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Stereochemical and Redox Properties of Palladium Complexes of 1,4,10,13-Tetrathia-7,16-diazacyclo-octadecane

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The square planar S_4 donor complex $[Pd(L^1)]^{2+}$ (L^1 = 7,16-dimethyl-1,4,10,13-tetrathia-7,16-diazacyclo-octadecane) shows a reversible $Pd^{II/I}$ redox couple at $E_{\frac{1}{2}}$ −0.74 V *vs.* Fc/Fc$^+$; in contrast, the complex $[Pd(L^2)]^{2+}$ (L^2 = 1,4,10,13-tetrathia-7,16-diazacyclo-octadecane) shows distorted octahedral N_2S_2 + S_2 co-ordination, and a reversible $Pd^{II/III}$ couple at $E_{\frac{1}{2}}$ +0.57 V *vs.* Fc/Fc$^+$ (ferrocene/ferrocinium).

Since the original report by Black and co-workers on the co-ordinative properties of the S_4N_2-donor macrocycle L^2 with first-row metal ions,[1] very little subsequent work on these systems has been reported.[2] In view of our recent results on the stereochemical and redox properties of platinum metal complexes of poly-thia and -aza macrocycles,[3,4] we undertook a study of the co-ordination of the potentially hexadentate ligands 7,16-dimethyl-1,4,10,13-tetrathia-7,16-diazacyclo-octadecane (L^1) and 1,4,10,13-tetrathia-7,16-diazacyclo-octadecane (L^2) with Pd^{II}.

Reaction of $PdCl_2$ with one mole equivalent of L^1 in refluxing MeCN–H_2O (3 : 1 v/v) under N_2 for 5 h afforded an orange solution from which the complex $[Pd(L^1)](PF_6)_2$ could be isolated as an orange product. ^{13}C N.m.r. spectroscopy of the complex shows resonances at δ 49.87, 40.31, 39.40(CH_2), and 41.57(CH_3); this, together with ^1H n.m.r. data, confirms the presence of only one isomer in solution. The single crystal *X*-ray structure of $[Pd(L^1)](PF_6)_2{\cdot}Me_2CO$ shows† square planar co-ordination of the four thioether donor atoms of L^1 to Pd^{II} [Pd–S(1) 2.3399(22), Pd–S(4) 2.3331(22), Pd–S(10) 2.3261(22), Pd–S(13) 2.3239(21) Å]. The two N-atoms are orientated away from, and do not interact with, the metal centre, [Pd···N(7) 3.744(7), Pd···N(16) 3.760(6) Å]. L^1, therefore, co-ordinates to the Pd^{II} ion as a simple tetradentate thioether donor (Figure 1).

The complex cation $[Pd(L^2)]^{2+}$ was prepared by reaction of $PdCl_2$ and L^2 in MeCN in the presence of $TlPF_6$, and was isolated as a green BPh_4^- salt or a blue PF_6^- salt. The single crystal *X*-ray structure of $[Pd(L^2)](BPh_4)_2$ (Figure 2) shows‡ the Pd^{II} ion co-ordinated to an N_2S_2-donor set in a square planar configuration, [Pd–S(1) 2.311(3), Pd–N(7) 2.123(7), Pd–S(13) 2.357(3), Pd–N(16) 2.068(7) Å], with S(1), N(16), and S(13) binding *meridionally* to the metal centre. The two remaining thioether donors interact at long range with Pd^{II}, [Pd–S(10) 2.954(4), Pd–S(4) 3.000(3) Å], and are displaced from the least-squares Pd–S(1)–N(7)–S(13)–N(16) plane by +2.863 and −2.901 Å, respectively, [∠S(4)–Pd–S(10) 158.94(9)°], to give a stereochemistry at Pd approaching distorted octahedral. Thus, by replacing NH by NMe moieties, the stereochemistry of the resultant Pd^{II} complexes is totally altered. The meridional binding of the macrocycle in $[Pd(L^2)]^{2+}$ reflects the bite and cone angles at the unsubsti-

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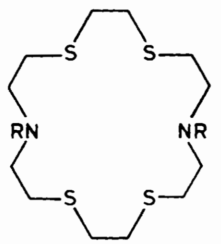
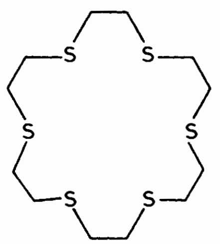
† *Crystal data* for $C_{14}H_{30}N_2PdS_4^{2+}{\cdot}2PF_6^-{\cdot}C_3H_6O$: M = 809.046, orthorhombic, space group *Pcab*, a = 14.3369(15), b = 17.6915(7), c = 24.2952(11) Å, U = 6162.24 Å^3 [from 2θ values of 58 reflections measured at ±ω (24 < 2θ < 25°, λ = 0.71073 Å)], Z = 8, D_c = 1.744 g cm^{-3}, μ(Mo-K_α) = 1.00 mm^{-1}. A yellow crystal (0.92 × 0.08 × 0.15 mm) was mounted in a glass capillary tube on a Stoe-Siemens AED2 four-circle diffractometer. Data collection used Mo-K_α radiation ($\bar{\lambda}$ = 0.71073 Å), ω–2θ scans and the learnt-profile method,[11] giving 4527 unique reflections ($2\theta_{max.}$ = 45°, $+h,+k,+l$) of which 2693 with $F > 6\sigma(F)$ were used in all calculations. A Patterson synthesis located the Pd atom and the structure was developed by least-squares refinement and difference Fourier synthesis. It was discovered that one PF_6^- and both –C–N(Me)–C– moieties were affected by disorder, but this was modelled successfully. The crystal lattice was found to contain one molecule of acetone per cation. At final convergence, R = 0.0450, R_w = 0.0606, S = 1.186 for 375 parameters and the final difference map showed no feature above 0.84 eÅ^{-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.

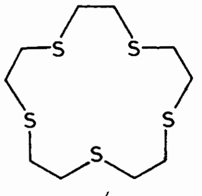
‡ *Crystal data* for $C_{12}H_{26}N_2PdS_4^{2+}{\cdot}2BC_{24}H_{20}^-$: M = 1071.45, monoclinic, space group $P2_1/c$, a = 16.8888(12), b = 16.5533(15), c = 18.5376(12) Å, β = 93.144(8)°, U = 5174.64 Å^3 [from 2θ values of 36 reflections measured at ±ω (15 < 2θ < 17°, λ = 0.71073 Å)], Z = 4, D_c = 1.375 g cm^{-3}, μ(Mo-K_α) = 0.52 mm^{-1}. A green columnar crystal (0.30 × 0.10 × 0.08 mm) was mounted in a glass capillary tube on a Stoe-Siemens AED2 four-circle diffractometer. Data collection used Mo-K_α radiation ($\bar{\lambda}$ = 0.71073 Å), ω–2θ scans and the learnt-profile method,[11] giving 6815 unique reflections ($2\theta_{max.}$ = 45°, $\pm h,+k,+l$) of which 4006 with $F > 4\sigma(F)$ were used in all calculations. A Patterson synthesis located the Pd atom, and DIRDIF[12] found all non-H atoms except for one macrocyclic C atom. The structure was developed by least-squares refinement and difference Fourier synthesis. At final convergence, R = 0.0623, R_w = 0.0786, S = 1.110 for 517 parameters and the final difference map showed no feature above 0.48 eÅ^{-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.



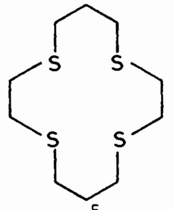
L^1; R = Me
L^2; R = H



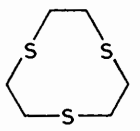
L^3



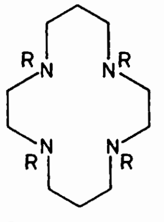
L^4



L^5



L^6



L^7; R = CH_2Ph
L^8; R = Me

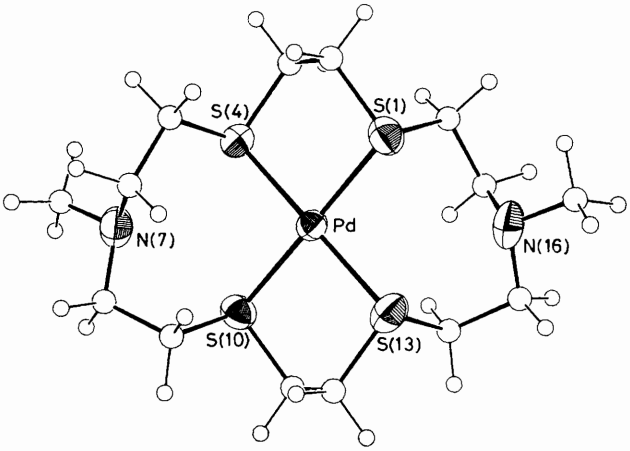


Figure 1. View of the structure of the $[Pd(L^1)]^{2+}$ cation showing the numbering scheme adopted.

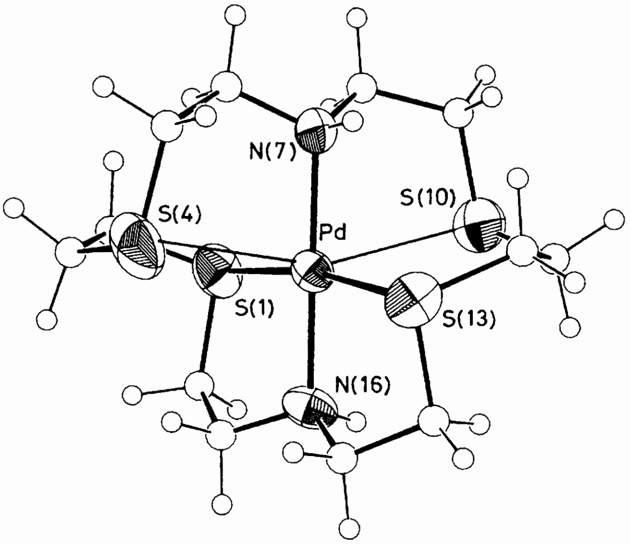


Figure 2. View of the structure of the $[Pd(L^2)]^{2+}$ cation showing the numbering scheme adopted.

tuted HN-donors; space-filling models of $[Pd(L^1)]^{2+}$ indicate that meridional binding of L^1 is inhibited due to the greater steric bulk of the NMe groups.

The stereochemical differences between these complexes are also reflected in their redox properties. Cyclic voltammetry of $[Pd(L^1)]^{2+}$ in MeCN (0.1 M Bu_4NPF_6) at platinum electrodes shows a reversible reduction at −0.74 V *vs.* Fc/Fc^+ (Fc/Fc^+ = ferrocene/ferrocinium), ΔE_p 72 mV at a scan rate of 100 mV s^{-1}. Coulometry confirms the reduction to be a one-electron process. The e.s.r. spectrum (77 K, MeCN glass) of the reduced product, generated by controlled potential electrolysis at −0.90 V in MeCN at a Pt gauze, is anisotropic ($g_{\parallel}$ 2.155, $g_{\perp}$ 2.049) with hyperfine coupling to ^{105}Pd ($I = 5/2$, 22.2%) with $A_{\parallel}$ 48 and $A_{\perp}$ 34 G (Figure 3), consistent with the formation of a mononuclear d^9 palladium(I) species.[5,6] Electrochemical conversion of $[Pd(L^1)]^{2+}$ [$\lambda_{max.}$ 373 nm ($\varepsilon_{max.}$ 2 175 mol^{-1} dm^3 cm^{-1}), 298(14 460), 232(15 070)] to $[Pd(L^1)]^+$ [$\lambda_{max.}$ 345 nm ($\varepsilon_{max.}$ 2 100 mol^{-1} dm^3 cm^{-1}, sh.), 289(8 700), 236(10 300)] occurs reversibly and isosbestically ($\lambda_{iso.}$ 275,225 nm). The related homoleptic thioether Pd^{II} complexes, $[Pd(L)]^{2+}$ (L = L^3—L^5) and $[Pd(L^6)_2]^{2+}$ show irreversible reductions at E_p −0.73 → −0.875 V *vs.* Fc/Fc^+ in MeCN at 293 K, although more reversible couples are observed for $[Pd(L^5)]^{2+}$ and $[Pd(L^6)_2]^{2+}$ at reduced temperatures (233 K).[7] Most importantly, $[Pd(L^1)]^{2+}$ is the only thioether complex we have studied which shows a reversible $Pd^{II/I}$ couple at 293 K. This couple occurs at a particularly anodic potential compared to the tetra-aza analogues $[Pd(L^7)]^{2+}$ ($E_{\frac{1}{2}}$ −1.27 V) and $[Pd(L^8)]^{2+}$ (−1.53 V *vs.* Fc/Fc^+).[6] These differences may be ascribed to the greater π-acidity of thioether donors, and to the ability of the larger and more flexible ring system of L^1 to accommodate the large Pd^I centre. In contrast, the tetra-aza complexes afford more reactive and transient paramagnetic species, with significant de-metallation occurring over a period of time. Sauvage and co-workers have shown[8] that tetrahedral catenand ligands stabilise d^9 Ni^I centres, and therefore, it seems likely that L^1 undergoes a tetrahedral distortion in the reduced complex $[Pd(L^1)]^+$.

In contrast to $[Pd(L^1)]^{2+}$, $[Pd(L^2)]^{2+}$ shows a chemically reversible oxidation at $E_{\frac{1}{2}}$ +0.57 V *vs.* Fc/Fc^+, ΔE_p 195 mV at a scan rate of 150 mV s^{-1}, indicative of a large stereochemical change occurring at the metal centre on oxidation. A totally irreversible reduction is observed at E_p −1.03 V at 293 K. Coulometry confirms the oxidation to be a one-electron process to form a bright red paramagnetic species which shows an anisotropic e.s.r. spectrum (77 K, MeCN; g_1 2.064, g_2 2.052, g_3 2.019) (Figure 4), assigned to the formation of a mononuclear d^7 palladium(III) species.[9,10] Electrochemical conversion of $[Pd(L^2)]^{2+}$ [$\lambda_{max.}$ 514 nm ($\varepsilon_{max.}$ 124 mol^{-1} dm^3 cm^{-1}), 332 (4 250), 266 (10 000), 233 (10 850)] to $[Pd(L^2)]^{3+}$ [$\lambda_{max.}$ 488 nm ($\varepsilon_{max.}$ 3 180 mol^{-1} dm^3 cm^{-1}), 341 (5 890), 264 (11 170)] occurs reversibly and isosbestically [$\lambda_{iso.}$ 241 nm].

The generation of Pd^{III} from the 4 + 2 co-ordinate $[Pd(L^2)]^{2+}$ is consistent with the availability of a distorted octahedral stereochemistry in this system. These results

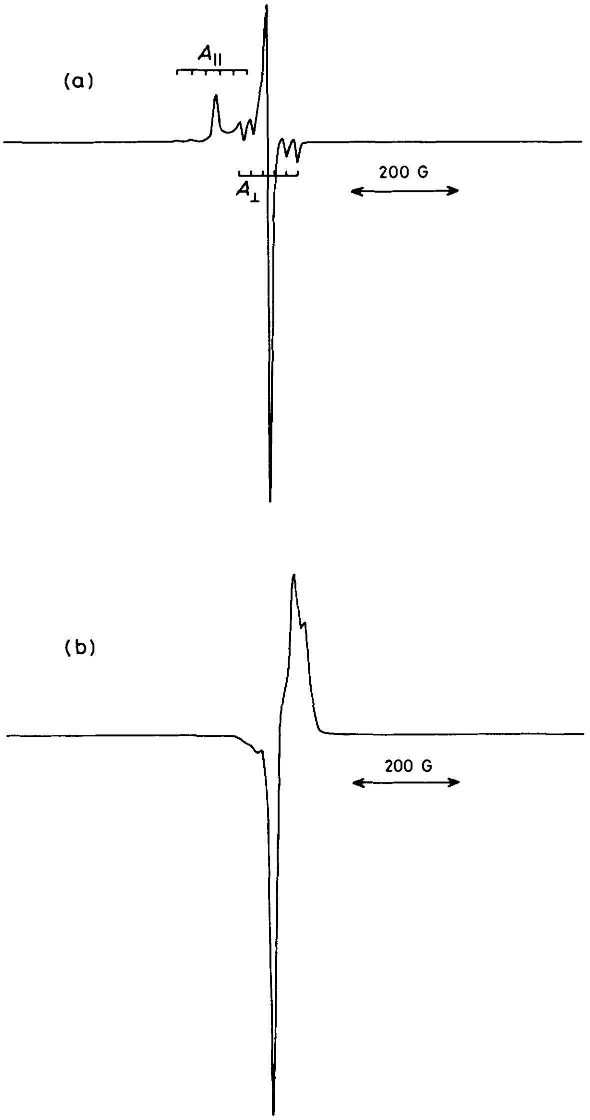


Figure 3. X-Band e.s.r. spectrum of (a) $[Pd(L^1)]^+$ and (b) $[Pd(L^2)]^{3+}$, both generated electrochemically; measured at 77 K in MeCN glass in the presence of 0.1 M $Bu^n_4NPF_6$. 1 G = 10^{-4} T.

suggest that there may be a significant kinetic/conformational barrier at room temperature to the formation of the corresponding Pd^{III} complex of L^3 (ref. 4).

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