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Synthesis and cyclic voltammetry of trinuclear selenido and tellurido clusters of nickel(II), palladium(II) and platinum(II) with 1,2-bis(diphenylphosphino)ethane and crystal structure of the tellurido cluster of platinum(II)

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Abstract

Reaction of M^{2+} (M = Ni, Pd or Pt) with 1,2-bis(diphenylphosphino)ethane (dppe) and NaSeH or NaTeH in acetonitrile (MeCN) and/or *N,N*-dimethylformamide (DMF) gives rise to $[Pd_3Se_2(dppe)_3][PF_6]_2$ (**2**), $[Pt_3Se_2(dppe)_3][BPh_4]_2$ (**3**), $[Ni_3Te_2(dppe)_3][BPh_4]_2$ (**4**), $[Pd_3Te_2(dppe)_3][BPh_4]_2$ (**5**) and $[Pt_3Te_2(dppe)_3][BPh_4]_2$ (**6**). The X-ray structure of **6** was determined and cyclic voltammograms of **2**–**6** at 293 and 255 K were recorded. The structure of $[Pt_3Te_2(dppe)_3]^{2+}$ comprises three square-planar $PtTe_2P_2$ coordination planes sharing two μ_3-Te^{2-} ligands. Interatomic distances are Te···Te 3.432(2), Pt···Pt 3.456, Pt–Te 2.634 and Pt–P 2.263 Å. Cyclic voltammograms of the reduction process of complex **4** in DMF at 293 K give two chemically reversible couples, while those of **2**, **3**, **5** and **6** show one reversible couple at 255 K.

Key words: Crystal structures; Electrochemistry; Nickel complexes; Palladium complexes; Platinum complexes; Selenido complexes; Tellurido complexes; Cluster complexes

Introduction

In a previous paper [1] we reported the synthesis of trinuclear $[M_3E_2(dppe)_3]^{2+}$ (M = Ni, Pd, Pt, E = S; M = Ni, E = Se) clusters and showed that cyclic voltammograms of the reduction process of $[M_3E_2(dppe)_3]^{2+}$ (M = Ni, E = S, Se) give two chemically reversible couples which involve one-electron reduction and oxidation processes in MeCN at 255 K, and $[Ni_3Se_2(dppe)_3]^{2+}$ is easier to reduce than $[Ni_3S_2(dppe)_3]^{2+}$. On the other hand $[M_3E_2(dppe)_3]^{2+}$ (M = Pd, Pt, E = S) are irreversibly reduced in DMF at 293 K, but at 255 K $[Pd_3S_2(dppe)_3]^{2+}$ is reversibly reduced. The process is a two-electron transfer. We have now extended our studies to include $[M_3E_2(dppe)_3]^{2+}$ (M = Pd, Pt, E = Se; M = Ni, Pd, Pt, E = Te) clusters and report our findings here.

Experimental

All manipulations were performed in dinitrogen atmosphere using solvent degassed prior to use. Acetonitrile (MeCN) and *N,N*-dimethylformamide (DMF) were dried over CaH_2 and $CuSO_4$, respectively, and distilled. NaSeH and NaTeH were prepared by the literature method [2]. The preparation of $[Ni_3Se_2(dppe)_3][BPh_4]_2$ (**1**) was described in a previous paper [1].

$[Pd_3Se_2(dppe)_3][PF_6]_2$ (2)

To a stirring solution of $Pd(MeCOO)_2$ (0.5 mmol, 112 mg) in MeCN (14 cm^3) was added dppe (0.5 mmol, 200 mg), and the solution was stirred for 1 h. After addition of NaSeH (0.45 mmol, 46 mg) in ethanol (1 cm^3) and triethylamine (0.3 mmol, 30 mg) the solution was stirred for 20 h, treated with $NaPF_6$ (0.6 mmol, 100 mg) and filtered. The filtrate was placed in air for a couple of days. Yellow crystals were obtained in 6.7% yield (22 mg). *Anal.* Found: C, 46.4; H, 3.7. Calc. for $[Pd_3Se_2(C_{28}H_{24}P_2)_3][PF_6]_2$: C, 47.7; H, 3.7%.

$[Pt_3Se_2(dppe)_3][BPh_4]_2$ (3)

A mixture of K_2PtCl_4 (0.5 mmol, 207 mg) and dppe (0.5 mmol, 200 mg) in 12 cm^3 MeCN was heated at 70 °C for 1 h. NaSeH (0.45 mmol, 46 mg) in ethanol (1 cm^3) and triethylamine (0.3 mmol, 30 mg) were

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added. The solution was stirred for 20 h, treated with $NaBPh_4$ (0.6 mmol, 205 mg) and filtered. The filtrate was placed in air for 1 day. Brownish yellow crystals were obtained in 21% yield (88 mg). *Anal.* Found: C, 58.2; H, 4.3. Calc. for $[Pt_3Se_2(C_{28}H_{24}P_2)_3][C_{24}H_{28}B]_2$: C, 58.7; H, 4.4%.

$[Ni_3Te_2(dppe)_3][BPh_4]_2$ (4)

To a stirring suspension of $NiCl_2$ (1 mmol, 130 mg) in MeCN (21 cm^3) was added dppe (1 mmol, 400 mg). After 3 h NaTeH (0.9 mmol, 137 mg) in ethanol (15 cm^3) was added. The solution was stirred for 20 h, treated with $NaBPh_4$ (0.7 mmol, 240 mg) and filtered. The filtrate was allowed to stand at room temperature for 3 days in air. Black–brown crystals were obtained in 10% yield (77 mg). *Anal.* Found: C, 66.5; H, 5.0. Calc. for $[Ni_3Te_2(C_{28}H_{24}P_2)_3][C_{24}H_{28}B]_2$: C, 66.8; H, 5.0%.

$[Pd_3Te_2(dppe)_3][BPh_4]_2$ (5)

To a stirring solution of $Pd(NO_3)_2$ (0.5 mmol, 115 mg) in MeCN (20 cm^3) and DMF (7 cm^3) was added dppe (0.5 mmol, 200 mg) and the solution was refluxed for 3 h at 120 °C. NaTeH (0.45 mmol, 68 mg) in ethanol (15 cm^3) and triethylamine (0.3 mmol, 30 mg) were then added. The solution was stirred for 20 h, treated with $NaBPh_4$ (0.3 mmol, 105 mg) and filtered. Dark brown crystals were obtained from the filtrate which had been left standing at room temperature for 3 days in air. Yield 37% (150 mg). *Anal.* Found: C, 62.4; H, 4.3. Calc. for $[Pd_3Te_2(C_{28}H_{24}P_2)_3][C_{24}H_{28}B]_2$: C, 62.8; H, 4.7%.

$[Pt_3Te_2(dppe)_3][BPh_4]_2$ (6)

K_2PtCl_4 (1 mmol, 415 mg) was suspended in MeCN (20 cm^3) and DMF (8 cm^3). After stirring for 20 min dppe (1 mmol, 400 mg) was added and refluxed for 4 h at 120 °C. NaTeH (0.9 mmol, 137 mg) in ethanol (15 cm^3) and triethylamine (0.3 mmol, 30 mg) were then added. The mixture was stirred for 20 h, treated with $NaBPh_4$ (0.7 mmol, 240 mg) and filtered. The filtrate was left standing in air for 3 days. Yellow crystals were obtained in 55% yield (490 mg). *Anal.* Found: C, 56.9; H, 4.0. Calc. for $[Pt_3Te_2(C_{28}H_{24}P_2)_3][C_{24}H_{28}B]_2$: C, 56.6; H, 4.2%.

X-ray structure analysis for 6

A Rigaku AFC-5R automated diffractometer was used to determine the space group of $P\bar{1}$ and lattice parameters from 13 centered reflections. Three standard reflections monitored every 150 reflections showed no decay. Semi-empirical absorption corrections were applied [3]. The crystal data and summary of data collection and structure refinement are given in Table 1.

TABLE 1. Crystal data and details of data collection and structure refinement for $[Pt_3Te_2(dppe)_3][BPh_4]_2$ (6)

Empirical formula	$C_{126}H_{112}B_2P_6Pt_3Te_2$
Formula weight	2674.2
Crystal size (mm)	0.65 × 0.34 × 0.06
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	16.035(3)
b (Å)	32.024(4)
c (Å)	11.774(3)
α (°)	94.73(2)
β (°)	111.05(2)
γ (°)	85.63(2)
V (Å^3)	5616.1(17)
Z	2
D_c (Mg m^{-3})	1.58
μ (mm^{-1})	4.20
F(000)	2612
2θ Range (°)	5–42
Scan type	ω
Scan speed (°min^{-1})	8
Scan range (°)	$1.0 + 0.3 \tan \theta$
h, k, l	0 to 16, −32 to 32, −12 to 12
Reflections collected	12797
Reflections $> 3\sigma(I)$	10063
Transmission factors: min., max.	0.273, 1.000
No. parameters	823
Final indices R, R'	0.068, 0.087
Goodness-of-fit	1.65
Largest Δ/σ	0.6
Largest difference peak, hole (e Å^{-3})	4 0, −1.7

MITHRIL and DIRDIF gave the positions of 11 heavy atoms [3]. The remaining non-hydrogen atoms were found with the use of SHELX 76 [4]. Refinement of the heavy atoms was performed using the anisotropic thermal parameters. Phenyl rings were refined as a rigid body using a C–C distance of 1.395 Å [4]. All hydrogen atoms were placed at calculated positions (C–H = 0.96 Å) with the isotropic temperature factor $B(\mathrm{H}) = 1.2B(\mathrm{C})$. The function minimized was $\Sigma w(F_o - |F_c|)^2$, where $w = \sigma[(F_o^2) + 0.001F_o^2]^{-1}$ was used. Atomic coordinates for non-hydrogen atoms are listed in Table 2. Figure 1 was drawn using ORTEPII [5]. UNICS(HBLS-IV and DAPH) [6] was used to make the F_o–F_c tables and to calculate the bond lengths and angles. Calculations were performed on an HITAC M-660K computer at Osaka City University.

Measurements

Cyclic voltammograms were recorded at 293 ± 1 and 255 ± 1 K with a Yanaco P-1100 system equipped with a Rikadenki RW201K x-y recorder. The working and counter electrodes were a glassy carbon disk and a platinum wire. The Ag–AgCl reference electrode was used in DMF solution. Potentials were measured against the ferrocenium–ferrocene couple as an internal standard. Tetrabutylammonium perchlorate (TBAP) was used as a supporting electrolyte.

Controlled potential coulometry of complexes **2–6** was carried out at 293 ± 1 K in a standard H-type cell with an Hokuto HA-501 potentiostat and a Rikadenki RW-11T x-y recorder using the t-y mode to obtain the total charge consumed. The working electrode was of reticulated vitreous carbon and the counter electrode was a platinum wire. The Ag–AgCl reference electrode was used in DMF solution.

Results and discussion

A perspective view of the cluster cation of **6** is shown in Fig. 1. The structure of the cluster consists of three square-planar $PtTe_2P_2$ coordination planes sharing two μ_3-Te^{2-} ligands. The cluster may alternatively be described by a central trigonal bipyramidal Pt_3Te_2 core with each Pt atom additionally coordinated by dppe in a square planar fashion. In the Pt_3Te_2 core of cluster **6** the Pt–Te bond length of 2.634 Å is 0.030 Å longer, while the Pt–Te–Pt angle of 82.05° is 4.7° smaller than those found in $[(Pt(PEt_3)_2)_3(\mu_3\text{-}Te)_2][PF_6]_2$ [7]. Consequently the non-bonded Te···Te distance of 3.432(2) Å is 0.260 Å longer and the Pt···Pt distance of 3.456 Å is 0.121 Å shorter, indicating elongation of the Pt_3Te_2 core of **6** in the Te···Te direction. An analogous elongation was observed in the Ni_3Se_2 core of $[Ni_3Se_2(dppe)_3]^{2+}$ [1] as compared with that of

TABLE 2. Atomic coordinates with standard deviations in parentheses for $[Pt_3Te_2(dppe)_3][BPh_4]_2$ (**6**)

Atom	*x*	*y*	*z*	*B*^{a}
Pt1	0.31225(5)	0.28629(2)	0.41051(6)	2.209(2)*
Pt2	0.26607(5)	0.18447(2)	0.31924(6)	2 197(2)*
Pt3	0.10265(5)	0.26752(3)	0.20658(6)	2.207(2)*
Te1	0.18464(8)	0.24120(4)	0.42561(10)	2.296(3)*
Te2	0.26099(8)	0.24815(4)	0.18876(10)	2.200(3)*
P1	0.3366(4)	0.3265(2)	0.5875(5)	2.9(1)*
P2	0 4329(4)	0.3151(2)	0.3985(5)	2.8(1)*
P3	0.2965(4)	0.1363(2)	0.4606(5)	2.7(1)*
P4	0.3042(4)	0.1319(2)	0.2012(5)	2.8(1)*
P5	−0.0380(4)	0.2734(2)	0.2121(5)	2.7(1)*
P6	0.0452(4)	0.3006(2)	0.0293(5)	2.8(1)*
C1	0.416(2)	0.362(1)	0.592(2)	3.8(4)
C2	0.486(2)	0.341(1)	0.546(2)	3.1(4)
C3	0.309(2)	0.086(1)	0.388(2)	3.3(4)
C4	0.362(2)	0.088(1)	0.303(2)	3.1(4)
C5	−0.104(2)	0.313(1)	0.103(2)	4.0(4)
C6	−0.077(2)	0.302(1)	−0.014(2)	3.7(4)
C7	0.192(2)	0.377(1)	0.477(2)	4.1(5)
C8	0.123(2)	0.407(1)	0.473(3)	6.7(7)
C9	0.104(3)	0.420(1)	0.579(3)	8.9(9)
C10	0.154(3)	0.403(1)	0.689(3)	8.7(9)
C11	0.223(2)	0.372(1)	0.693(2)	5.8(6)
C12	0.242(2)	0.360(1)	0.588(2)	3.7(4)
C13	0.462(2)	0.310(1)	0.824(2)	5.0(5)
C14	0.489(2)	0.292(1)	0.937(2)	6.0(6)
C15	0.434(2)	0.265(1)	0.960(3)	6.5(7)
C16	0.352(2)	0.255(1)	0.871(3)	6.1(6)
C17	0.325(2)	0.273(1)	0.758(2)	4.9(5)
C18	0.380(2)	0.300(1)	0.734(2)	3.2(4)
C19	0.379(2)	0.341(1)	0.161(2)	4.7(5)
C20	0.370(2)	0.369(1)	0.073(3)	6.6(7)
C21	0.394(3)	0.411(1)	0.109(3)	9.2(9)
C22	0.427(2)	0.424(1)	0.232(3)	7.9(8)
C23	0.436(2)	0.395(1)	0.320(3)	6.2(6)
C24	0.412(1)	0.354(1)	0.284(2)	3.0(4)
C25	0.529(2)	0.242(1)	0.446(2)	3.6(4)
C26	0.597(2)	0.212(1)	0.446(2)	5.4(6)
C27	0.654(2)	0.218(1)	0.382(3)	6.9(7)
C28	0.641(2)	0.255(1)	0.318(2)	5.4(6)
C29	0.572(2)	0.284(1)	0.318(2)	4.3(5)
C30	0.516(2)	0.278(1)	0.382(2)	3.4(4)
C31	0.477(2)	0.118(1)	0.614(3)	6.5(6)
C32	0.560(2)	0.129(1)	0.698(3)	6.4(6)
C33	0.574(2)	0.170(1)	0.745(2)	5.3(5)
C34	0.505(2)	0 201(1)	0.709(2)	5.9(6)
C35	0.422(2)	0.190(1)	0.625(2)	5.0(5)
C36	0.408(2)	0.149(1)	0.578(2)	3 3(4)
C37	0.240(2)	0.129(1)	0.658(3)	6.2(6)
C38	0.176(2)	0.121(1)	0.708(2)	5.7(6)
C39	0.089(2)	0.112(1)	0.632(2)	5.8(6)
C40	0.066(2)	0.111(1)	0.506(3)	6.2(6)
C41	0.129(2)	0.119(1)	0.455(2)	5.8(6)
C42	0.216(2)	0.128(1)	0.531(2)	3.7(4)
C43	0.205(2)	0.070(1)	0.047(2)	5.7(6)
C44	0.127(2)	0.054(1)	−0.039(3)	7.3(7)
C45	0.050(2)	0.080(1)	−0.083(2)	5.3(6)
C46	0.052(2)	0.123(1)	−0.041(2)	4.9(5)
C47	0.130(2)	0.138(1)	0.045(2)	4.6(5)
C48	0.206(1)	0.112(1)	0.089(2)	2.9(4)
C49	0.447(2)	0.166(1)	0.169(3)	6.6(7)

(*continued*)

TABLE 2 (*continued*)

Atom	x	y	z	B^a
C50	0.511(3)	0.168(1)	0.114(3)	8.5(9)
C51	0.508(2)	0.141(1)	0.012(3)	7.3(7)
C52	0.440(3)	0.113(1)	−0.035(3)	9.5(10)
C53	0.376(2)	0.111(1)	0.019(2)	6.0(6)
C54	0.380(2)	0.137(1)	0.122(2)	3.3(4)
C55	−0.190(2)	0.227(1)	0.119(2)	4.8(5)
C56	−0.236(2)	0.190(1)	0.087(3)	6.1(6)
C57	−0.189(3)	0.151(1)	0.094(3)	8.2(8)
C58	−0.095(2)	0.149(1)	0.132(3)	7.2(7)
C59	−0.049(2)	0.186(1)	0.163(2)	5.1(5)
C60	−0.096(1)	0.225(1)	0.157(2)	3.0(4)
C61	−0.042(2)	0.335(1)	0.393(3)	6.8(7)
C62	−0.060(3)	0.350(1)	0.497(3)	8.0(8)
C63	−0.092(2)	0.324(1)	0.559(3)	6.0(6)
C64	−0.107(2)	0.282(1)	0.517(3)	6.2(6)
C65	−0.089(2)	0.267(1)	0.413(2)	5.0(5)
C66	−0.057(2)	0.293(1)	0.351(2)	3.9(4)
C67	0.094(2)	0.296(1)	−0.181(2)	4.6(5)
C68	0.109(2)	0.275(1)	−0.281(3)	7.0(7)
C69	0.096(2)	0.232(1)	−0.302(2)	5.8(6)
C70	0.068(2)	0.210(1)	−0.224(2)	5.1(5)
C71	0.053(2)	0.232(1)	−0.124(2)	4.9(5)
C72	0.066(1)	0.275(1)	−0.103(2)	3.1(4)
C73	0.151(2)	0.367(1)	0.147(2)	5.5(6)
C74	0.175(2)	0.409(1)	0.164(2)	5.6(6)
C75	0.123(2)	0.438(1)	0.082(3)	7.6(7)
C76	0.047(3)	0.426(1)	−0.016(4)	10.1(10)
C77	0.024(2)	0.384(1)	−0.032(3)	8.1(8)
C78	0.076(2)	0.354(1)	0.049(2)	3.3(4)
C101	0.719(2)	0.355(1)	0.681(2)	5.3(5)
C102	0.716(2)	0.312(1)	0.662(3)	5.9(6)
C103	0.697(2)	0.288(1)	0.744(2)	5.9(6)
C104	0.681(2)	0.309(1)	0.845(2)	4.3(5)
C105	0.684(2)	0.352(1)	0.864(2)	4.6(5)
C106	0.703(2)	0.376(1)	0.782(2)	3.9(4)
C107	0.837(2)	0.430(1)	0.726(3)	5.9(6)
C108	0.890(2)	0.447(1)	0.672(3)	6.9(7)
C109	0.863(2)	0.486(1)	0.619(3)	6.8(7)
C110	0.784(2)	0.507(1)	0.620(3)	5.9(6)
C111	0.730(2)	0.489(1)	0.674(2)	5.2(5)
C112	0.757(2)	0.451(1)	0.727(2)	4.4(5)
C113	0.825(2)	0.419(1)	1.018(3)	7.4(7)
C114	0.876(3)	0.434(2)	1.136(4)	12.1(13)
C115	0.855(3)	0.474(2)	1.180(4)	12.3(13)
C116	0.784(3)	0.499(1)	1.106(3)	8.7(9)
C117	0.733(2)	0.484(1)	0.989(3)	7.5(7)
C118	0.754(2)	0.444(1)	0.944(2)	4.7(5)
C119	0.545(2)	0.455(1)	0.641(2)	4.3(5)
C120	0.455(2)	0.468(1)	0.606(2)	5.2(5)
C121	0.413(2)	0.473(1)	0.693(3)	6.1(6)
C122	0.461(2)	0.465(1)	0.814(3)	7.8(8)
C123	0.551(2)	0.452(1)	0.849(3)	6.7(7)
C124	0.593(2)	0.447(1)	0.762(2)	4.8(5)
C201	0.064(2)	−0.022(1)	0.377(2)	5.5(6)
C202	−0.016(2)	0.003(1)	0.343(2)	5.3(5)
C203	−0.032(2)	0.033(1)	0.259(2)	5.8(6)
C204	0.033(2)	0.039(1)	0.208(3)	6.4(6)
C205	0.113(2)	0.015(1)	0.241(2)	5.2(5)
C206	0.128(2)	−0.016(1)	0.326(2)	3.3(4)
C207	0.252(2)	−0.042(1)	0.161(2)	4.4(5)
C208	0.306(2)	−0.036(1)	0.093(3)	7.1(7)
C209	0.393(2)	−0.023(1)	0.152(3)	6.4(6)
C210	0.427(2)	−0.016(1)	0.279(3)	6.1(6)
C211	0.373(2)	−0.023(1)	0.347(2)	4.8(5)
C212	0.286(2)	−0.035(1)	0.288(2)	4.3(5)
C213	0.209(2)	−0.123(1)	0.241(2)	5.4(6)
C214	0.186(2)	−0.165(1)	0.222(3)	6.9(7)
C215	0.156(3)	−0.182(1)	0.305(4)	10.1(10)
C216	0.150(3)	−0.158(1)	0.407(3)	9.4(9)
C217	0.173(3)	−0.116(1)	0.426(3)	8.0(8)
C218	0.203(2)	−0.099(1)	0.343(2)	4.8(5)
C219	0.261(2)	0.003(1)	0.578(2)	5.2(5)
C220	0.305(2)	0.010(1)	0.704(3)	8.0(8)
C221	0.367(3)	−0.020(1)	0.769(4)	9.8(10)
C222	0.385(2)	−0.057(1)	0.709(3)	8.0(8)
C223	0.341(2)	−0.065(1)	0.584(2)	5.6(6)
C224	0.279(2)	−0.034(1)	0.518(2)	4.7(5)
B100	0.702(2)	0.430(1)	0.798(2)	3.9(5)
B200	0.225(2)	−0.045(1)	0.373(2)	3.6(5)

[a] B = isotropic temperature factor, $(8\pi^2u^2)$. Starred items: $B_{eq} = (8\pi^2)/3\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$.

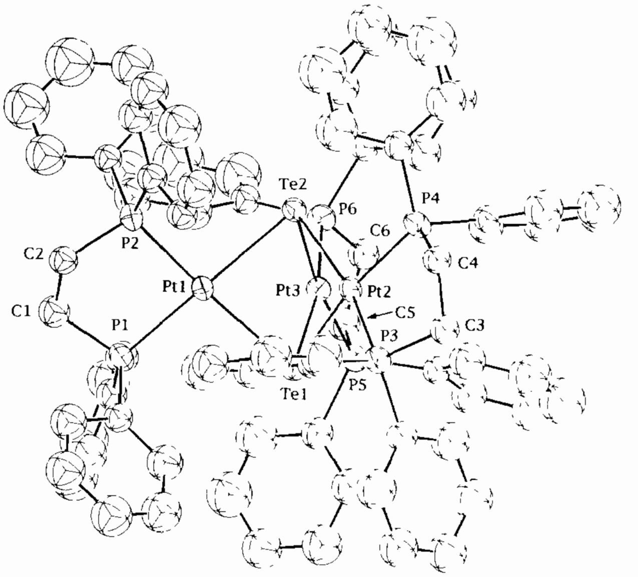

Fig. 1. ORTEP drawing of the cluster cation $[Pt_3Te_2(dppe)_3]^{2+}$ of **6**

$[Ni_3Se_2(PEt_3)_6]^{2+}$ [8]. The three Pt atoms form an asymmetric triangle. The Pt···Pt distances of 3.388(2), 3.420(1) and 3.561(1) Å, which are much longer than that (2.77 Å) found in platinum metal, are too long to be assigned as any Pt–Pt interaction. As each Pt atom is well isolated, the Pt···Pt length would be influenced by bulky ligands and/or crystal packing. An asymmetric arrangement of three metal atoms has also been reported in previous works [1, 8]. The shorter Pt–P bond length of 2.263 Å, smaller P–Pt–P angle of 86.2°, less acute Te–Pt–Te angle of 81.32° and elongation

TABLE 3. Selected interatomic distances (Å) and angles (°) for $[Pt_3Te_2(dppe)_3][PBh_4]_2$ (**6**)

Pt1···Pt2	3.388(2)	Pt2–Pt1–Pt3	63.07(3)
Pt1···Pt3	3.420(1)	Te1–Pt1–Te2	80.76(5)
Pt1–Te1	2.648(2)	P1–Pt1–P2	86.4(2)
Pt1–Te2	2.650(2)	Pt1–Pt2–Pt3	58.90(3)
Pt1–P1	2.271(6)	Te1–Pt2–Te2	81.51(5)
Pt1–P2	2.250(6)	P3–Pt2–P4	85.7(2)
Pt2···Pt3	3.561(1)	Pt1–Pt3–Pt2	58.03(3)
Pt2–Te1	2.632(2)	Te1–Pt3–Te2	81.70(5)
Pt2–Te2	2.626(2)	P5–Pt3–P6	86.4(2)
Pt2–P3	2.257(6)	Pt1–Te1–Pt2	79.85(5)
Pt2–P4	2.269(6)	Pt1–Te1–Pt3	81.08(5)
Pt3–Te1	2.614(2)	Pt2–Te1–Pt3	85.51(5)
Pt3–Te2	2.633(2)	Pt1–Te2–Pt2	79.92(5)
Te1···Te2	3.432(2)	Pt1–Te2–Pt3	80.69(5)
Pt3–P5	2.263(6)	Pt2–Te2–Pt3	85.24(5)
Pt3–P6	2.269(6)	Pt1–P1–C1	105.6(8)
P1–C1	1.75(3)	Pt1–P2–C2	105.4(7)
P2–C2	1.79(2)	Pt2–P3–C3	108.0(8)
P3–C3	1.79(2)	Pt2–P4–C4	107.5(7)
P4–C4	1.88(2)	Pt3–P5–C5	108.4(8)
P5–C5	1.85(3)	Pt3–P6–C6	106.7(8)
P6–C6	1.83(3)	P1–C1–C2	111(2)
C1–C2	1.49(3)	P2–C2–C1	110(2)
C3–C4	1.54(3)	P3–C3–C4	111(2)
C5–C6	1.58(4)	P4–C4–C3	105(2)
		P5–C5–C6	105(2)
		P6–C6–C5	111(2)

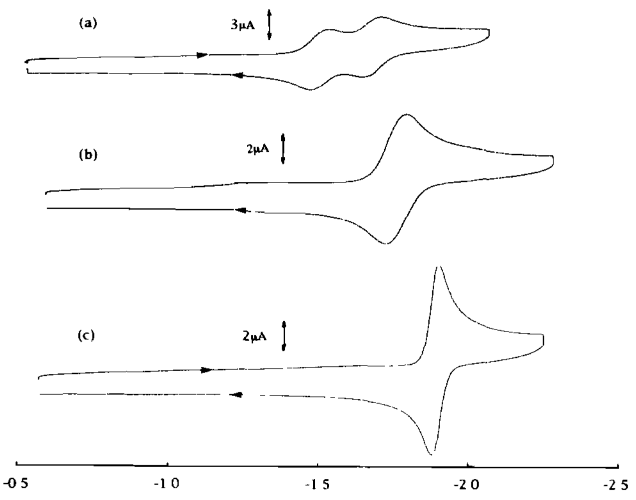

Fig. 2. Cyclic voltammograms of 3×10^{-4} mol dm^{-3} cluster **4** (a), **5** (b) and **6** (c) containing 0.1 mol dm^{-3} TBAP at a scan rate of 50 mV s^{-1} at 293 K.

of the Te···Te distance in **6** than those found in $[(Pt(PEt_3)_2)_3(\mu_3\text{-}Te)_2][PF_6]_2$ [7] result from the formation of the Pt–dppe five-membered chelate ring. Each $PtTe_2P_2$ coordination plane is tetrahedrally distorted square-planar (maximum deviation : 0.32 Å for P4). The angle between the Pt2Te1Te2 and Pt2P3P4 planes is 18.7°. Bond lengths and angles of the $PtTe_2P_2$ coordination planes for **6** are virtually identical to those observed in $[(Ph_2PC_2H_4PPh_2)Pt(\mu\text{-}Te)_2Pt(Ph_2PC_2H_4PPh_2)]\cdot2DMF$ [9]. Selected bond lengths and angles are given in Table 3.

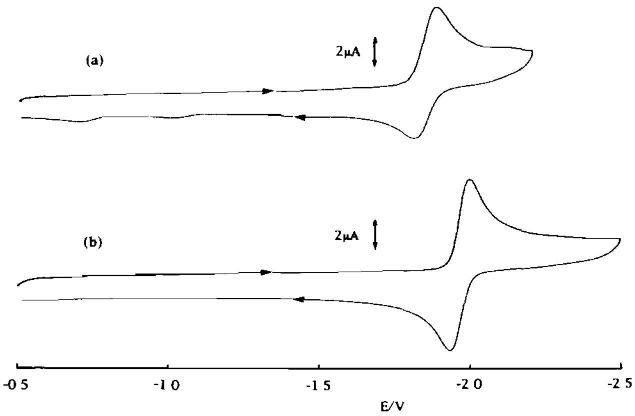

Fig. 3. Cyclic voltammograms of 3×10^{-4} mol dm^{-3} cluster **2** (a) and **3** (b) containing 0.1 mol dm^{-3} TBAP at a scan rate of 50 mV s^{-1} at 293 K.

Numerical data from cyclic voltammograms for complexes **1**–**6** are summarized in Table 4. All potentials are reported with respect to the ferrocenium-ferrocene couple. Figure 2 gives the cyclic voltammograms for **4**. Two chemically reversible couples at −1.51 and −1.69 V are found in DMF solution at 293 K. Controlled-potential coulometry for **4** in DMF solution at −1.85 V indicates that each process involves a one-electron reduction. Cluster **1**, previously reported [1], is reversibly reduced at −1.61 and −1.88 V at 293 K, indicating **4** is easier to reduce than **1**.

The cyclic voltammogram for **2** at 293 K is shown in Fig. 3. Cluster **2** gives a reduction peak at −1.89 V with an associated oxidation peak at −1.82 V and a broad oxidation peak at −0.73 V. Thus the product of reduction at −1.89 V is partly decomposed and oxidized at −0.73 V. At 255 K a chemically reversible couple is, however, exhibited at −1.84 V. Clusters **3**, **5** and **6** are reversibly reduced and oxidized at 293 K. The process is a two-electron transfer for **2**, **3**, **5** and **6**. The electrode reactions for **2**, **3**, **5** and **6** at 255 K are shown in the following equation.

$$[M_3E_2(dppe)_3]^{2+} \underset{-2e}{\overset{+2e}{\rightleftharpoons}} [M_3E_2(dppe)_3]^0$$

2: M = Pd, E = Se −1.84 V
3: M = Pt, E = Se −2.01
5: M = Pd, E = Te −1.76
6: M = Pt, E = Te −1.91

The ease of reduction follows the order Te > Se > S regarding the chalconido ligands for the $[M_3E_2(dppe)_3]^{2+}$ (M = Ni, Pd, Pt; E = S, Se, Te) clusters containing the same metal ion. Chemical reversibility is also improved in the order Te > Se > S.

TABLE 4. Numerical data[a] from cyclic voltammograms of complexes **1**–**6** (3×10^{-4} mol dm^{-3}) containing 0.1 mol dm^{-3} TBAP at a scan rate of 50 mV s^{-1}

Complex	E_{pa} (V)	E_{pc} (V)	E_{pa} (V)	E_{pc} (V)	E_{pa} (V)
$[Ni_3Se_2(dppe)_3][BPh_4]_2$ (**1**)		−1.64 (−1.66)	−1.58 (−1.61)	−1.96 (−1.93)	−1.80 (−1.87)
$[Pd_3Se_2(dppe)_3][PF_6]_2$ (**2**)	−0.73	−1.89 (−1.87)	−1.82 (−1.80)		
$[Pt_3Se_2(dppe)_3][BPh_4]_2$ (**3**)		−2.00 (−2.06)	(−1.95)		−1.94
$[Ni_3Te_2(dppe)_3][BPh_4]_2$ (**4**)		−1.54 (−1.59)	−1.48 (−1.55)	−1.71 (−1.73)	−1.66 (−1.67)
$[Pd_3Te_2(dppe)_3][BPh_4]_2$ (**5**)		−1.79 (−1.78)	−1.72 (−1.74)		
$[Pt_3Te_2(dppe)_3][BPh_4]_2$ (**6**)		−1.91 (−1.93)	−1.88 (−1.88)		

[a]Values at 293 K, those in parentheses refer to 255 K.

Supplementary material

H atom coordinates, thermal parameters, remaining bond lengths and angles, and observed and calculated structure factors for $[Pt_3Te_2(dppe)_3][BPh_4]_2$ (**6**) are available from the authors on request.

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