Stabilisation of Mononuclear Palladium(III). The Single Crystal *X*-Ray Structure of the $[Pd(L)_2]^{3+}$ Cation (L = 1,4,7-trithiacyclononane)

Alexander J. Blake, Alan J. Holder, Timothy I. Hyde, and Martin Schröder*

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland, U.K.

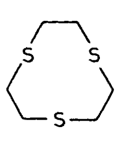
Oxidation of the green $[Pd(1)_2]^{2+}$ cation [(1) = 1,4,7-trithiacyclononane] in 70% aqueous $HClO_4$ affords the red $[Pd(1)_2]^{3+}$ cation, the single crystal *X*-ray structure of which shows a tetragonally distorted geometry about the Pd^{III} centre with Pd–S(1) 2.5448(15), Pd–S(4) 2.3558(14), and Pd–S(7) 2.3692(15) Å.

The tridentate macrocyclic ligand (**1**) [(**1**) = 1,4,7-trithiacyclononane] forms stable bis-sandwich complexes $[M(\mathbf{1})_2]^{x+}$ with first row transition metal centres.[1,2] We have been investigating the binding of (**1**) to platinum group metal ions and have recently reported[3] the generation of mononuclear platinum(III) species from the square-based pyramidal $[Pt(\mathbf{1})_2]^{2+}$ cation. We have extended this work to the corresponding palladium complexes, and report here the crystal structure of the mononuclear palladium(III) species $[Pd(\mathbf{1})_2]^{3+}$.

Cyclic voltammetry of $[Pd(\mathbf{1})_2](PF_6)_2$ in MeCN at 20 °C (0.1 M $Bu^n{}_4NPF_6$) shows a reversible oxidation at E_{pa} = 0.65 and E_{pc} = +0.56 V, $E_{\frac{1}{2}}$ = +0.605 V, ΔE_p = 84 mV *vs.* Fc^0/Fc^+ (Fc = ferrocene), I_{pa}/I_{pc} = 1.0. Controlled potential oxidation of this complex at +0.7 V at a platinum gauze in MeCN affords an orange solution ($\lambda_{max.}$ 476 nm, ε 5350 $dm^3\,mol^{-1}\,cm^{-1}$), the e.s.r. spectrum of which as a frozen glass at 77 K shows an anisotropic signal with $g_{\parallel}$ = 2.008, $g_{\perp}$ = 2.048, $g_{av.}$ = 2.032. Attempts to isolate the oxidised product from these reactions failed, with the product decomposing slowly in solution. Further investigations showed that the oxidation product could be stabilised in acidic media.

Oxidation of $[Pd(\mathbf{1})_2]^{2+}$ [$\lambda_{max.}$ 615 nm (ε 55 $dm^3\,mol^{-1}\,cm^{-1}$), 296 (15 000), 198 (9900)] with 70% $HClO_4$ yielded, in an isosbestic manner ($\lambda_{iso.}$ 603, 316, 260, and 216 nm), a deep orange solution with the same electronic spectrum [$\lambda_{max.}$ 477 nm (ε 5350 $dm^3\,mol^{-1}\,cm^{-1}$), 341 (16 100), 230 (8100)] as obtained in the electrogeneration experiments. The e.s.r. spectrum of the oxidised complex, measured as a frozen aqueous $HClO_4$ glass at 77 K, showed an anisotropic signal with $g_{\parallel}$ = 2.009, $g_{\perp}$ = 2.049 with partially discernible coupling to ^{105}Pd ($I = \frac{5}{2}$, 22.8%) $A_{\perp}$ = 20 G, $A_{\parallel} \simeq$ 5 G (1 G = 10^{-4} T).

The voltammetric, electronic, and e.s.r. data are consistent



(1)

with the formation of paramagnetic palladium(III) species in these experiments. Oxidation of the metal-free ligand (**1**) and of the ligand site in $[Ni(\mathbf{1})_2]^{2+}$ has been previously shown[2] to occur at +0.99 V (irrev.) and +0.97 V respectively suggesting that the oxidation ($E_{\frac{1}{2}}$ = +0.605 V) of $[Pd(\mathbf{1})_2]^{2+}$ was indeed a predominantly metal-based process. Cooling of the aqueous $HClO_4$ solution of the oxidised cation afforded red paramagnetic crystals suitable for an *X*-ray diffraction study.

The single crystal *X*-ray structure of $[Pd(\mathbf{1})_2](ClO_4)_4 \cdot H_3O \cdot 3H_2O$ shows† the $[Pd(\mathbf{1})_2]^{3+}$ cation to have a tetragonally elongated octahedral stereochemistry as expected for a Jahn–Teller distorted d^7 palladium(III) complex. A view of the $[Pd(\mathbf{1})_2]^{3+}$ cation is shown in Figure 1. The Pd atom lies on an inversion centre with Pd–S(1) 2.5448(15), Pd–S(4) 2.3558(14), Pd–S(7) 2.3692(15) Å, and the SPdS angles [87.33, 87.17, 88.88(5)°] close to octahedral. In comparison, the $[Pd(\mathbf{1})_2]^{2+}$ cation shows[4] a greater elongation of the axial bond lengths with Pd–S(1) 2.952(4), Pd–S(4) 2.332(3), Pd–S(7) 2.311(3) Å. The mean differences between the axial and equatorial bond lengths in these homoleptic thia palladium(III) and palladium(II) complexes are 0.182 and 0.631 Å respectively. On oxidising palladium(II) to palladium(III), the axial thia donors S(1) are brought in towards the more positive 3+ metal centre; this is linked to a slight elongation in the equatorial Pd–S distances due to the restricted conformation of the co-ordinated macrocycles. The resulting structure for the $[Pd(\mathbf{1})_2]^{3+}$ cation is a compromise between the facially co-ordinating trithia ligands and the Jahn–Teller distortion of the d^7 metal centre. A Jahn–Teller distortion has been postulated[5] on the basis of solid state e.s.r. spectral evidence for $NaPdF_4$, while for the related homoleptic octahedral d^6 complex cations $[Ru(\mathbf{1})_2]^{2+}$ [6] and $[Rh(\mathbf{1})_2]^{3+}$,[7] the M–S bond lengths have been found to be essentially equal. Likewise, d^6 palladium(IV) species would be expected to show symmetrical, octahedral stereochemistries. The $[Rh(\mathbf{1})_2]^{3+}$ cation shows two reversible one electron reductions at −0.64 and −1.0 V *vs.* Fc^0/Fc^+ in MeCN assigned to Rh^{III}/Rh^{II} and Rh^{II}/Rh^{I} redox couples respectively. Electrochemical reduction of $[Rh(\mathbf{1})_2]^{3+}$ at −0.75 V affords $[Rh(\mathbf{1})_2]^{2+}$ ($g_{\parallel}$ = 2.007, $g_{\perp}$ = 2.088 at 77 K in MeCN glass) which is isoelectronic with the $[Pd(\mathbf{1})_2]^{3+}$ cation.

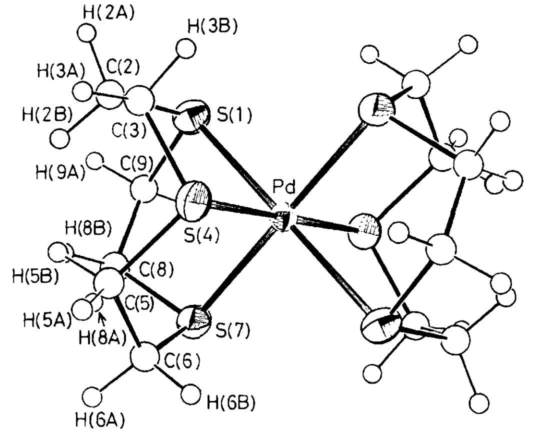


Figure 1. Structure of the $[Pd(\mathbf{1})_2]^{3+}$ cation with numbering scheme adopted. H(9B) is wholly obscured by S(4).

The $[Pd(\mathbf{1})_2]^{3+}$ cation represents the first example of a structurally characterised mononuclear trivalent palladium complex and is related to the $[Pt(\mathbf{1})_2]^{3+}$ cation that we reported[3] recently. Presumably the thia donors can accommodate positive charge from the metal centre; future work is aimed at elucidating the charge distribution and reactivities of these activated cations, and the role of $HClO_4$ as an apparent one electron oxidant in these systems.[9]

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† *Crystal data* for $[Pd(\mathbf{1})_2](ClO_4)_4 \cdot H_3O \cdot 3H_2O$. The highly air-sensitive crystal was protected by sealing in a Lindemann tube containing mother liquor (aqueous $HClO_4$): $C_{12}H_{24}PdS_6 \cdot 4ClO_4 \cdot H_3O \cdot 3H_2O$, monoclinic, *C*2/*c*, *a* = 20.664(4), *b* = 9.2335(17), *c* = 20.218(4) Å, β = 124.514(13)°, *U* = 3179 Å³, D_{calc} = 1.959 g cm⁻³, *Z* = 4; 3104 data measured to θ = 25°, refinement based on 1809 data with $F \geqslant 6\sigma(F)$. At convergence, R, R_w = 0.0311, 0.0390 respectively for 184 parameters. The Pd position was deduced from a Patterson synthesis and the remaining non-hydrogen atoms from iterative rounds of least-squares cycles and difference Fourier syntheses.[8] Methylene H atoms were included in fixed, calculated positions and the H_3O^+ ion refined as a rigid group.[8] Anisotropic thermal parameters were refined for Pd, S, Cl, and for those O atoms with the full occupancy appropriate to their site. Although the structure contains some disordered water molecules, the remainder is well-ordered and the final difference map exhibits no feature above 0.50 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.