Synthesis, Structure and Electrochemistry of $[Pt([10]aneS_3)_2][PF_6]_2$ ($[10]aneS_3$ = 1,4,7-trithiacyclodecane)

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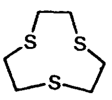
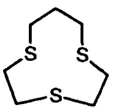
The orange complex $[Pt([10]aneS_3)_2][PF_6]_2$ ($[10]aneS_3$ = 1,4,7-trithiacyclodecane) is centrosymmetric with primary S_4 co-ordination, Pt–S(5) 2.297(4), Pt–S(8) 2.309(4) Å, with long-range interactions to the two remaining S-donors, Pt···S(1) 3.233(4) Å; $[Pt([10]aneS_3)_2]^{2+}$ shows a broad two-electron oxidation centred at $E_{\frac{1}{2}}$ = +0.35 V (*vs.* ferrocene–ferrocenium) assigned to a Pt^{II}–Pt^{IV} couple.

We have studied a range of platinum(II) complexes of S-donor macrocyclic ligands.[1–3] Our aims in this work were to generate complexes of unusual co-ordination geometries and to investigate their redox behaviour. One such complex, $[Pt([9]aneS_3)_2][PF_6]_2$, ($[9]aneS_3$ = 1,4,7-trithiacyclononane) is particularly interesting since it exhibits an unusual elongated square-based pyramidal geometry at Pt^{II} (Fig. 1).[2] This cation has a square-planar arrangement of two S-donors from each of the two macrocyclic crowns, Pt–S 2.246(8)–2.305(8) Å, with a third S-donor from one of the ligands interacting at an apical position, Pt···S 2.885(7) Å. The sixth S-donor is non-interacting, Pt···S 4.04 Å. Thus, the co-ordination geometry around Pt^{II} in $[Pt([9]aneS_3)_2][PF_6]_2$ can be described as [4 + 1] with one non-interacting S-donor.


$[9]aneS_3$


$[10]aneS_3$

We wished to determine whether a similar stereochemistry would be observed for the complex cation $[Pt([10]aneS_3)_2]^{2+}$ ($[10]aneS_3$ = 1,4,7-trithiacyclodecane) incorporating the corresponding 10-membered macrocycle, or whether the greater flexibility of $[10]aneS_3$ (ref. 4) would lead to a different overall geometry. We have, therefore, undertaken a structural and electrochemical study of $[Pt([10]aneS_3)_2][PF_6]_2$.

Reaction of K_2PtCl_6 with 2 molar equivalents of $[10]aneS_3$ in water–methanol–acetonitrile (1 : 1 : 1 v/v/v) affords, on addition of an excess of NH_4PF_6, the orange complex $[Pt([10]aneS_3)_2][PF_6]_2$. Analytical data, fast atom bombardment mass spectrometry, IR, ^1H and ^{13}C NMR spectroscopy are all consistent with this formulation.† The single-crystal X-ray structure of $[Pt([10]aneS_3)_2][PF_6]_2$ shows‡ primary S_4 co-ordination in a square-planar arrangement, Pt–S(5) 2.297(4), Pt–S(8) 2.309(4) Å, with long-range interactions to *both* the remaining S-donors, Pt···S(1) 3.233(4) Å. This [4 + 2] co-ordination at Pt^{II} contrasts with the [4 + 1] binding observed in $[Pt([9]aneS_3)_2][PF_6]_2$; the latter complex also shows a significantly shorter Pt···S_{apical} interaction. These structural differences are consistent with the larger, more flexible $[10]aneS_3$ ring conferring a less strained geometry at Pt^{II}. The [4 + 2] co-ordination mode at Pt^{II} has also been found for the larger ring complex $[Pt([18]aneS_6)]^{2+}$ ($[18]aneS_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane).[3]

Recently, we have discovered that the solid-state structures of cationic thioether macrocyclic complexes can be dependent upon the counter anion present,[7] especially when stereochemical mismatches between metal and ligand exist. We were therefore concerned that the structural differences between [Pt([9]ane-

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† The salt K_2PtCl_6 (33.4 mg, 0.08 mmol) was treated with $[10]aneS_3$ (29.2 mg, 0.15 mmol) under reflux in a 1 : 1 : 1 mixture of distilled water, methanol and acetonitrile (30 cm^3) for 3 h under N_2. To the resulting bright yellow solution an excess of NH_4PF_6 was added. The solvent was removed, and the resulting orange precipitate was recrystallised from nitromethane and diethyl ether and dried *in vacuo* (Found: C, 18.9; H, 3.20. $C_{14}H_{28}F_{12}P_2PtS_6$ requires C, 19.2; H, 3.20%). NMR [$(CD_3)_2CO$, 298 K]: ^{13}C (50.32 MHz), δ 35.60, 34.90, 31.36 and 25.84 (CH_2); ^1H (360.13 MHz), δ 3.47–3.87 (m, 12 H, CH_2) and 2.22–2.60 (m, 2 H, CH_2).

‡ Crystals of $[Pt([10]aneS_3)_2][PF_6]_2$ were grown by vapour diffusion of diethyl ether into a solution of the complex in $MeNO_2$. A yellow tablet (0.23 × 0.19 × 0.06 mm) suitable for X-ray analysis was selected and mounted on a Stoë Stadi-4 four-circle diffractometer.

Crystal data: $C_{14}H_{28}F_{12}P_2PtS_6 \cdot 1.75CH_3NO_2$, M = 980.4, monoclinic, space group $C2/c$, a = 23.3767(19), b = 12.0450(12), c = 11.2155(15) Å, β = 94.346(10)°, U = 3148.9 $Å^3$ (from 2θ values of 59 reflections measured at ±ω, 2θ = 26–28°, λ = 0.710 73 Å), Z = 4, D_c = 2.068 g cm^{-3}, μ = 5.08 mm^{-1}, $F(000)$ = 1920.

Data collection and processing: Stoë Stadi-4 diffractometer, graphite monochromated Mo-Kα X-radiation, T = 298 K, ω–2θ scans with omega widths (0.99 + 0.347 tanθ), 2662 data measured (5 ⩽ 2θ ⩽ 45°), h −25 to 25, k 0–12, l 0–12), 1877 unique (R_{int} = 0.027), giving 1467 with $F \geq 4\sigma(F)$ for use in all calculations. Initial absorption correction was made using ψ scans (maximum, minimum transmission 0.397, 0.267). Linear isotropic decay (*ca.* 52%) was corrected for during data reduction.

Structure solution and refinement: A Patterson synthesis located the Pt atom and iterative cycles of least-squares refinement and Fourier difference synthesis located the remaining non-hydrogen atoms. At isotropic convergence, corrections (minimum 0.894, maximum 1.192) for absorption were applied using DIFABS.[5] Refinement (by least squares on F)[6] with anisotropic thermal parameters for all ordered non-H atoms [except C(10)], and with H atoms in fixed calculated positions, converged at R,R' = 0.0506, 0.0598, S = 1.150 for 187 parameters, and the final ΔF synthesis showed no feature above 2.19 e $Å^{-3}$. The weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,292F^2$ gave satisfactory agreement analysis and in the final cycle $(\Delta/\sigma)_{max}$ was 0.013. 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.

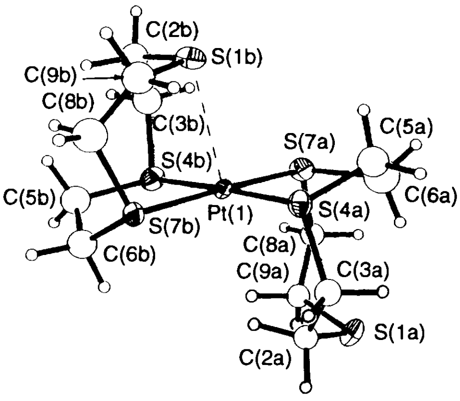

Fig. 1 View of $[Pt([9]aneS_3)_2]^{2+}$ with numbering scheme adopted[2]

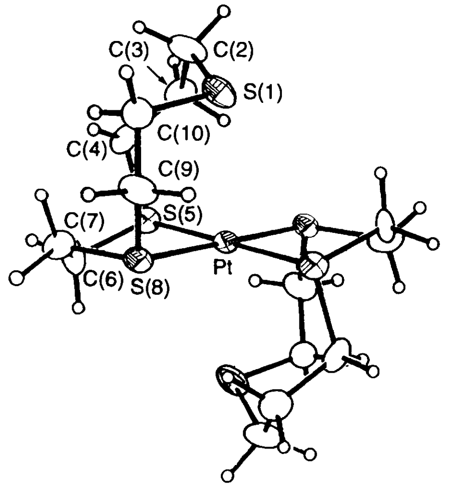

Fig. 2 View of $[Pt([10]aneS_3)_2]^{2+}$ with numbering scheme adopted. Selected bond lengths (Å) and angles (°): Pt–S(5) 2.297(4), Pt–S(8) 2.309(4), Pt···S(1) 3.233(4), S(5)–Pt–S(8) 88.90(13), S(1)···Pt–S(5) 94.19(12), S(1)···Pt–S(8) 80.28(12)

$S_3)_2]^{2+}$ and $[Pt([10]aneS_3)_2]^{2+}$ observed above might be due to packing effects and therefore potentially dependent upon the counter ion, rather than any conformational and configurational differences between the 9- and 10-membered thioether macrocycles. A range of different salts of $[Pt([9]aneS_3)_2]^{2+}$ and $[Pt([10]aneS_3)_2]^{2+}$ were prepared by metathesis reactions. Importantly, the single-crystal X-ray structures of $[Pt([9]aneS_3)_2]X_2$ (X = BPh_4 or PF_6) both confirm [4 + 1] co-ordination at Pt^{II}, with $[Pt([10]aneS_3)_2]X_2$ (X = PF_6 or BF_4) both showing [4 + 2] co-ordination.[8] Interestingly, the structures of $[Pd([9]aneS_3)_2][PF_6]_2$[9] and $[Pd([10]aneS_3)_2][PF_6]_2$[10] show [4 + 2] co-ordination at Pd^{II}. These results suggest that [4 + 1] co-ordination is indeed preferred for Pt^{II} with $[9]aneS_3$,[11] while [4 + 2] co-ordination is preferred with $[10]aneS_3$.

Cyclic voltammetry of $[Pt([10]aneS_3)_2]^{2+}$ shows a broad, quasi-reversible oxidation centred at $E_{\frac{1}{2}} = +0.35$ V *vs.* ferrocene–ferrocenium, assigned to a Pt^{II}–Pt^{IV} couple. The large peak-to-peak separation (*ca.* 300 mV) suggests a significant change in co-ordination geometry at the platinum centre during the redox change. Coulometry confirms this oxidation to be an overall two-electron process. Quantitative electrochemical oxidation of $[Pt([10]aneS_3)_2]^{2+}$ in MeCN at a Pt gauze at a potential of +1.1 V (*vs.* ferrocene–ferrocenium) affords an initial yellow colour {assigned to the presence of $[Pt([10]aneS_3)_2]^{3+}$} which fades to a pale yellow solution of $[Pt([10]aneS_3)_2]^{4+}$. A weak ESR spectrum for the intermediate $[Pt([10]aneS_3)_2]^{3+}$ species can be obtained and this shows an anisotropic signal at 77 K (as a frozen glass) with $g_{\perp} = 2.062$ and $g_{\parallel} = 1.989$. No hyperfine coupling was discerned. The oxidation of $[Pt([10]aneS_3)_2]^{2+}$ to $[Pt([10]aneS_3)_2]^{4+}$ can also be monitored using electronic spectroelectrochemistry. Thus, *in situ* electrooxidation of $[Pt([10]aneS_3)_2]^{2+}$ [λ_{max} = 245 (ε_{max} = 12 000) and 276 (ε_{max} = 8700 $dm^3\ mol^{-1}\ cm^{-1}$)] at 243 K in an optically transparent electrode cell proceeds isosbestically (λ_{iso} = 230 and 250 nm) and quantitatively to afford $[Pt([10]aneS_3)_2]^{4+}$ [λ_{max} = 299 (ε_{max} = 31 000) and 342 nm (sh) (ε_{max} = 9500 $dm^3\ mol^{-1}\ cm^{-1}$)]. The platinum(III) intermediate can be detected *via* a low intensity absorption band at 405 nm which forms and decays during the course of the electrooxidation. This contrasts with the spectroelectrochemistry of $[Pt([9]aneS_3)_2]^{2+}$ which, despite showing an overall two-electron oxidation, affords a relatively stable mononuclear platinum(III) intermediate. Reduction of $[Pt([10]aneS_3)_2]^{4+}$ at +0.1 V (*vs.* ferrocene–ferrocenium) affords a product, assigned as a new platinum species [λ_{max} = 342 nm (ε_{max} = 4000 $dm^3\ mol^{-1}\ cm^{-1}$)]; interestingly, reoxidation of this species to the platinum(IV) product occurs reversibly and isosbestically.

Current work is aimed at assessing further the stereochemical and redox properties of these and related platinum(II) thioether complexes.

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