

Unprecedented Coordination Environment in Poly- $\{\mu$ -bis(methylthienyltellane)(chlorido)(thienyl)platinum(II) $\}$

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The reaction of methylthienyltellane TeMeTh (Th = thienyl, C₄H₃S) and [PtCl₂(NCPh)₂] affords in addition to the main product [PtCl₂(TeMeTh)₂], also small amounts of yellow crystalline [PtCl(Th)(TeMeTh)₂]_n that exhibits unprecedented quasi-octahedral coordination environment around platinum(II). There are four weak Pt-Te bonds of 2.898(1) and 3.419(1) Å forming an approximate square-plane the quasi-octahedral coordination being completed by a Pt-Cl bond of 2.400(2) Å and a Pt-C bond of 1.998(8) Å of a discrete thienyl ring. The TeMeTh acts as a bridging ligand. Tellurium shows a distorted tetrahedral coordination and the weak Pt-Te bonds can be rationalized in terms of sharing one tellurium electron lone-pair by two adjacent platinum centers. The closest contacts between the polymer chains involve thienyl rings.

Key words: Poly $\{\mu$ -bis(methylthienyltellane)(chlorido)-(thienyl)platinum(II) $\}$, Crystal Structure, Quasi-Octahedral Coordination

Introduction

During recent years, a number of mononuclear telluroether complexes of platinum(II) has been prepared and structurally characterized (for two recent reviews, see Refs. [1–2]). In the solid state, they generally form discrete complexes with square-planar coordination around the metal. In addition, many of the complexes show weak tellurium-halogen contacts linking the complexes together as dimeric units [3–5] or as continuous chains [6]. Telluroether complexes of palladium(II) exhibit a similar tendency [1, 2]. By contrast, the platinum(IV) and palladium(IV) complexes gener-

ally show octahedral coordination, as exemplified by [PtX(Me)₂{Se(Me)C₂H₄SeMe}] (X = Cl, I) [7].

We have recently reported the preparation of [PtCl₂(TeMeTh)₂] as a part of a systematic study of the structural and bonding trends in the series [MCl₂(ERR')₂] (M = Pd, Pt; E = Te, Se; R = Me; R' = Th, C₄H₃S or Fu, C₄H₃O) [3]. Whereas the ¹²⁵Te and ¹³C NMR spectra of the main product in the reaction solution could be assigned in terms of [PtCl₂(TeMeTh)₂], the crystallized bulk material was microcrystalline and consequently no single crystal X-ray structure could be determined. However, in some cases the reaction also afforded a very minor side product. The determination of the X-ray structure of these crystals revealed them to be polymeric [PtCl(Th)(TeMeTh)₂]_n with an unprecedented quasi-octahedral coordination environment around platinum(II).

Experimental Section

[PtCl(Th)(TeMeTh)₂]_n was obtained during the preparation of [PtCl₂(TeMeTh)₂] from methylthienyltellane and [PtCl₂(NCPh)₂] as a side product (for preparative details, see ref. [3]). It was isolated as few yellow crystals from the filtrate that was obtained upon precipitation of the main product by hexane and washing the precipitate with small further aliquots.

Crystal data for C₁₄H₁₅S₃ClTe₂Pt. FW = 765.18, yellow plates, monoclinic, C2/c, *a* = 16.534(3), *b* = 13.776(3), *c* = 9.653(2) Å, β = 112.22(3)°, *U* = 2035.3(7) Å³; *Z* = 4; *D_c* = 2.497 g cm⁻³, *F*(000) = 1384; μ (Mo-K α) = 10.134 mm⁻¹, *T* = 120(2) K, crystal dimensions 0.20 × 0.15 × 0.08 mm³. Reflections (11190 total, 1626 unique, θ range 3.38–24.98°, *R_{int}* = 0.0566). *R*₁ = 0.0323 [*I* ≥ 2σ(*I*)], *wR*₂ = 0.0856 (all data). Diffraction data were collected on a Nonius kappa CCD diffractometer using graphite monochromated Mo-K α radiation (λ = 0.71073 Å).^{*} The data were corrected for Lorentz and polarization effects and the empirical absorption correction was applied to the net intensities. The structures were solved by direct methods using SHELXS-97 [8] and refined using SHELXL-97 [9]. After the full-matrix least-squares refinement of the non-hydrogen atoms with

^{*}Crystallographic information (excluding tables of structure factors) has been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 225729. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

anisotropic thermal parameters the hydrogen atoms were placed in calculated positions in aromatic rings ($C-H = 0.95 \text{ \AA}$) and methyl groups ($C-H = 0.98 \text{ \AA}$) for the final refinement. The scattering factors for the neutral atoms were those incorporated with the programs.

Results and Discussion

The crystal structure of $[PtCl(Th)(TeMeTh)_2]_n$ is shown in Fig. 1 together with selected bond lengths and angles. Interestingly, the two telluroether molecules act as bridging ligands between adjacent platinum(II) centers resulting in the formation of an infinite polynuclear chain. Consequently, there are two pairs of long Pt-Te distances of 2.898(1) and 3.419(1) \AA {*c.f.* the Pt-Te single bonds of 2.578–2.586 \AA and 2.595 \AA for $[PtI_2(TeMePh)_2]$ [4] and $[PtCl_2\{Te(CH_2)_4Te\}_2]$ [6], respectively} for each platinum atom. These weak bonds can be conceived to be formed by sharing one of the two lone electron pairs of the tellurium atom by two adjacent platinum centers. Indeed, tellurium shows a distorted tetrahedral environment (see Fig. 1). It is interesting to note that the shorter Pt-Te bond lies closer to the normal of the $C(11)-Te(1)-C(15)$ plane than the longer bond. This is to be expected, since the lone electron pair of the tellurium donor corresponds to the p orbital that is perpendicular to the $C(11)-Te(1)-C(15)$ bonding plane.

The quasi-octahedral coordination environment around platinum is completed by a Pt-Cl bond of 2.400(2) \AA and by a Pt-C bond of 1.998(8) \AA . These bond lengths are quite normal, as exemplified by the Pt-Cl bond of 2.383(8) \AA and the Pt-C bond of 1.988(8) \AA found in $[PtCl(Th)(PPh_3)_2]$ [10]. We note that the Pt-C bonds in $[Pt_3Te_2(Th)(PPh_3)_5]Cl$ [2.12(3) \AA ; ref. 11] and in $[PtX(Me)_2\{Se(Me)C_2H_4SeMe\}]$ ($X = Cl, I$) [2.03(3)–2.12(2) \AA , ref. 7] are somewhat longer. This is likely a consequence of a smaller *trans*-influence of the Cl donor compared to that of Te or Se.

The thienyl group that is directly bonded to platinum lies on a symmetry element (two-fold axis C_2). There are three independent atoms in the five-membered ring the two other atoms being generated by symmetry. This thienyl ring is disordered exhibiting two alternative orientations with the site occupation factors constrained by symmetry to 0.5. These two disordered thienyl rings consist of the atoms $C(1)-C(2A)-C(3A)-C(3B)^a-S(1B)^a$ and $C(1)-C(2A)^a-C(3A)^a-C(3B)-S(1B)$ (the symmetry operation a is $-x+1, y, -z+3/2$; see Fig. 1). We explored this disorder further by refining the structure in the space group Cc that removes the symmetry constraints in the case of this thienyl group that consequently then contains five independent atoms. The refinement of the site occupation factors of the two alternative orientations afforded the value close to 0.5 for both rings. Therefore, the higher symmetry space group $C2/c$ is applicable for the complex. The thienyl group bound to tellurium does not exhibit disorder.

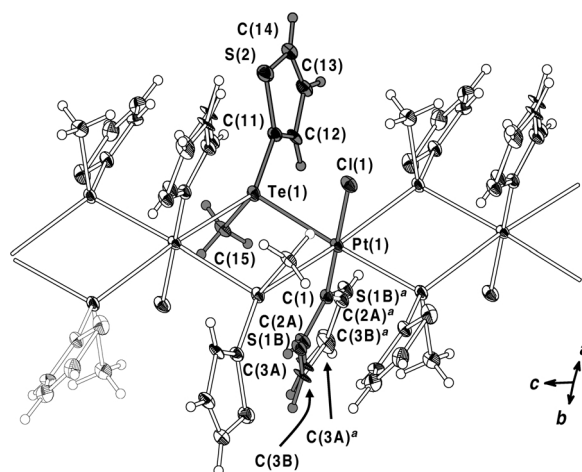


Fig. 1. The crystal structure of $[PtCl(Th)(TeMeTh)_2]_n$ indicating the numbering of atoms. The thermal ellipsoids have been drawn at 50% probability level. The thienyl ring bound directly to platinum is disordered showing two alternative orientations $C(1)-C(2A)-C(3A)-C(3B)^a-S(1B)^a$ and $C(1)-C(2A)^a-C(3A)^a-C(3B)-S(1B)$ (site occupation factors are 0.5 for both orientations). The asymmetric unit is high-lighted in grey. Selected bond lengths (\AA): Pt(1)-Te(1) 2.898(1), Pt(1)-Te(1)^a 3.419(1), Pt(1)-Cl(1) 2.400(2), Pt(1)-C(1) 1.998(8), Te(1)-C(11) 2.083(6), Te(1)-C(15) 2.166(6). Selected bond angles (deg): Te(1)-Pt(1)-Te(1)^a 176.20(2), Te(1)-Pt(1)-Te(1)^b 99.37(2), Te(1)-Pt(1)-Te(1)^c 80.39(2), Cl(1)-Pt(1)-Te(1) 88.20(1), Cl(1)-Pt(1)-Te(1)^a 88.100(9), Cl(1)-Pt(1)-Te(1)^b 86.349(9), Cl(1)-Pt(1)-Te(1)^c 86.349(9), C(1)-Pt(1)-Te(1) 91.900(9), C(1)-Pt(1)-Te(1)^a 91.900(9), C(1)-Pt(1)-Te(1)^b 93.651(9), C(1)-Pt(1)-Te(1)^c 93.651(9), Cl(1)-Pt(1)-C(1) 180.0, C(11)-Te(1)-C(15) 92.2(2), C(11)-Te(1)-Pt(1) 107.70(2), C(15)-Te(1)-Pt(1) 109.5(2), C(11)-Te(1)-Pt(1)^c 148.5(2), C(15)-Te(1)-Pt(1)^c 93.2(2), Pt(1)-Te(1)-Pt(1)^c 99.61(2). Symmetry operations: $a: -x+1, y, -z+3/2$; $b: x, -y, z+1/2$; $c: -x+1, -y, -z+1$.

$C(3A)^a-C(3B)-S(1B)$ (the symmetry operation a is $-x+1, y, -z+3/2$; see Fig. 1). We explored this disorder further by refining the structure in the space group Cc that removes the symmetry constraints in the case of this thienyl group that consequently then contains five independent atoms. The refinement of the site occupation factors of the two alternative orientations afforded the value close to 0.5 for both rings. Therefore, the higher symmetry space group $C2/c$ is applicable for the complex. The thienyl group bound to tellurium does not exhibit disorder.

The polymeric chains are packed together by weak van der Waals' forces the closest contacts involving the thienyl rings.

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