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[{(C5Me5)2Nb}2PdTe4], a heterometallic palladium telluride cluster with a planar PdTe4 fragment

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Dedicated to Professor Dr. Dieter Fenske on the occasion of his 65th birthday.

Abstract

The reaction of $[Cp_2^*Nb(Te_2H)]$ $(Cp^* = \eta^5\text{-}C_5Me_5)$ with $[Pd(DBA)_2]$ (DBA = dibenzylidenacetone) and dppm (bis(diphenylphosphanyl)methane) gave the new tetratelluropalladate cluster $[(Cp_2^*Nb)_2PdTe_4]$ (**1**), which has been characterised by means of elemental analysis, FD-MS and X-ray crystallography. The structure of compound **1** contains a planar PdTe4 rectangle to which two niobocene groups are coordinated. DFT calculations on the hypothetical $[PdTe_4]^{2-}$ anion and comparison of the results with those of the W and Ni homologues show that the planar arrangement of Te ligands in **1** is due to the intrinsic property of the central Pd atom.
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1. Introduction

The chemistry of nickel telluride compounds is characterised by an impressing variety of polyhedral structures [1]. The preferred cluster types belong to cubic [2] and icosahedral geometries [3], which may be regarded as intermediate steps on the route to binary solid state phases [2]. By contrast, comparatively little is known about palladium telluride complexes [4]. We have recently shown that use of $[Cp_2^*Nb(Te_2H)]$ as tellurium transfer reagent [5] in the reaction with $[Ni(COD)_2]$ in the presence of $Ph_2PCH_2PPh_2$ (dppm) provides access to the mixed early–late transition metal clusters $[(Cp_2^*Nb)_2NiTe_4]$ and $[(Cp^*Nb)_2Ni_5Te_7(dppm)_2]$ [6]. Of particular interest for us has been the electronic structure of the tetratelluronickelate cluster. In

this work, we report on the synthesis and structural characterisation of a related tetratelluropalladate cluster as a further member of the rare class of telluro metallates with coordination number four [7].

2. Results

Reaction of $[Cp_2^*Nb(Te_2H)]$ $(Cp^* = \eta^5\text{-}C_5Me_5)$ with $[Pd(DBA)_2]$ (DBA = dibenzylidenacetone) and half an equivalent of dppm (bis(diphenylphosphanyl)methane) in boiling toluene gave a brown solution. After chromatographic work-up $[(Cp_2^*Nb)_2PdTe_4]$ (**1**) was isolated as a brown, analytically pure solid in 22% yield. Complex **1** is soluble in common solvents, its solutions are extremely air sensitive. The field desorption (FD) mass spectrum of **1** exhibits the parent ion at m/z 1343. The ^1H NMR spectrum of **1** reveals a singlet at $\delta = 1.79$ ppm (C_6D_6) for the C_5Me_5 rings. The trimetallic cluster **1** also forms in the presence of PEt_3 or when increasing the Pd/dppm ratio

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to 1. Generally, the presence of phosphine increases the yield of **1** from 12% (without dppm) to 22%, but is not essential.

The reaction of [(tBuC$_5$H$_4$)$_2$NbTe$_2$H] with [Pd(DBA)$_2$] and dppm in boiling toluene was also investigated in order to find analogies to the corresponding nickel telluride chemistry [6]. However, the only hint for the formation of larger Pd/Te clusters was provided by FD-MS, which reveals peaks at m/z 2098 and 2298 with isotope patterns typical of a polynuclear heavy atom skeleton, or part of it.

Crystallisation of **1** from toluene gave brown, air sensitive crystals, which have been suitable for X-ray diffraction. The unit cell contains one [(Cp$_2^*$Nb)$_2$PdTe$_4$] and four toluene molecules, the palladium atom lies on an inversion centre. Central feature of the molecular structure is a planar PdTe$_4$ rectangle to which two niobocene units are coordinated. Perpendicular to the PdTe$_4$ plane there is another plane through Nb1, Pd and Nb1a bisecting the C$_5$Me$_5$ rings (Fig. 1). Consequently, a perfectly linear axis passes through Nb1, Pd and Nb1a. Compound **1** is the first tetratelluropalladate complex and it is a further example of the extremely rare coordination compounds incorporating an MTe$_4$ structural unit.

In contrast to the tetrahedral MTe$_4$ derivatives [{(tBuC$_5$H$_4$)$_2$NbTe$_2$}$_2$W · W(CO)$_4$] (**2**) [8] and [(Cp$_2^*$Nb)$_2$NiTe$_4$] (**3**) [6] the heavy atom core of **1** has a deck-chair like structure with angles of 160° between the planes Te1/Nb1/Te2 and Te1/Te2/Pd (Fig. 2). The Nb–Te distances are of the same order [2.759 versus 2.766 Å (mean)] in **1** and **3**, but significantly longer in **2** (2.832 Å). The M–Nb and M–Te distances in **1** are 0.1–0.15 Å longer than those in **3** which may be due to the larger covalent radius of Pd. However, the Pd–Te distances are longer by 0.06 Å than the W–Te distances in **2** (Table 1).

The core of the molecule may also be described by containing two folded four-membered NbTe$_2$Pd rings being

linked together by Pd. A preliminary analysis of the bonding situation in **1** has to consider the formal built-up of the cluster from Pd^{2+} plus two [Cp$_2^*$NbTe$_2$]$^-$ moieties or, alternatively, from [Pd(Te$_2$)$_2$]$^{2-}$ plus two [Cp$_2^*$Nb]$^+$ fragments. The latter view is supported by looking on the Te–Te distances around Pd. Sets of two short (3.157 Å inter-annular) and two long (4.214 Å intra-annular) Te–Te distances are observed. This is also the case in compound **3**, whereas in **2** only long distances (>4 Å) have been found (Table 1). These long distances are typical of nonbonding intra- and inter-annular interactions. Less clear is the bonding situation between Te1 and Te2a [$d = 3.157(1)$ Å], which are neighbouring Te atoms of two different NbTe$_2$Pd rings.

DFT calculations carried out on the hypothetical [NiTe$_4$]$^{2-}$ anion led to an optimised structure containing two ditelluride (Te$_2^{2-}$) ligands around severely distorted Ni^{2+}. The calculated distance [d(Te–Te) = 2.970 Å] is 0.18 Å shorter than that in **1**, but the latter is still at the border of the wide range of compounds with Te–Te bonding interactions [1,6].

The Pd atom in the triclinic crystal structure of **1** occupies the set of special positions (symmetry centre) that implies a planar geometry of PdTe$_4$ unit, while the Ni atoms in analogous **3** are placed in no symmetry general positions. The local symmetry of [NiTe$_4$]$^{2-}$ in **3** is close to D_2 while that of Pd in **1** roughly reaches D_{2h}. The obvious question is: is the symmetry of central MTe$_4$ unit governed by crystallographic requirements or by intrinsic properties of Ni versus Pd atoms? We have already described the electronic properties of [NiTe$_4$]$^{2-}$ [6] for which no planar structure could be stabilised. Similar calculations with GAUSSIAN 03 [9] (DFT, B3LYP/3-21G*) on [PdTe$_4$]$^{2-}$ starting from slightly broken D_{4h}, D_{2h}, D_{2d} and T_d geometries invariantly lead to the planar close to D_{2h} [PdTe$_4$]$^{2-}$ ion. Two short Te–Te distances of 2.789 Å correspond clearly to two Te$_2^{2-}$ anions, while two sets of long
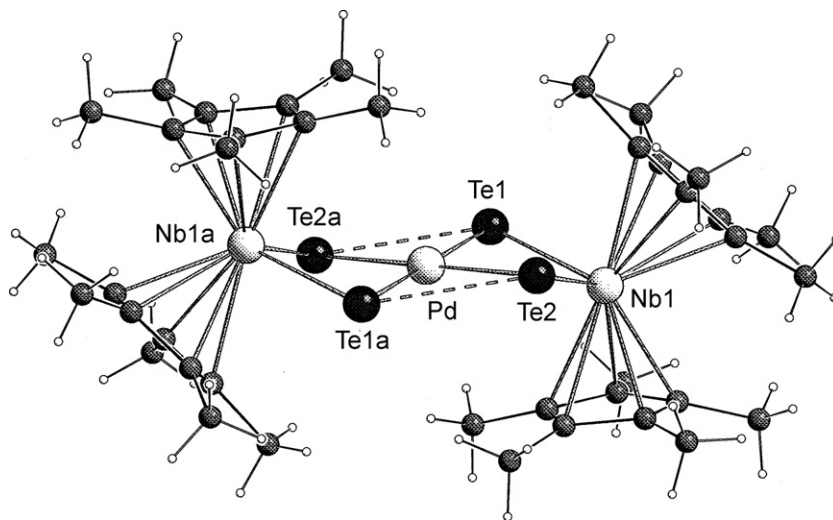

Fig. 1. Structure of [(Cp$_2^*$Nb)$_2$PdTe$_4$] (**1**). Selected distances (Å) and angles (°): Nb1–Te1 2.758(1), Nb1–Te2 2.760(1), Nb1···Pd 3.250(1), Te1···Te2 4.214(1), Te1–Te2a 3.157(1), Pd–Te1 2.631(1), Pd–Te2 2.635(1); Te1–Pd–Te2a 73.7(1), Te1–Pd–Te2 106.3(1), Te1–Pd–Te1a 180.0, Te1–Nb1–Te2 99.6(1). The Pd atom lies on an inversion centre.
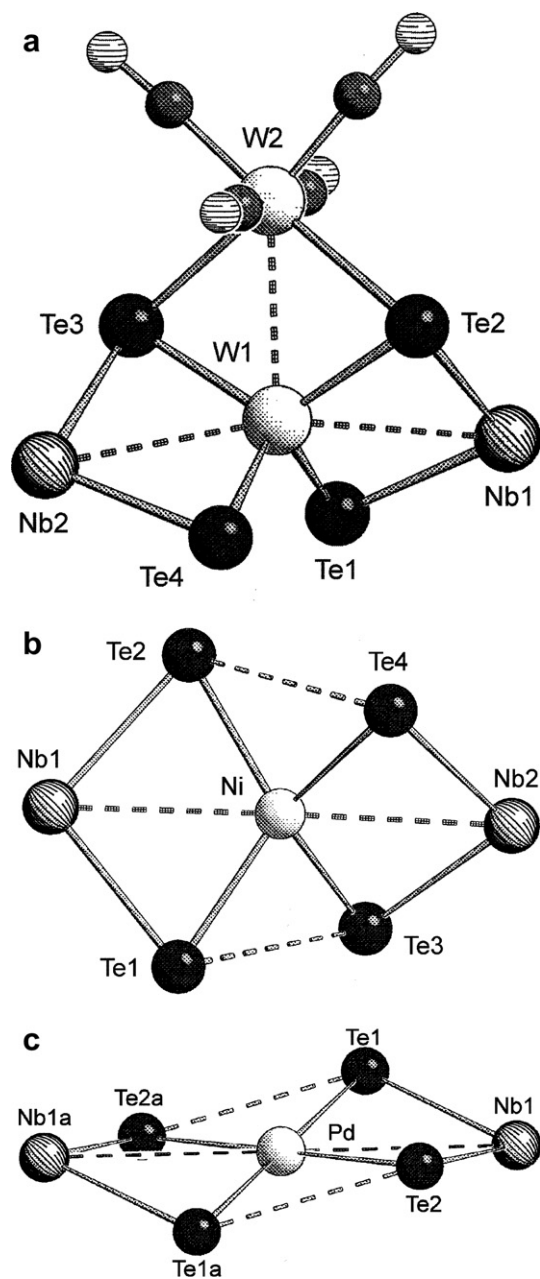
Fig. 2. Structural comparison of the heavy atom cores of [{(*t*BuC$_5$H$_4$)$_2$NbTe$_2$}$_2$W · W(CO)$_4$] (**2**) (a), [(Cp$_2^*$Nb)$_2$NiTe$_4$] (**3**) (b) and [(Cp$_2^*$Nb)$_2$PdTe$_4$] (**1**) (c).

Te···Te distances of 4.623 and 5.400 Å complete the overall description. The calculated Te–Te bond in free [PdTe$_4$]$^{2-}$ is shorter than the crystallographic one [3.157(1) Å]. This is not surprising because the Te$_2^{2-}$ units are responsible of [PdTe$_4$]$^{2-}$ coordination with niobocene fragments. Note also that the calculated (B3LYP/all electron diffuse basis set 3-21G*) short Te–Te bond in [NiTe$_4$]$^{2-}$ is equal to 2.858 Å and shorter than the 2.970 Å calculated from 3-21G/SDD basis [6]. The still shorter Te–Te bond (2.789 Å) in [PdTe$_4$]$^{2-}$ (with Pd–Te distances of 2.700 Å) than in [NiTe$_4$]$^{2-}$ (2.858 Å) with Ni–Te ones of 2.415 Å (larger covalent radius of Pd than that of Ni) argue strongly for the presence of ditelluride

Table 1
Comparison of distances (Å) and angles (°) of the central Nb$_2$MTe$_4$ moieties in [(Cp$_2^*$Nb)$_2$PdTe$_4$] (**1**), [{(*t*BuC$_5$H$_4$)$_2$NbTe$_2$}$_2$W · W(CO)$_4$] (**2**) [8] and [(Cp$_2^*$Nb)$_2$NiTe$_4$] (**3**) [6]

	1[a]	**2**	**3**
M–Te1	2.631(1)	2.539(2)	2.481(1)
M–Te2	2.635(1)	2.600(2)	2.475(1)
M–Te3	2.631(1)	2.604(2)	2.470(1)
M–Te4	2.635(1)	2.553(2)	2.475(1)
M···Nb1	3.250(1)	3.35(1)	3.100(4)
M···Nb2	3.250(1)	3.33(2)	3.147(4)
Nb1–Te1	2.758(1)	2.823(3)	2.766(1)
Nb1–Te2	2.760(1)	2.827(2)	2.766(1)
Nb2–Te3	2.758(1)	2.844(3)	2.774(1)
Nb2–Te4	2.760(1)	2.834(3)	2.757(1)
Te1···Te3	3.157(1)	4.04(1)	3.122(1)
Te2···Te4	3.157(1)	4.08(1)	3.201(1)
Te1···Te2	4.214(1)	4.22(3)	4.212(1)
Te3···Te4	4.214(1)	4.25(2)	4.169(1)
Te1–Nb1–Te2	99.6(1)	96.2(1)	99.2(1)
Te3–Nb2–Te4	99.6(1)	96.6(1)	97.8(1)
Te1–M–Te2	106.3(1)	109.9(1)	116.4(1)
Te1–M–Te3	73.7(1)	103.5(1)	78.2(1)
Te1–M–Te4	180.0	108.4(1)	138.2(1)
Te2–M–Te3	180.0	119.3(1)	139.2(1)
Te2–M–Te4	73.7(1)	104.8(1)	80.6(1)
Te3–M–Te4	106.3(1)	110.6(1)	115.0(1)
Nb1–M–Nb2	180.0	163.8(1)	178.6(1)

[a] Atom labels "Te3" and "Te4" are employed instead of "Te2a" and "Te1a".

Te$_2^{2-}$ as well in the hypothetical tetratellurides as in their niobocene complexes. It is clear from DFT calculations that the planarity of Pd polyhedron is its intrinsic property, whereas the Ni in [NiTe$_4$]$^{2-}$ and in complex **3** prefers an intermediate planar/tetrahedral D_2 geometry.

In conclusion, the novel heterometallic tetratelluropalladate cluster [(Cp$_2^*$Nb)$_2$PdTe$_4$] (**1**) has been obtained by the reaction of [Pd(DBA)$_2$] with [Cp$_2^*$Nb(Te$_2$H)]. The presence of the chelating phosphane dppm increases the yield but is not essential for the formation of **1**. The outstanding structural feature of **1** is the planar character of the electron-rich PdTe$_4$ bridge. This moiety exhibits short and long Te–Te distances similar to those in [(Cp$_2^*$NbTe$_2$)$_2$Ni] (**3**) [6]. Following the DFT calculations for **3** the complexation of the elusive [PdTe$_4$]$^{2-}$ dianion may be assisted by Nb–Pd and Te–Te bonding interactions. Finally, the distorted tetrahedral cluster **3** may be regarded as a structural transition state between the planar structure of **1** and the almost perfect tetrahedral structure of [{(*t*BuC$_5$H$_4$)$_2$Nb-Te$_2$}$_2$W · W(CO)$_4$] (**2**) [8].

3. Experimental

All procedures were carried out under N$_2$ using dry solvents with schlenktube techniques. Elemental analyses (C, H) were performed at the Mikroanalytisches Laboratorium, Universität Regensburg. NMR spectra were measured on a Bruker Avance 400 instrument. FD mass spectra were obtained on a Finnigan MAT 95 spectrometer.

$[Cp_2^*Nb(Te_2H)]$ [10] and $[Pd(DBA)_2]$ [11] were prepared due to the literature methods.

3.1. Synthesis of $[(Cp_2^*Nb)_2PdTe_4]$ (1)

To the solution of 186 mg (0.32 mmol) of $[Pd(DBA)_2]$ in 70 ml of toluene a solution of 56 mg (0.14 mmol) of bis(diphenylphosphanyl)methane in 10 ml of toluene was added. To the mixture a solution of 162 mg (0.26 mmol) of $[Cp_2^*Nb(Te_2H)]$ in 20 ml of toluene was added dropwise. After stirring for 20 h the colour has changed from dark red to brown. Then toluene was evaporated in vacuo and the resulting brownish residue was dissolved in 20 ml of toluene. Chromatography on SiO_2 (column 15×3 cm) gave upon elution with toluene an orange band containing $[Cp_2^*Nb(Te_2H)]$ followed by a brown band containing 102 mg (0.07 mmol, 22% related to Pd) of analytically pure 1.

Anal. Calc. for $C_{40}H_{60}Nb_2PdTe_4$ (1343.54): C, 35.76; H, 4.50. Found: C, 35.58; H, 4.59%. FD-MS (toluene): m/z 1343.8 (M$^+$). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.79$ ppm.

4. Crystal structure determination

Brown plates suitable for X-ray diffraction analysis were grown from toluene at -24 °C. The data were collected on a STOE imaging plate diffraction system (IPDS) at 123 K. The structure was solved by direct methods (SIR97) and refined by full-matrix least-squares procedures on F_2, using all data, with the SHELX 97 program. During the structure refinement two disordered toluene molecules have been found per asymmetric unit. The crystallographic data are summarised in Table 2.

Appendix A. Supplementary material

CCDC 641948 contains the supplementary crystallographic data for 1. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, fax: (+44) 1223-336-033, or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.05.047.

Table 2
Crystal data and structure refinement for $[(Cp_2^*Nb)_2PdTe_4] \cdot 4(C_7H_8)$ (1)

Empirical formula	$C_{40}H_{60}Nb_2PdTe_4 \cdot 4(C_7H_8)$
Formula weight	1712.0
Crystal system	Triclinic
Crystal size	$0.26 \times 0.20 \times 0.05$ mm^3
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	10.194(2)
b (Å)	12.739(2)
c (Å)	15.177(2)
α (°)	98.7(1)
β (°)	108.1(1)
γ (°)	113.4(1)
Volume (Å^3)	1631.2(5)
Z	1
Density (calculated)	1.743 g/cm^3
$F(000)$	836
Absorption coefficient	2.409 mm^{-1}
Wavelength	0.71073 Å
Diffractometer	STOE-IPDS
Temperature	123 K
Θ Range for data collection	2.39–26.82°
Reflections collected	25099
Reflections unique [R_{int}]	6410 [0.0392]
Reflections observed [$I > 2\sigma(I)$]	5484
Parameters	317
Absorption correction	Analytical
Goodness-of-fit on F^2	1.064
Largest difference in peak and hole (e/Å^3)	1.448 and -0.729
Maximum and minimum transmission	0.8822 and 0.4973
Final R indices [$I > 2\sigma$]	$R_1 = 0.038$, $wR_2 = 0.104$
R indices (all data)	$R_1 = 0.043$, $wR_2 = 0.107$

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