

Tellurium azamacrocycles: synthesis, characterization and coordination studies [☆]

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Abstract

The metal-free condensation of bis(2-formylphenyl) telluride (**1**) with a series of diamines affords macrocyclic tellurium ligands **2–7**. Crystals of the protonated macrocycle **8** are monoclinic, space group $P2_1/n$ with $a = 10.890(5)$, $b = 7.414(4)$, $c = 24.334(13)$ Å, $Z = 2$. The reaction of tellurium containing macrocyclic Schiff base **2** with $\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$ gives the expected 1:1 product $[\text{Pd}(\text{II}) \mathbf{2}] \text{Cl}_2$ (**9**). Complex **9** was treated with excess of NH_4PF_6 in methanol to give the analogous PF_6^- salt $[\text{Pd}(\text{II}) \mathbf{2}] (\text{PF}_6)_2$ (**10**). The crystals of **10** are monoclinic, space group $P2_1/n$, $a = 8.2250(10)$, $b = 21.280(4)$, $c = 21.150(4)$, $Z = 4$. However, the reaction of **2** with $\text{Pt}(\text{COD})\text{Cl}_2$ proceeds via novel transmetalation to yield an organoplatinum complex (**11**). The crystals of **11** are also monoclinic, space group $P2_1/n$, $a = 12.3253(14)$, $b = 14.6557(14)$, $c = 13.4054(11)$, $Z = 4$. The octahedral Ni(II) complex **12** was prepared by the reaction of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with **2** and NH_4PF_6 under an inert atmosphere. For **12**: triclinic, space group $P1$; $Z = 2$; $a = 10.800(8)$, $b = 13.468(9)$, $c = 13.918(11)$, $\alpha = 89.67(6)^\circ$, $\beta = 101.53(7)^\circ$, $\gamma = 81.49(3)^\circ$ and $V = 1961(3)$. Cyclic voltammetry of **12** in MeCN solution shows a well-behaved quasi-reversible ($\Delta E = 100$ mV) Ni(III) \leftrightarrow Ni(II) couple.

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1. Introduction

The thioether macrocycles have proved to be very good ligands for a wide range of d- and p-block ions [1]. An important feature of these systems is their ability to adopt unpredictable geometries and stabilize unusual oxidation states. In the field of acyclic ligands the systems bearing heavy chalcogens selenium and tellurium exhibit a rich coordination chemistry [2]. Polyseleno-

ether macrocycles have been shown to have an equally good potential to serve as ligands [3,4]. Some efforts have also been directed to extend this chemistry to the corresponding tellurium macrocycles [5]. The lower electronegativity and hence the greater σ electron-donating properties of Te compared to Se and/or S suggest that incorporation of telluroether (TeR_2) as donors in a macrocyclic arrangement should yield ligands with rich coordination chemistry. Recently, we have reported an easy, high yield synthesis, structure and preliminary coordination of a novel tellurium azamacrocycle (**2**) with Pd(II) and Pt(II) [6]. In continuation to that, in this full paper we report the synthesis and characterization of some new related tellurium macrocycles, the crystal structure of the protonated macrocycle **8** and detailed ligand chemistry of **2**.

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2. Results and discussion

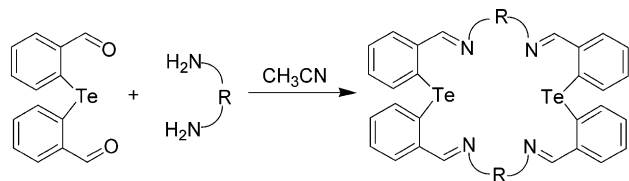
2.1. Ligand synthesis

The macrocyclic tellurium ligands **2–7** were easily isolated in good yields (32–80%) via one step dipodal 2+2 condensation of bis(2-formylphenyl) telluride (**1**) [7] with a series of diamines without recourse to a metal ion template or high dilution reaction (Scheme 1). There was no evidence for the formation of the 1+1 condensation product in EI-MS and ^{125}Te NMR spectra [5h].

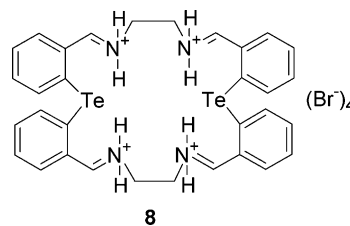
The presence of secondary intramolecular $\text{Te}\cdots\text{N}$ coordination in the macrocycles plays an important role in their formation by reducing the unfavorable lone pair–lone pair repulsion between the nitrogen atoms in the ring. The macrocycles with varying ring size i.e. from 22 to 34 and donor atoms from 6 to 10 were readily formed at room temperature by stirring the diamines and the bis(aldehyde) **1** in acetonitrile. The yields of the reactions were found to be highly dependent on the purity of the solvent. In general, all these compounds show poor solubility in common organic solvents. However, they were soluble to some extent in chloroform and dichloromethane, but insoluble in more polar solvents like CH_3OH and DMSO.

Attempts to synthesize analogous macrocycles by reacting **1** with *o*-phenylenediamine, 1,8-diaminonaphthalene and hydrazine hydrate were unsuccessful. This is probably due to the rigid nature of the amines. Attempts were also made to synthesize these macrocycles in the presence of metal templates such as lanthanum nitrate. The bright yellow product formed after refluxing **1** and *o*-phenylenediamine with lanthanum nitrate for 2 h in methanol was found to be soluble in dichloromethane and chloroform. Although this gave an indication of formation of the metal free macrocyclic ligand by IR and elemental analysis, its NMR spectrum was very complex.

The reduction of **2** with NaBH_4 followed by protonation with hydrogen bromide resulted in the formation of **8** [6a]. This was obtained in very good yield and was recrystallized from water/ methanol (1:1) mixture as colourless needles. This compound should be able to bind to a variety of anionic substrates and has been characterized by X-ray diffraction studies (vide infra).

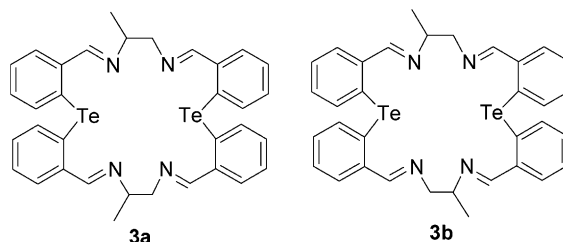


Scheme 1. R = CH_2CH_2 (**2**) [6a], $\text{CH}_2\text{CH}(\text{Me})$ (**3**), $\text{CH}_2\text{CH}_2\text{CH}_2$ (**4**), $\text{CH}_2(\text{CH}_2)_4\text{CH}_2$ (**5**), $\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2$ (**6**), and $\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2$ (**7**).



The macrocyclic Schiff base ligands (**3–7**) show IR absorption frequencies characteristic of $\nu_{\text{C=N}}$ stretching around 1640 cm^{-1} . The NMR spectra of the Schiff base ligands (**3–7**) were recorded in CDCl_3 . Due to the poor solubility, satisfactory ^{13}C NMR spectra of the compounds other than **5** could not be recorded. In the case of **4** and **5**, the ^1H NMR spectra obtained were as expected. The very symmetric NMR spectrum is probably due to a fast (on NMR time scale) $\text{Te}\cdots\text{N}(1)$, $\text{Te}\cdots\text{N}(2)$ bond scrambling. This leads to a dynamic equilibrium between the two-topomeric 10-Te-3 structures, which apparently takes place via a 12-Te-4 tellurane intermediate as reported by Minkin and co-workers [8].

The CH=N proton signals for the Schiff bases are observed at $\sim 8.5\text{--}8.6$ ppm being shifted to $1.5\text{--}1.6$ ppm upfield in comparison with the signal of the formyl proton in the precursor bis(2-formylphenyl) telluride (10.1 ppm). In the case of **3** although elemental analysis and mass spectral data suggested the formation of the 2+2 product, the ^1H NMR spectrum was complex. This could be due to the existence of different geometrical and optical isomeric structures. The CH_3 group in the product can have at least two different positions, thus giving structures **3a** and **3b**.



Though the products obtained by the (2+2) Schiff base condensation of triethylenetetraamine (TRIEEN) (**6**) and diethylenetriamine (DIEN) (**7**) with **1** gave satisfactory elemental analysis, their ^1H NMR spectra were quite complex. A ring contraction of the macrocyclic cavity of Schiff bases, often leading to the stabilization of metal free ligands, has been observed when there is a group such as NH or OH available for addition to the imine bond in the related macrocycles. Four closely related examples of such inner ring contractions, where Schiff base condensation reactions of diethylenetriamine and dialdehydes 2,6-diacetylpyridine, isophthalaldehyde and 2,6-diformyl-4-chlorophenol, have been reported by Drew et al. [9], Menif et al. [10] and Aguiari et al. [11],

respectively. Very recently NMR evidences for inter-conversion between two enantiomeric forms of lanthanide complexes of this ligand through reversible ring contraction and expansion has been described [12]. In our case the product probably consists of a mixture of the desired macrocycles with the isomers formed by the [34]–[28]–[22] or [28]–[22] ring contraction as a consequence of the nucleophilic addition of the secondary amine function (NH) across the imine bond. Here also metal ions were not involved in the ring contraction and expansion. Neither chemical analysis nor IR spectra allow a distinction to be made between the Schiff bases (**6** and **7**) and their isomeric forms which were the expected ring-contracted products [11].

^{125}Te NMR spectra were recorded for $\text{CDCl}_3/\text{DMSO-d}_6$ solutions of macrocycles. The spectrum of **3** displays four signals, thus again indicating the presence of more than one tellurium containing species in solution.

Electron impact (EI) or fast atom bombardment (FAB) mass spectra of all macrocycles were recorded in order to confirm the formation of 2+2 cyclocondensation product. Unfortunately compound **6** does not show molecular ion peak. The highest recorded peak at m/e 732 was assigned due to loss of $\text{C}_6\text{H}_4\text{CHNC}_2\text{H}_4\text{NHCH}_2$ group (735).

2.2. Complexation studies

In view of the excellent yield and simple ^1H NMR spectra the coordination properties of potential hexadentate ligand **2** towards Pd(II), Pt(II) and Ni(II) ions were studied (Scheme 2).

2.2.1. Reaction with Pd(II) ions

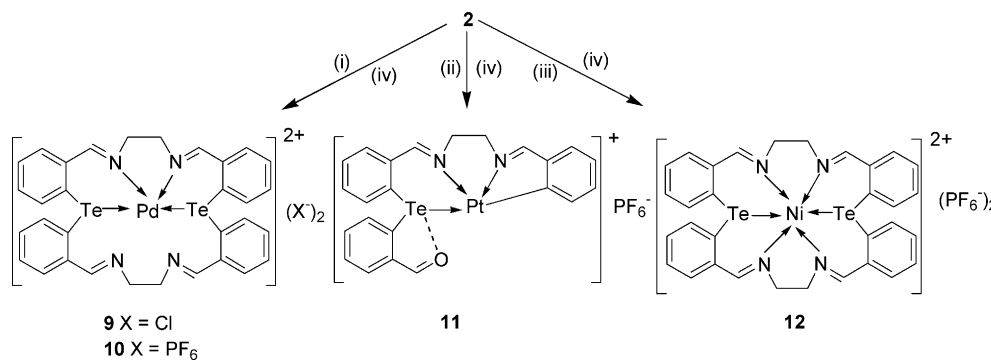
When the reaction of **2** was carried out with one equivalent of $\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$ in CHCl_3 , light yellow precipitate formed immediately after addition. However, it re-dissolved on stirring for some time to give a clear reddish yellow solution. The reddish yellow powder of the complex left after evaporation of the solvent was re-

crystallized from methanol as yellow needles of complex **9** by vapour diffusion of diethylether. Crystal structure of this complex could not be determined due to fact that the crystals lost its luster on removing it out from the solvent. The complex was found to be a 1:2 electrolyte in methanol (Λ_M $142.68 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$). The IR spectrum shows $\nu_{\text{C}=\text{N}}$ absorption frequency at 1639cm^{-1} . The ^{125}Te NMR spectrum shows a single signal at 722 ppm, a deshielded position compared to the free ligand **2** (607 ppm). The elemental analysis data suggested the formation of the 1:1 product. The FAB mass spectrum of the crystals shows the highest mass peak at m/z 867 (80%) and base peak at m/z 830 which are assignable to $[\text{2}+\text{PdCl}]^+$ and $[\text{2}+\text{Pd}]^+$. Hence the formulation $[\text{Pd}(\text{2})]\text{Cl}_2$ (**9**) is suggested. Thus a noticeable difference in behaviour of the products obtained from 2:1 (metal:ligand) molar reaction reported [6a] earlier and the 1:1 (metal:ligand) molar reaction has been observed. The 1:1 product is more soluble and ionic in nature compared with the less soluble nonionic 2:1 complex [6a].

In order to get suitable crystal of the palladium complex (vide supra), we thought of changing the chloride ions with bulkier PF_6^- anions. Complex **9** was treated with an excess of ammonium hexafluorophosphate in methanol to give a yellow precipitate of **10**. Washing the product with methanol followed by re-crystallization from acetonitrile by vapour diffusion of diethyl ether afforded yellow needles of **10** [6b]. This compound was characterized by routine spectroscopic techniques. The IR spectrum shows a broad absorption peak at 836cm^{-1} which indicates the presence of the PF_6^- ion in addition to the azomethine stretching frequency at 1639.8cm^{-1} . The ^1H , ^{13}C or ^{125}Te NMR data were very similar to that of **9** with some shifts. The structure was further confirmed by single crystal X-ray diffraction studies.

2.2.2. Reaction with Pt(II) ion

The reaction of $\text{Pt}(\text{COD})\text{Cl}_2$ with the ligand **2** (metal ligand ratio 1:1) in dichloromethane at room temperature gave a reddish brown solution from which a solid



Scheme 2. Reagents and conditions: (i) $\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$, CHCl_3 , 2 h; (ii) $\text{Pt}(\text{COD})\text{Cl}_2$, CH_2Cl_2 , 16 h; (iii) $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.5 h, MeOH, reflux (iv) MeOH, NH_4PF_6 , rt.

was obtained by filtration after concentrating the solution. This was dissolved in methanol by warming and an excess of ammonium hexafluorophosphate was added. A reddish brown precipitate of the complex **11** separated out immediately [6b]. This could be recrystallized by slow evaporation of the acetonitrile solution. In contrast to the reaction of Pd(II) with **2**, in this case the reaction proceeds via novel transmetallation to yield an organoplatinum complex **11** [6b]. The elemental analysis, NMR and FAB mass spectral data suggested the formation of complex. The IR spectra showed peaks consistent with the presence of C=O and C=N stretching frequencies at 1697 and 1646 cm^{-1} , respectively. The unexpected organoplatinum complex, presumably, results from the facile cleavage of one of the Te–C bonds activated by the Te–N interaction; transfer of electron density from nitrogen to the σ^* orbital of *trans* Te–C bond leading to significant Te–C bond weakening. The crystal structure of **11** was further confirmed further by a single crystal X-ray diffraction study.

2.2.3. Reactions with Ni(II) ion

Reaction of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with one mole of **2** in refluxing methanol followed by the addition of excess of PF_6^- afforded air stable red Ni(II) paramagnetic complex (**12**) (Scheme 2). Complex **12** is insoluble in chlorocarbons and hydrocarbons. However, it dissolves in coordinating solvents such as MeCN, DMF and DMSO. However, it results in rapid decomposition via displacement of the azatelluromacrocycle **2** in DMSO. This was confirmed by ^1H NMR spectroscopic studies on the compound in DMSO-d_6 . A similar observation has been observed by Reid and co-workers [4m] for the seven-coordinate Mo(II) and W(II) species derived from the selenoether ligands 1,5,9,13-tetraselenacyclohexadecane ($[\text{16janeSe}_4]$) and 1,6-diselena-3,4-benzocyclononane. The infrared spectroscopic measurements showed the presence of the PF_6^- anion. The $\nu_{\text{C=N}}$ absorption stretching frequency for **12** was found at 1644 cm^{-1} . The electronic spectrum of the complex was recorded at room temperature in CH_3CN in the range 190–900 nm. The solution phase electronic spectra (>200 nm) of the ligand **2** consists of two intense bands centered at 291.6, 368.0 nm which can be assigned to the intraligand $\pi-\pi^*$ transitions. For the complex **12** intense peak is found at 294.8 nm which may be attributed to the charge-transfer transitions. The bands observed at 367, 488 and 809.5 nm are due to $\pi-\pi^*$ and d–d transitions, respectively. The diffuse reflectance spectrum of the complex showed peaks at 370, 534 and 802 nm, thus confirming the presence of same species in solution and solid state.

In the FAB Ms the peaks at m/z 927 and 784 for the complex **12** were for $[\text{12-PF}_6]$ and $[\text{12-2PF}_6]$, respectively. The cyclic voltammogram of **12** showed the oxidation and reduction peaks at 0.8 and 0.9 V, respectively, at scan rate 100 mV/s. It reveals a well-

behaved quasi-reversible ($\Delta E = 100$ mV) Ni(III) \leftrightarrow Ni(II) couple (Fig. 1). The assignment of octahedral geometries to $[\text{Ni(II) 2}](\text{PF}_6)_2$ (**12**) follows from its paramagnetism, $\mu_{\text{eff}} = 3.06$ BM, which indicates $S = 1$ and this was further confirmed by single-crystal X-ray study (vide infra). Thus, from the elemental analysis data, IR, UV/visible, ^{125}Te NMR, FAB mass spectrum, magnetic susceptibility the formation of $[\text{Ni(II) 2}](\text{PF}_6)_2$ is suggested.

2.3. Crystal structure of **8**

The protonated salt (**8**) crystallizes from a solution consisting of water and methanol (1:1) with solvent of crystallization (H_2O) which is hydrogen bonded to the macrocycle. The thermal ellipsoid plot [13] with 50% probability together with the atomic labeling scheme is shown in Fig. 2. Selected bond lengths and angles are collected in the Table 1. The crystal structure confirmed the reduction of CH=N bonds and the formation of macrocyclic polyamine as well as protonation at nitrogen centres. The asymmetric unit contains half the macrocycle similar to its parent Schiff base (**2**) [6a]. In **8** none of the bromide counter ions are situated inside the macrocyclic cavity, but one lies above the macrocycle and forms intermolecular hydrogen bonding with the amine and water hydrogens [14]. These distances $\text{Br}(1)\cdots\text{H}(1\text{B})$ 2.369 Å, $\text{Br}(1)\cdots\text{H}(2\text{B})$ 2.431 Å, $\text{Br}(2)\cdots\text{H}(1\text{W}1)$ 2.860 Å, $\text{Br}(2)\cdots\text{H}(1\text{A})$ 2.498 Å, $\text{N}(2)\cdots\text{H}(2\text{A})$ 0.900 Å and $\text{N}(2)\cdots\text{H}(2\text{B})$ 0.900 Å indicate presence of strong hydrogen bonds. The macrocycle is highly puckered. All four nitrogens are not planar and the mean plane deviation from the plane is 0.7766 Å. The intramolecular distance between symmetry related nitrogen atom is 5.473 Å while intramolecular Te \cdots Te distance is 7.108 Å. The intramolecular Te \cdots Te distance is greater than the corresponding distance (4.979 Å) in the Schiff base **2**.

The Te(1)–C(11) distance of [2.121(5) Å] and Te(1)–C(21) distance of [2.131(4) Å] compares well with the mean value of Te–C (aromatic) of 2.166 Å given by

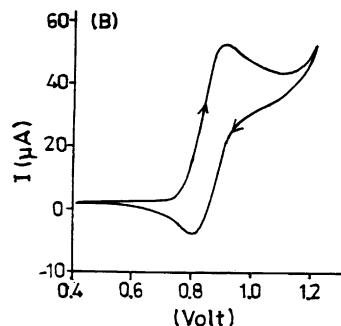
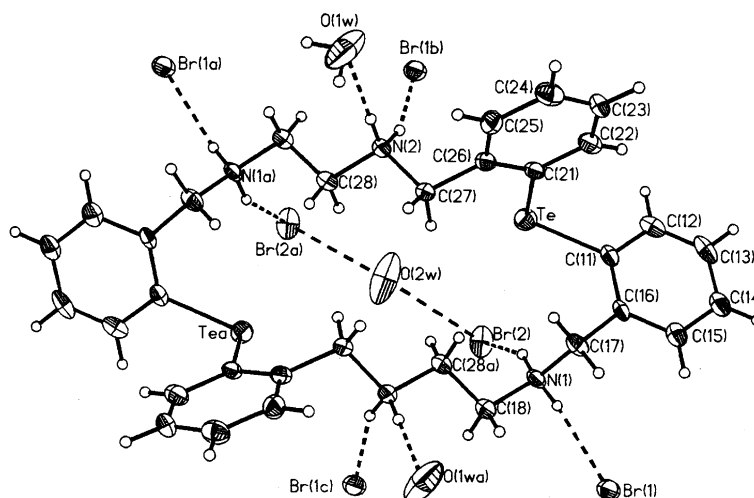


Fig. 1. Cyclic voltammogram of **12**.

Fig. 2. An ORTEP diagram of **8**.Table 1
Significant bond lengths (Å) and angles (°) for **8**

Te–C(11)	2.121(5)	Te–C(21)	2.131(4)
O(1WA)–O(1WB)	0.67(3)	O(2W)–O(2W)#1	0.64(5)
N(1)–C(17)	1.509(5)	N(1)–C(18)	1.510(6)
N(2)–C(28)	1.490(5)	N(2)–C(27)	1.503(5)
C(11)–Te–C(21)	96.34(17)	C(17)–N(1)–C(18)	114.0(3)
C(28)–N(2)–C(27)	110.7(3)	C(12)–C(11)–Te	118.9(4)
C(16)–C(11)–Te	122.0(3)	C(16)–C(17)–N(1)	111.5(4)
C(28)#1–C(18)–N(1)	111.0(4)	C(22)–C(21)–Te	119.3(3)
C(26)–C(21)–Te	121.2(3)	N(2)–C(27)–C(26)	111.9(3)
N(2)–C(28)–C(18)#1	111.8(4)		

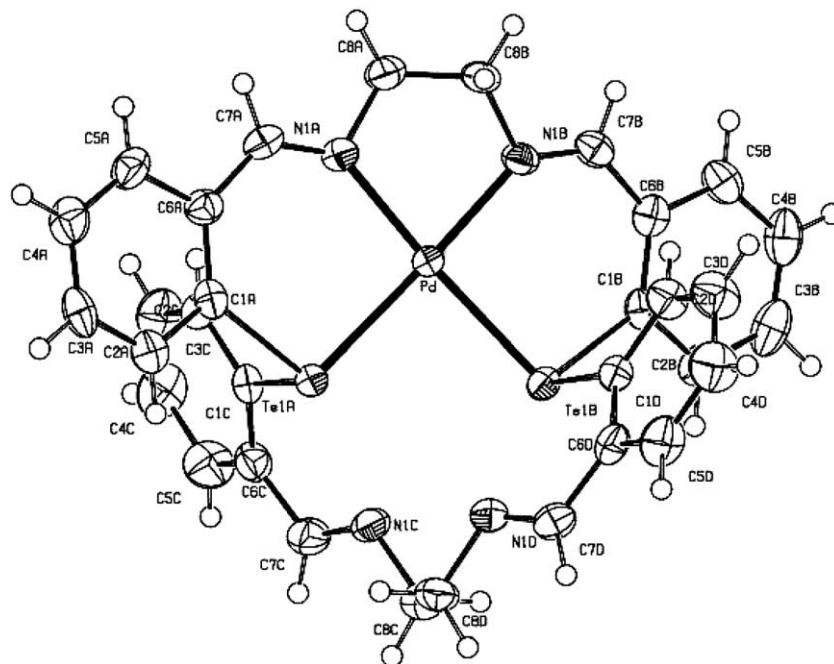
Allen et al. [15] and with 2.125(16) Å observed for Te–C in 2-bromotelluro-*N*-(*p*-tolyl)benzylamine [16]. The angle C(11)–Te–C(21) is 96.34° and geometry around tellurium can be considered as V-shaped.

2.4. Crystal structure of **10**

The molecular structure of **10** is shown in Fig. 3 and selected bond lengths and bond angles are given in Table 2. In complex **10**, the Pd²⁺ cation is interestingly coordinated to only two nitrogen atoms of same diaminomethane unit and two tellurium atoms. The adaptability of **2** to form *cis*-square planar complex with Te₂N₂ donor sets forces a twofold symmetry. The average Pd–N distance of 2.098 Å is slightly higher than the sum of Pauling's single bond covalent radii (2.01 Å) while the mean Pd–Te distance (2.5463 Å) is significantly shorter than the sum of the covalent radii (2.68 Å) of Te and Pd. This shortening in Pd–Te bond distance may be due to the soft–soft interaction. The Pd–Te distances are, however, comparable to the Pd(1)–Te(1) 2.540(2) Å and Pd(3)–Te(5) 2.554(2) Å, respectively, in [Pd(OC₆H₄)(TeMe)TeI₄][17] which has *cis*-disposition

of Te atoms. In contrast, in square planar Pd complexes having two *trans* Pd–Te bonds [18–20], the Pd–Te bond lengths are in the range from 2.589 to 2.606 Å (average 2.597 Å), thus indicating a strong donor and trans influences of Te donor.

The geometry around Pd is trapezoid planar with mean Te, N bite angle of 93.7° and smaller bite angles of N–Te (82.8(2)°) and Te–Te 89.68(2)°. The smaller Te(1A) and Te(1B) bite angles force the telluriums to be at a strong interacting distance of 3.591 Å which is 4.971 Å in the free ligand [6a]. The mean Te–C bond distance (2.14 Å) is close to the sum of the Pauling's single bond covalent radii for tellurium (1.37 Å) and the sp² hybridized carbon (0.74 Å). Both the telluriums have identical pyramidal geometry. The angles around Te [C(1D)–Te(1B)–C(1B)] and [C(1C)–Te(1A)–(1A)] average 94.3° and are close to the corresponding angle in the free ligand [6a]. Interestingly the tellurium atoms in addition to acting as donor atoms to Pd, also act as acceptors to N and Te. The mean Te···N intramolecular distances [Te(B)···N(1D)] and [Te(1A)···N(1C)] are 2.738 Å well within the van der Waal's distance of 3.7 Å and the Te–C–C–N moieties are planar.

Fig. 3. An ORTEP diagram of complex **10** cation.Table 2
Significant bond lengths (Å) and angles (°) for **10**

Te(1A)–C(1C)	2.129(7)	Te(1A)–C(1A)	2.150(7)
Te(1A)–Pd	2.5443(7)	Te(1B)–C(1B)	2.138(7)
Te(1B)–C(1D)	2.145(7)	Te(1B)–Pd	2.5483(7)
Pd–N(1A)	2.097(6)	Pd–N(1B)	2.099(6)
N(1A)–C(7A)	1.284(9)	N(1A)–C(8A)	1.479(9)
N(1B)–C(7B)	1.275(9)	N(1B)–C(8B)	1.475(9)
N(1C)–C(7C)	1.254(10)	N(1C)–C(8C)	1.458(10)
N(1D)–C(7D)	1.266(10)	N(1D)–C(8D)	1.457(9)
C(1C)–Te(1A)–C(1A)	94.9(3)	C(1C)–Te(1A)–Pd	99.0(2)
C(1A)–Te(1A)–Pd	99.8(2)	C(1B)–Te(1B)–C(1D)	93.7(2)
C(1B)–Te(1B)–Pd	99.5(2)	C(1D)–Te(1B)–Pd	99.5(2)
N(1A)–Pd–N(1B)	82.8(2)	N(1A)–Pd–Te(1A)	94.4(2)
N(1B)–Pd–Te(1A)	176.9(2)	N(1A)–Pd–Te(1B)	175.9(2)
N(1B)–Pd–Te(1B)	93.1(2)	Te(1A)–Pd–Te(1B)	89.68(2)
C(7A)–N(1A)–Pd	136.9(5)	C(8A)–N(1A)–Pd	107.5(4)
C(7B)–N(1B)–C(8B)	116.4(6)	C(7B)–N(1B)–Pd	137.1(5)
C(8B)–N(1B)–Pd	106.4(4)	C(7C)–N(1C)–C(8C)	119.9(7)
C(7D)–N(1D)–C(8D)	119.0(6)	C(6A)–C(1A)–Te(1A)	128.7(5)
C(2A)–C(1A)–Te(1A)	111.0(5)	N(1A)–C(7A)–C(6A)	129.2(7)
N(1A)–C(8A)–C(8B)	108.0(6)	C(2B)–C(1B)–Te(1B)	111.8(5)
C(6B)–C(1B)–Te(1B)	129.0(5)	N(1B)–C(7B)–C(6B)	129.8(7)
N(1B)–C(8B)–C(8A)	107.6(6)	C(2C)–C(1C)–Te(1A)	121.2(5)
C(6C)–C(1C)–Te(1A)	118.9(5)	N(1C)–C(7C)–C(6C)	120.8(7)
C(2D)–C(1D)–Te(1B)	121.3(5)	C(6D)–C(1D)–Te(1B)	118.8(5)
N(1D)–C(7D)–C(6D)	120.2(7)	N(1D)–C(8D)–C(8C)	108.9(7)
C(7A)–N(1A)–C(8A)	115.4(6)	N(1C)–C(8C)–C(8D)	109.7(7)

2.5. Crystal structure of **11**

Complex **11** also crystallizes in monoclinic system with space group $P2_1/n$. The selected bond length and angles are given in Table 3 and the molecule is shown in

Fig. 4. The crystal structure shows a trapezoid planar geometry around Pt(II) cation which is coordinated by two nitrogen atoms of the same diaminomethane unit, a tellurium and a carbon atom. The average Pt–N distance is in excellent agreement with the sum of covalent

Table 3
Significant bond lengths (Å) and angles (°) for **11**

Pt–N(1A)	1.994(7)	Pt–C(1A)	2.028(8)
Pt–N(1B)	2.087(7)	Pt–Te	2.5180(6)
Te–C(1C)	2.149(7)	Te–C(1B)	2.149(8)
N(1B)–C(7B)	1.273(12)	N(1B)–C(8B)	1.472(11)
N(1A)–C(7A)	1.259(13)	N(1A)–C(8A)	1.445(13)
O–C(7C)	1.186(10)	N(1A)–Pt–C(1A)	80.3(4)
N(1A)–Pt–N(1B)	82.4(3)	C(1A)–Pt–N(1B)	162.4(3)
N(1A)–Pt–Te	177.0(2)	C(1A)–Pt–Te	100.7(2)
N(1B)–Pt–Te	96.8(2)	C(1C)–Te–C(1B)	90.5(3)
C(1C)–Te–Pt	97.1(2)	C(1B)–Te–Pt	100.0(2)
C(7B)–N(1B)–C(8B)	117.1(8)	C(7B)–N(1B)–Pt	134.4(6)
C(8B)–N(1B)–Pt	108.4(6)	C(7A)–N(1A)–C(8A)	126.6(8)
C(7A)–N(1A)–Pt	118.4(7)	C(8A)–N(1A)–Pt	115.0(6)
N(1B)–C(7B)–C(6B)	130.0(8)	C(2B)–C(1B)–Te	112.5(7)
C(6B)–C(1B)–Te	127.7(6)	C(2C)–C(1C)–Te	118.2(5)
C(6C)–C(1C)–Te	121.8(5)	N(1B)–C(8B)–C(8A)	110.2(8)
N(1A)–C(7A)–C(6A)	114.9(8)	N(1A)–C(8A)–C(8B)	108.6(8)
O–C(7C)–C(6C)	126.1(8)	C(2A)–C(1A)–Pt	132.6(7)
C(6A)–C(1A)–Pt	111.3(7)		

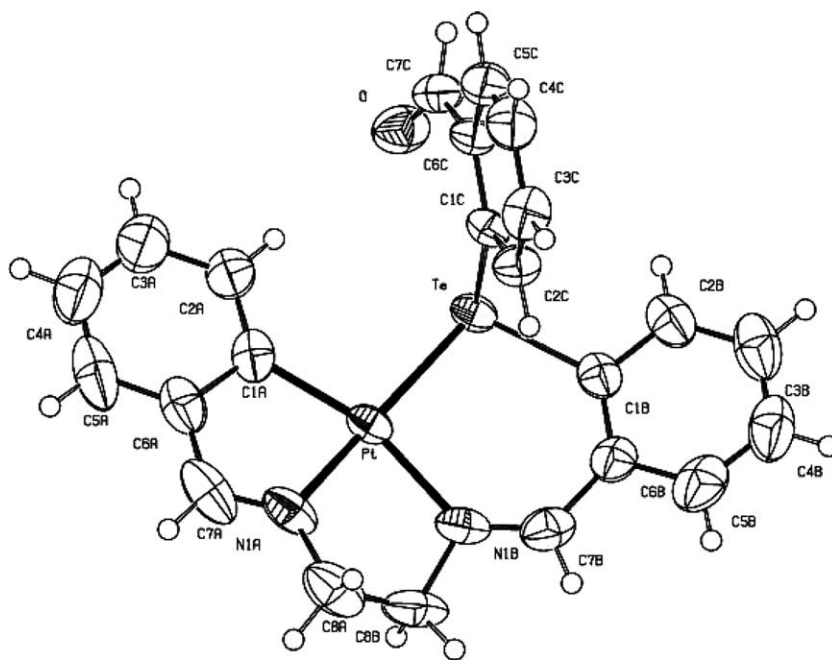


Fig. 4. An ORTEP diagram of complex **11** cation.

radii of Pt and N. The Pt–Te distance of 2.5180(6) Å observed in complex is considerably shorter than the sum of covalent radii (2.68 Å), however, it is comparable with the Pt–Te distance of 2.512(1) Å observed in [Pt{NC₅H₄–2-(CH₂)–Te–C₆H₄–4-OMe}Cl₂] [21]. The transmetalation of Te with Pt leads to unsymmetrical chelate rings. The Te···N chelate ring in this case is six membered with a large bite angle of 96.8(2)° whereas the opposite CN bite angle is 80.3°. This leads to a highly distorted square planar geometry.

The intramolecular Te···O distance of 3.004 Å implies a weak coordination of oxygen to tellurium as it is significantly shorter than the van der Waal's radii of 3.6 Å. However, this is much larger than the mean intra-

molecular distance of 2.76 Å observed in bis(2-formyl)ditelluride [22]. Further, the cations are linked into weak dimers by weak Te···Pt contacts (3.483 Å) (Fig. 5) giving dimeric complex. Interestingly, such dimers have been proposed as possible intermediates in reaction [23]. Complex **11**, is the first example of a structurally characterised complex having both intra and intermolecular Pt–Te bonding.

2.6. Crystal structure of **12**

Crystals of complex **12** were obtained by vapour diffusion of diethyl ether into a solution of the complex in CH₃CN. The ORTEP diagram of **12** is given in Fig. 6.

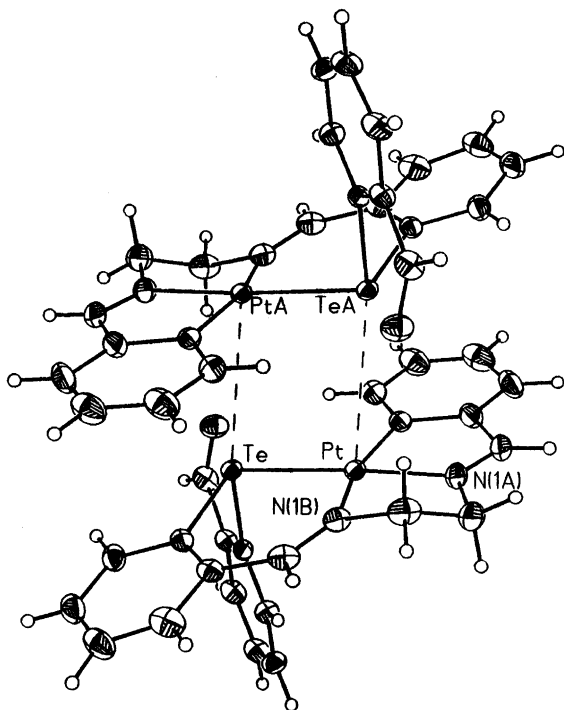


Fig. 5. Packing diagram of **11**.

Complex **12** crystallizes in the triclinic system (space group $P1$) with $Z = 2$. Though the R value is not satisfactory, it confirms the proposed structure beyond doubt.

The Ni–Te mean bond distance 2.66 Å as expected is longer than the sum of the single bond covalent radii of Ni(II) in octahedral environment (0.83 Å) and Te (1.37) Å. This is due to “hard” N and “soft” Te bonding. This

bond distance is significantly longer than the Ni–Te distance 2.485(1) Å in $[(\eta^5\text{-Cp})\text{Ni}(\text{PET}_3)\text{TeMes}]$ [24]. Here again adaptability of **2** leads to a *cis*-disposition of Te donors.

3. Experimental

The complex precursors, i.e., $\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$ [25] and $\text{Pt}(\text{COD})\text{Cl}_2$ [26] were prepared by following the reported procedures. Bis(*o*-formylphenyl) telluride was prepared as described in the literature [7]. 1,2-Diaminoethane (EN), 1,2-diaminopropane (1-MeEN), 1,3-diaminopropane (PN), 1,6-diaminohexane (HN), triethylenetetraamine (TRIEEN) and diethylenetriamine (DIEN) were distilled before use. FAB MS analyses were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using Xenon (6 kV) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature. In case of isotopic pattern, the value given is for the most intense peak. EI mass spectra were obtained on a Jeol D-300(EI/CI) spectrometer and are reported as m/z (ion percent relative intensity). The melting points are uncorrected and were determined on a Veego melting point apparatus using a capillary tube. Elemental analyses were performed on a Carlo Erba elemental analyser model 1106. Electronic absorption spectra were obtained in $\text{CHCl}_3/\text{CH}_3\text{CN}$ at 25 °C in a 1 cm quartz cuvette on a thermostat Shimadzu UV-2100 apparatus. The IR spectra were recorded on a Perkin–Elmer 681 spectrometer. The solid samples were examined as KBr pellets. FAR IR spectra of polyethylene pellet were recorded on Bruker

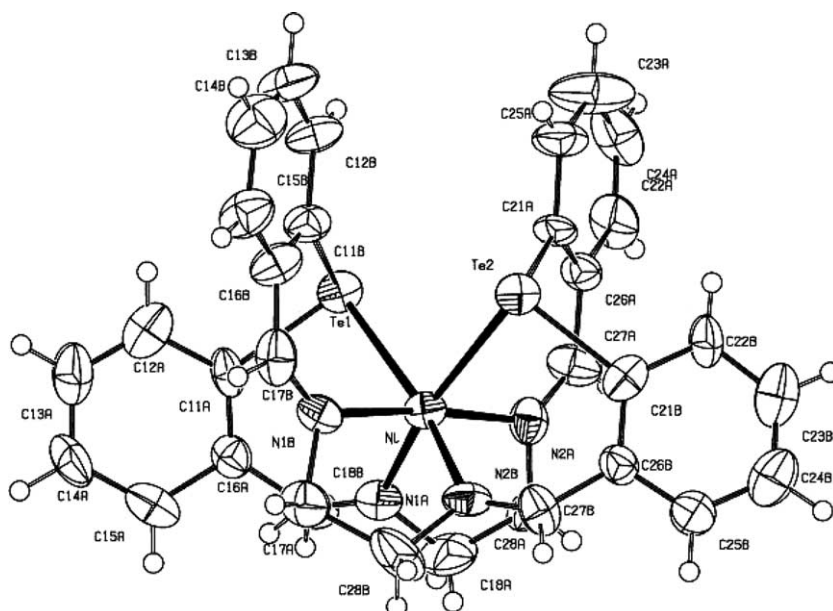


Fig. 6. An ORTEP diagram of complex **12** cation.

IFS 66V FT-IR spectrometer. Nuclear magnetic resonance spectra, ^1H (299.94 MHz), ^{13}C (75.42 MHz), ^{125}Te (94.75 MHz) were recorded on a Varian VXR 300S spectrometer. Chemical shifts are cited with respect to SiMe_4 as internal standard (^1H and ^{13}C) and TeMe_2 as external standard (^{125}Te). Magnetic susceptibility of the complexes has been studied at room temperature. Complex $\text{Hg}[\text{Co}(\text{SCN})_4]$ was used as the standard. Cyclic voltammetry (CV) experiments were performed on a Scanning Potentiostat EG and G PARC Model 362 instrument which consists of one-compartment cell with platinum working and counter electrodes and a standard Ag/AgCl reference electrode. Tetrabutylammonium tetrafluoroborate (Aldrich) was used as the supporting electrolyte. All solutions were purged with nitrogen before the CV data were recorded. Measurements were conducted in 0.1 mol dm^{-3} NBu_4BF_4 in acetonitrile with sample concentration 0.05 mM with the scan rates of 100 mV/s. Under these conditions $[\text{Fe}(\text{C}_5\text{H}_5)_2]/[\text{Fe}(\text{C}_5\text{H}_5)_2]^+$ has $E_{1/2}$ 0.46 mV.

3.1. Synthesis of macrocyclic Schiff bases: general procedure

A solution of bis(*o*-formylphenyl) telluride (**1**) (0.2 g, 0.59 mmol) in acetonitrile (100 ml) was added to a stirred solution of α, ω -diamine (0.5 mmol) in CH_3CN (100 ml) over a period of 1 h. The mixture was stirred for 5 h and the precipitated pale yellow powder was filtered off, washed with acetonitrile and recrystallized from $\text{CHCl}_3/\text{CH}_3\text{CN}$ (1:1).

3.1.1. Synthesis of bis(diphenyltelluride)BIS-1-MeEN Schiff base (3)

Yield: 0.157 g, 71%; m.p. 230–232 °C (d). Anal. Calc. for $\text{C}_{34}\text{H}_{32}\text{N}_4\text{Te}_2 \cdot 0.5\text{H}_2\text{O}$: C, 53.67; H, 4.37; N, 7.36. Found: C, 53.4; H, 4.2; N, 7.06%. MS (ED): m/z 751 (M^+ for ^{128}Te), 609, 376, 288, 248, 232. ^{125}Te NMR (CDCl_3): δ -745 (major), -721, -731, -750. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1631.4 (C=N stretching).

3.1.2. Synthesis of bis(diphenyltelluride)BISPN Schiff base (4)

Yield: 0.136 g, 61%; m.p. 255–256 °C (d). Anal. Calc. for $\text{C}_{34}\text{H}_{32}\text{N}_4\text{Te}_2 \cdot 1.5\text{H}_2\text{O}$: C, 52.43; H, 4.53; N, 7.19. Found: C, 52.42; H, 4.18; N, 7.12%. MS (FAB): m/z 769 ($\text{M}^+ + \text{H}_2\text{O}$), 753 (M^+), ^1H NMR (CDCl_3): δ 8.60 (s, 4H, azomethine-H), 7.71–7.68 (m, 4H, aromatic H) 7.46–7.43 (m, 4H, aromatic H) 7.37–7.31 (m, 4H, aromatic H) 7.18–7.12 (m, 4H, aromatic H), 4.78 (bs, 8H, H_2O) 3.75 (t, $J = 6$ Hz, 8H, $\text{NCH}_2\text{-CH}_2$), 2.08 (quintet, $J = 6$ Hz, 4H, $\text{CH}_2\text{-CH}_2\text{-CH}_2$); ^{125}Te (CDCl_3): δ -410.4. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1700, 1680 (C=N stretching).

3.1.3. Synthesis of bis(diphenyltelluride)BISHN Schiff base (5)

Yield: 0.15 g, 61%; m.p. 120 °C. Anal. Calc. for $\text{C}_{40}\text{H}_{44}\text{N}_4\text{Te}_2$: C, 57.47; H, 5.30; N, 6.70. Found: C, 57.43; H, 5.57; N, 6.62%. MS (FAB): m/z 838 (M^+ for ^{128}Te), 648, 627, 419, 329, 314, 214, ^1H NMR (CDCl_3): δ 8.60 (s, 4H, azomethine-H), 7.76–7.72 (m, 4H, aromatic H) 7.50–7.48 (d, $J = 6$ Hz, 4H, aromatic H) 7.33–7.27 (m, 4H, aromatic H) 7.17–7.09 (m, 4H, aromatic H), 3.64–3.56 (m, 8H, NCH_2) 1.66–1.64 (m, 8H, $\text{NCH}_2\text{-CH}_2$) 1.35 (bs, 8H $\text{NCH}_2\text{-CH}_2\text{-CH}_2$); ^{13}C NMR (CDCl_3): δ 125.85, 138.14, 130.67, 127.39, 129.76, 138.14 (aromatic C), 165.5 (azomethine-C), 60.09 (NCH_2), 31.11 (NCH_2CH_2), 27.12; ^{125}Te NMR (CDCl_3): δ -242.9. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1624 (C=N stretching).

3.1.4. Synthesis of bis(diphenyltelluride)BISTRIN Schiff base (6)

Yield: 0.085 g, 32%; m.p. 180 °C. Anal. Calc. for $\text{C}_{40}\text{H}_{48}\text{N}_8\text{Te}_2$: C, 53.62; H, 5.40; N, 12.50. Found: C, 53.86; H, 4.88; N, 11.76%. MS (FAB): m/z 732, 582, 502, 462, 369. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1640 (CH=N stretching).

3.1.5. Synthesis of bis(diphenyltelluride)BISDIEN Schiff base (7)

Yield: 0.15 g, 60%; m.p. 213–215 °C (d). Anal. Calc. for $\text{C}_{36}\text{H}_{38}\text{N}_6\text{Te}_2$: C, 53.39; H, 4.73; N, 10.38. Found: C, 53.46; H, 4.93; N, 10.59%. FAB mass spectrum m/z 828 ($\text{M}^+ + \text{H}_2\text{O}$), 810 (M^+ for ^{128}Te), 613, 460, 307, 289, 154; ^1H NMR (CDCl_3): δ 8.67 (s, 4H, azomethine-H), 8.65–7.00 (m, 16H, aromatic H), 3.82 (m, 8H, $\text{NCH}_2\text{-C}$) 3.06 (t, $J = 6$ Hz, 8H $\text{NCH}_2\text{-CH}_2\text{-NH}$); ^{125}Te NMR (CDCl_3): δ -745.5. IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1636 (CH=N).

3.2. Synthetic procedures for the transition metal complexes

3.2.1. Synthesis of $[\text{Pd}(\text{II}) 2]\text{Cl}_2$ (9)

To a chloroform (10 ml) solution of **2** (0.1 gm, 0.138 mmol), $\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$ (0.053 g, 0.138 mmol) in dichloromethane (10 ml) was added dropwise. On stirring for 2 h, the yellow precipitate initially formed redissolved and a clear red solution was obtained. The solvent was evaporated and the residue was dissolved in methanol (5 ml). From this solution yellow crystals of $[\text{Pd}(\text{II}) 2]\text{Cl}_2$ were obtained by vapour diffusion of diethyl ether. Yield: 0.11 g, 88.3%; m.p. 180 °C (d). Anal. Calc. for $\text{C}_{32}\text{H}_{28}\text{N}_4\text{Te}_2 \cdot \text{PdCl}_2 \cdot 2\text{H}_2\text{O}$: C, 41.01; H, 3.44; N, 5.98. Found: C, 40.75; H, 3.78; N, 6.48%. FAB mass spectrum m/z 867 ($\text{M}^+ - \text{Cl}$), 830 ($\text{M}^+ - 2\text{Cl}$); ^1H NMR (CD_3OD): δ 9.02 (s, 2H, azomethine-H), 8.91 (s, 2H, azomethine-H), 7.98–7.92 (m, 4H, aromatic H), 7.77–7.70 (m, 4H, aromatic-H), 7.67–7.54 (m, 4H, aromatic H), 7.33–7.28 (m, 2H, aromatic H), 7.07 (d, 2H, $J = 7.9$

Hz, aromatic H), 4.53–4.45 (m, 2H, CH₂), 4.31–4.11 (m, 4H, CH₂), 4.06–3.98 (m, 2H, CH₂); ¹³C NMR (DMSO-d₆): δ 175.0, 168.1 (coordinated and uncoordinated azomethine C), 143.7, 143, 141.7, 140.6, 138.3, 138.0, 136.8, 135.6, 126.0, 124.5 (aromatic C), 68.8, 63.0(CH₂); ¹²⁵Te NMR (DMSO-d₆): δ 722; IR (KBr) ν_{max}/cm⁻¹: 1638.8 (C=N stretching), 439.1 bw, 391 bw, 342 bw, 281 bw, 249, 236 (polyethylene). Conductance (Λ_M): 142.68 Ω⁻¹ cm² mol⁻¹: (methanol).

3.2.2. Synthesis of [Pd(II) 2](PF₆)₂[6b] (10)

To a chloroform (10 mL) solution of **2** (0.1 g, 0.14 mmol), Pd(C₆H₅CN)₂Cl₂ (0.053 g, 0.14 mmol) in dichloromethane (10 mL) was added dropwise. On stirring for 2 h the yellow precipitate formed initially redissolved and a clear red solution resulted. The solvent was evaporated and the residue was dissolved in methanol (5 mL). To this an excess of NH₄PF₆ was added. The precipitated yellow product was filtered off, washed with methanol and recrystallized from CH₃CN by vapour diffusion of diethyl ether. Yield: 0.13g, (87%); m.p: 202–204 °C (d). Anal. Calc. for C₃₂H₂₈N₄Te₂PdP₂F₁₂: C, 34.29; H, 5.00; N, 2.5. Found: C, 34.42; H, 5.13; N, 2.45%. MS (FAB): *m/z* 977 (M⁺-PF₆), 832 (M⁺-2PF₆), 483, 331, 291, 178, 152, 120; ¹H NMR (CD₃CN): δ 8.99 (s, 2H, azomethine-H), 8.82 (s, 2H, azomethine-H), 7.97 (d, 2H, aromatic-H), 7.91 (d, 2H, aromatic-H), 7.81 (m, 4H, aromatic-H), 7.66 (m, 4H, aromatic-H), 7.37 (t, 2H, aromatic-H), 7.14 (d, 2H, aromatic-H), 4.51 (d, 2H, CH₂), 4.23 (d, 2H, CH₂), 4.12 (d, 2H, CH₂) 3.92 (d, 2H, CH₂); ¹³C NMR (CD₃CN): δ 170.81, 163.76 (coordinated and uncoordinated azomethine C), 139.32, 138.73, 136.90, 136.30, 134.16, 133.93, 132.81, 131.73 (aromatic carbon), 63.75, 58.11 (CH₂); ¹²⁵Te NMR (CD₃CN): δ 740. IR (KBr): 1639.8 (C=N stretching), 834.8 (PF₆⁻) cm⁻¹

3.2.3. Synthesis of 11

To the ligand **2** (0.1 g, 0.14 mmol) in dichloromethane (15 mL) was added Pt(COD)Cl₂ (0.051 g, 0.14 mmol) in dichloromethane (2 mL). The reaction was stirred for 16 h, during that time it turned to reddish brown in colour. The solvent was evaporated and the residue was dissolved in methanol by warming. Excess methanol was evaporated to get 15 ml of the reaction mixture. To this an excess of ammonium hexafluorophosphate was added. A reddish brown precipitate that separated out immediately was recrystallized from acetonitrile by vapour diffusion of diethyl ether. Yield: 0.060 g., (46%); m.p. 260–262 °C (d). Anal. Calc. for C₂₃H₁₉N₂TePtOPF₆: C, 34.20; H, 2.35; N, 3.47. Found: C, 34.24; H, 2.43; N, 3.45%. ¹H NMR (acetone-d₆): δ 10.24 (d, 1H, aldehydic H), 9.17 (s, 1H, azomethine H), 8.73 (t, 1H, azomethine H), 8.47–7.1 (m, 12H, aromatic H), 4.59–4.03 (m, 4H, =NCH₂CH₂N=); ¹²⁵Te NMR (CD₃CN): δ 708.39 and 684.12; MS (FAB): *m/z* 663 (M⁺-PF₆), 558, 429, 309,

291, 152, 120; IR (KBr): 1697 ν(C=O), 1646 ν(C=N) cm⁻¹.

3.2.4. Synthesis of [Ni(II) 2](PF₆)₂ (12)

The ligand **2** (0.1 g, 0.14 mmol) was added to 20 ml of methanol under nitrogen. This was brought to reflux and then NiCl₂ · 6H₂O (0.033 g, 0.14 mmol) was added. The suspension changed to clear red solution within 5 min. It was allowed to reflux for additional 15 min. The solution was filtered and to the filtrate an excess of NH₄PF₆ was added. Immediately a red precipitate was obtained which was filtered and washed with methanol. Crystals were grown from this sample by diffusing diethyl ether into the nitromethane solution. Yield: 0.135 g, (90%); m.p. 238–240 °C (d). Anal. Calc. for C₃₂H₂₈N₄Te₂NiP₂F₁₂: C, 35.84; H, 2.63; N, 5.22. Found: C, 35.69; H, 2.56; N, 4.86%. MS (FAB): 927 (M⁺-PF₆), 784 (M⁺-2PF₆), 490, 391, 309, 292, 273, 178, 152, 120; UV/Vis (MeCN, λ, nm (ε, M⁻¹ cm⁻¹)): 294.8 (15,890), 367 (4630), 488 (630), 809.5 (84). μ_{eff}: 3.06 BM.; IR (KBr): 1644 ν(C=N) 838 ν(P-F), 557 δ(F-P-F) cm⁻¹.

3.3. Crystal-structure determination of compounds **8**, **10**, **11**, and **12**

3.3.1. Data collection, structure solution and refinement

The diffraction measurements were carried out on a Siemens R3m/V diffractometer using graphite-monochromated Mo Kα radiation (= 0.71073 Å). The structure solutions and refinement were routine [27–29]. Some details of data collection and refinement are given in Tables 4 and 5. The high *R* value of complex **12** re-

Table 4
Crystal data and structure refinement for **8** and **10**

	8	10
Empirical formula	C ₃₂ H ₄₆ Br ₄ N ₄ O ₃ Te ₂	C ₃₂ H ₂₈ F ₁₂ N ₄ P ₂ PdTe ₂
<i>F</i> _w	1109.57	1120.12
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2/ <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	10.890(5)	8.2250(10)
<i>b</i> (Å)	7.414(4)	21.280(4)
<i>c</i> (Å)	24.334(13)	21.150(4)
β (°)	96.43	94.190(10)
<i>V</i> (Å ³)	1952.3(17)	3691.9(11)
<i>Z</i>	2	4
Temperature (K)	293(2)	293(2)
Absolute coefficients (mm ⁻¹)	5.623	2.230
Observed reflections [<i>I</i> > 2σ]	6957	8467
Final <i>R</i> (<i>F</i>) [<i>I</i> > 2σ] ^a	0.0449	0.0512
<i>wR</i> (<i>F</i> ²) indices [<i>I</i> > 2σ]	0.1040	0.1162

^a Definition: $R(F_0) = \sum ||F_0| - F_c| / \sum |F_0|$ and $wR(F_0^2) = \{ \sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_c^2)^2] \}^{1/2}$.

Table 5
Crystal data and structure refinement for **11** and **12**

	Compound	
	11	12
Empirical formula	C ₂₃ H ₁₉ F ₆ N ₂ OP- PtTe	C ₃₂ H ₂₈ F ₁₂ N ₄ Ni- P ₂ Te ₂
<i>F</i> _w	807.06	1072.43
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1
<i>a</i> (Å)	12.3253(14)	10.800(8)
<i>b</i> (Å)	14.6557(14)	13.468(9)
<i>c</i> (Å)	13.4054(11)	13.918(11)
α (°)	90	89.67(6)
β (°)	97.000(7)	101.53(7)
γ (°)	90	81.49(3)
<i>V</i> (Å ³)	2403.4(4)	1961(3)
<i>Z</i>	4	2
<i>D</i> (calcd) (Mg/m ³)	2.230	1.817
Temperature (K)	293(2)	293(2)
λ (Å)	0.71073	0.71073
Absolute coefficients (mm ⁻¹)	7.161	2.121
Observed reflections [<i>I</i> > 2 σ]	5108	6592
Final <i>R</i> (<i>F</i>) [<i>I</i> > 2 σ] ^a	0.0422	0.1240
<i>wR</i> (<i>F</i> ²) indices [<i>I</i> > 2 σ]	0.1071	0.3268
Data/restraints/parameters	5107/106/409	6538/40/526
Goodness-of-fit on <i>F</i> ²	1.029	1.099

^a Definition: $R(F_0) = \sum ||F_0| - F_c| / \sum |F_0|$ and $wR(F_0^2) = \{ \sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_c^2)^2] \}^{1/2}$.

quires some comments. In fact the crystal had split reflections and a wide scan was required to collect data. Even then, due to the variable width broad reflections, some were not collected well which resulted in the *R* factor observed. Due to the split reflections the Ψ -scans for absorption correction could not be applied, however, SHELXA (a Difabs type correction) has to be used. This only works well with good data. In addition because of the crystal shape faces also could not indexed.

4. Supplementary material

Crystallographic data for H-atom coordinates, anisotropic thermal parameters and full listings of bond lengths and bond angles for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre CCDC Nos. 168448, 168449, 136087 and 136088 for compounds **8**, **12**, **10**, and **11**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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