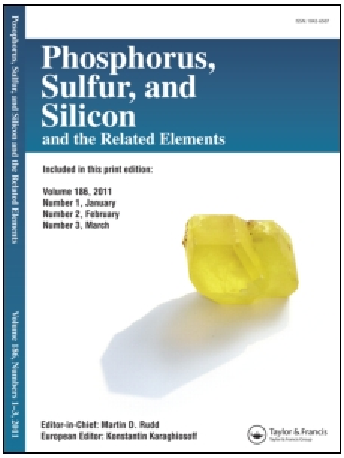

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PALLADIUM AND PLATINUM COMPLEXES FROM METHYL(2-THIENYL) CHALCOGENIDES AND BIS(2-THIENYL) DICHALCOGENIDES

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The preparation of [$M(C_4H_3SECH_3)_2Cl_2$] (M = Pd, Pt; E = Se, Te) and [$Pd_6Te_6(C_4H_3S)_2(PPh_3)_6Cl_2$] from methyl(2-thienyl)chalcogenides and bis(2-thienyl) ditelluride is reported. The products are identified and characterized by X-ray crystallography and by ^{77}Se and ^{125}Te NMR spectroscopy.

Keywords: Methyl(2-thienyl) chalcogenides, bis(2-thienyl) ditelluride, palladium and platinum complexes, X-ray crystallography, NMR spectroscopy

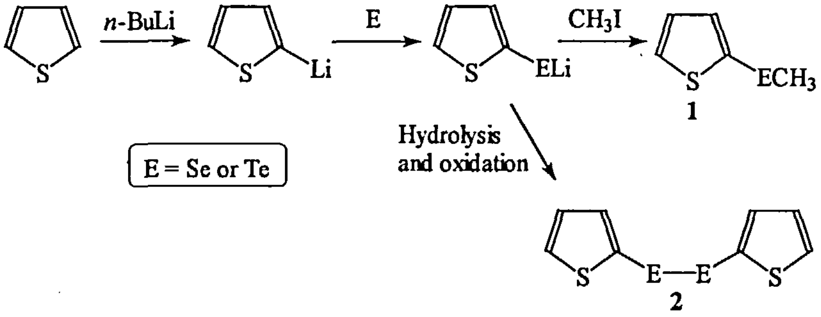
INTRODUCTION

Transition metal complexes with ligands containing chalcogen elements exhibit a rich structural chemistry and they have attracted attention in recent years because of their potential utility in materials chemistry.[1] For instance, Brennan *et al.*[2] have shown that molecular palladium telluride complexes provide a convenient low-energy route to solid state tellurides that can serve as catalysts precursors for specific purposes.

In this work we report the synthesis and characterization of some palladium and platinum complexes derived from 2-thienyl monochalcogenides and ditelluride. In addition to the expected dinuclear palladium complex [3] the latter ligand produced a cyclic hexanuclear species with the Pd-Te framework analogous to that reported earlier by Brennan *et al.*[2]

EXPERIMENTAL

The chalcogen-containing thienyl ligands were prepared by applying the method described by Engman and Cava.[4]



The preparation of the palladium and platinum complexes from the ligands 1 and 2 is shown below:

$$\mathbf{1} \quad + \quad [M(PhCN)_2Cl_2] \longrightarrow [M(C_4H_3SECH_3)_2Cl_2]$$

$$\boxed{E = Se\ or\ Te;\ M = Pd\ or\ Pt}$$

$$\nearrow [Pd_2Te_4(C_4H_3S)_4(PPh_3)_2]$$

$$[Pd(PPh_3)_2Cl_2] \xrightarrow[PPh_3]{N_2H_4(aq)} \xrightarrow{\mathbf{2}} [Pd_6Te_6(C_4H_3S)_2(PPh_3)_6Cl_2]$$

The crystal structure determinations of $[Pd\{(C_4H_3S)ECH_3\}_2Cl_2]$ and $[Pd_6Te_6(C_4H_3S)_2(PPh_3)_6Cl_2]$ were carried out at room temperature.

RESULTS AND DISCUSSION

[M{(C_4H_3S)ECH_3}$_2$$Cl_2$] (M = Pd, Pt; E = Se, Te)

The ^{125}Te NMR spectrum of the [Pd{(C_4H_3S)TeCH_3}$_2$$Cl_2$] solution indicates that both *cis* and *trans* isomers are present in the solution. Two resonances at 421 and 429 ppm are observed (see Table I) and they can be assigned to the *cis* and *trans* isomers.[5] Upon crystallization we obtained the *cis* form (see Figure 1).

The analogous selenium complex crystallizes in the *trans* form.[6] It is worth noting that only one ^{77}Se resonance is observed in the NMR spectrum of the complex (Table I). It implies that in contrast to the tellurium complex, only the *trans* isomer is present in solution. The smaller size of the selenium atom compared to that of the tellurium atom is likely render the formation of *cis*-[Pd{(C_4H_3S)SeCH_3}$_2$$Cl_2$] less favourable than in the case of the tellurium complex.

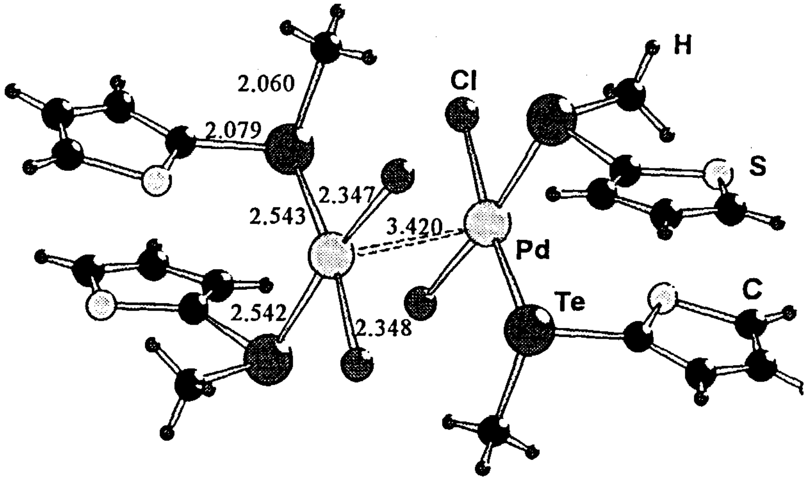


FIGURE 1. [Pd{(C_4H_3S)TeCH_3}$_2$$Cl_2$]. Crystal data: a = 23.698 (4) Å, b = 14.259 (3) Å, c = 10.820 (2) Å, β = 114.410 (10) °, V = 3329.4 (11) Å^3, Sp. Gr. $C2/c$, Z = 8, R = 0.0536

TABLE I ^{77}Se and ^{125}Te NMR data of $(C_4H_3S)ECH_3$ (E = Se, Te) and their palladium and platinum complexes

Compound	δ(^{77}Se) / ppm	δ(^{125}Te) / ppm
$(C_4H_3S)SeCH_3$	133	
$(C_4H_3S)TeCH_3$		218
$[Pd\{(C_4H_3S)SeCH_3\}_2Cl_2]$	233	
$[Pd\{(C_4H_3S)TeCH_3\}_2Cl_2]$		421 429
$[Pt\{(C_4H_3S)SeCH_3\}_2Cl_2]$	231 [a]	

[a] $^1J_{PtSe}$ = 450 Hz

$[Pd_6Te_6(C_4H_3S)_2(PPh_3)_6Cl_2]$

$[Pd_6Te_6(C_4H_3S)_2(PPh_3)_6Cl_2]$ has a similar Pd-Te framework that has previously been observed by Brennan *et al.*[2] for the product $[Pd_6Te_6(Et_3P)_8]$ from the reaction of $[Pd(PPh_3)_4]$ with Et_3PTe in excess of Et_3P. All palladium atoms in both complexes show a square planar coordination with all Pd-Te bond lengths and bond angles very similar. There are chemical differences, however. The bridging μ-tellurium atoms in the complex of Brennan *et al.*[2] are best described as Te^{2-} whereas in our complex the ligand in the corresponding site is $(C_4H_3S)Te^-$. In both complexes all palladium atoms show a formal oxidation state +II. The electron count in our complex is balanced by two Cl^--ligands, since in the complex of Brennan *et al.*[2] there are only electrically neutral ligands in addition to tellurium.

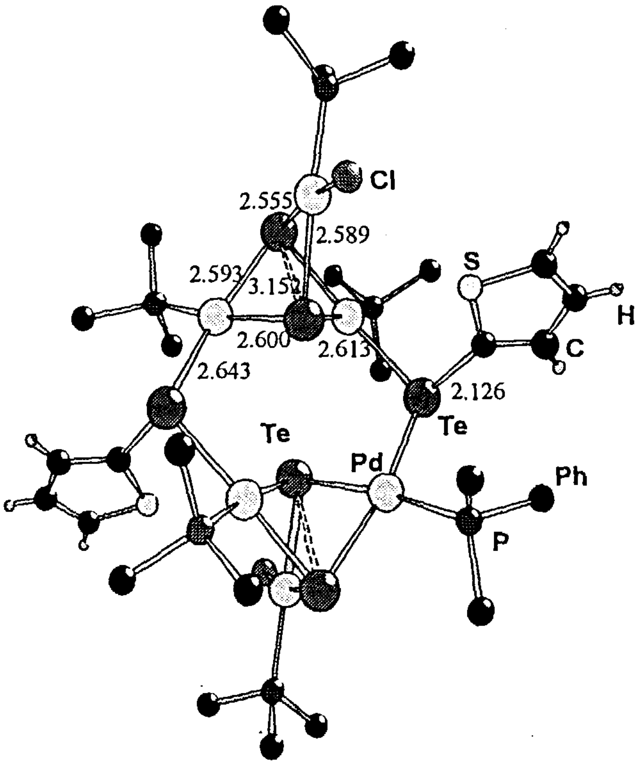


FIGURE 2. $[Pd_6Te_6(C_4H_3S)_2(PPh_3)_6Cl_2]$. Crystal data: $a = 22.538$ (5) Å, $b = 22.145$ (4) Å, $c = 23.920$ (5) Å, $\beta = 104.42$ (3) °, $V = 11562.46$ Å^3, Sp. Gr. $C2/c$, $Z = 8$, $R = 0.0482$

An interesting feature in the two Pd_6Te_6 complexes are the short distances between the two μ_3-Te atoms (see Figure 2). In our complex this distance (Te1···Te2) is 3.15 Å that is significantly shorter than the sum of the van der Waal's radii of two tellurium atoms (4.20 Å). In $[Pd_6Te_6(Et_3P)_8]$ the corresponding distance is somewhat longer (3.29 Å).[2] The situation is analogous in $[Pd_3S_2Cl_2(PPh_3)_4]$ and

$[Pd_3Se_2(SeSiMe_3)_2(PPh_3)_4]$.[7] The μ_3-S distance (S1···S2) is 2.93 Å and the μ_3-Se distance (Se1···Se2) 3.08 Å both well shorter than the sums of the corresponding van der Waals' radii (3.60 and 3.80 Å, respectively).

The Pd_6Te_6 framework seems to be rather stable. In the case of $[Pd_6Te_6(Et_3P)_8]$ [2] the excess of Et_3P displaces PPh_3 from palladium and the facile decomposition of Et_3PTe provides Te^{2-}. In our complex (4) the situation is slightly different. The reversible decomposition of the starting palladium complex provides free PPh_3 that will cleave bis(2-thienyl) ditelluride and the resulting equilibrium mixture contains both RTe^- and Ph_3PTe that again provides Te^{2-}.

$$RTeTeR + PPh_3 \rightleftharpoons R\overset{\ominus}{Te} + Ph_3\overset{\oplus}{P}TeR \rightleftharpoons RTeR + Ph_3PTe$$

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References

[1.] L.C. Roof and J.W. Kolis, *Chem. Rev.*, **93** 1037 (1993).
[2.] J.G. Brennan, T. Siegrist, S.M. Stuczynski, and M.L. Steigerwald, *J. Am. Chem. Soc.* **112** 9233 (1990).
[3.] L.Y. Chia and W.R. McWhinnie, *J. Organomet. Chem.* **148** 165 (1978).
[4.] L. Engman and M.P. Cava, *Organometallics*, **1** 470 (1982).
[5.] E.G. Hope and W. Levason, *Coord. Chem. Rev.*, **122** 109 (1993).
[6.] R. Oilunkaniemi, R.S. Laitinen, J. Pursiainen, and M. Ahlgren, in preparation.
[7.] D. Fenske, H. Fleischer, H. Krautscheid, and J. Magull, *Z. Naturforsch.*, **45b** 127 (1990).