DALTON
FULL PAPER

Synthesis and electrochemistry of $[Pt(tame)_2]^{4+}$: crystallographic analysis of bis[1,1,1-tris(aminomethyl)ethane-*N*,*N′*]platinum(II) bis(tetrachlorozincate) dihydrate

Kylie N. Brown,[a] **David C. R. Hockless**[a] **and Alan M. Sargeson**[b]

[a] *Research School of Chemistry, Australian National University, A.C.T., 0200 Australia*
[b] *Chemistry Department, Australian National University, A.C.T., 0200 Australia*

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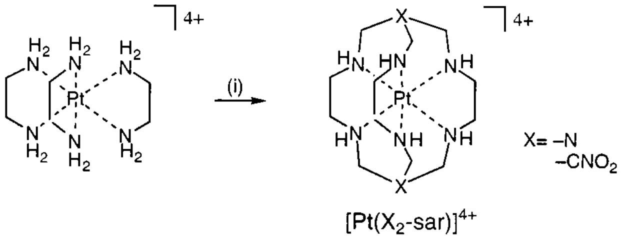
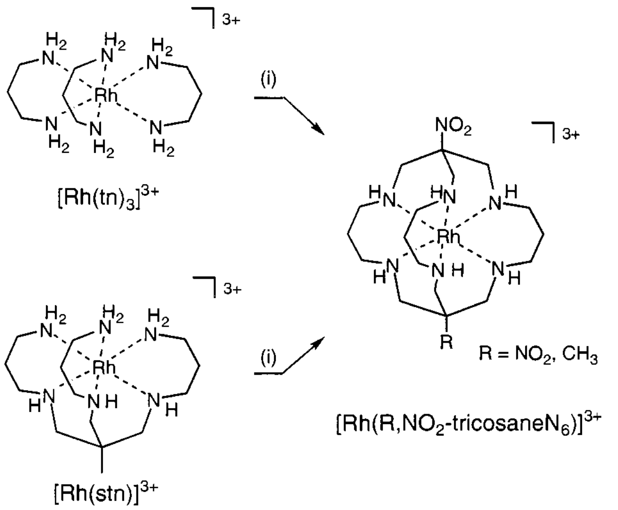
Reaction of K_2PtCl_6 with the tripodal ligand tame [1,1,1-tris(aminomethyl)ethane] in dimethylformamide catalysed by K_2PtCl_4 afforded the octahedral bis(tridentate ligand) $[Pt(tame)_2]^{4+}$ ion. The cyclic voltammogram of $[Pt(tame)_2]^{4+}$ in aqueous media showed an irreversible reduction of the six-co-ordinate platinum(IV) species to Pt^{II} and bulk electrochemical reduction of the $[Pt^{IV}(tame)_2]^{4+}$ ion quantitatively produced a square planar platinum(II) complex $[Pt(tame)_2]^{2+}$. Crystallographic analysis of the protonated complex $[Pt^{II}(Htame)_2][ZnCl_4]_2{\cdot}2H_2O$, showed two dissociated nitrogen atoms on opposite sides of the PtN_4^{2+} co-ordination plane which has typical Pt^{II}–N bond lengths (2.042(6) Å). The routes to the formation of the $[Pt^{IV}(tame)_2]^{4+}$ ion and its reduced product are addressed.

Introduction

Platinum(IV) sarcophagine† cage complexes, namely $[Pt(sep)]^{4+}$, $[Pt((NO_2)_2sar)]^{4+}$, and $[Pt((NHOH)_2sar)]^{4+}$, have been synthesized previously using $[Pt(en)_3]^{4+}$ as a template,[1] in analogy to the aqueous capping methods devised for $[Co(en)_3]^{3+}$ encapsulation[2] (Scheme 1). It was also anticipated that the platinum(IV) cage complexes with expanded cavities, such as $[Pt(tricosaneN_6)]^{4+}$, could be synthesized using the capping strategy described for $[Rh(tricosaneN_6)]^{3+}$ complexes, where tris(propane-1,3-diamine)rhodium(III) ($[Rh(tn)_3]^{3+}$) and [1,1,1-tris(5-amino-2-azapentyl)ethane]rhodium(III) ($[Rh(stn)]^{3+}$) ions were used as templates (Scheme 2).[3] Since the anticipated Pt^{IV}–N bond length for the saturated PtN_6^{4+} cage (≈ 2.07 Å) is comparable to that of Rh–N in saturated RhN_6^{3+} systems (2.09 Å),[3] the synthesis of platinum(IV) tricosaneN_6 complexes should be feasible using either $[Pt(tn)_3]^{4+}$ or $[Pt(stn)]^{4+}$ complexes as templates. However, the syntheses of the necessary precursors for the platinum(IV) capping reactions, namely $[Pt(tn)_3]^{4+}$ and $[Pt(stn)]^{4+}$, have not been reported and surprisingly attempts to synthesize the $[Pt(tn)_3]^{4+}$ ion were not fruitful using modified syntheses which had been successful for $[Pt(en)_3]^{4+}$ [4] and $[Pt(en)_x(pn)_{3-x}]^{4+}$ ($x = 3$, 2, 1 or 0).[5] These routes produced mostly $[Pt(tn)Cl_2]$, $[Pt(tn)_2]^{2+}$, *trans*-$[Pt(tn)_2Cl_2]^{2+}$ and red polymeric species of unknown constitution, regardless of the temperature and solvents including dimethylformamide, water, dimethyl sulfoxide and ethanol. In no case was the target $[Pt(tn)_3]^{4+}$ ion isolated even after using ion-exchange chromatography.[6] Similar attempts to synthesize $[Pt(stn)]^{4+}$ were also unsuccessful. Red oils were obtained when free stn was treated with $K_2[PtCl_6]$ in the presence of $K_2[PtCl_4]$ in a variety of solvents (*e.g.* water, DMF, DMSO, alcohols). NMR Spectroscopy and ion exchange chromatography also showed these oils to be complex mixtures.



Scheme 1 Capping $[Pt(en)_3]^{4+}$. (i) CH_3NO_2 or NH_3, CH_2O and base, in water.



Scheme 2 Capping $[Rh(tn)_3]^{3+}$ and $[Rh(stn)]^{3+}$. (i) CH_3NO_2, CH_2O and base, in water.

An alternative route to the synthesis of bicyclic platinum(IV) tricosaneN_6 cage complexes was envisaged by strapping the template $[Pt(tame)_2]^{4+}$ from top to bottom (Scheme 3). A precedent for such a path existed for the analogous cobalt(III) template, which when treated with formaldehyde and a range of aldehydes in acetonitrile gave the $[Co(tricosanetriimineN_6)]^{3+}$ framework.[7] The synthesis for the simple $[Pt(tame)_2]^{4+}$ complex had not been reported, however, and this paper addresses its synthesis and redox properties. The tripodal tame ligand co-ordinates facially to the metal ion, in analogy to the [9]aneN_3 and [9]aneS_3 (trithiacyclononane) ligands, but is more flexible.

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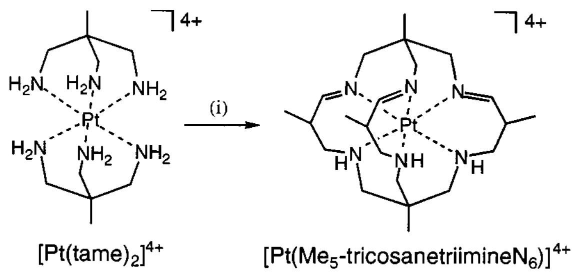
† Abbreviated ligand names used: sar, sarcophagine = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane; sep, sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane; tricosaneN_6 = 3,7,11,15,18,22-hexaazabicyclo[7.7.7]tricosane; Me_5-tricosanetriimineN_6 = 1,5,9,13,20-pentamethyl-3,7,11,15,18,22-hexaazabicyclo[7.7.7]tricosa-3,14,18-triene; tame = 1,1,1-tris(aminomethyl)ethane; [9]aneN_3 = 1,4,7-triazacyclononane; pn = propane-1,2-diamine.



Scheme 3 Strapping [Pt(tame)$_2$]$^{4+}$ to form [Pt(Me$_5$-tricosanetriimineN_6)]$^{4+}$. (i) CH$_3$CH$_2$CHO, CH$_2$O and base, in acetonitrile.

The reactivities of the three bis(tridentate ligand) complexes are compared.

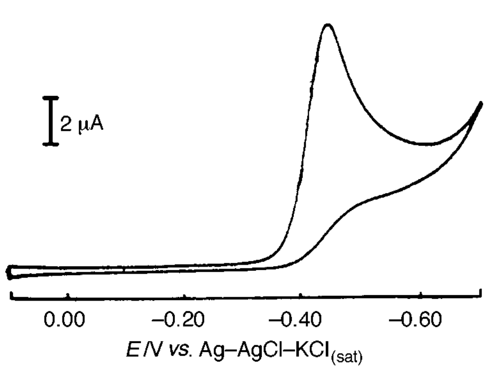
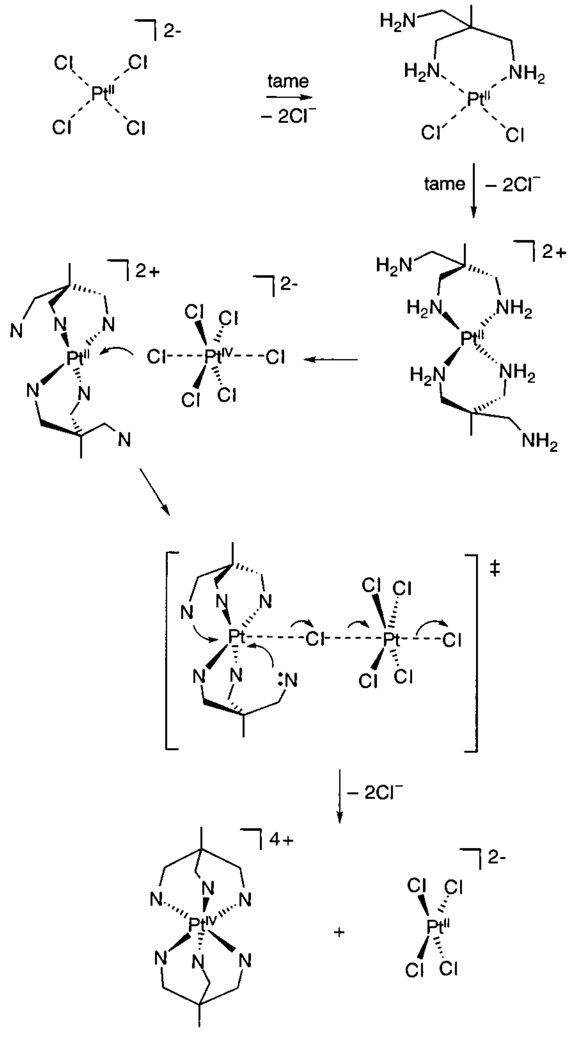


Fig. 1 Cyclic voltammogram of [Pt(tame)$_2$]$^{4+}$ in 1 M HClO$_4$ (100 mV s^{-1}, *vs.* Ag–AgCl–KCl (sat.), hanging mercury drop electrode).



Scheme 4 Proposed mechanism for [Pt(tame)$_2$]$^{4+}$ synthesis (some amine protons have been omitted for clarity).

Results and discussion

A good yield of [Pt(tame)$_2$]Cl$_4$ (75%) was obtained after 40 h when free tame was added to a solution of K$_2$[PtCl$_6$] dissolved in warm dimethylformamide at 40 °C with a catalytic amount of K$_2$[PtCl$_4$]. When the reaction was performed in ethanol and heated for three hours at 70 °C a slightly lower yield of the desired product was obtained. The ^{1}H and ^{13}C NMR spectra for [Pt(tame)$_2$]Cl$_4$ in D$_2$O were consistent with that for an octahedral bis(tridentate ligand) complex with D_{3h} symmetry. For example, the methyl, quaternary and methylene carbon atom resonances occurred respectively at δ 21.80, 45.15 and 47.20 in D$_2$O. The ^{195}Pt coupling constants with the methylene and quaternary carbon atoms are typical for complexes of this type ($^2J_{\text{Pt–C}} = 8.4$; $^3J_{\text{Pt–C}} = 44.2$ Hz, respectively).[8] The nitrogen protons rapidly exchange with D$_2$O and were not observed. This is consistent with the first pK_a (7.0 ± 0.1) which is characteristic for simple hexaamine platinum(IV) complexes.[9]

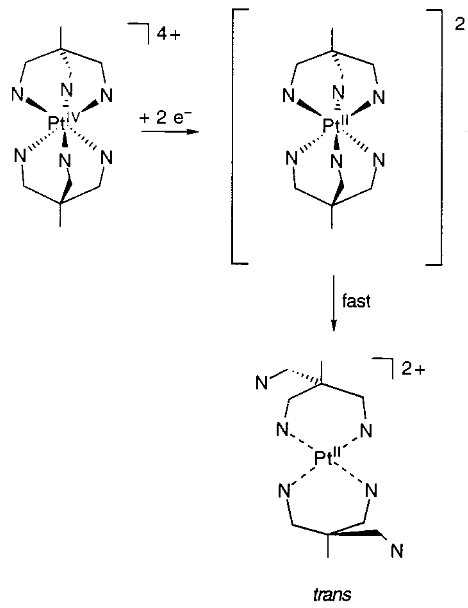
The formation of the [Pt(tame)$_2$]$^{4+}$ template is likely to be initiated by tame substitution at the catalytic platinum(II) ion to form a square planar complex, as outlined in Scheme 4. Oxidation by PtCl$_6^{2-}$ then takes place *via* a bridged intermediate, accompanied by co-ordination of the pendant amines on the two tame residues, to generate the six-co-ordinate hexaamine geometry preferred by Pt$^{\text{IV}}$. An equivalent amount of the catalyst PtCl$_4^{2-}$ ion is also regenerated. This proposal parallels the mechanism for ligand substitution about the platinum(IV) ion in the presence of Pt$^{\text{II}}$ described previously for didentate ligands.[10–13]

It was hoped that the Pt$^{\text{IV}}$–Pt$^{\text{III}}$ couple would show a degree of reversibility, given the bis(tridentate ligand) nature of the complex. However, the cyclic voltammetry (CV) of the parent [Pt(tame)$_2$]Cl$_4$ in aqueous 1 M HClO$_4$ using a hanging mercury drop electrode showed an irreversible electrochemical reduction wave at $E_{pc} = +0.02$ V (*vs.* SHE, 100 mV s^{-1}, Fig. 1). The reduction potential was largely insensitive to electrolyte, acid and scan rate up to 0.5 V s^{-1}, and was slightly more positive than that for [Pt(en)$_3$]$^{4+}$,[1] presumably because of the larger bite size of the tame chelate. The response was also irreversible in acetone at 295 K, using edge-plane pyrolytic graphite and gold disc electrodes. No response was observed using a platinum disc electrode in acetone. Formation of the [Pt(tame)$_2$]$^{3+}$ complex was not evident in either aqueous media or acetone. The response was also irreversible up to 5 V s^{-1}. The electrochemical data are attributed to a two-electron reduction of Pt$^{\text{IV}}$, accompanied by dissociation of two nitrogen donor atoms, to give a square planar platinum(II) complex as shown in Scheme 5. This is supported by the coulometric reduction of [Pt(tame)$_2$]Cl$_4$ at −0.80 V *vs.* SCE in 0.1 M CF$_3$CO$_2$H and also in 0.1 M NaClO$_4$ using a mercury pool working electrode which clearly showed a two-electron process. The ^{1}H and ^{13}C NMR spectra of the bulk electrolysis product were relatively simple and indicated that only one product was formed. The microanalysis of the isolated tetrachlorozincate salt also implied that the two dissociated amine groups were protonated.

The ^{1}H NMR spectrum of [Pt$^{\text{II}}$(Htame)$_2$]Cl$_4$ in D$_2$O showed that the signals for the methylene protons on the dissociated strand of the tame ligand were poorly resolved, and vicinal platinum-195 coupling was not discernible. The splitting pattern of the methylene protons of the co-ordinated methylene amine strands was consistent with that expected for an AA′ system, presumably due to the less flexible environment induced by co-ordination. However, the configuration about the platinum(II) ion was not defined by the NMR data. Two amine donor groups clearly had dissociated *cis* or *trans* as a result of the reduction, to form a complex with either C_{2h} or C_{2v}

Table 1 Selected interatomic distances (Å) and bond angles (°) for $[Pt^{II}(Htame)_2][ZnCl_4]_2{\cdot}2H_2O$

Pt(1)–N(1)	2.042(6)	N(1)–C(3)	1.50(1)
Pt(1)–N(2)	2.042(6)	N(2)–C(4)	1.49(1)
N(3)–C(5)	1.51(1)	C(1)–C(2)	1.53(1)
C(2)–C(3)	1.53(1)	C(2)–C(4)	1.53(1)
C(2)–C(5)	1.53(1)		
N(1)–Pt(1)–N(1)	180.0	N(1)–Pt(1)–N(2)	92.1(3)
N(1)–Pt(1)–N(2)	87.9(3)	N(2)–Pt(1)–N(2)	180.0
Pt(1)–N(1)–C(3)	116.3(5)	Pt(1)–N(2)–C(4)	118.6(5)
C(1)–C(2)–C(3)	111.8(7)	C(1)–C(2)–C(4)	111.3(6)
C(1)–C(2)–C(5)	110.3(7)	C(3)–C(2)–C(4)	110.0(6)
C(3)–C(2)–C(5)	108.8(6)	C(4)–C(2)–C(5)	104.4(6)
N(1)–C(3)–C(2)	113.3(7)	N(2)–C(4)–C(2)	114.6(7)
N(3)–C(5)–C(2)	115.1(7)		



Scheme 5 Electrochemical reduction of $[Pt^{IV}(tame)_2]^{4+}$ (amine protons have been omitted for clarity).

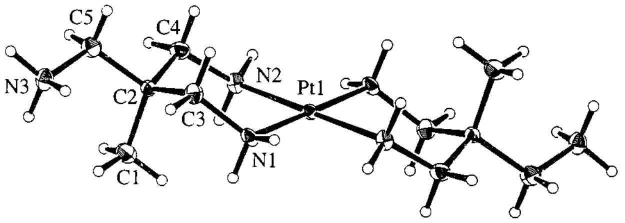


Fig. 2 An ORTEP diagram of the cation in $[Pt^{II}(Htame)_2][ZnCl_4]_2{\cdot}2H_2O$.

symmetry respectively. However, both isomers would give rise to the same number of ^{13}C signals and similar ^{1}H NMR splitting patterns.

An X-ray crystallographic analysis of a single crystal of the tetrachlorozincate salt of the product was therefore necessary to determine its structure. The structural analysis confirmed that two *trans* nitrogen atoms had dissociated. The ORTEP[14] plot of the cation in $[Pt^{II}(Htame)_2][ZnCl_4]_2{\cdot}2H_2O$ is presented in Fig. 2. Similar *trans* stereochemistry has been observed for the two ligands in $[Pt([9]aneN_3H)_2]^{4+}$.[15] The interatomic distances and angles are listed in Table 1 and other relevant crystallographic data are in Table 2. The Pt–N bond lengths are consistent with those of platinum(II) saturated amine complexes. The six-membered chelate rings of both tame residues are in a chair conformation with their dissociated pendant amines in equatorial positions and far from the feasible *trans* bonding sites on the Pt.

Table 2 Crystal data for $[Pt^{II}(Htame)_2][ZnCl_4]_2{\cdot}2H_2O$

Chemical formula	$C_{10}H_{36}Cl_8N_6O_2PtZn_2$
M	881.91
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14)
a/Å	12.012(2)
b/Å	10.194(2)
c/Å	12.012(1)
β/°	112.276(7)
V/Å^3	1361.1(3)
Z	2
μ(Cu-Kα)/cm^{-1}	185.33
No. reflections measured	2284
unique	2171
R_{int}	0.049
Residuals R, R'	0.036, 0.047

It is not surprising that the two amine groups *trans* to each other dissociated during the reduction process since this is the pathway that requires the least rearrangement. It is also well known that square planar platinum(II) complexes interact weakly with most nucleophiles at these axial sites. It is instructive therefore to look at the reduction of the $[Pt(en)_3]^{4+}$ ion. NMR Spectrometry was used to monitor the hydrogenation of $[Pt(en)_3]^{4+}$ in the presence of Pd/C in 1 M DCl. The experiment was undertaken under acidic conditions in order to trap the dissociated amines and limit their reco-ordination to the platinum(II) centre. After 20 min of hydrogenation at pH ≈ 1 the ^{1}H NMR spectrum showed four signals: three triplets at δ 2.68 (≈ 1 H), 3.11 (1 H) and 3.32 (1 H) and a singlet at δ 3.38 (0.2 H). Four signals were observed in the ^{13}C NMR spectrum at δ 37.4, 40.1, 44.6 and 48.1. None of these spectra had signals consistent with those of the parent $[Pt(en)_3]^{4+}$ ion, whose ^{1}H and ^{13}C resonances occur at δ 3.26 and 49.4, respectively. These data are consistent with the sample containing mostly $[Pt(en)(NH_2CH_2CH_2NH_3)_2]^{4+}$ ion with about 20% $[Pt(en)_2]^{2+}$ and free ethylenediamine: the triplet at δ 2.68 is attributed to the methylene protons of the chelate in $[Pt(en)(NH_2CH_2CH_2NH_3)_2]^{4+}$ and the two triplets at δ 3.11 and 3.32 are attributed to the methylene protons of the unidentate ethylenediamine ligands. The singlet at δ 3.38 is ascribed to the methylene protons of the dissociated and protonated ethylenediamine; the ethylenediamine protons of $[Pt(en)_2]^{2+}$ (at δ 2.65) overlap with those of the chelate in $[Pt(en)(NH_2CH_2CH_2NH_3)_2]^{4+}$. Likewise, the assignment of the ^{13}C spectrum is as follows: δ 37.4 (free ethylenediamine), 40.1 and 44.6 (unidentate ethylenediamine) and 48.1 (didentate ethylenediamine for the $[Pt(en)(NH_2CH_2CH_2NH_3)_2]^{4+}$ ion overlapped with those of the $[Pt(en)_2]^{2+}$ ion, δ 47.6). The ^{1}H and ^{13}C NMR spectra of the products from the hydrogenation performed under neutral conditions were very different. After 30 min of hydrogenation, followed by addition of DCl, only two major signals were evident in the ^{1}H NMR spectrum, a triplet at δ 2.67 and a singlet at δ 3.39 and are attributed to $[Pt(en)_2]^{2+}$ and protonated ethylenediamine, respectively. The ^{13}C NMR spectrum also showed two major resonances, at δ 47.6 ($[Pt(en)_2]^{2+}$) and 37.4 (free ethylenediamine). However, in both the NMR spectra, signals of very low intensity were observed which were consistent with traces of the $[Pt(en)(NH_2CH_2CH_2NH_3)_2]^{4+}$ ion.

The implication of these two results is that Pt^{IV} will preferentially dissociate two *trans* groups. The formation of $[Pt(en)_2]^{2+}$ and ethylenediamine in the neutral reduction may seem to be an exception to this requirement. However, this product almost certainly arises from rapid intramolecular amine addition, rearrangement and diamine dissociation in the initially formed complex $[Pt^{II}(en)(NH_2CH_2CH_2NH_2)]^{2+}$ ion. There will also be other occasions when such facile subsequent events obscure the initial product, particularly with multidentate systems.[16]

Formation of the platinum(III) ion was, likewise, not evident in attempts electrochemically to oxidise the platinum(II) counterpart in aqueous media and in acetone, in contrast to the behaviour of the analogous $[Pt([9]aneS_3)_2]^{3+/2+}$ couple in acetonitrile, where $[Pt([9]aneS_3)_2]^{3+}$ was produced from the bulk oxidation of $[Pt([9]aneS_3)_2]^{2+}$.[17] The more polarisable sulfur donor atoms appear to help to stabilise Pt^{III}. The difficulty in reco-ordinating nitrogen atoms compared to the sulfur atoms in the transformation from square planar Pt^{II} to octahedral Pt^{III} might be explained by initial oxidation of the sulfur atoms followed by their intramolecular reduction by the platinum(II) ion to form Pt^{III}. The same type of path is much less accessible for the nitrogen-containing ligands. Attempts chemically to generate the platinum(III) complex were also unsuccessful: the absorbance changes of a solution containing equimolar amounts of $[Pt^{II}(Htame)_2]Cl_4$ and the one electron oxidant ferrocenium tetrafluoroborate were negligible over 120 min at 298 K. The inability to regenerate the $[Pt^{IV}(tame)_2]^{4+}$ from $[Pt^{II}(Htame)_2]^{4+}$ was also evident when a solution of $[Pt^{II}(Htame)_2]Cl_4$ in D_2O was purged with oxygen for 3 d at 323 K. This behaviour, however, is not inconsistent with that of the similar complex $[Pt^{II}([9]aneN_3H)_2]^{4+}$ which took 20 h to oxidise to its related platinum(IV) hexaamine complex at 90 °C.[15] The CV of the bulk-reduced $[Pt^{II}(Htame)_2]^{4+}$ solution in 0.1 M aqueous $NaClO_4$ showed an irreversible anodic response at 0.22 V *vs.* SCE using the edge-plane pyrolytic graphite electrode which disappeared after a second sweep. This is akin to passivation of the electrode which has been observed with more complicated platinum(II) tetraamine complexes.[7,18] Bulk electrochemical oxidation of the same reduced solution using a carbon rod electrode at 0.4 V *vs.* SCE for 12 h was likewise unsuccessful: the ^1H and ^{13}C NMR spectra of the desalted electrolysed solution showed that no oxidation had occurred. It is not clear why the oxidation to reform the platinum(IV) hexaamine complex was unsuccessful, especially since the steric demands of the tame ligand are not high and access of oxidants is not hindered. It might be that effective oxidation requires an inner-sphere pathway and the oxidants used here were not suitable. Despite the inability to regenerate the platinum(IV) hexaamine complex readily, it is clear that the synthetic pathway involves cycling between platinum-(II) and -(IV) species and this process requires further investigation.

The use of the $[Pt(tame)_2]^{4+}$ ion in encapsulation reactions will be described in subsequent publications.

Experimental

Syntheses

All chemicals (AR grade) were used as received unless otherwise specified. Bio-Rad analytical grade Dowex 50W-X2 (200–400 mesh, H^+ form) was used in the cation exchange chromatography. All evaporations were conducted with Buchi rotatory evaporators at Torr ≈ 16–20 using a water-bath (< 50 °C).

1,1,1-Tris(aminomethyl)ethane (tame). The compound tame·3HCl (25.5 g) prepared as described previously[19] was suspended in hot ethanol (1 L) and added slowly to a warm solution of NaOH (13.5 g) in ethanol (200 mL). The mixture was heated at reflux under a stream of nitrogen for 3 h. The ethanol was evaporated and the tame ligand extracted from the white residue using hot chloroform. The suspension was filtered and the solvent evaporated to yield a pale yellow oil. NMR (D_2O): ^1H, δ 0.80 (s, 1 H, CH_3) and 2.45 (s, 2 H, CH_2); ^{13}C, δ 18.64 (CH_3), 39.81 (quaternary carbon) and 45.64 (CH_2).

Bis[1,1,1-tris(aminomethyl)ethane-*N*,*N′*,*N″*]platinum(IV) tetrachloride monohydrate, $[Pt(tame)_2]Cl_4{\cdot}H_2O$. Free tame (2 equivalents, 1.0 g) was added dropwise to a stirring suspension of K_2PtCl_6 (2 g) in dimethylformamide (15 mL) in the dark; K_2PtCl_4 (≈ 5 mg) was added to catalyse the reaction. A clear orange solution formed after the tame was added and within ≈5 min a colourless precipitate was evident. The reaction was heated at 40 °C for 30 h. The reaction mixture was diluted to 500 mL with water, the pH adjusted to 4–5 with HCl and then the solution was sorbed onto a column (15 × 3 cm) of Dowex 50W-X2 cation exchange resin. The column was washed with water (500 mL) and 2 M HCl (500 mL) and the complex then eluted with 6 M HCl. Evaporation of the eluate to near dryness yielded a colourless powder which was filtered off, washed with ethanol and then 2-propanol. The powder was dried *in vacuo* over molecular sieves. Yield: 75% (Calc. for $C_{10}H_{30}Cl_4N_6Pt{\cdot}H_2O$: C, 20.38; H, 5.47; Cl, 24.06; N, 14.26; Pt, 33.11. Found: C, 20.35; H, 5.71; Cl, 24.67; N, 14.13; Pt, 32.95%). pK_{a1} 7.0 ± 0.1, pK_{a2} 11 ± 0.1 at 25 °C (0.1 mmol titrated with 0.100 M NaOH in 10 mL H_2O potentiometrically; data were analysed with SUPERQUAD).[20] NMR (D_2O): ^1H, δ 1.10 (s, 1 H, CH_3) and 2.87 (t, 1 H, CH_2, $^3J_{Pt\text{–}H} = 10.3$ Hz); ^{13}C, δ 21.80 (s, CH_3), 45.15 (t, quaternary, $^3J_{Pt\text{–}C} = 44.2$) and 47.20 (t, CH_2, $^2J_{Pt\text{–}C} = 8.4$ Hz).

$[Pt^{II}(Htame)_2]Cl_4$. Controlled potential electrolysis of $[Pt(tame)_2]Cl_4{\cdot}H_2O$ (207 mg) in 0.1 M $NaClO_4$ (≈ 20 mL) at −800 mV *vs.* SCE using a mercury pool working electrode indicated that 1.96 electrons per platinum(IV) ion were consumed. After electrolysing for 12 h the solution was decanted. The mercury pool was rinsed three times with water (≈10 ml). The combined washings and the electrolysed solution were loaded onto a 2 × 5 cm column of Dowex cation exchange resin which was then washed with water (500 mL), 1 M HCl (500 mL) and the product eluted with 6 M HCl. The 6 M eluate was evaporated to dryness to yield a cream-coloured powder (90%). Crystals of *trans*-$[Pt^{II}(Htame)_2][ZnCl_4]_2{\cdot}2H_2O$ were slowly grown from an aqueous solution containing two drops of a saturated solution of $ZnCl_2$ in 4 M HCl. NMR (D_2O): ^1H, δ 1.20 (s, 3 H, CH_3), 2.74 (m, 4 H, CH_2), 3.10 (s, 2 H, CH_2), 5.08 (broad s, NH_2) and 5.35 (broad s, NH_2); ^{13}C, δ 18.4 (CH_3), 37.3 (quaternary), 46.1 (CH_2), 48.9 (CH_2) and 49.2 (CH_2).

Hydrogenation of $[Pt(en)_3]Cl_4$. The complex $[Pt(en)_3]Cl_4$ (20 mg) was dissolved in 1 M DCl (0.7 mL) in an NMR tube and Pd/C catalyst (10%, ≈3 mg) was introduced. The suspension was purged gently with hydrogen for 20 min and then with nitrogen for 5 min. The sample was sealed and centrifuged for 5 min before the ^1H and ^{13}C NMR spectra were acquired. Assignment of the signals was aided by doping the sample with ethylenediamine after the spectrum had been acquired and by comparing the NMR spectra of separate samples of the precursors and products in 1 M DCl. NMR (1 M DCl): ^1H, δ 2.68 (t, ≈1 H, co-ordinated ethylenediamine of $[Pt(en)(NH_2CH_2CH_2NH_3)_2]^{4+}$, overlapping a small signal from $[Pt(en)_2]^{2+}$), 3.11 (t, 1 H, unidentate ethylenediamine of $[Pt(en)(NH_2CH_2CH_2NH_3)_2]^{4+}$), 3.32 (t, 1 H, unidentate ethylenediamine of $[Pt(en)(NH_2CH_2CH_2NH_3)_2]^{4+}$) and 3.38 (s, 0.2 H, unco-ordinated ethylenediamine); ^{13}C, δ 37.4 (unco-ordinated ethylenediamine), 40.1 (unidentate ethylenediamine of $[Pt(en)(NH_2CH_2CH_2NH_3)_2]^{4+}$), 44.6 (unidentate ethylenediamine of $[Pt(en)(NH_2CH_2CH_2NH_3)_2]^{4+}$) and 48.1 (co-ordinated ethylenediamine of $[Pt(en)(NH_2CH_2CH_2NH_3)_2]^{4+}$, overlapping a small signal from $[Pt(en)_2]^{2+}$).

The above procedure was repeated in neutral D_2O, using 20 mg $[Pt(en)_3]Cl_4$ and hydrogenating for 30 min instead. Assignment of the signals was aided by doping the sample with ethylenediamine after the spectrum had been acquired and by comparing the NMR spectra of separate samples of the precursors and products in neutral D_2O. NMR after acidification (≈ 0.1 M DCl): ^1H, δ 2.67 (t, 2 H, $[Pt(en)_2]^{2+}$) and 3.39 (s, 1 H, unco-ordinated ethylenediamine); ^{13}C, δ 37.4 (unco-ordinated ethylenediamine) and 47.6 ($[Pt(en)_2]^{2+}$).

Physical methods

All ^1H and ^{13}C NMR spectra were acquired using a Varian Gemini 300 MHz spectrometer and standard Varian software.

The solvents D_2O and DCl (Merck) were used without further purification. All spectra were referenced internally against 1,4-dioxane (δ 3.744 *vs.* $(CH_3)_4Si$ for the ^1H NMR spectra and δ 67.3 *vs.* $(CH_3)_4Si$ for ^{13}C NMR spectra).[21] The electrolytes used in the aqueous electrochemistry were of AR grade. The electrolyte concentration was typically 0.1 or 1.0 M. The concentration of the electroactive species was ≈1 mM. The samples were purged for ≈15 min with a continuous flow of argon or nitrogen prior to data acquisition. Measurements were acquired under a blanket of dinitrogen or argon at ≈293 ± 1 K unless otherwise specified. The cyclic voltammograms using a mercury drop working electrode were recorded using a Princeton Applied Research Model-170 Polarographic Analyser or Model-173 Universal Programmer in conjunction with a Model-175 Potentiostat/Galvanostat (PAR-175). Both systems were interfaced with a Hewlett-Packard 7046A (X,Y) plotter. The mercury electrode (Metrohm 663 VA stand with an RSC Model-411 interface unit) was generally used in the hanging mercury drop mode. The three-electrode configuration included an auxiliary electrode, which was a carbon rod (≈0.4 cm diameter, ≈8 cm in length), and the reference electrode, which was either a Ag–AgCl–KCl(sat) (199 mV *vs.* SHE)[22] or a saturated calomel electrode (SCE, 241 mV *vs.* SHE).[22]

Structure determination

The X-ray crystallographic analysis of a single crystal of $[Pt(Htame)_2][ZnCl_4]_2\cdot 2H_2O$ was made using a Rigaku AFC-6R diffractometer with graphite monochromated Cu-Kα (λ = 1.54178 Å) radiation and a rotating anode generator. The data (Table 2) were collected using the ω–2θ scan technique to a maximum 2θ value of 120.1°. No decay correction was applied. The refinement reflections, 1799 [$I > 3\sigma(I)$], were corrected for Lorentz-polarisation effects. The structure was solved by direct methods[23] and expanded using Fourier techniques.[24] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Neutral atom scattering factors were taken from Cromer and Waber.[25] Anomalous dispersion effects were included in F_{calc};[26] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[27] The values of the mass attenuation coefficients were those of Creagh and Hubbel.[28]

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