffi, R. L. O. R. Cunha, J. Zuckerman-Schpector, H. A. Stefani, and J. V. Comasetto, *Organometallics*, **18,** 803 (1999).

[19] J. V. Comasetto, *Rev. Heteroatom Chem.*, **9,** 61 (1993).

[20] J. V. Comasetto, L. W. Ling, N. Petragnani, and H. A. Stefani, *Synthesis*, 373 (1997).

[21] K. J. Irgolic, *The Organic Chemistry of Tellurium* (Gordon and Breach, New York, 1974), chap. 6, pp. 59.

[22] S. Husebye and K. W. Törnroos, *Acta Crystallogr.*, **C56,** 1242 (2000).

[23] G. T. Morgan and R. E. Kellett, *J. Chem. Soc.*, 1080 (1926).

[24] SHELXTL (Version 5.03), Bruker AXS, Madison WI (1995).

[25] G. M. Sheldrick, University of Göttingen, Germany (1997).

[26] I. W. J. Still, N. Plavac, D. M. McKinnon, and M. S. Chauhan, *Can. J. Chem.*, **54,** 1660 (1976).

[27] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. II*, S1 (1987).

[28] P. J. Wheatley, *J. Chem. Soc.*, 4379 (1961).

[29] S. Husebye, S. Kudis, and S. V. Lindeman, *Acta Crystallogr.*, **C52,** 429 (1996).