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Structures of $(\text{PPh}_4)_2[\text{Pd}(\text{Te}_4)_2]\cdot\text{DMF}$ and $[(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)\text{Pt}(\mu\text{-Te})_2\text{Pt}(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)]\cdot 2\text{DMF}$. ^{125}Te Gamma Ray Resonance of $(\text{PPh}_4)_2[\text{Pd}(\text{Te}_4)_2]\cdot\text{DMF}$

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Abstract. Bis(tetraphenylphosphonium) octatelluro-palladate-*N,N*-dimethylformamide (1/1), $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Pd}(\text{Te}_4)_2]\cdot\text{C}_3\text{H}_7\text{NO}$ (I), $M_r = 1879.11$, orthorhombic, *Pbca*, $a = 16.320$ (8), $b = 23.409$ (11), $c = 29.606$ (13) Å, $V = 11310.7$ (10) Å³, $Z = 8$, $D_x = 2.20$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 41.5$ cm⁻¹, $F(000) = 6880$, $T = 293$ K, $R = 0.049$ for 6931 observed unique reflections. The structure consists of PPh_4^+ cations and $[\text{Pd}(\text{Te}_4)_2]^{2-}$ anions with nearly square-planar coordination of palladium with two chelated Te_4^{2-} ligands. ^{125}Te gamma resonance yields a large quadrupole splitting indicative of a significantly asymmetric population of the $5p$ orbitals similar to that observed for transition metal ditellurides. $\text{Di}[1,2\text{-bis}(\text{diphenylphosphino})\text{ethane-}P,P']\text{-di-}\mu\text{-tellurio-di-platinum-dimethylformamide}$ (1/2), $\text{Pt}_2\text{Te}_2[(\text{C}_6\text{H}_5)_2\text{PC}_2\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2]_2\cdot 2\text{C}_3\text{H}_7\text{NO}$ (II), $M_r = 1588.40$, triclinic, $P\bar{1}$, $a = 9.474$ (6), $b = 12.342$ (8), $c = 14.222$ (9) Å, $\alpha = 114.41$ (3), $\beta = 97.44$ (3), $\gamma = 100.85$ (3)°, $V = 1446.7$ (8) Å³, $Z = 1$, $D_x = 1.78$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu =$

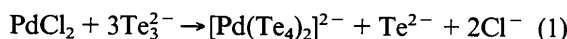
56.9 cm⁻¹, $F(000) = 760$, $T = 200$ K, $R = 0.048$ for 5212 observed unique reflections. The complex has a centrosymmetric molecular structure with a planar Pt_2Te_2 ring, and two chelating (tetraphenyldiphosphino)ethane ligands.

Introduction. Recently, the interest in polytellurium and polyselenium complexes has increased significantly, mainly because of their expected semiconducting properties (Böttcher, 1988; Ansari & Ibers, 1990; Kanatzidis, 1990). In this paper, the syntheses of two different polytellurium complexes, their crystal structures, and some data obtained from ^{125}Te gamma ray resonance are reported. Adams, Wolfe, Eichhorn & Haushalter (1989) had obtained a triclinic form (space group $P\bar{1}$) of solvate-free $(\text{PPh}_4)_2[\text{Pd}(\text{Te}_4)_2]$ by reacting PdCl_2 with K_2Te_4 in dimethylformamide (DMF) in the presence of PPh_4Br dissolved in ethylenediamine. Subsequently, Kanatzidis (1990) replaced ethylenediamine by ether, otherwise using a similar procedure. His result was orthorhombic $(\text{PPh}_4)_2[\text{Pd}(\text{Te}_4)_2]$ with the same space group as $(\text{PPh}_4)_2[\text{Pd}(\text{Te}_4)_2]\cdot\text{DMF}$ (I) of this study.

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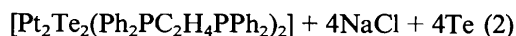
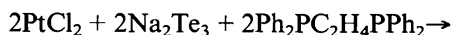
Adams, Wolfe, Eichhorn & Haushalter (1989) also synthesized the complex Pt₂Te₂(PPh₃)₄.3DMF which comprises a planar Pt₂Te₂ four-ring framework similar to that of Pt₂Te₂(Ph₂PC₂H₄PPh₂)₂.2DMF (II) described in this paper. This was obtained by reacting (NBu₄)₄Hg₄Te₁₂ with Pt(PPh₃)₄ in DMF solution.

Experimental. (PPh₄)₂[Pd(Te₄)₂].DMF (I) was prepared by reacting a solution of Na₂Te₃ (Zintl, Goubeau & Dullenkopf, 1931; Schultz & Koehler, 1987) in dimethylformamide (DMF) with a suspension of PPh₄Cl and PdCl₂ in DMF at room temperature over several hours. After filtration of NaCl, metallicly reflecting needles of (I) were obtained by adding tetrahydrofuran, according to reaction (1):



Dimensions of crystal used for measurement 0.46 × 0.30 × 0.20 mm. Stoe-Stadi IV diffractometer, graphite-crystal monochromator, Mo K α radiation, unit-cell parameters determined from the angular settings of 45 reflections. 9155 independent reflections measured at 293 K up to 2 θ ≤ 52° by θ -2 θ scan technique; range of *hkl*: *h* = 0 → 16, *k* = 0 → 28, *l* = 0 → 36; standard reflections 200, 004, variations ≤ 2%; scan speed: 2 s step⁻¹. 2224 reflections unobserved [*I*_{net} < 2 σ (*I*)], empirical absorption correction $\mu(\text{Mo K}\alpha) = 41.5 \text{ cm}^{-1}$; transmission factors from 0.30 to 0.51; data corrected for Lorentz and polarization effect; 6931 unique observed reflections, *R*_{int} = 0.026. Atomic scattering factors of Cromer & Mann (1968), *f'*, *f''* of Cromer & Liberman (1970). Calculations with *SHELX76* and *SHELXS86* (Sheldrick, 1976, 1986) and *SCHAKAL86* (Keller, 1986). H atoms calculated with *r* C—H = 0.96 Å, atoms of the disordered DMF molecule isotropic, all other atoms anisotropic with full-matrix least-squares refinements on *wF*_o. Final *R* = 0.049, *wR* = 0.038, *w* = 0.0006. Residual electron density in last difference Fourier synthesis < 0.6 e Å⁻³, $\Delta/\sigma_{\text{max}} = 0.003$.

[Pt₂Te₂(Ph₂PC₂H₄PPh₂)₂] (II) resulted from the reaction of Na₂Te₃ with PtCl₂ in the presence of tetraphenyldiphosphinoethane in DMF at 373 K, filtration of NaCl/Te, and cooling to room temperature, according to equation (2):



(II) forms black crystals, dimensions of crystal used for measurement 0.60 × 0.30 × 0.25 mm. Stoe-Stadi IV diffractometer, graphite-crystal monochromator, Mo K α radiation, unit-cell parameters determined from the angular settings of 30 reflections. 5936 independent reflections measured at 183 K up to 2 θ ≤ 54° by θ -2 θ scan technique; range of *hkl*: *h* = 0 → 8, *k* = -15 → 15, *l* = -16 → 16; standard reflection

Table 1. Atomic coordinates and equivalent isotropic thermal parameters *U*_{eq} (Å²) (Hamilton, 1959) for (I)

	x	y	z	<i>U</i> _{eq}
Te(1)	0.81742 (5)	0.38431 (4)	0.06091 (3)	0.0575 (3)
Te(2)	0.82183 (5)	0.48678 (4)	0.10752 (3)	0.0584 (3)
Te(3)	0.65933 (5)	0.48849 (4)	0.12490 (3)	0.0662 (4)
Te(4)	0.65620 (5)	0.38197 (4)	0.16521 (3)	0.0553 (3)
Te(5)	0.84590 (5)	0.24766 (4)	0.07663 (3)	0.0507 (3)
Te(6)	0.77099 (5)	0.14178 (4)	0.06989 (3)	0.0584 (3)
Te(7)	0.71073 (5)	0.14176 (4)	0.15503 (3)	0.0576 (3)
Te(8)	0.62973 (4)	0.24434 (4)	0.14563 (3)	0.0493 (3)
Pd(1)	0.73700 (5)	0.31446 (4)	0.11233 (3)	0.0422 (3)
P(1)	0.1241 (2)	0.2550 (2)	0.1676 (1)	0.044 (1)
C(1)	0.0697 (7)	0.3189 (5)	0.1831 (3)	0.044 (4)
C(2)	0.1094 (7)	0.3632 (6)	0.2056 (4)	0.054 (5)
C(3)	0.0666 (8)	0.4129 (6)	0.2156 (4)	0.061 (5)
C(4)	-0.0129 (8)	0.4181 (6)	0.2036 (4)	0.064 (6)
C(5)	-0.0530 (8)	0.3749 (7)	0.1824 (4)	0.063 (6)
C(6)	-0.0133 (7)	0.3256 (6)	0.1718 (4)	0.053 (5)
C(7)	0.1243 (6)	0.2493 (6)	0.1077 (3)	0.043 (4)
C(8)	0.1551 (7)	0.2014 (6)	0.0871 (4)	0.060 (5)
C(9)	0.1627 (8)	0.1974 (7)	0.0406 (4)	0.069 (6)
C(10)	0.1386 (8)	0.2424 (8)	0.0142 (5)	0.072 (7)
C(11)	0.1070 (8)	0.2901 (7)	0.0338 (5)	0.070 (6)
C(12)	0.0997 (7)	0.2945 (6)	0.0803 (4)	0.057 (5)
C(13)	0.2267 (6)	0.2576 (5)	0.1892 (4)	0.042 (4)
C(14)	0.2384 (7)	0.2614 (5)	0.2359 (4)	0.054 (5)
C(15)	0.3164 (7)	0.2641 (6)	0.2530 (5)	0.061 (5)
C(16)	0.3828 (9)	0.2618 (6)	0.2251 (5)	0.073 (6)
C(17)	0.3722 (8)	0.2589 (6)	0.1785 (5)	0.068 (6)
C(18)	0.2933 (7)	0.2566 (5)	0.1609 (4)	0.051 (5)
C(19)	0.0724 (6)	0.1920 (5)	0.1897 (3)	0.045 (4)
C(20)	0.1031 (9)	0.1610 (7)	0.2235 (5)	0.086 (7)
C(21)	0.0610 (9)	0.1146 (7)	0.2406 (5)	0.088 (7)
C(22)	-0.0152 (9)	0.1021 (7)	0.2229 (5)	0.079 (7)
C(23)	-0.0471 (9)	0.1336 (7)	0.1881 (5)	0.082 (7)
C(24)	-0.0027 (8)	0.1790 (6)	0.1720 (5)	0.073 (6)
P(2)	0.3142 (2)	0.4638 (2)	0.0950 (1)	0.047 (1)
C(25)	0.3589 (7)	0.3949 (5)	0.0806 (4)	0.045 (4)
C(26)	0.3138 (8)	0.3531 (6)	0.0595 (4)	0.060 (5)
C(27)	0.3513 (9)	0.3013 (6)	0.0473 (4)	0.066 (6)
C(28)	0.433 (1)	0.2933 (7)	0.0545 (5)	0.074 (7)
C(29)	0.4790 (9)	0.3356 (7)	0.0748 (4)	0.070 (6)
C(30)	0.4415 (7)	0.3871 (6)	0.0882 (4)	0.058 (5)
C(31)	0.3093 (7)	0.4719 (6)	0.1551 (4)	0.045 (4)
C(32)	0.2825 (8)	0.5206 (7)	0.1740 (4)	0.077 (7)
C(33)	0.2696 (9)	0.5249 (8)	0.2200 (5)	0.084 (7)
C(34)	0.2825 (9)	0.4801 (8)	0.2467 (5)	0.081 (7)
C(35)	0.3115 (9)	0.4301 (8)	0.2295 (5)	0.079 (7)
C(36)	0.3248 (7)	0.4250 (7)	0.1830 (4)	0.060 (5)
C(37)	0.3780 (7)	0.5179 (6)	0.0704 (4)	0.054 (5)
C(38)	0.4351 (7)	0.5492 (6)	0.0958 (4)	0.059 (5)
C(39)	0.4905 (8)	0.5844 (6)	0.0760 (5)	0.064 (6)
C(40)	0.4891 (8)	0.5919 (7)	0.0316 (5)	0.073 (6)
C(41)	0.433 (1)	0.5642 (8)	0.0057 (5)	0.13 (1)
C(42)	0.377 (1)	0.5280 (9)	0.0249 (5)	0.14 (1)
C(43)	0.2103 (6)	0.4652 (5)	0.0750 (3)	0.041 (4)
C(44)	0.1916 (7)	0.4662 (6)	0.0299 (4)	0.073 (6)
C(45)	0.1121 (8)	0.4617 (7)	0.0152 (5)	0.085 (7)
C(46)	0.0512 (8)	0.4553 (6)	0.0450 (5)	0.066 (6)
C(47)	0.0663 (8)	0.4535 (7)	0.0890 (5)	0.072 (6)
C(48)	0.1472 (7)	0.4591 (6)	0.1046 (4)	0.064 (6)
O(1)	0.3017 (8)	0.1174 (7)	0.1102 (5)	0.146 (6)*
N(1)	0.4333 (8)	0.1170 (6)	0.1006 (5)	0.107 (4)*
C(50)	0.446 (1)	0.1060 (8)	0.1471 (6)	0.109 (6)*
C(51)	0.497 (1)	0.1212 (8)	0.0688 (6)	0.122 (6)*
C(52)	0.357 (1)	0.1212 (8)	0.0803 (6)	0.106 (6)*

* Refined isotropically.

040, variations ≤ 3%; ω -scan speed: 2 s step⁻¹. 724 reflections unobserved [*I*_{net} < 2 σ (*I*)], empirical absorption correction $\mu(\text{Mo K}\alpha) = 56.9 \text{ cm}^{-1}$; transmission factors from 0.26 to 0.48; data corrected for Lorentz and polarization effects; 5212 unique observed reflections, *R*_{int} = 0.028. Atomic scattering factors of Cromer & Mann (1968), *f'*, *f''* of Cromer & Liberman (1970). Calculations with *SHELX76* and *SHELXS86* (Sheldrick, 1976, 1986) and *SCHAKAL86* (Keller, 1986). H atoms not con-

Table 2. Atomic coordinates and equivalent isotropic thermal parameters U_{eq} (\AA^2) (Hamilton, 1959) for (II)

	x	y	z	U_{eq}
Pt(1)	1-13414 (5)	1-13221 (4)	0-13395 (4)	0-0392 (2)
Te(1)	0-9491 (1)	0-91277 (7)	0-06531 (6)	0-0498 (3)
P(1)	1-1798 (4)	1-1772 (3)	0-3070 (2)	0-049 (1)
P(2)	1-3065 (4)	1-3107 (3)	0-1835 (3)	0-046 (1)
C(1)	1-210 (2)	1-058 (1)	0-351 (1)	0-061 (4)*
C(2)	1-248 (3)	0-945 (3)	0-282 (2)	0-061 (7)*
C(3)	1-270 (4)	0-848 (3)	0-308 (3)	0-09 (1)*
C(4)	1-258 (2)	0-880 (2)	0-411 (1)	0-118 (6)*
C(5)	1-144 (5)	0-915 (4)	0-422 (3)	0-07 (1)*
C(6)	1-114 (4)	1-007 (3)	0-379 (3)	0-07 (1)*
C(7)	1-039 (1)	1-238 (1)	0-3723 (9)	0-044 (4)
C(8)	0-897 (2)	1-203 (1)	0-312 (1)	0-066 (6)
C(9)	0-783 (2)	1-246 (1)	0-358 (1)	0-072 (6)
C(10)	0-814 (2)	1-328 (1)	0-463 (1)	0-074 (7)
C(11)	0-957 (2)	1-366 (2)	0-523 (1)	0-098 (8)
C(12)	1-073 (2)	1-321 (1)	0-479 (1)	0-071 (6)
C(13)	1-265 (1)	1-429 (1)	0-142 (1)	0-063 (5)
C(14)	1-148 (2)	1-478 (2)	0-181 (2)	0-13 (1)
C(15)	1-111 (2)	1-569 (2)	0-153 (2)	0-16 (2)
C(16)	1-185 (2)	1-601 (2)	0-086 (2)	0-11 (1)
C(17)	1-298 (2)	1-557 (2)	0-052 (2)	0-099 (9)
C(18)	1-342 (2)	1-468 (2)	0-084 (1)	0-083 (8)
C(19)	1-481 (1)	1-292 (1)	0-150 (1)	0-046 (4)
C(20)	1-484 (2)	1-180 (1)	0-065 (1)	0-068 (6)
C(21)	1-619 (2)	1-163 (1)	0-036 (1)	0-076 (7)
C(22)	1-748 (2)	1-257 (2)	0-094 (2)	0-087 (9)
C(23)	1-748 (2)	1-371 (2)	0-179 (1)	0-083 (8)
C(24)	1-613 (1)	1-388 (1)	0-206 (1)	0-063 (5)
C(25)	1-356 (2)	1-299 (1)	0-377 (1)	0-071 (5)
C(26)	1-356 (2)	1-397 (1)	0-333 (1)	0-074 (5)
C(201)	1-368 (4)	1-052 (3)	0-357 (3)	0-09 (1)*
C(301)	1-396 (5)	0-964 (4)	0-399 (3)	0-11 (2)*
C(501)	1-203 (2)	0-971 (1)	0-486 (1)	0-045 (3)*
C(601)	1-165 (1)	1-051 (1)	0-4478 (9)	0-035 (2)*
O(1)	0-388 (1)	0-328 (1)	0-6332 (8)	0-093 (5)
N(1)	0-334 (2)	0-225 (1)	0-730 (1)	0-092 (7)
C(28)	0-416 (3)	0-258 (2)	0-668 (2)	0-14 (1)
C(29)	0-210 (3)	0-268 (2)	0-749 (2)	0-14 (1)
C(30)	0-378 (3)	0-145 (3)	0-770 (2)	0-20 (2)

* Refined isotropically.

sidered, C atoms of the phenyl group C(1)–C(6), which is disordered in two perpendicular positions, isotropic, all other atoms anisotropic with full-matrix least-squares refinements on wF_o . Final $R = 0.048$, $wR = 0.050$, $w = 0.0008$. Residual electron density in last difference Fourier synthesis $< 0.6 \text{ e \AA}^{-3}$, $\Delta/\sigma_{max} = 0.003$.

The absorption spectra in the far infrared (FIR) region between 100 and 300 cm^{-1} were recorded with an IFS-88 Bruker spectrometer, using the polyethylene disc Nujol technique. The gamma ray resonance of ^{125}Te (Mössbauer effect) was performed using a $\text{Mg}_3^{125m}\text{TeO}_6$ source (Pasternak, van der Heyden & Langousche, 1984), which has a half-life of 58 d. The matrix for the source was enriched in ^{125}Te to 97% ^{125}Te . It was activated at KFA Jülich. It had an original activation strength of about 20 mCi. The comparatively high Debye temperature θ_D of the source ($\theta_D = 350 \text{ K}$) permits the recording of ^{125}Te spectra, the source being at room temperature, whereas the absorber may be in a conventional He gas-flow cryostat at the temperature of interest. The spectra were recorded using 512 channels (before folding) with a mechanical drive at constant acceleration with a symmetrical velocity dependence as commonly used for ^{57}Fe resonance. The detecting

Table 3. Selected bond distances (\AA) and angles ($^\circ$) for $(\text{PPh}_4)_2[\text{Pd}(\text{Te}_4)_2]\cdot\text{DMF}$ (I)

Pd—Te(1)	2.591 (2)	P(1)—C(1)	1.80 (1)
Pd—Te(4)	2.586 (2)	P(1)—C(7)	1.78 (1)
Pd—Te(5)	2.592 (2)	P(1)—C(13)	1.79 (1)
Pd—Te(8)	2.594 (2)	P(1)—C(19)	1.82 (1)
Te(1)—Te(2)	2.768 (2)	P(2)—C(25)	1.82 (1)
Te(2)—Te(3)	2.702 (2)	P(2)—C(31)	1.79 (1)
Te(3)—Te(4)	2.765 (2)	P(2)—C(37)	1.79 (1)
Te(5)—Te(6)	2.771 (2)	P(2)—C(43)	1.80 (1)
Te(6)—Te(7)	2.706 (2)		
Te(7)—Te(8)	2.755 (2)		
Te(1)—Pd—Te(4)	103.20 (4)	C(1)—P(1)—C(7)	108.5 (5)
Te(5)—Pd—Te(8)	103.64 (4)	C(1)—P(1)—C(13)	110.0 (5)
Te(1)—Pd—Te(5)	78.10 (4)	C(1)—P(1)—C(19)	110.7 (5)
Te(4)—Pd—Te(8)	79.19 (4)	C(7)—P(1)—C(13)	110.9 (5)
Te(1)—Pd—Te(8)	164.65 (5)	C(7)—P(1)—C(19)	107.4 (5)
Te(4)—Pd—Te(5)	164.80 (5)	C(13)—P(1)—C(19)	109.4 (5)
Pd—Te(1)—Te(2)	105.49 (4)	C(25)—P(2)—C(31)	110.2 (6)
Pd—Te(4)—Te(3)	106.28 (4)	C(25)—P(2)—C(37)	107.3 (6)
Pd—Te(5)—Te(6)	105.45 (4)	C(25)—P(2)—C(43)	108.4 (5)
Pd—Te(8)—Te(7)	105.43 (4)	C(31)—P(2)—C(37)	110.8 (6)
Te(1)—Te(2)—Te(3)	94.72 (4)	C(31)—P(2)—C(43)	106.5 (5)
Te(2)—Te(3)—Te(4)	94.99 (4)	C(37)—P(2)—C(43)	113.7 (5)
Te(5)—Te(6)—Te(7)	95.36 (4)		
Te(6)—Te(7)—Te(8)	94.60 (4)		

Table 4. Selected distances (\AA) and angles ($^\circ$) for $[(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2\text{Pt}(\mu\text{-Te})_2\text{Pt}(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)]\cdot 2\text{DMF}$ (II)

Pt(1)—Te(1)	2.636 (3)	C(25)—C(26)	1.58 (2)
Pt(1)—Te(1A)	2.630 (3)	P(1)—C(1)	1.88 (2)
Pt(1)—P(1)	2.248 (4)	P(1)—C(7)	1.83 (1)
Pt(1)—P(2)	2.254 (4)	P(2)—C(13)	1.87 (2)
Pt(1)—C(25)	1.85 (2)	P(2)—C(19)	1.81 (2)
P(2)—C(26)	1.88 (1)	Pt(1)···Pt(1A)	3.965 (1)
Te(1)—Pt(1)—Te(1A)	82.31 (4)	Pt(1)—P(2)—C(13)	120.5 (5)
Te(1)—Pt(1)—P(1)	96.5 (1)	Pt(1)—P(2)—C(19)	114.7 (5)
Te(1)—Pt(1)—P(2)	174.6 (1)	C(1)—P(1)—C(7)	104.9 (6)
Te(1A)—Pt(1)—P(1)	173.1 (1)	C(1)—P(1)—C(25)	101.3 (7)
Te(1A)—Pt(1)—P(2)	95.77 (9)	C(7)—P(1)—C(25)	106.3 (6)
P(1)—Pt(1)—P(2)	86.0 (1)	C(13)—P(2)—C(19)	104.2 (7)
Pt(1)—Te(1)—Pt(1A)	97.69 (4)	C(13)—P(2)—C(26)	103.0 (7)
Pt(1)—P(1)—C(25)	109.0 (5)	C(19)—P(2)—C(26)	103.9 (6)
Pt(1)—P(2)—C(26)	108.7 (5)	P(1)—C(25)—C(26)	106.9 (9)
Pt(1)—P(1)—C(1)	121.1 (5)	P(2)—C(26)—C(25)	107 (1)
Pt(1)—P(1)—C(7)	112.9 (4)		

system was a high purity Ge detector at 78 K. The spectra were fitted on the mean least-squares basis by a conventional procedure, assuming single lines or quadrupole-split doublets.

Polycrystalline absorbers containing about 4 mg cm^{-2} natural Te were prepared in a nitrogen chamber to prevent decomposition. The area of the absorber was about 0.40 cm^2 . Only compound (I) was studied.

Discussion. Atomic coordinates and equivalent isotropic thermal parameters of (I) and (II) are listed in Tables 1 and 2, and selected bond distances and angles in Tables 3 and 4.*

* Lists of structure factors, anisotropic thermal parameters, full bond lengths, angles, torsion angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54036 (74 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The structure of the [Pd(Te₄)₂]²⁻ anions in (I) can be recognized in Fig. 1. The bond lengths and bond angles are quite similar to those reported previously (Adams, Wolfe, Eichhorn & Haushalter, 1989; Kanatzidis, 1990) and so are the two undulating PdTe₄ rings. In view of the geometrical similarity of the orthorhombic form (Kanatzidis, 1990) and the data shown here, the question is open whether the two forms which exhibit the same space group are identical phases despite the quite different syntheses and the missing DMF in Kanatzidis's compound.

Comparable 'envelope' structured molecular anions were also found for the anions of (PPh₄)₂[Cr(CO)₄Te₄] (Flomer, O'Neal, Kolis, Jeter & Cordes, 1988) and (PPh₄)₂[MoO(Te₄)₂] (Flomer & Kolis, 1989). It is interesting to note that the local environment of the Pd atoms deviates somewhat from being planar. The angle between the planes Te(1)—Pd—Te(4) vs Te(5)—Pd—Te(8) is 19.5°, yielding a local symmetry of 42m (*D*_{2d}) for the Pd atom. This angle is greater than that of the monoclinic crystals of the selenium compound (PPh₄)₂[Pd(Se₄)₂] (Kräuter, Dehnicke & Fenske, 1990) by about 3°. The reason may be the somewhat greater rejection of the adjacent chalcogenic atoms which depends on the values of the chelate angles *E*—Pd—*E* (*E* = Se, Te): the chelate angles in the Te complex of (I) are 103.2 and 103.6° compared with 100.7 and 101.0° in (PPh₄)₂[Pd(Se₄)₂]. The intense band at 200 cm⁻¹ of the FIR spectrum of (I) is probably owing to a Te—Te stretching vibration which may be compared with the Se—Se band of similar intensity at 274 cm⁻¹ in (PPh₄)₂[Pd(Se₄)₂] (Kräuter, Dehnicke & Fenske, 1990).

The structural topology of compound (II), which is shown in Fig. 2, is similar to that of (PPh₃)₂Pt(μ-Te)₂Pt(PPh₃)₂ (Adams, Wolfe, Eichhorn & Haushalter, 1989). However, some significant differences may be observed from the bond angles of the Pt₂Te₂ rings as shown in Table 4. Moreover, the Pt—P bond distances are somewhat shorter in (II) compared to Pt₂Te₂(PPh₃)₄, the chelating effect yield-

ing an increase of the bond angle Te—Pt—Te. This angle is greater by 5.4° in (II) compared to that in the triphenylphosphine complex. The angle at the μ-Te atoms in (II) is comparatively smaller, resulting in a decrease of the Pt—Pt distances from 412 pm to 396.5 pm in (II). Nevertheless, there is no transannular relationship in those compounds. The local environment of the Pt atoms is quasi-planar, the

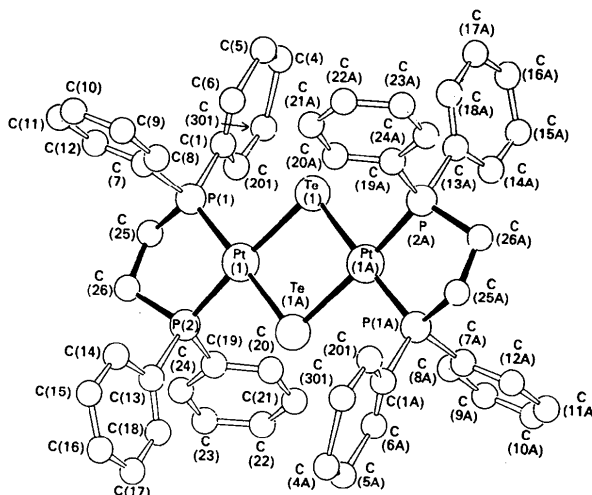


Fig. 2. SCHAKAL (Keller, 1986) drawing of [Pt₂Te₂-(Ph₂PC₂H₄PPh₂)₂]²⁻DMF (without DMF molecules) with the atom-labelling scheme.

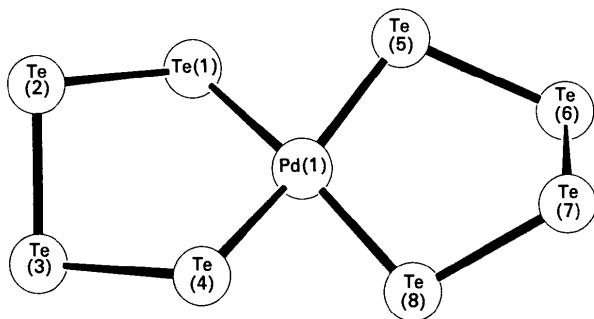


Fig. 1. SCHAKAL (Keller, 1986) drawing of the [Pd(Te₄)₂]²⁻ ion in (PPh₄)₂[Pd(Te₄)₂].DMF with the atom-labelling scheme.

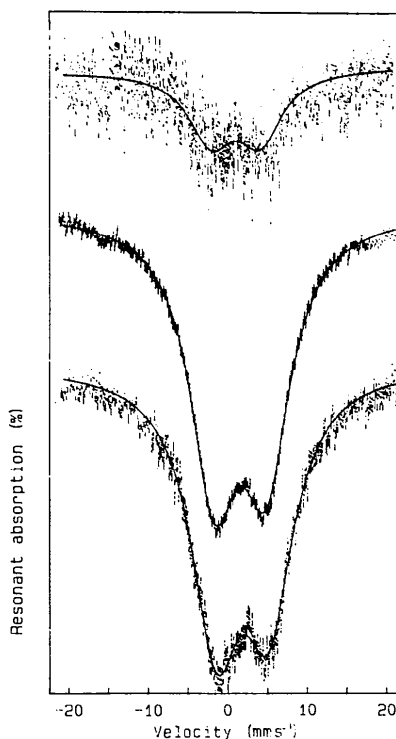


Fig. 3. ¹²⁵Te Mössbauer spectra of (PPh₄)₂[Pd(Te₄)₂].DMF.

Table 5. ^{125}Te Mössbauer parameters of (I)

IS = isomer shift, standard $\text{Mg}_3^{125}\text{TeO}_6$, QS = quadrupole splitting, A = amplitude of absorption, Γ = half width.

	IS (mm s^{-1})	QS (mm s^{-1})	A (%)	Γ (mm s^{-1})
$T = 78 \text{ K}$	1.3 (2)	6.2 (4)	0.21 (2)	6.7 (10)
$T = 7 \text{ K}$	1.51 (3)	6.58 (5)	1.17–1.37 (3)	6.95–7.67 (24)

angle between the planes P(1)—Pt—P(2) vs Te(1)—Pt(1)—Te(1A) being as small as 8.8° . The six distinct bands observed on the FIR spectrum of (II) (110, 147, 201, 235, 270, 317 cm^{-1}) cannot be interpreted at this time.

^{125}Te Mössbauer spectra of (I). With respect to the short life time of the first excited state of ^{125}Te and the large energy of the transition to the ground state of 35.46 keV, the electronic state of Te at its positions in the crystal structure cannot be analyzed with the precision commonly expected e.g. in the case of ^{57}Fe . Some qualitative conclusions are, however, possible. For example, the nominal valence state of Te in Te compounds may vary nominally between $6+$ and $2-$. Thus, information on the effective valence state of Te can be derived from the hyperfine data of ^{125}Te .

The observed apparent two-line spectrum in (I) (Fig. 3) is due to an apparently single quadrupole-split doublet. It cannot be interpreted in terms of two distinct single resonant lines of Te at crystallographically non-equivalent positions. Small crystallographic distinctions within the group of polytelluride complexes described in the present paper cannot be resolved in ^{125}Te spectra at this time. For this reason, only compound (I) was studied. ^{125}Te data of (II) are expected to be quite similar. The data obtained are summarized in Table 5.

The ^{125}Te doublet is distinctly asymmetric in intensity as recognized clearly in the spectrum at 20 K. This is interpreted in terms of a textured absorber. It cannot be due primarily to anisotropic vibration of the Te atom since the asymmetry appears to be maintained at the same level at a lower temperature (cf. spectrum at 7 K, Fig. 3). However, it cannot be analyzed at higher temperatures with precision because of the accordingly smaller recoilless fraction which produces a correspondingly lower intensity of the resonant absorption.

The plot of the isomer shift (IS) vs nuclear quadrupole splitting (QS) of ^{125}Te for (I) and a few other Te compounds in Fig. 4 shows some interesting trends. The IS results from two contributions of opposite sign: (i) a major contribution of positive sign by the density of s electrons at the nucleus ^{125}Te , its variation in Te compounds being mainly due to a different population of $5s$ orbitals; (ii) a minor contribution of negative sign due to s electron shielding by $5p$ electrons.

The major part of the electric field gradient (EFG) at the ^{125}Te nucleus is produced by electrons with non-zero orbital momentum. The observed QS may be interpreted in terms of the partly filled $5p$ shell, the completely filled inner shells yielding negligible contributions. IS and QS values which depend on $5s$ and $5p$ orbital populations reflect a particular Te bonding state at the lattice position. It may be assumed that a $5s$ electron contributes about $+2.4 \text{ mm s}^{-1}$ to the IS and a $5p$ electron contributes -0.4 mm s^{-1} to the IS by s shielding; it may also be assumed that a $5p$ electron contributes about -12 mm s^{-1} to the QS value (Binczycka, Hafner, Moh & Stanek, 1990).

In order to explain the observed QS, it may be estimated that the two $5p$ orbitals in the bonding plane of the Te_4Pd ring are occupied less than the $5p$ orbital perpendicular to the plane by approximately 0.5 e. Adopting the orbital population of the rather well studied compound TeO_2 (Dobud & Jones, 1976) as reference, the $5s$, $5p$ shell population of Te in polytelluride complexes can be estimated as being not higher than 5.0 for $5p$ and about 1.3 for $5s$. According to this, the net charge of the Te atom is -0.3 e .

The electronic state of Te in polytellurium complexes appears to be rather similar to that of the transition metal ditellurides (cf. Fig. 4), especially MnTe_2 or FeTe_2 (Binczycka, Hafner, Moh & Stanek, 1990). A significant difference should be noted, however: the EFG in the ditellurides is produced by a non-occupied $5p$ orbital (hole), connecting the two Te atoms in the molecular anion Te_2^{2-} , whereas the EFG in the polytellurium complexes is produced by the filled $5p$ orbital perpendicular to the Te_4Pd plane,

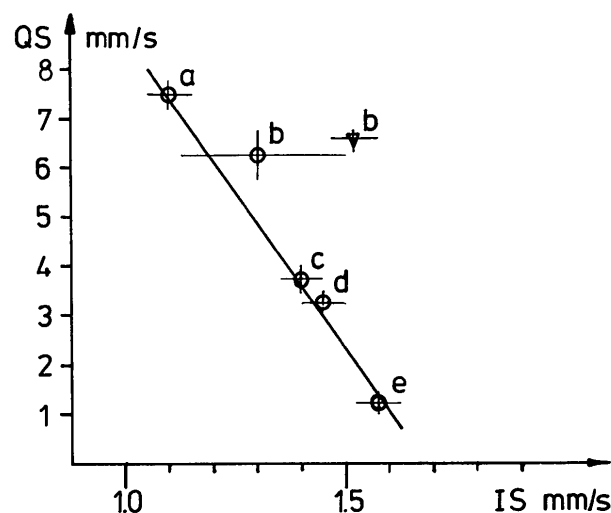


Fig. 4. Plot of isomer shift (IS) vs nuclear quadrupole splitting (QS) for (I) and a few ditellurides: a = MnTe_2 , b = (I) (\circ at 78 K, ∇ at 7 K), c = FeTe_2 , d = CoTe_2 , e = NiTe_2 .

the holes being located in the 5*p* orbitals within the plane.

It may be predicted, therefore, that the signs of the EFG, or QS, in the ditellurides and the Te₄Pd rings of the polytellurium complexes are opposite. At any rate, the study of ¹²⁵Te gamma ray resonance may reveal simple relationships *e.g.* between planar and linear bonding of tellurium in different compounds, adopting a scheme of partly filled 5*s* and 5*p* shells.

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Structure of Aqua(di-2-pyridylcarbonylaminato)isothiocyanatocopper(II)

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Abstract. [Cu(C₁₂H₈N₃O₂)(NCS)(H₂O)], *M_r* = 365.78, triclinic, *P* $\bar{1}$, *a* = 7.281 (2), *b* = 10.646 (3), *c* = 10.345 (2) Å, α = 92.70 (2), β = 85.55 (2), γ = 116.26 (2)°, *V* = 717 (1) Å³, *Z* = 2, *D_x* = 1.69 (1) g cm⁻³, *Mo K α* , λ = 0.71069 Å, μ = 17.36 cm⁻¹, *F*(000) = 370, room temperature, *R* = 0.033, *wR* = 0.037 for 2799 unique reflections with *I* > 3 σ (*I*). The structure consists of discrete neutral units linked through hydrogen bonds. The coordination geometry around copper ions can be described as tetragonal square pyramidal, the O atoms from the coordinated water molecule occupying the axial position and the N atoms from the pyridinecarboximidate and the thiocyanate groups the basal plane.

Introduction. In the course of our study on the interactions between Cu^{II} and easily stackable ligands we have recently reported the synthesis and characterization of a set of Cu^{II} pcpci [pcpci = *N*-(2'-pyridylcarbonyl)pyridine-2-carboximidate anion] complexes (Folgado, Escrivá, Beltrán-Porter & Beltrán-Porter, 1987; Folgado, Coronado, Beltrán-Porter, Burriel, Fuertes & Miravittles, 1988). pcpci is a tridentate rigid quasi-planar *N*-donor ligand whose monoanionic character makes it different from other related ligands such as terpy (2,2':6',2''-terpyridine), paphy (pyridine-2-aldehyde-2'-pyridyl hydrazone), or tpt [2,4,6-tris(2-pyridyl)-1,3,5-triazine]. This renders possible the isolation of neutral Cu(pcpci)*X* entities (*X* = monoanion). When *X* is a potentially bridging ligand, condensed systems may result. Such an ability is well established for halide and pseudohalide

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