

Pyridine- and 3-/6-Methylpyridine-2-tellurolate Complexes of Palladium(II) and Platinum(II)

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The reaction of py_2Te_2 or $(3\text{-MeC}_5\text{H}_3\text{N})_2\text{Te}_2$ with Na_2PdCl_4 in methanol yields an insoluble brown complex, $[\text{PdCl}(\text{TeNC}_5\text{H}_3\text{R})]_n$ ($\text{R} = \text{H}$ or Me). Several reactions of pyTe^- , $(3\text{-MeC}_5\text{H}_3\text{N})\text{Te}^-$, or $(6\text{-MeC}_5\text{H}_3\text{N})\text{Te}^-$ with various palladium(II) and platinum(II) complexes have been carried out. Complexes of the types $[\text{MCl}(\text{Te-N})(\text{PR}_3)]$, $[\text{Pt}(\text{Te-N})_2(\text{dppe})]$, $[\text{Pt}(\text{Te-N})_2(\text{PPh}_3)_2]$, and $[\text{Pt}_2(\mu\text{-Te-N})_2(\text{dppe})_2][\text{BPh}_4]_2$ [$\text{M} = \text{Pd}$ or Pt ; $\text{Te-N} = \text{pyTe}$, $(3\text{- or } 6\text{-MeC}_5\text{H}_3\text{N})\text{Te}$] have been prepared and characterized by elemental analyses, UV/Vis, IR, and NMR (^1H , ^{31}P , ^{195}Pt) spectroscopy. The complexes

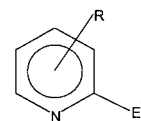
$[\text{MCl}(\text{Te-N})(\text{PR}_3)]$ show irreversible oxidation and reduction by CV in DMF. The molecular structure of $[\text{PdCl}(\text{Te}(3\text{-MeC}_5\text{H}_3\text{N}))(\text{PPh}_3)]$ (**2c**) has been established by single-crystal X-ray diffraction analysis. The palladium atom is bound to the chelating 3-methylpyridinetellurolate ligand, a chlorine atom and a PPh_3 ligand. The pyrolysis of $[\text{PdCl}(\text{Te}(3\text{-MeC}_5\text{H}_3\text{N}))(\text{PR}_3)]$ ($\text{PR}_3 = \text{PEt}_3$ or PPh_3) at 340°C yields PdTe .

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Introduction

The synthesis and characterization of metal chalcogenolates continues to be an area of considerable interest. Their emerging applications as single-source precursors for a low-temperature preparation of solid-state chalcogenide materials has further accelerated work in this area.^[1–4] The area of metal chalcogenolates has been dominated by molecules containing the M-SR linkage.^[5] In most cases, these molecules have been isolated as non-volatile insoluble (or sparingly soluble) polymers, thus making them inconvenient precursors for the preparation of metal chalcogenides. To suppress polymerization, several strategies have been explored. These include use of (a) a strongly coordinating ligand, such as tertiary phosphanes,^[6,7] (b) a sterically demanding chalcogenolate ion,^[8] (c) internally functionalized small-bite ligands.^[9–13] One of the families of the latter class of ligands is the pyridine-2-chalcogenolate ion **I**. While the ligand chemistry of $\text{C}_5\text{H}_4\text{NO}^-$ ^[14] and $\text{C}_5\text{H}_4\text{NS}^-$ ^[15] has been well documented, the coordination chemistry of the pyridine-2-selenolate ion has been explored only re-

cently by us^[11,16] and others.^[17–21] In contrast, metal complexes with pyridine-2-tellurolate are virtually non-existent, although py_2Te_2 has been known for some time.^[22,23] Possibly, a rather tedious preparation (“difficult to reproduce”^[22]) of py_2Te_2 , the precursor for $\text{C}_5\text{H}_4\text{NTe}^-$, appears to be a limiting factor for its use as a ligand.



I

($\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}$; $\text{R} = \text{H}$ or Me)

Group-10 metal chalcogenides (M_xE_y ; $\text{M} = \text{Pd}$ or Pt ; $\text{E} = \text{S}, \text{Se}, \text{Te}$) have found several applications in catalysis^[24] (PdTe supported on carbon is employed industrially) and in the electronic industry.^[25,26] Besides their wide structural diversity^[5] and relevance in catalysis,^[9,27,28] platinum-group metal chalcogenolates offer an attractive possibility of serving as precursors for the synthesis of metal chalcogenides.^[12,29] In continuation of our program on the molecular design of platinum-group metal precursors, we have now synthesized bis(2-pyridyl) and bis(methyl-substituted 2-pyridyl) ditelluride, and have investigated the chemistry of their palladium and platinum complexes.

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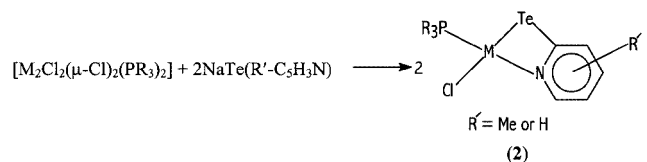
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Results and Discussion

Synthesis and NMR Spectroscopic Data

A methanolic solution of Na₂PdCl₄ was treated with py₂Te₂ or (3-MeC₅H₃N)₂Te₂ at room temperature to give a brown insoluble product, [PdCl{Te(3-RC₅H₃N)}]_n [R = H (**1a**) or Me (**1b**)]. The IR spectrum of **1b** exhibits a band at 281 cm⁻¹ which is assigned to the terminal ν_{Pd-Cl} stretching. On treatment with tertiary phosphanes, the mononuclear complexes [MCl{Te(3-MeC₅H₃N)}(PR₃)] are obtained. The latter complexes and their platinum analogues can readily be prepared by the reaction of [M₂Cl₂(μ-Cl)₂(PR₃)₂] with 2 equiv. of NaTe(RC₅H₃N) (R = H, 3-Me, or 6-Me) [(Scheme 1), prepared by the cleavage of the Te-Te bond in bis(2-pyridyl) ditelluride with NaBH₄ in methanol]. The reaction exclusively gives [MCl{Te(RC₅H₃N)}(PR₃)] (**2**).

Similar reactions with pyO⁻ afford 2-pyridinol-bridged dinuclear complexes, [M₂Cl₂(μ-OC₅H₄N)₂-



(M = Pd or Pt; PR₃ = PEt₃, PnPr₃, PMe₂Ph, PMePh₂, PPh₃, Ptol₃, PPh₂py)

Scheme 1

(PR₃)₂]^[30] while in the reactions with pyS⁻, both mono- and dinuclear complexes [MCl(SC₅H₄N)(PR₃)] and [M₂Cl₂(μ-SC₅H₄N)₂(PR₃)₂] are formed, depending on the nature of the phosphane ligand.^[31–35] In solution a dimer ⇌ monomer equilibrium is established, which is shifted to either side by subtle energetic factors. The reactions with C₅H₄NSe⁻ preferentially yield mononuclear complexes, [MCl(SeC₅H₄N)(PR₃)]. However, dinuclear species are formed in small concentration (ca. 5%) in certain cases when trialkylphosphanes are used.^[11] Clearly, as the Pd-E

Table 1. ³¹P{¹H} and ¹H NMR spectroscopic data for the 2-pyridine- and methyl-2-pyridinetellurolate complexes of palladium(II) and platinum(II)

Complex	³¹ P{ ¹ H} NMR (δ)	¹ H NMR (δ)
[PdCl{Te(3-MeC ₅ H ₃ N)}(PEt ₃)] ^[a]	33.2	1.23 [dt, <i>J</i> (d) = 17.4, <i>J</i> (t) = 7.6 Hz, PCH ₂ CH ₃]; 1.88 (dq, 10.6 (d), 7.6 (q, PCH ₂); 6.98 (m, 5-H); 7.47 (d, <i>J</i> = 7.6 Hz, 4-H); 8.19 (br, 6-H)
[PdCl{Te(3-MeC ₅ H ₃ N)}(PMePh ₂)] ^[a]	17.8	2.27 (d, <i>J</i> = 11.4 Hz, PMe); 6.99 (m, 5-H); 7.46–7.51 (m, 4-H + C ₆ H ₅); 7.72–7.79 (m, C ₆ H ₅); 8.29 (br, 6-H)
[PdCl{Te(3-MeC ₅ H ₃ N)}(PPh ₃)] ^[a]	29.8	7.05 (m, 5-H); 7.50–7.54 (m, 4-H + C ₆ H ₅); 7.74–7.78 (m, C ₆ H ₅); 8.45 (br, 6-H)
[PdCl{Te(3-MeC ₅ H ₃ N)}(Ptol ₃)] ^[a]	27.8	2.38 (s, tol-Me); 7.00 (m, 5-H); 7.30 (m, C ₆ H ₄); 7.51 (d, <i>J</i> = 7.6 Hz, 4-H); 7.64 (dd, <i>J</i> = 8 Hz, <i>J</i> = 11.6 Hz, C ₆ H ₄); 8.42 (br, 6-H)
[PdCl{Te(3-MeC ₅ H ₃ N)}(PPh ₂ py)] ^[a]	30.1	6.99 (m, 5-H); 7.50 (m, 4-H + C ₆ H ₅ , C ₅ H ₄ N); 7.83 (br, C ₆ H ₅ + C ₅ H ₄ N); 8.38 (br, 6-H); 8.83 (br, 6-H, pyP)
[PdCl(TeC ₅ H ₄ N)(PMePh ₂)] ^[a]	17.6	2.33 (d, <i>J</i> = 11 Hz, PMe), 7.05 (br), 7.33–7.64 (br, m); 7.80 (br), 8.40 (br) (Ph + C ₅ H ₄)
[PtCl{Te(3-MeC ₅ H ₃ N)}(PnPr ₃)] ^[a]	-9.3 ¹ <i>J</i> (Pt-P) = 3575 Hz	1.05 (t, <i>J</i> = 7.2 Hz, PCH ₂ CH ₂ Me); 1.64–1.88 (m, PCH ₂ CH ₂); 7.10 (t, <i>J</i> = 5.7 Hz, 5-H); 7.49 (d, <i>J</i> = 7.5 Hz, 4-H); 8.34 [br, ³ <i>J</i> (Pt-H) = 41 Hz, 6-H]
[PtCl{Te(3-MeC ₅ H ₃ N)}(PMe ₂ Ph)] ^[b]	-26.0 ¹ <i>J</i> (Pt-P) = 3605 Hz	1.93 [d, <i>J</i> = 11 Hz, ³ <i>J</i> (Pt-H) = 37 Hz, PMe ₂]; 2.01 (s, MeC ₅ H ₃ N); 6.92 (m, 5-H); 7.27 (d, <i>J</i> = 7.1 Hz, 4-H); 7.45 (m, C ₆ H ₅); 7.69–7.77 (m, C ₆ H ₅); 8.44 [br, ³ <i>J</i> (Pt-H) = 37 Hz, 6-H]
[PtCl{Te(3-MeC ₅ H ₃ N)}(PMePh ₂)] ^[b]	-10.4 ¹ <i>J</i> (Pt-P) = 3699 Hz	1.97 (s, MeC ₅ H ₃ N); 2.25 [d, <i>J</i> = 11.1 Hz, ³ <i>J</i> (Pt-H) = 33 Hz, PMe]; 6.93 (m, 5-H); 7.27 (d, <i>J</i> = 7 Hz, 4-H); 7.43 (m, C ₆ H ₅); 7.66–7.73 (m, C ₆ H ₅); 8.51 [br, ³ <i>J</i> (Pt-H) = 41 Hz, 6-H]
[PtCl(TeC ₅ H ₄ N)(PMePh ₂)] ^[a]	-2.6 ¹ <i>J</i> (Pt-P) = 3814 Hz	2.34 [d, <i>J</i> = 11 Hz, ³ <i>J</i> (Pt-H) = 36 Hz, PMe]; 6.61 (m), 7.22 (m), 7.45 (m), 7.76 (m), 8.00 (m), 8.20 (m) (Ph + C ₅ H ₄)
[Pt{Te(3-MeC ₅ H ₃ N)} ₂ (dppe)] ^[b]	44.8 ¹ <i>J</i> (Pt-P) = 2947 Hz	2.08 (s, MeC ₅ H ₃ N); 2.02 (m, CH ₂ CH ₂); 6.57 (dd, <i>J</i> = 5 Hz, <i>J</i> = 7 Hz, 5-H); 6.77 (d, 7.5 Hz, 4-H); 7.27–7.37 (m, C ₆ H ₅); 7.56 (d, <i>J</i> = 5 Hz, 6-H); 7.71–7.77 (m, C ₆ H ₅)
[Pt{Te(6-MeC ₅ H ₃ N)} ₂ (dppe)] ^[b]	46.8 ¹ <i>J</i> (Pt-P) = 2900 Hz	2.05 (s, MeC ₅ H ₃ N); 2.09 (m, CH ₂ CH ₂); 6.48 (d, <i>J</i> = 7.4 Hz, 3-H); 6.61 (t, <i>J</i> = 7.5 Hz, 4-H); 7.27–7.36 (m, Ph); 7.69–7.76 (m, Ph, 5-H)
[Pt ₂ {Te(3-MeC ₅ H ₃ N)} ₂ (dppe) ₂][BPh ₄] ^[b]	37.1 42.1 ¹ <i>J</i> (Pt-P) = 2944 Hz, ¹ <i>J</i> (Pt-P) = 3259 Hz	2.02 (s, MeC ₅ H ₃ N); 1.85–2.00 (m, CH ₂ CH ₂); 6.55 (m, 5-H); 6.73–6.88 (m), 7.31 (br), 7.47–7.60 (m) [C ₆ H ₅ + 4-H, 6-H]
[Pt{Te(3-MeC ₅ H ₃ N)} ₂ (PPh ₃) ₂] ^[b]	6.6 ¹ <i>J</i> (Pt-P) = 3725 Hz -4.5 (PPh ₃)	2.15 (s, MeC ₅ H ₃ N); 6.65 (br, 5-H); 7.10 (br, 4-H); 7.35 (m), 7.80 (m) (C ₆ H ₅); 8.20 (br, 6-H)

^[a] Recorded in [D₆]acetone; methyl resonance of the 3-MeC₅H₃N merged in the multiplet of [D₆]acetone. ^[b] Recorded in CDCl₃.

distance (Pd–O $\approx$ 2.10 Å; Pd–S $\approx$ 2.28 Å; Pd–Se $\approx$ 2.45 Å; Pd–Te $\approx$ 2.55 Å) increases with increasing size of the chalcogen atom, the Pd–N interaction of these small-bite ligands with a single metal center is facilitated.

The reaction of $\text{PtCl}_2(\text{dppe})$ with 2 equiv. of $\text{NaTe}(3\text{-MeC}_5\text{H}_3\text{N})$ yields the yellow mononuclear complex $[\text{Pt}\{\text{Te}(3\text{-MeC}_5\text{H}_3\text{N})\}_2(\text{dppe})]$. The NMR spectroscopic data (^1H , ^{31}P , and ^{195}Pt) are consistent with several organochalcogenolates, *cis*- $[\text{Pt}(\text{ER})_2(\text{P-P})]$.^[6,7,11–13] The reaction, performed in a 1:1 ratio in the presence of NaBPh_4 , gives a cationic complex $[\text{Pt}_2\{\text{Te}(3\text{-MeC}_5\text{H}_3\text{N})\}_2(\text{dppe})_2][\text{BPh}_4]_2$. The ^{31}P and ^{195}Pt NMR spectra show two sets of resonances and doublets of doublets, respectively; a pattern which can be attributed to the non-equivalence of the phosphorus nuclei of the P–P ligand. Similar spectral features have been reported for $[\text{Pt}_2(\mu\text{-SeCH}_2\text{CH}_2\text{NMe}_2)_2(\text{dppe})_2]^{2+}$ ^[13] for which the existence of an asymmetric M–Se bridge has been suggested.

Treatment of $\text{PtCl}_2(\text{PPh}_3)_2$ with 2 equiv. of $\text{NaTe}(3\text{-MeC}_5\text{H}_3\text{N})$ affords $[\text{Pt}\{\text{Te}(3\text{-MeC}_5\text{H}_3\text{N})\}_2(\text{PPh}_3)_2]$. The ^{31}P NMR spectrum of the complex exhibits a resonance at $\delta = 6.6$ ppm, with $^1J(\text{Pt-P}) = 3725$ Hz, together with a signal which is assigned to PPh_3 ($\delta = -4.5$ ppm) (Table 1). A dynamic equilibrium between free PPh_3 and $[\text{M}(\text{EC}_5\text{H}_4\text{N})_2(\text{PPh}_3)]$ (M = Pd or Pt; E = S or Se)^[11,16] has been reported earlier.

The ^1H NMR spectra of **2** show characteristic resonances for the ligand protons. The 6-H proton signal for the (3-MeC₅H₃N)Te ligand in the platinum complexes is flanked by ^{195}Pt satellites with $^3J(\text{Pt-H}) \approx 40$ Hz. The ^{31}P NMR spectra of these complexes display a single resonance indicating the formation of only one isomer. The magnitude of $^1J(^{195}\text{Pt-}^{31}\text{P})$ in the platinum complexes suggests that the phosphane ligand is *trans* to the nitrogen atom of the chelating 2-pyridinetellurolate ligands,^[11–13] and this is confirmed by the X-ray structural analysis. The ^{195}Pt NMR spectra (Table 2) show a doublet due to coupling with the single phosphorus nucleus. The ^{195}Pt resonance is considerably shielded relative to the signal for the corresponding 2-pyridineselenolate complexes.^[11]

Table 2. $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectra of the 2-pyridinetellurolates of platinum(II)

Complex	^{195}Pt NMR (δ)
$[\text{PtCl}\{\text{Te}(3\text{-MeC}_5\text{H}_3\text{N})\}(\text{PnPr}_3)]$	–4347 [d, $^1J(\text{Pt-P}) = 3580$ Hz]
$[\text{PtCl}\{\text{Te}(3\text{-MeC}_5\text{H}_3\text{N})\}(\text{PMe}_2\text{Ph})]$	–4312 [d, $^1J(\text{Pt-P}) = 3634$ Hz]
$[\text{PtCl}\{\text{Te}(3\text{-MeC}_5\text{H}_3\text{N})\}(\text{PMePh}_2)]$	–4314 [d, $^1J(\text{Pt-P}) = 3690$ Hz]
$[\text{PtCl}(\text{TeC}_5\text{H}_4\text{N})(\text{PMePh}_2)]$	–3830 [d, $^1J(\text{Pt-P}) = 3820$ Hz]
$[\text{Pt}\{\text{Te}(3\text{-MeC}_5\text{H}_3\text{N})\}_2(\text{dppe})]$	–5311 [t, $^1J(\text{Pt-P}) = 2952$ Hz]
$[\text{Pt}_2\{\text{Te}(3\text{-MeC}_5\text{H}_3\text{N})\}_2(\text{dppe})_2][\text{BPh}_4]_2$	–4843 [dd, $^1J(\text{Pt-P}) = 2962$ Hz]

UV/Vis Spectroscopy

All these complexes are deeply colored crystalline solids. The UV/Vis spectra (Table 3) in dichloromethane show a well-separated relatively weak broad band in the visible region, and this is responsible for the deep colors observed for these complexes. The platinum complexes have an absorbance band at higher energies than that of the corresponding palladium analogues. For both the series of complexes (Pd or Pt), this band is hypsochromically shifted with increasing donor strength of the phosphane ligand. The DFT calculations of $[\text{MCl}(\text{TeCH}_2\text{CH}_2\text{NMe}_2)(\text{PR}_3)]$ (M = Pd or Pt) reveal a metal-mediated charge-transfer between coordinated ligands. The highest occupied molecular orbital (HOMO) is predominantly centered on the tellurolate ligand, whereas the lowest unoccupied molecular orbital (LUMO) is delocalized over the system, with significant phosphane contributions. The low-energy electronic transitions between the frontier orbitals give rise to the colors.^[35]

Table 3. UV/Vis data for the 2-pyridinechalcogenolate complexes of $[\text{MCl}\{\text{E}(3\text{-MeC}_5\text{H}_3\text{N})\}(\text{PR}_3)]$ (M = Pd^{II} and Pt^{II}; E = Se, Te) in CH_2Cl_2

Complex	$\lambda_{\text{max}}^{[\text{a}]}$ [nm]
$[\text{PdCl}\{\text{Te}(3\text{-MeC}_5\text{H}_3\text{N})\}(\text{PEt}_3)]$ (2a)	283 (13860), 371 (3280), 567 (190)
$[\text{PdCl}\{\text{Te}(3\text{-MeC}_5\text{H}_3\text{N})\}(\text{PMePh}_2)]$ (2b)	294 (16560), 377 (4670), 595 (240)
$[\text{PdCl}\{\text{Te}(3\text{-MeC}_5\text{H}_3\text{N})\}(\text{PPh}_3)]$ (2c)	277 (16930), 297 (15710), 380 (4400), 614 (210)
$[\text{PdCl}\{\text{Te}(3\text{-MeC}_5\text{H}_3\text{N})\}(\text{Ptol}_3)]$ (2d)	299 (15040), 381 (4660), 609 (210)
$[\text{PdCl}(\text{TeC}_5\text{H}_4\text{N})(\text{PMePh}_2)]$ (2f)	293 (sh, 13170), 373 (4200), 570 (320)
$[\text{PtCl}\{\text{Te}(3\text{-MeC}_5\text{H}_3\text{N})\}(\text{PnPr}_3)]$ (3a)	286 (sh, 7420), 402 (1880)
$[\text{PtCl}\{\text{Te}(3\text{-MeC}_5\text{H}_3\text{N})\}(\text{PMe}_2\text{Ph})]$ (3b)	285 (6430), 313 (sh, 3940), 404 (1342)
$[\text{PtCl}\{\text{Te}(3\text{-MeC}_5\text{H}_3\text{N})\}(\text{PMePh}_2)]$ (3c)	286 (sh, 8090), 316 (3950), 408 (1760)
$[\text{PdCl}(\text{SeC}_5\text{H}_4\text{N})(\text{PnPr}_3)]^{[\text{b}]}$	293 (26070), 475 (89)
$[\text{PtCl}(\text{SeC}_5\text{H}_4\text{N})(\text{PnPr}_3)]^{[\text{b}]}$	282 (7350), 376 (1480)

[a] Wavelengths λ_{max} at the absorbance maxima in nm, molar extinction coefficients ϵ in $\text{M}^{-1} \text{cm}^{-1}$. [b] Prepared according to ref.^[11]

Cyclic Voltammetry

The complexes show irreversible oxidation and reduction in DMF/0.01 M Et_4NClO_4 (Table 4). The lower oxidation potential of the Pt/Te system indicates that the HOMO (Te) is destabilized relative to that of the corresponding Pd/Te system. Such behavior has been reported for $[\text{MCl}(\text{TeCH}_2\text{CH}_2\text{NMe}_2)(\text{PR}_3)]$ complexes.^[35] It was difficult to oxidize the 2-pyridineselenolates $[\text{MCl}(\text{SeC}_5\text{H}_4\text{N})(\text{PR}_3)]$ (high oxidation potential values).

Structure of $[\text{PdCl}\{\text{Te}(3\text{-MeC}_5\text{H}_3\text{N})\}(\text{PPh}_3)]$ (**2c**)

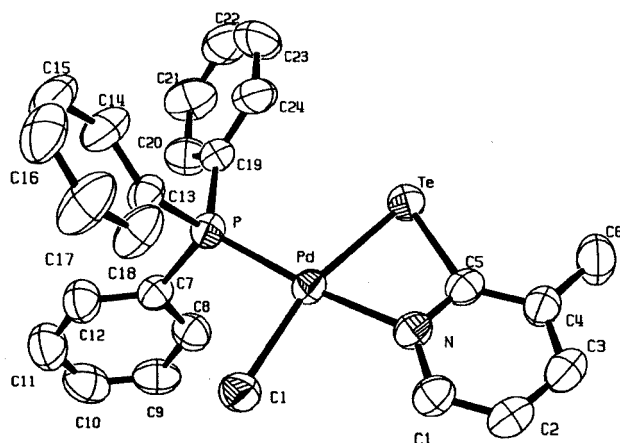
The molecular structure of $[\text{PdCl}\{\text{Te}(3\text{-MeC}_5\text{H}_3\text{N})\}(\text{PPh}_3)]$ (**2c**) was established by single-crystal X-ray diffrac-

Table 4. Electrochemical data

Complex	E_{pa} (ox) ^[a]	E_{pc} (red) ^[a]
[PdCl{Te(3-MeC ₅ H ₃ N)}(PEt ₃)] (2a)	0.46	−2.13
[PdCl{Te(3-MeC ₅ H ₃ N)}(PMePh ₂)] (2b)	0.40	−1.78
[PtCl{Te(3-MeC ₅ H ₃ N)}(PMe ₂ Ph)] (3b)	0.36	−2.26
[PtCl{Te(3-MeC ₅ H ₃ N)}(PMePh ₂)] (3c)	0.39	−2.30
[PdCl(SeC ₅ H ₄ N)(PnPr ₃)] ^[b]	0.98	−1.98
[PtCl(SeC ₅ H ₄ N)(PnPr ₃)]	0.80	−1.63

^[a] Scan rate 100 mV·s^{−1}, peak potentials for irreversible processes in V vs. FeCp₂/FeCp₂⁺. ^[b] Measurement in DMF/Et₄NClO₄.

tion analysis. The ORTEP^[36] plot with the atomic numbering scheme is shown in Figure 1, and the selected bond lengths and angles are given in Table 5. The molecule consists of a distorted square-planar palladium atom that is bound to the chelating 3-methyl-2-pyridinetellurolate ligand, a chlorine atom and a PPh₃ ligand. The neutral donors (N, P) are mutually *trans*, and as a consequence the chloride ion and the Te atom adopt a *trans* arrangement, a configuration that has been reported previously for selenolate and tellurolate complexes, [MCl(E-N)(PR₃)] (M = Pd or Pt; E-N = SeCH₂CH₂NMe₂,

Figure 1. Molecular structure of [PdCl{Te(3-MeC₅H₃N)}(PPh₃)] (**2c**) with the atomic numbering schemeTable 5. Selected bond lengths [Å] and angles [°] for [PdCl{Te(3-MeC₅H₃N)}(PPh₃)] (**2c**)

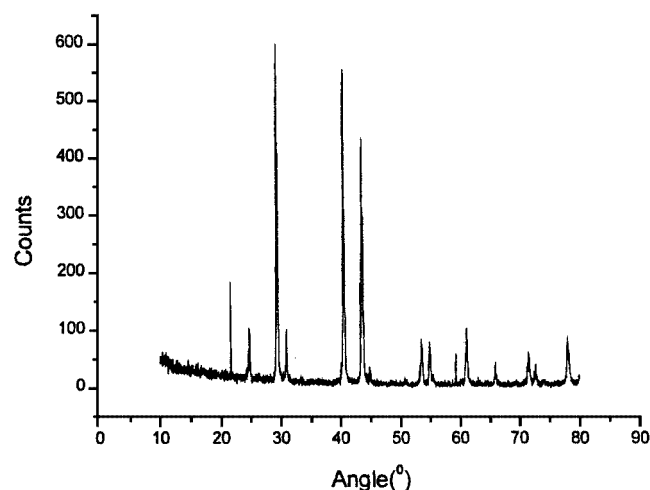
Pd–Te	2.5606(8)	Te–C(5)	2.118(5)
Pd–N	2.085(4)	N–C(1)	1.337(7)
Pd–Cl	2.3620(16)	N–C(5)	1.330(7)
Pd–P	2.2420(15)	P–C(av)	1.821
N–Pd–P	173.76(13)	Pd–Te–C(5)	72.71(15)
N–Pd–Cl	94.17(13)	Te–C(5)–N	106.1(4)
P–Pd–Cl	92.07(5)	Te–C(5)–C(4)	131.1(4)
N–Pd–Te	73.18(12)	C(7)–P–C(13)	107.1(3)
P–Pd–Te	100.67(4)	C(7)–P–C(19)	104.0(3)
Cl–Pd–Te	165.21(4)	C(13)–P–C(19)	103.0(3)

TeCH₂CH₂NMe₂).^[12,13,35] The square plane of the palladium atom (defined by the N, Cl, P, Te atoms), the four-membered chelate ring [Pd, N, C(5), Te], and the pyridine ring are almost coplanar, with the interplanar angles varying between 3.68 and 6.68°. The Te atom lies 0.1 Å out of the plane defined by the Pd, N, Cl, and P atoms.

The various angles around the Pd atom differ significantly from [PdCl(TeCH₂CH₂NMe₂)(PR₃)] (PR₃ = PnPr₃, PMePh₂),^[35] owing to the small bite of the four-membered (3-MeC₅H₃N)Te moiety. The Pd–Te distance is slightly longer [2.5606(8) Å] than that observed for [PdCl(TeCH₂CH₂NMe₂)(PR₃)] [PR₃ = PnPr₃ 2.5095(8) and PMePh₂ 2.5156(6) Å],^[35] while the Pd–N distance [2.085(4) Å] is shorter than that reported for [PdCl(TeCH₂CH₂NMe₂)(PR₃)].^[35] These distances, as well as the Pd–Cl, Pd–P and Te–C bond lengths are not unusual.^[33–35,37–40]

Thermal Behavior

Thermogravimetric analysis of [PdCl{Te(3-MeC₅H₃N)}(PPh₃)] (**2c**) was carried out under a dynamic argon pressure. The TG curve shows a one-step decomposition (290°C), leading to the formation of PdTe as inferred from the calculated weight loss. In order to prepare large quantities of the telluride, a substantial amount (100–350 mg) of the complexes (**2a**, **2c**) was heated in a furnace at 340°C for 2 h under a dynamic dry argon pressure. The weight loss and XRD pattern (Figure 2) of the residue obtained after decomposition in each case matches the product obtained from TG. The XRD patterns (Figure 2) of all these samples are in agreement with the standard pattern of PdTe^[41] [analysis of the prepared PdTe: sample from **2a**: C 1.8, H < 0.2, N < 0.2; sample from **2c**: C < 0.2, H < 0.2, N < 0.2 (detection limit 0.2%)]. The scanning electron micrographs

Figure 2. XRD pattern of PdTe obtained from [PdCl{Te(3-MeC₅H₃N)}(PPh₃)]

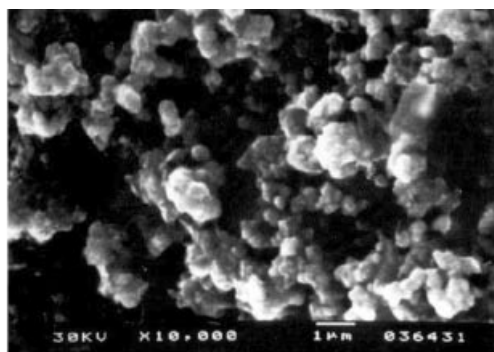


Figure 3. SEM picture of PdTe obtained from $[\text{PdCl}\{\text{Te}(\text{3-MeC}_5\text{H}_3\text{N})\}(\text{PPh}_3)]$

(Figure 3) of PdTe obtained from **2c** taken at different resolutions show large aggregates of microcrystals.

Experimental Section

General: The complexes Na_2PdCl_4 , $[\text{PtCl}_2(\text{PPh}_3)_2]$, $[\text{M}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PR}_3)_2]$ ($\text{M} = \text{Pd}$ or Pt ; $\text{PR}_3 = \text{PEt}_3$, $\text{P}n\text{Pr}_3$, PMe_2Ph , PMePh_2 , PPh_3), $[\text{PtCl}_2(\text{dppe})]$,^[42] py_2Te_2 ,^[43a] $(3\text{-}/6\text{-MeC}_5\text{H}_3\text{N})_2\text{Te}_2$,^[43b] and the methyl-substituted 2-bromopyridines^[44] were prepared according to literature methods. The phosphanes were obtained from Strem Chemicals (USA). All reactions were carried out under nitrogen, in dry and distilled analytical grade solvents. Microanalyses were carried out in the Analytical Chemistry Division of B.A.R.C. ^1H , $^{31}\text{P}\{^1\text{H}\}$, $^{125}\text{Te}\{^1\text{H}\}$, and $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectra were recorded with a Bruker DPX-300 NMR spectrometer, operating at 300, 121.49, 94.86, and 64.52 MHz, respectively. Chemical shifts are relative to the internal chloroform peak ($\delta = 7.26$ ppm) for ^1H , external 85% H_3PO_4 for ^{31}P , $\text{Te}(\text{dte})_2$ ($\text{dte} = \text{Et}_2\text{NCS}_2$) for ^{125}Te , and $\text{Na}_2[\text{PtCl}_6]$ in D_2O for ^{195}Pt . A 90° pulse was used in every case. The IR spectra were recorded as Nujol mulls between CsI plates with a Bomen MB-102 FT-IR spectrometer. UV/Vis absorbance spectra were recorded with a JASCO V-530 spectrometer using quartz cuvettes with a diameter of 1 cm. Cyclic voltammetry was carried out at a scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$ in DMF/0.01 M Et_4NClO_4 , using a three-electrode configuration (glassy carbon electrode, platinum counter electrode, calomel reference electrode) and an Ecochemie potentiostat 100 with autolab software. The ferrocene/ferrocenium couple served as the external reference. Mass spectra were recorded with a VG-705 11-250J spectrometer at RSIC, Panjab University, Chandigarh. Thermogravimetric analysis (TGA) was carried out using a Setaram 92-16-18 instrument calibrated with $\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O}$. The TG curves were recorded at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ under a flow of argon. X-ray powder diffraction was measured using Cu-K_α radiation. SEM photographs were taken using a JEOL JSM-T330A instrument.

Preparations

Preparation of Bis(3- and 6-methyl-2-pyridyl) Ditelluride: Sodium borohydride (4.0 g, 108 mmol) was added slowly under a flow of nitrogen to a suspension of tellurium powder (9.65 g, 76 mmol) in 2-ethoxyethanol. The resulting colorless solution was refluxed for 30 min and then cooled to room temperature; 3- or 6-methyl-substituted 2-bromopyridine (13.07 g, 76 mmol) was added and the resulting solution was refluxed until all the 2-bromopyridine was con-

sumed (48–96 h). The progress of the reaction was monitored by TLC. The nitrogen flow was stopped and the mixture was subjected to oxidation in air. The solvent was removed under vacuum and the crude residue was washed with water, and extracted with diethyl ether ($4 \times 100 \text{ mL}$). The extract was dried with anhydrous sodium sulfate and the solvent removed using a rotary evaporator, leaving the crude ditelluride. This was purified by column chromatography (silica gel; hexane/ethyl acetate, 10:1).

Bis(3-methyl-2-pyridyl) Ditelluride $\{[(3\text{-MeC}_5\text{H}_3\text{N})\text{Te}]_2\}$: Yield 52%, m.p. $125\text{--}128^\circ\text{C}$. $\text{C}_{12}\text{H}_{12}\text{N}_2\text{Te}_2$ (439.4): calcd. C 32.8, H 2.7, N 6.4; found C 32.6, H 2.42, N 6.18. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 297 (3260), 346 (sh, 1340), 412 (510) nm. ^1H NMR (CDCl_3): δ = 2.41 (s, Me), 6.96 (dd, J = 3.2, 5.0 Hz, 5-H), 7.25 (d, J = 4.6 Hz, 4-H); 8.20 (dd, J = 0.8, 3.5 Hz, 6-H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ = 24.4 (s, Me), 122.1 (C-4), 134.9 (C-5), 137.8 (C-2), 140.7 (C-3), 148.3 (C-6) ppm. $^{125}\text{Te}\{^1\text{H}\}$ NMR (CDCl_3): δ = -382.7 ppm. IR (KBr): $\tilde{\nu}$ = 3060, 2960, 2920, 1580, 1540, 1430, 1120, 1090, 1020, 840, 780, 660, 540 cm^{-1} . MS (EI): m/z (%) = 440 (7.33) $[\text{M} (^{130}\text{Te})]^+$, 314 (14.51) $[\text{M} - \text{Te}]^+$, 216 (1.47) $[\text{M} - \text{MeC}_5\text{H}_3\text{NTe}]$, 183 (76.62) $[\text{M} - \text{Te}_2\text{H}]^+$, 92 (100) $[\text{M} - \text{CH}_3\text{pyTe}_2]^+$.

Bis(6-methyl-2-pyridyl) Ditelluride: Yield 24%, m.p. $55\text{--}56^\circ\text{C}$. $\text{C}_{12}\text{H}_{12}\text{N}_2\text{Te}_2$ (439.4): calcd. C 32.8, H 2.7, N 6.4; found C 32.21, H 2.52, N 6.18. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 292 (sh, 8110), 386 (850) nm. ^1H NMR (CDCl_3): δ = 2.50 (s, Me), 6.85 (d, J = 5.0 Hz, 3-H), 7.25 (t, J = 5.0 Hz, 4-H), 7.84 (d, J = 5.0 Hz, 5-H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ = 24.2 (s, Me), 121.0 (C-4), 128.0 (C-5), 134.9 (C-2), 137.0 (C-3), 158.9 (C-6) ppm. $^{125}\text{Te}\{^1\text{H}\}$ NMR (CDCl_3): δ = -426.4 ppm. IR (KBr): $\tilde{\nu}$ = 3042, 2916, 1571, 1429, 1376, 1242, 1163, 1083, 988, 826, 781, 655, 545 cm^{-1} . MS (EI): m/z (%) = 444 (5.5) $[\text{M} (^{130}\text{Te})]^+$, 314 (6.5) $[\text{M} - \text{Te}]^+$, 216 (0.6) $[\text{M} - \text{MeC}_5\text{H}_3\text{NTe}]$, 183 (30.9) $[\text{M} - \text{Te}_2\text{H}]^+$, 92 (100) $[\text{M} - \text{CH}_3\text{pyTe}_2]^+$.

$[\text{PdCl}\{\text{Te}(\text{3-MeC}_5\text{H}_3\text{N})\}]_n$ (1b**):** A methanolic solution (10 mL) of Na_2PdCl_4 (342 mg, 1.16 mmol) was added to a methanolic solution (20 mL) of $(3\text{-MeC}_5\text{H}_3\text{N})_2\text{Te}_2$ (256 mg, 0.58 mmol) while stirring at room temperature, whereupon a brown precipitate formed. Stirring was continued for 3 h. The brown precipitate was filtered, washed with methanol, water, acetone, and diethyl ether and dried in vacuo (yield: 235 mg, 56%). Complex **1a** was also prepared in a similar manner.

$[\text{PdCl}\{\text{Te}(\text{3-MeC}_5\text{H}_3\text{N})\}(\text{PEt}_3)]$ (2a**):** An acetone suspension (20 mL) of $[\text{Pd}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PEt}_3)_2]$ (108 mg, 0.18 mmol) was added to a freshly prepared methanolic solution (5 mL) of $\text{NaTe}(\text{3-MeC}_5\text{H}_3\text{N})$ [prepared from $(3\text{-MeC}_5\text{H}_3\text{N})_2\text{Te}_2$ (82 mg, 0.19 mmol) and NaBH_4 (15 mg, 0.39 mmol)], and the mixture was stirred for 4 h at room temperature. The solvents were evaporated in vacuo and the residue was extracted with acetone ($3 \times 8 \text{ mL}$). The solution was passed through a Florisil column. The blue solution was concentrated to 3 mL, a few drops of hexane were added, and the solution was kept at -5°C in a freezer giving blue-violet crystals (130 mg, 74%). Similarly, other palladium (**2b**, **2c**, **2f**) and platinum (**3a–3d**) complexes were prepared. The most important data are summarized in Table 6.

$[\text{PdCl}\{\text{Te}(\text{3-MeC}_5\text{H}_3\text{N})\}(\text{Ptol}_3)]$ (2d**):** Solid Ptol_3 ($\text{tol} = 4\text{-MeC}_6\text{H}_4$) (26 mg, 0.09 mmol) was added to an acetone suspension (20 mL) of **1** (30 mg, 0.08 mmol), and the mixture was stirred for 1 h. The green solution was dried in vacuo and the residue was washed with hexane, diethyl ether and recrystallized from acetone/hexane to yield green crystals (38 mg, 68%). The complexes **2c** and **2e** were prepared in an analogous manner.

Table 6. Physical and analytical data for 3-methyl- and 6-methyl-2-pyridinetellurolate complexes of Pd^{II} and Pt^{II}

Complex	Color	Recrystallization solvent (yield [%])	M.p. [°C]	Analysis: found (calcd.)		
				C	H	N
[PdCl(TeC ₅ H ₄ N)] _n (1a)	brown		164 (dec.)	17.0 (17.3)	1.2 (1.2)	4.1 (4.0)
[PdCl{Te(3-MeC ₅ H ₃ N)}] _n (1b)	brown		185 (dec.)	18.6 (19.9)	1.3 (1.7)	3.6 (3.9)
[PdCl{Te(3-MeC ₅ H ₃ N)}(PET ₃)] (2a)	blue-violet	hexane (74)	116	30.5 (30.1)	4.2 (4.4)	2.8 (2.9)
[PdCl{Te(3-MeC ₅ H ₃ N)}(PMePh ₂)] (2b)	blue	acetone/hexane (72)	163	40.6 (40.7)	3.3 (3.4)	2.4 (2.5)
[PdCl{Te(3-MeC ₅ H ₃ N)}(PPh ₃)] (2c)	green	acetone (76)	150	45.4 (46.2)	3.2 (3.4)	2.3 (2.2)
[PdCl{Te(3-MeC ₅ H ₃ N)}(P(tol) ₃)] (2d)	green	acetone/hexane (68)	167	48.6 (48.7)	3.7 (4.1)	2.2 (2.1)
[PdCl{Te(3-MeC ₅ H ₃ N)}(PPh ₂ py)] (2e)	green	acetone (60)	78	45.0 (44.2)	3.0 (3.2)	4.8 (4.5)
[PdCl(TeC ₅ H ₄ N)(PMePh ₂)] (2f)	green	acetone/hexane (56)	102	38.9 (39.5)	3.3 (3.1)	2.8 (2.6)
[PtCl{Te(3-MeC ₅ H ₃ N)}(PnPr ₃)] (3a)	orange-red	hexane (66)	98	29.5 (29.5)	4.2 (4.5)	2.2 (2.3)
[PtCl{Te(3-MeC ₅ H ₃ N)}(PMe ₂ Ph)] (3b)	red	diethyl ether/hexane (58)	124	28.8 (28.6)	2.7 (2.9)	2.3 (2.4)
[PtCl{Te(3-MeC ₅ H ₃ N)}(PMePh ₂)] (3c)	red	acetone (62)	187	35.1 (35.1)	2.6 (2.9)	2.1 (2.2)
[PtCl(TeC ₅ H ₄ N)(PMePh ₂)] (3d)	brown	acetone/hexane (52)	166	(34.0)	(2.7)	(2.2)
[Pt{Te(3-MeC ₅ H ₃ N)} ₂ (dppe)] (4a)	yellow	CH ₂ Cl ₂ /hexane (64)	192	45.0 (44.2)	3.2 (3.5)	2.8 (2.7)
[Pt{Te(6-MeC ₅ H ₃ N)} ₂ (dppe)] (4b)	yellow	acetone/hexane (56)	167	43.4 (44.2)	3.2 (3.5)	2.4 (2.7)
[Pt{Te(3-MeC ₅ H ₃ N)} ₂ (PPh ₃) ₂] (5)	yellow	acetone/benzene (42)	168	49.3 (49.8)	2.5 (3.6)	2.1 (2.4)
[Pt ₂ {Te(3-MeC ₅ H ₃ N)} ₂ (dppe) ₂][BPh ₄] ₂ (6)	yellow	acetone (60)	213	59.5 (59.4)	4.2 (4.4)	1.4 (1.2)

[Pt{Te(3-MeC₅H₃N)}₂(dppe)] (**4a**): This compound was prepared analogously to **2a** by using [PtCl₂(dppe)] (110 mg, 0.17 mmol) and NaTe(3-MeC₅H₃N) [prepared from (3-MeC₅H₃N)₂Te₂ (73 mg, 0.17 mmol) and NaBH₄ (13 mg, 0.34 mmol)]. The yellow residue was recrystallized from a CH₂Cl₂/hexane mixture (yield: 109 mg, 64%). Complex **4b** was prepared in a similar manner.

[Pt{Te(3-MeC₅H₃N)}₂(PPh₃)₂] (**5**): A benzene suspension of [PtCl₂(PPh₃)₂] (154 mg, 0.19 mmol) was added to a freshly prepared methanolic solution (5 mL) of NaTe(3-MeC₅H₃N) [prepared from (3-MeC₅H₃N)₂Te₂ (85 mg, 0.19 mmol) and NaBH₄ (15 mg, 0.39 mmol)], and the yellow-orange mixture was stirred for 4 h. The solvents were evaporated in vacuo and the residue was washed thoroughly with hexane, diethyl ether, and acetone and then extracted with benzene (3 × 8 mL). The solution was passed through a Florisil column and concentrated to 5 mL, a few drops of acetone were added, and the solution was kept at −5°C in a freezer, giving a yellow powder (95 mg, 42%).

[Pt₂{Te(3-MeC₅H₃N)}₂(dppe)₂][BPh₄]₂ (**6**): An acetone suspension (20 mL) of [PtCl₂(dppe)] (203 mg, 0.31 mmol) was added to a freshly prepared methanolic solution (5 mL) of NaTe(3-MeC₅H₃N) [prepared from (3-MeC₅H₃N)₂Te₂ (68 mg, 0.16 mmol) and NaBH₄ (12 mg, 0.32 mmol)], while stirring. After 2 h, an acetone solution (8 mL) of NaBPh₄ (107 mg, 0.31 mmol) was added, while stirring was continued for 3 h. The solvents were evaporated under vacuum. The yellow residue was extracted with acetone (3 × 8 mL) and passed through a Florisil column. The solution was concentrated to 5 mL and yellow crystals were obtained (207 mg, 60%).

Crystallography: X-ray data on dark green crystals of [PdCl{Te(3-MeC₅H₃N)}(PPh₃)] (**2c**) were collected at room temperature with an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), employing the ω-2θ scan technique. Crystal data are given in Table 7. The unit cell parameters were determined from 25 reflections measured by random search routine and indexed by the method of short vectors followed by least-squares refinement. The intensity data were corrected for Lorentz polarization and absorption effects. The structure was solved using the SHELXS86^[45] and refined using the SHELXL97^[46] computer programs. The non-hydrogen atoms were refined anisotropically. CCDC-181928 contains the supplementary crystallographic data for this paper. These data can be obtained

Table 7. Crystallographic and structure refinement details for [PdCl{Te(3-MeC₅H₃N)}(PPh₃)] (**2c**)

Empirical formula	C ₂₄ H ₂₁ ClNPPdTe
Formula mass	623.84
Crystal size [mm]	0.3 × 0.3 × 0.2
<i>T</i> [K]	293(2)
λ [Å]	0.71073
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	
<i>a</i> [Å]	8.607(2)
<i>b</i> [Å]	11.088(3)
<i>c</i> [Å]	24.552(5)
β [°]	98.83(2)
<i>V</i> [Å ³]	2315.4(9)
ρ _{calcd.} [Mg·m ^{−3}]	1.790
<i>Z</i>	4
μ [mm ^{−1}]	2.231
θ for data collection/°	2.02 to 24.96
Reflections collected/unique	4349/4059 [<i>R</i> _{int} = 0.03–0.01]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Absorption correction	ψ scan
Data/restraints/parameters	4059/0/263
Goodness of fit on <i>F</i> ²	1.104
Final <i>R</i> ₁ , <i>wR</i> ₂ indices	0.0376, 0.0955
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0563, 0.1265
Largest diff peak and hole [e·Å ^{−3}]	0.944 and −1.058

free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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