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Pentanuclear cluster of palladium(II) bridged by telluride ions: synthesis and crystal structure of $[Pd_5(\mu_3\text{-}Te)_4(Ph_2PCH_2CH_2PPh_2)_4]^{2+}$

Keiji Matsumoto,*[a] **Chiaki Nishitani,**[a] **Makoto Tadokoro**[a] **and Seichi Okeya**[b]

[a] *Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan*
[b] *Faculty of Education, Wakayama University, Sakaedani, Wakayama 640, Japan*

A pentanuclear palladium(II) cluster $[Pd_5(\mu_3\text{-}Te)_4(dppe)_4]^{2+}$ [dppe = 1,2-bis(diphenylphosphino)ethane] has been synthesized and characterized by an X-ray diffraction study; the cluster comprises two dinuclear $[Pd_2Te_2(dppe)_2]$ units the PdP_2Te_2 co-ordination planes of which fold along the common Te · · · Te axis with the four telluride ions of the two dinuclear units additionally co-ordinated to a central palladium(II).

In order to extend our redox study of trinuclear clusters $[M_3(\mu_3\text{-}E)_2L_3]^{2+}$ [M = Ni, Pd or Pt; E = S, Se or Te; L = $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PCH_2CH_2PPh_2$ (dppe),[1,2] $Ph_2PCH_2CH_2CH_2PPh_2$ (dppp) or $Ph_2PCH_2CH_2CH_2CH_2PPh_2$ (dppb)[3]] we tried to synthesize a trinuclear $[Pd_3(\mu_3\text{-}Te)_2(dpae)_3]^{2+}$ [dpae = 1,2-bis(diphenylarsino)ethane] cluster,[3] but unexpectedly obtained a complex which may be formulated as dinuclear $[Pd_2(\mu\text{-}Te_2)(dpae)_2]^{2+}$ and may have a Te–Te bond.† The cyclic voltammogram of the trinuclear cluster $[Pd_3(\mu_3\text{-}Te)_2(dpae)_3]^{2+}$ shows a reversible couple at −1.41 V with respect to the ferrocenium–ferrocene couple at 293 K, while that of the dinuclear complex $[Pd_2(\mu\text{-}Te_2)(dpae)_2]^{2+}$ exhibits two couples at −0.83 and −1.60 V. For the dinuclear complex, we have tentatively assigned the couple at −0.83 V to $Te_2^{2-} + 2e \rightleftharpoons 2Te^{2-}$,[5] and that at −1.60 V to $2Pd^{2+} + 2e \rightleftharpoons 2Pd^{+}$. Unfortunately a good single crystal of $[Pd_2(\mu\text{-}Te_2)(dpae)_2][BPh_4]_2$ suitable for an X-ray diffraction study was not obtained and consequently the structure has not yet been confirmed. In order to investigate the system in detail we tried to synthesize a corresponding dinuclear phosphine complex $[Pd_2(\mu\text{-}Te_2)(dppe)_2][BPh_4]_2$ containing dppe from the reaction system $Pd(MeCO_2)_2$–dppe–Te_n^{2-}. We, however, obtained a new pentanuclear palladium(II) cluster $[Pd_5(\mu_3\text{-}Te)_4(dppe)_4][BPh_4]_2$·dmf·MeCN·EtOH·$H_2O$.† In this communication the synthesis and crystal-structure determination of the pentanuclear cluster are described.

Black crystals of $[Pd_5(\mu_3\text{-}Te)_4(dppe)_4][BPh_4]$·dmf·MeCN·EtOH·$H_2O$ are air stable in their mother-liquor. In air, in the absence of the mother-liquor the crystal loses the solvent of crystallization. An ORTEP view[6] of the pentanuclear cluster $[Pd_5(\mu\text{-}Te)_4(dppe)_4]^{2+}$ together with selected bond lengths and angles is listed in Fig. 1.‡ The two PdP_2Te_2 co-ordination planes of each dinuclear $[Pd_2Te_2(dppe)_2]$ unit largely fold along the common Te · · · Te axis to form a bent Pd_2Te_2 rhombus and the four telluride ions of the two dinuclear units additionally co-ordinate to a central palladium(II). The cluster cation has a crystallographically imposed two-fold axis passing through Pd(1) and the central point between Te(1) and Te(1′) $(-x, y, -\frac{1}{2} - z)$. The co-ordination around Pd(1) is square planar [deviations of the atoms: +0.060 for Te(1), +0.061 for Te(2), −0.056 for Te(1′), −0.063 for Te(2′) and 0.001 Å for Pd(1)] with a Pd(1)–Te(1) bond length of 2.595(2) Å and Pd(1)–Te(2) of 2.595(2) Å, similar to the values observed in $[Pd(Te_4)_2]^{2-}$.[9] The [Pd(1),Te(1,2),Te(1′,2′)] and [Pd(2),Te(1,2′),P(1,2)] planes make an angle of 107.5°, [Pd(1),Te(1,2),Te(1′,2′)] and [Pd(3′),Te(1,2′),P(3′,4′)] one of 137.9°. The Te(1) · · · Te(1′) distance is 3.889(2) Å. In the dinuclear unit, each PdP_2Te_2 co-ordination plane is also planar [maximum deviation of the atom: 0.10 Å for Te(1) and 0.23 Å for P(3′)] and the dihedral angle between the two PdP_2Te_2 planes is 113.2°. The Pd(2,3)–Te bond lengths range from 2.609(2) to 2.619(2) Å,[10] close to the sum of the covalent radii (2.64 Å), however, slightly longer than the Pd(1)–Te(1,2) bonds. The Te(1) · · · Te(2′) distance of 3.424(2) Å is much longer than reported Te–Te bonds (2.7–2.8 Å),[5,11] indicating the absence of a Te–Te bond. The Pd(2) · · · Pd(3′) distance in the dinuclear unit is 3.289(2) Å. The Pd–P bond lengths are between 2.260(6) and 2.293(6) Å, which are comparable to the Pd–P bonds observed in $[Pd_6Te_6(Et_3P)_8]$.[10]

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of $[Pd_5(\mu_3\text{-}Te)_4(dppe)_4]$-

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† Reaction between $Pd(NO_3)_2$ (115 mg, 0.5 mmol), dpae (210 mg, 0.5 mmol), NaTeH (80 mg, 0.5 mmol) and $NaBPh_4$ (120 mg, 0.4 mmol) in acetonitrile (20 cm³) afforded a mixture of $[Pd_3(\mu\text{-}Te)_2(dpae)_3][BPh_4]_2$ and $[Pd_2(\mu\text{-}Te_2)(dpae)_2][BPh_4]_2$. Concentrated *N*,*N*-dimethylformamide (dmf) solution of the compounds was put on the top of a Sephadex LH-20 column (3.5 cm diameter and 30 cm in length) and was eluted with methanol–acetone (1 : 1). As purification was unsatisfactory, reddish brown $[Pd_3(\mu_3\text{-}Te)_2(dpae)_3][BPh_4]_2$ and dark brown $[Pd_2(\mu\text{-}Te_2)(dpae)_2][BPh_4]_2$ crystals were visually separated {Found: C, 56.8; H, 4.30; N, 0.45. $[Pd_3Te_2(C_{26}H_{24}As_2)_3][B(C_6H_5)_4]_2$·$CH_3CN$ requires C, 56.6; H, 4.25; N, 0.50%. Found: C, 57.1; H, 4.20. $[Pd_2Te_2(C_{26}H_{24}As_2)_2][B(C_6H_5)_4]_2$ requires C, 57.6; H, 4.25%}.[4]

Preparation of $[Pd_5(\mu_3\text{-}Te)_4(dppe)_4][BPh_4]_2$·dmf·MeCN·EtOH·$H_2O$: $Pd(MeCO_2)_2$ (112 mg, 0.5 mmol) was dissolved in a mixture of dmf (5 cm³) and acetonitrile (15 cm³) and dppe (200 mg, 0.5 mmol) was added. After stirring for 3 h, a product of oxidation of NaTeH (75 mg, 0.5 mmol) by air (20 cm³) in ethanol (5 cm³) and triethylamine (30 mg, 0.3 mmol) were added and stirred overnight to afford a brownish black solution. Sodium tetraphenylborate (110 mg, 0.3 mmol) was added, the solution filtered and the filtrate gave black crystals upon standing in the air at room temperature for 3 d. Yield 16% (51 mg) {Found: C, 54.1; H, 4.10; N, 0.45. $[Pd_5Te_4(C_{26}H_{24}P_2)_4][B(C_6H_5)_4]_2$·$(CH_3)_2NCHO$·$CH_3CN$·$CH_3CH_2OH$·$H_2O$ requires C, 55.7; H, 4.60; N, 0.80%}.

‡ $[Pd_5(\mu_3\text{-}Te)_4(dppe)_4][BPh_4]_2$·dmf·MeCN·EtOH·$H_2O$: $M = 3452.8$, monoclinic, space group $C2/c$, $a = 37.398(6)$, $b = 17.504(7)$, $c = 33.173(5)$ Å, $\beta = 125.839(8)°$, $U = 17\,603(7)$ Å³, $Z = 4$, $D_m = 1.28$ g cm⁻³, $D_c = 1.30$ g cm⁻³, μ(Mo-Kα) = 12.7 cm⁻¹, $F(000) = 6856$, $T = 293$ K, black prism, 0.34 × 0.45 × 0.72 mm. Data (16 336 intensities to 2θ 42°, absorption corrected, 16 065 unique) were collected on a Rigaku AFC7S diffractometer using graphite-monochromated Mo-Kα radiation (0.710 69 Å). The structure was solved by direct methods with SHELXS 86[7] and refined by full-matrix least squares {refinement on *F* for 8148 reflections [$I > 3\sigma(I)$] with TEXSAN}.[8] All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were placed at calculated positions with $B(H) = 1.2\,B(C)$. The final *R* was 0.062 and *R′* 0.091 for 819 parameters with $w = 1/\sigma^2(F_o)$. Solvents of crystallization are disordered over two sites with occupancies 0.5 and 0.5 and their hydrogen atoms were excluded from the refinement. The maximum and minimum electron densities on the final Fourier-difference synthesis were 1.8 and −0.65 e Å⁻³, respectively. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/172.

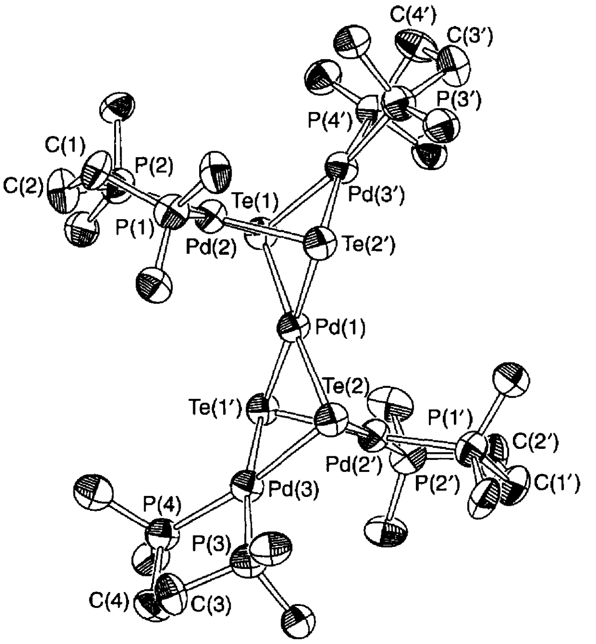

Fig. 1 Structure of the pentanuclear cluster $[Pd_5(\mu_3\text{-}Te)_4(dppe)_4]^{2+}$. Phenyl rings and hydrogen atoms are omitted for clarity. Only the *ipso* carbon atoms of the phenyl rings are drawn. Selected bond lengths (Å) and angles (°): Pd(1)–Te(1) 2.595(2), Pd(1)–Te(2) 2.595(2), Pd(2)–Te(1) 2.619(2), Pd(2)–Te(2') 2.610(2), Pd(3)–Te(1') 2.609(2), Pd(3)–Te(2) 2.611(2), Pd(2)–P(1) 2.264(6), Pd(2)–P(2) 2.261(6), Pd(3)–P(3) 2.278(6), Pd(3)–P(4) 2.293(6); Te(1)–Pd(1)–Te(1') 97.02(4), Te(1)–Pd(1)–Te(2') 82.53(4), Pd(1)–Te(1)–Pd(2) 75.12(7), Pd(1)–Te(2')–Pd(2) 75.27(7), Pd(1)–Te(1)–Pd(3') 89.72(8), Pd(1)–Te(2)–Pd(3) 89.70(7), Te(1)–Pd(2)–Te(2') 81.83(5), Te(1')–Pd(3)–Te(2) 82.01(5), P(1)–Pd(2)–P(2) 86.8(2), P(3)–Pd(3)–P(4) 85.3(2)

$[BPh_4]_2$ in dmf at 300 K shows one singlet at δ 42.8 *vs.* external H_3PO_4, indicating the presence of only one magnetic environment for the phosphorus of the co-ordinated dppe. For $[Pd_3(\mu_3\text{-}Te)_2(dppe)_3][BPh_4]_2$ one resonance is also observed at δ 46.7. Two such values in close proximity are consistent with the similar dppe environment for both clusters. The cyclic voltammogram of $[Pd_5(\mu_3\text{-}Te)_4(dppe)_4][BPh_4]_2$ in dmf exhibits irreversible reduction waves at −1.84 and −2.44 V and oxidation waves at −1.32 and −1.00 V *vs.* the ferrocenium–ferrocene couple at 293 K. Controlled-potential coulometry for the cluster at −2.10 V indicates that the reductions at −1.84 and −2.44 V involve a two-electron process. It is assumed that the cluster is reduced at −1.84 V and a product of this reduction is itself reduced at −2.44 V. As the oxidation peak at −1.32 V is observed after cathodic scanning to −2.10 V and the peak at −1.00 V disappears, it is concluded that a product of the reduction at −2.44 V is oxidized at −1.00 V and that at −1.84 V is oxidized at −1.32 V.

References

1 K. Matsumoto, N. Saiga, S. Tanaka and S. Ooi, *J. Chem. Soc., Dalton Trans.*, 1991, 1265.
2 K. Matsumoto, M. Ikuzawa, M. Kamikubo and S. Ooi, *Inorg. Chim. Acta*, 1994, **217**, 129.
3 K. Matsumoto and S. Ooi, *Proceedings of the 30th International Conference on Coordination Chemistry*, Kyoto, 1994, PS8-05, p. 356.
4 K. Matsumoto, M. Ikuzawa and K. Takahashi, unpublished work.
5 A. L. Ma, J. B. Thoden and L. F. Dahl, *J. Chem. Soc., Chem. Commun.*, 1992, 1516.
6 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
7 G. M. Sheldrick, SHELXS 86, Program for the Solution of Crystal Structures, University of Göttingen, 1986.
8 TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985.
9 H. Wolkers, K. Dehnicke, D. Fenske, A. Khassanov and S. S. Hafner, *Acta Crystallogr., Sect. C*, 1991, **47**, 1627; R. D. Adams, T. A. Wolfe, B. W. Eicthorn and R. C. Haushalter, *Polyhedron*, 1989, **8**, 701.
10 J. G. Brennan, T. Siegrist, S. M. Stuczynski and M. L. Steigerwald, *J. Am. Chem. Soc.*, 1990, **112**, 9233.
11 M. D. Vaira, M. Peruzzini and P. Stoppioni, *J. Chem. Soc., Chem. Commun.*, 1986, 374.

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