Synthesis, Structure and Electrochemistry of $[Pd([9]aneNS_2)_2][BF_4]_2$ ($[9]aneNS_2$ = 1,4-Dithia-7-azacyclononane)

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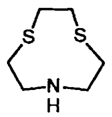
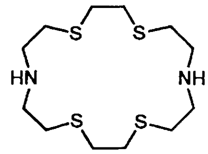
The centrosymmetric purple-blue complex $[Pd([9]aneNS_2)_2][BF_4]_2$ ($[9]aneNS_2$ = 1,4-dithia-7-azacyclononane) shows a primary N_2S_2 co-ordination, Pd–N(1) 2.081(9), Pd–S(7) 2.322(3) Å, with long-range interactions to the two remaining S donors, Pd $\cdots$ S(4) 3.011(3) Å; $[Pd([9]aneNS_2)_2]^{2+}$ shows two one-electron oxidations at ${}^1E_{\frac{1}{2}} = +0.43$ V and ${}^2E_{\frac{1}{2}} = +0.84$ V *vs.* ferrocene–ferrocenium assigned to Pd^{II}–Pd^{III} and Pd^{III}–Pd^{IV} couples respectively.

We have studied a range of palladium(II) complexes of S- and N-donor macrocyclic ligands.[1–3] Our aims in this work were to generate complexes which showed unusual co-ordination geometries at Pd^{II} and to investigate their redox behaviour. One such complex, $[Pd([18]aneN_2S_4)]^{2+}$ ($[18]aneN_2S_4$ = 1,4,10,13-tetrathia-7,16-diazacyclooctadecane), was of particular interest since it shows a distorted *rac* configuration with the palladium(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 the two remaining thioether S donors interacting with the metal centre at long range, Pd $\cdots$ S(10) 2.954(4), Pd $\cdots$ S(4) 3.000(3) Å.[2] The overall stereochemistry at Pd^{II} is therefore tetragonally distorted octahedral with a formal $N_2S_2 + S_2$ co-ordination sphere. We wished to ascertain whether the observed stereochemistry in *rac*-$[Pd([18]aneN_2S_4)]^{2+}$ was controlled by the configurational and conformational restrictions of the co-ordinated macrocycle, or whether the co-ordination at Pd^{II} is simply electronically controlled by the metal–donor atom interactions. We have therefore undertaken a study of the related palladium(II) complex $[Pd([9]aneNS_2)_2]^{2+}$ where there would be no configurational or conformational restriction with respect to N- or S-co-ordination.

Treatment of $[Pd(NCMe)_4][BF_4]_2$ with 2 molar equivalents of $[9]aneNS_2$† in MeCN afforded the purple-blue complex $[Pd([9]aneNS_2)_2][BF_4]_2$ in high yield.‡ Analytical data, IR, FAB mass, ^1H and ^{13}C NMR spectroscopy are all consistent with this formulation. The unusual colour of the complex suggested a 4 + 2 co-ordination at the palladium(II) centre as observed in the related complexes $[Pd([9]aneS_3)_2]^{2+}$ [3] and $[Pd([18]aneN_2S_4)]^{2+}$.[2] In order to confirm this, and to ascertain the N,S ligation in the complex, a single-crystal structure determination was undertaken. The crystal structure of $[Pd([9]aneNS_2)_2][BF_4]_2$ shows§ (Fig. 1) primary N_2S_2 co-ordination, Pd–N(1) 2.081(9), Pd–S(7) 2.322(3) Å, with long-range interactions to the two remaining S donors, Pd $\cdots$ S(4) 3.011(3) Å. In the 4 + 2 co-ordination at Pd^{II} in $[Pd([9]aneNS_2)_2]^{2+}$, it is therefore the two S donors rather than the N donors that interact with Pd^{II} at long range. This is consistent with the relative size and polarisability of thioether S donors compared to the stronger σ-donor N atoms. The co-ordination at Pd^{II} in $[Pd([9]aneNS_2)_2]^{2+}$ is therefore very similar to that in $[Pd([18]aneN_2S_4)]^{2+}$ [2] except that the former adopts a *fac* configuration as expected for the face-capping tridentate ligand, while the latter shows a *rac* configuration.



$[9]aneNS_2$



$[18]aneN_2S_4$

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† The macrocycle $[9]aneNS_2$ was prepared by the method of McAuley[4] and Parker[5] and their respective co-workers.

‡ The complex $[Pd(NCMe)_4][BF_4]_2$ (36 mg, 0.08 mmol) was treated with $[9]aneNS_2$ (30 mg, 0.18 mmol) in dry and degassed MeCN (2 cm^3) for 1 h at room temperature. The resultant red-brown solution was reduced in volume to 1 cm^3, and on addition of Et_2O (5 cm^3) a purple-blue precipitate was formed which was collected, recrystallised from MeCN–Et_2O and dried *in vacuo*. Yield = 62% (Found: C, 23.20; H, 3.85; N, 4.50. Calc. for $[Pd([9]aneNS_2)_2][BF_4]_2$: C, 23.8; H, 4.30; N, 4.60%). FAB mass spectrum (3-nitrobenzyl alcohol): *m/z* 519 and 432. Calc. for $[Pd([9]aneNS_2)_2(BF_4)]^+$ *m/z* = 519 and $[Pd([9]aneNS_2)_2]^+$ *m/z* = 432. NMR (CD_3CN, 298 K): ^{13}C (50.32 MHz), δ 52.0 (CH_2N), 32.9 and 32.3 (CH_2S); ^1H (80 MHz), δ 5.42 (br s, 2 H, NH), 3.35–2.89 (m, 14 H, CH_2).

§ Crystals of $[Pd([9]aneNS_2)_2][BF_4]_2$ were grown by slow evaporation of a solution of the complex in MeCN. A purple block (0.56 × 0.56 × 0.74 mm) suitable for X-ray analysis was mounted in the cold stream of an Oxford Cryosystems low-temperature device,[6] on a Stoë Stadi-4 four-circle diffractometer. Crystal data. $C_{12}H_{26}B_2F_8N_2PdS_4$, M = 642.54, monoclinic, space group $P2_1/c$, a = 9.662(12), b = 7.419(5), c = 16.291(9) Å, β = 94.52(11)°, U = 1164 $Å^3$ (from 2θ values of 14 reflections measured at $\pm\omega$, 2θ = 28–32°, λ = 0.710 73 Å), D_c = 1.833 g cm^{-3}, Z = 2 (implying that each cation lies on a crystallographic inversion centre), μ = 1.206 mm^{-1}, $F(000)$ = 648. Graphite-monochromated Mo-Kα X-radiation, T = 150 K, ω–2θ scans with ω scan width (1.50 + 0.347 tan θ)°, 1668 unique data measured ($5 \leqslant 2\theta \leqslant 45°$), h −10 to 10, k 0–7, l 0–17, giving 1348 with $F \geqslant 4\sigma(F)$ for use in all calculations. A Patterson synthesis located the Pd atom and iterative cycles of least-squares refinement and Fourier difference synthesis located the remaining non-H atoms. At isotropic convergence, corrections (minimum 0.345, maximum 1.288) for absorption were applied using DIFABS.[7] Refinement (by least-squares on F)[8] with anisotropic thermal parameters for all non-H atoms (except B) and with H-atoms (amine H atoms not found) in fixed calculated positions converged at R, R' = 0.0892, 0.1133, S = 0.911 for 133 parameters, and the final ΔF synthesis showed no feature above 2.14 e $Å^{-3}$. The weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,250F^2$ gave satisfactory agreement analyses and in the final cycle $(\Delta/\sigma)_{max}$ was 0.066. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

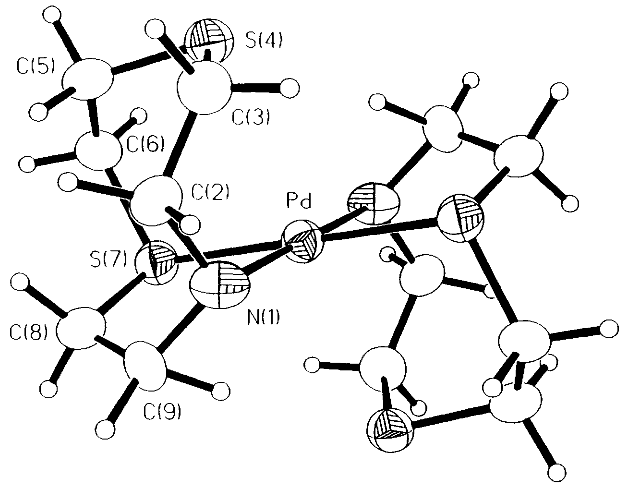

Fig. 1 Structure of $[Pd([9]aneNS_2)_2]^{2+}$ with the numbering scheme adopted: Pd–N(1) 2.081(9), Pd···S(4) 3.011(3), Pd–S(7) 2.322(3) Å; N(1)–Pd–S(7) 81.7(3), N(1)–Pd···S(4) 85.8(3), S(7)–Pd···S(4) 82.49(9)°

Cyclic voltammetry of $[Pd([9]aneNS_2)_2]^{2+}$ shows two chemically-reversible oxidations at $^1E_{\frac{1}{2}} = +0.43$ V (ΔE = 140 mV) and $^2E_{\frac{1}{2}} = +0.84$ V (ΔE = 130 mV) *vs.* ferrocene–ferrocenium assigned to Pd^{II}–Pd^{III} and Pd^{III}–Pd^{IV} couples respectively. The large peak-to-peak separations suggest significant changes in co-ordination geometry at Pd during these redox changes. Coulometry confirms these to be one-electron processes. Quantitative electrochemical oxidation of $[Pd([9]aneNS_2)_2]^{2+}$ in MeCN at a Pt gauze at +0.7 V affords an orange solution of $[Pd([9]aneNS_2)_2]^{3+}$, the ESR spectrum of which shows (Fig. 2) a strong signal with $g_{\parallel} = 2.008$, $g_{\perp} = 2.058$ consistent with a d^7 palladium(III) centre.[2,3,9] Superhyperfine coupling to N donors is not observed for this species suggesting, on the basis of previous work on related nickel(III) and palladium(III) complexes,[3,9,10] that the N donors are bound in the equatorial *xy* plane, with S donors bound along the *z* axis, probably at a distance of *ca.* 2.5 Å from the palladium(III) centre.[3] The oxidation of $[Pd([9]aneNS_2)_2]^{2+}$ to $[Pd([9]aneNS_2)_2]^{3+}$ can also by monitored using electronic spectroelectrochemistry. Thus, *in situ* electrooxidation of $[Pd([9]aneNS_2)_2]^{2+}$ [λ_{max} = 260 nm (ε_{max} = 11 450 dm^3 mol^{-1} cm^{-1})] at 243 K in an optically transparent electrode cell proceeds isosbestically (λ_{iso} = 280 nm) and quantitatively to afford $[Pd([9]aneNS_2)_2]^{3+}$ [λ_{max} = 245 (5400), 265(sh) (9600), 328 (9000), 455 nm (ε_{max} = 5400 dm^3 mol^{-1} cm^{-1})]. Reduction back to the palladium(II) starting material occurs quantitatively reversibly and isosbestically.

We have established that the observed $N_2S_2 + S_2$ co-ordination (rather than the alternative $S_4 + N_2$ binding) in $[Pd([9]aneNS_2)_2]^{2+}$ and $[Pd([18]aneN_2S_4)]^{2+}$ is electronically controlled by the metal–donor atom interactions rather than by any conformational and configurational constraints of the macrocyclic ligands. The stabilisation of mononuclear radical species, in this instance d^7 Pd^{III}, reflects the imposed stereochemistry in the precursor palladium(II) complexes.

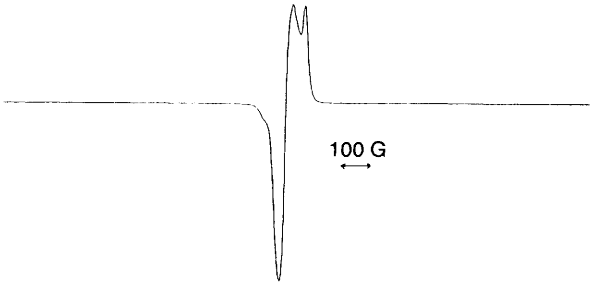

Fig. 2 X-Band ESR spectrum (77K, MeCN–0.1 mol dm^{-3} NBu_4PF_6) of electrochemically generated d^7 $[Pd([9]aneNS_2)_2]^{3+}$

Acknowledgements

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