Palladium(II)/(III) Complexes of Triaza Macrocycles: Synthesis and Single Crystal *X*-Ray Structures of $[Pd^{III}(tacn)_2]^{3+}$ and $[Pd^{II}(tacn)(tacnH)]^{3+}$ (tacn = 1,4,7-triazacyclononane)

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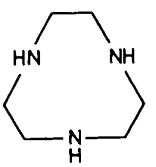
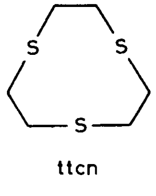
The complex cation $[Pd(tacn)_2]^{2+}$ (tacn = 1,4,7-triazacyclononane) shows a one-electron oxidation at $E_{\frac{1}{2}} = +0.07$ V *vs.* Fc/Fc^+ (ferrocene/ferrocinium) to afford the stable mononuclear Pd^{III} species $[Pd(tacn)_2]^{3+}$, which has a tetragonally-distorted octahedral structure with Pd–N(1) = 2.180(9), Pd–N(4) = 2.118(9), Pd–N(7) = 2.111(9) Å.

We have been investigating the stereochemical and redox properties of tridentate macrocyclic ligands with Pd^{II} and Pt^{II}.[1] The stabilisation of M^{III} species by 1,4,7-trithiacyclononane (ttcn) in the complexes $[M(ttcn)_2]^{3+}$ (M = Pd, Pt)[2,3] has prompted us to study the analogous chemistry with the triaza analogue 1,4,7-triazacyclononane (tacn).[4]

Reaction of K_2PdCl_4 with two molar equiv. of tacn.$3HNO_3$ in water in the presence of NaOH affords an orange solution from which the complex $[Pd(tacn)_2](PF_6)_2$† can be isolated by addition of excess of NH_4PF_6. In addition, by controlling the pH of the reaction solution, the protonated complex cation $[Pd(tacn)(tacnH)]^{3+}$† can be isolated. Single crystals of $[Pd(tacn)(tacnH)](PF_6)_2(NO_3).H_2O$ were grown from



tacn



ttcn

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† All complexes have been characterised by spectroscopic and analytical methods.

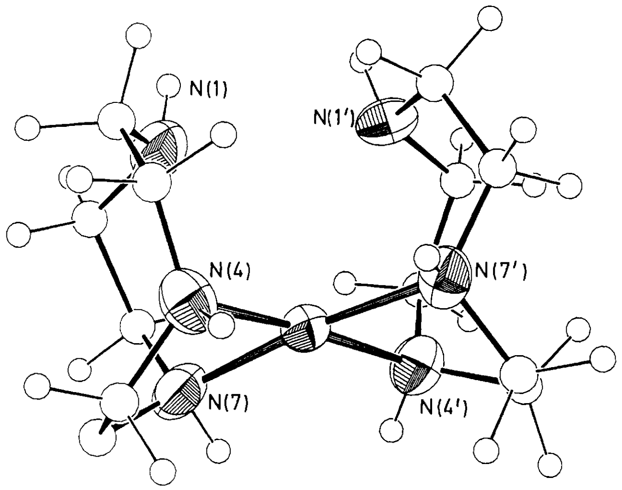

Figure 1. Single crystal *X*-Ray structure of $[Pd(tacn)(tacnH)]^{3+}$ with numbering scheme adopted.

aqueous solution and the single crystal *X*-ray structure of the complex was determined.

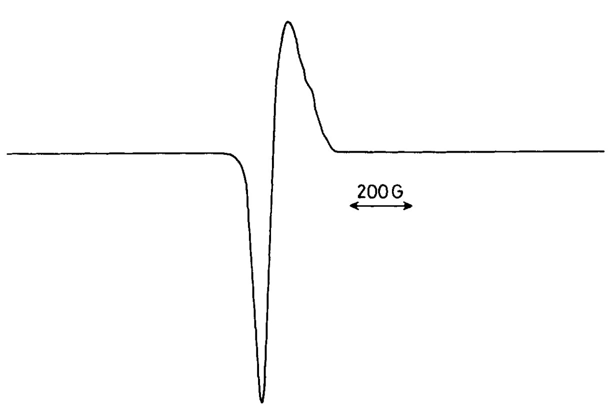

Figure 2. *X*-Band e.s.r. spectrum of $[Pd(tacn)_2]^{3+}$ measured at 77 K (MeCN glass).

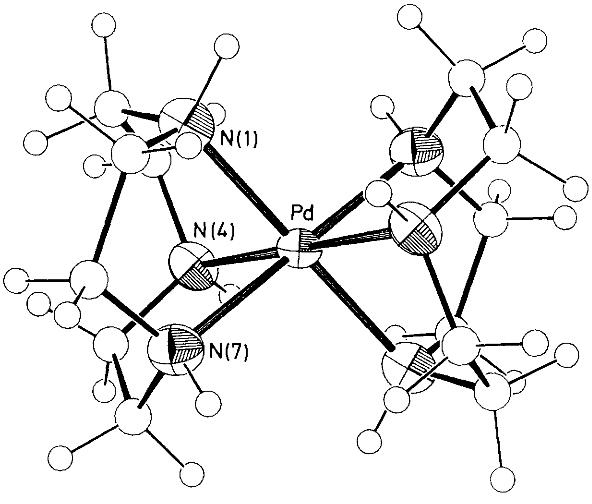

Figure 3. Single crystal *X*-ray structure of $[Pd(tacn)_2]^{2+}$ with numbering scheme adopted.

Figure 1 shows the structure of the $[Pd(tacn)(tacnH)]^{3+}$ cation.‡ The triaza ligands are each co-ordinated *via* two N-donors to the Pd^{II} centre to give a square planar complex, Pd–N(4) = 2.017(14), Pd–N(7) = 2.087(14), Pd–N(4′) = 2.051(12), Pd–N(7′) = 2.067(13) Å. The unusual feature of the structure is that the two non-bonding N-donors, N(1) and N(1′), lie on the same side of the PdN_4 plane to give a *syn* configuration for the complex, Pd–N(1) = 2.982(11), Pd–N(1′) = 3.079(11) Å. The N(1) · · · N(1′) distance is 2.954(15) Å. This structure contrasts with that of the Pt^{II} analogue $[Pt(tacn)_2]^{2+}$ in which the two non-bonding N-donors lie on opposite sides of the PtN_4 plane to give an *anti* configuration of macrocyclic ligands.[5] Extensive H-bonding occurs in the Pd^{II} complex between the cation and the NO_3^- and H_2O molecules. This may explain the net stabilisation of the *syn* over the *anti* isomer for this species, and suggests that H-bonding may be used to control the configuration of co-ordinated polyaza macrocycles. In the absence of H-bonding, we would expect the complex cation $[Pd(tacn)_2]^{2+}$ to adopt an *anti* configuration, and be isostructural with its Pt^{II} analogue.§

Cyclic voltammetry of $[Pd(tacn)_2](PF_6)_2$ in MeCN (0.1 M, $Bu^n_4NPF_6$) at platinum electrodes shows a chemically reversible oxidation at $E_{\frac{1}{2}}$ = +0.07 V *vs.* Fc/Fc$^+$ (ferrocene/ferrocinium).[6] A more sluggish, second oxidation is observed at +0.45 V. Coulometry confirms both these oxidations to be one-electron processes. Since the triaza ligand is redox-inactive within this potential range, these oxidations are

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‡ *Crystal data* for $C_{12}H_{31}N_6Pd^{2+}.NO_3^-.2PF_6^-.H_2O$: A yellow columnar crystal (0.10 × 0.14 × 0.55 mm) was mounted on a Stöe–Siemens AED2 four-circle diffractometer. Orthorhombic, space group $P2_12_12_1$, $a = 8.4574(15)$, $b = 16.2641(27)$, $c = 18.756(4)$ Å, $U = 2579.9$ Å^3 (by least-squares refinement on diffractometer angles for 11 reflections with $15 < \theta < 17°$, $\lambda = 1.54184$ Å), $M = 735.62$, $D_c = 1.894$ g cm^{-3}, $Z = 4$, $\mu(\text{Cu-}K_\alpha) = 83.10$ cm^{-1}. Data collection using Cu-K_α *X*-radiation yielded 2155 unique reflections ($2\theta_{max.}$ 120°, h 0→9, k 0→18, l 0→21). These were corrected for absorption using ψ scans, and 1663 with $F > 6\sigma(F)$ were used in all calculations. Aftcr location of the Pd atom from a Patterson synthesis, its position was used in DIRDIF[11] to develop the structure. Using this method, followed by iterative cycles of least-squares refinement and difference Fourier synthesis,[12] all non-H atoms were found. With the exception of a carbon atom in one of the ligands, for which disorder had to be modelled, all non-H atoms were refined anisotropically. H atoms were included in fixed, calculated positions. At final convergence, $R = 0.0492$, $R_w = 0.0674$, $S = 1.112$ for 338 parameters and the final difference map showed no feature above +1.04 or below −0.72 eÅ^{-3}.

For $C_{12}H_{30}N_6Pd^{3+}.3PF_6^-$: A yellow plate (0.40 × 0.45 × 0.025 mm) was mounted on a Stöe–Siemens AED2 four-circle diffractometer. Triclinic, space group $P\bar{1}$, with $a = 9.3663(22)$, $b = 9.3853(24)$, $c = 17.314(5)$ Å, $\alpha = 80.661(13)$, $\beta = 79.832(13)$, $\gamma = 61.199(10)°$, $U = 1307.5$ Å^3 [from 2θ values of 18 reflections measured at $\pm\omega$ ($24 < 2\theta < 25°$, $\lambda = 0.71073$ Å)], $M = 799.70$, $D_c = 2.03$ g cm^{-3}, $Z = 2$, $\mu(\text{Mo-}K_\alpha) = 9.69$ cm^{-1}, $T = 298$ K. Data collection using Mo-K_α *X*-radiation gave 3415 unique reflections ($2\theta_{max.}$ 45°, h − 9→10, k −9→10, l 0→18) of which 2452 with $F > 2\sigma(F)$ were used in all calculations. A Patterson synthesis located two Pd atoms on inversion centres. DIRDIF[11] found all non-H atoms. The structure was developed by least-squares refinement and difference Fourier synthesis.[12] The Pd, C, N, P, and F atoms were refined anisotropically. H Atoms were included in fixed calculated positions. One cation was significantly better determined than the other; all parameters quoted in the text refer to the former. At final convergence, $R = 0.0594$, $R_w = 0.0828$, $S = 1.050$ for 364 parameters and the final difference map showed no feature above +1.7 or below −0.48 e Å^{-3}. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ Since the submission of this paper, McAuley *et al.*[13] have reported the crystal structure of $[Pd(tacn)_2]^{2+}$ with the two ligands in an *anti* configuration.[13]

therefore assigned to $Pd^{II/III}$ and $Pd^{III/IV}$ couples, respectively. Controlled potential electrolysis of $[Pd(tacn)_2]^{2+}$ at +0.3 V affords the bright yellow Pd^{III} complex, the e.s.r. spectrum of which (77 K, MeCN glass) shows a strong, broad, near-isotropic signal with, $g_{\perp} = 2.123$, $g_{\parallel} = 2.007$ (Figure 2). Super-hyperfine coupling to two N-donors (1:2:3:2:1 quintet) is more apparent in the second derivative spectrum with $A_{II} = 27$ G (1G = 10^{-4} T). Similar coupling to two N-donors has been observed for octahedral Ni^{III} tetra-aza macrocyclic complexes with a d_{z^2} ground state.[7] Further oxidation at +0.7 V leads to the formation of a product which is e.s.r. silent and is therefore assigned to the octahedral Pd^{IV} species $[Pd(tacn)_2]^{4+}$. The reversible interconversion of the $Pd^{II/III/IV}$ complexes was confirmed by *in situ* electronic spectral measurements using an optically transparent thin layer electrode (OTTLE) system.

The complex $[Pd(tacn)_2](PF_6)_3$† was isolated by careful addition of diethyl ether to an electrolysed solution. Crystals of the complex were grown from MeCN/diethyl ether and the single crystal *X*-ray structure determined. The structure of $[Pd(tacn)_2](PF_6)_3$‡ (Figure 3) shows tetragonally distorted N_6 co-ordination around the Pd^{III} centre with Pd–N(1) = 2.180(9), Pd–N(4) = 2.118(9), Pd–N(7) = 2.111(9) Å, consistent with a Jahn–Teller distorted d^7 complex. The structure of $[Pd(tacn)_2]^{3+}$ is therefore related to that of $[Pd(ttcn)_2]^{3+}$ which is the only other reported crystal structure of a mononuclear Pd^{III} species.[2] However, the trithia complex $[Pd(ttcn)_2]^{3+}$ is generated at a higher anodic potential ($E_{\frac{1}{2}}$ = 0.605 V *vs.* Fc/Fc^+), and is also much less stable than the triaza analogue in the solid state and in solution. $[Pd(tacn)_2]^{3+}$ is stable indefinitely in MeCN and $MeNO_2$ and may be manipulated readily in non-reducing solvents; in contrast, $[Pd(ttcn)_2]^{3+}$ decomposes slowly in these solvents, and is stabilised indefinitely only in acidic media. Interestingly, the solid state structure of $[Ni(tacn)_2]^{3+}$ shows a greater tetragonal distortion than the Pd^{III} complex, Ni–N = 1.964(5), 1.985(5), 1.970(5), 1.965(5) Å and 2.107(5), 2.111(5) Å.[8] This may reflect the greater size of Pd^{III} *vs.* Ni^{III}, with the cavity generated by two tacn ligands being too large for Ni^{III}.[8,9]

The stabilisation of Pd^{III} by the triaza macrocycle (tacn) contrasts with the redox properties of square planar Pd^{II} tetra-aza complexes which, in general, do not show $Pd^{II/III}$ couples.[1,10] This difference can be ascribed to the availability of distorted octahedral stereochemistry in the complexes of tacn.

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