Stabilisation of Trivalent Platinum by Structurally Accommodating Thiamacrocycles

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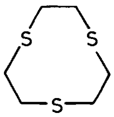
The complex cation $[Pt(\mathbf{1})_2]^{2+}$ [($\mathbf{1}$) = 1,4,7-trithiacyclononane] shows a quasi square based pyramidal structure with one non-bonding sulphur donor atom; electrochemical oxidation at +0.5 V. *vs.* Fc^0/Fc^+ (Fc = ferrocene) at 20 °C in MeCN affords a paramagnetic platinum(III) species.

The majority of platinum(III) compounds are diamagnetic Pt–Pt dimers.[1,2] Few monomeric platinum(III) species have been generated, the well-documented examples including $[Pt(C_6Cl_5)_4]^-$,[3] $[Pt(L)_2]^+$ (L = diphenylglyoximate),[4] and $[Pt(diamsar)]^{3+}$ (diamsar = 1,8-diamino-3,6,10,13,16,19-hexa-azabicyclo[6.6.6.]icosane).[5] In view of the ability of macrocyclic ligands to stabilise unusual, otherwise unstable metal oxidation states, we undertook a study of the redox chemistry of platinum(II) macrocyclic complexes and report here structural and electrochemical results on the homoleptic bis-macrocyclic species $[Pt(\mathbf{1})_2]^{2+}$ [($\mathbf{1}$) = 1,4,7-trithiacyclononane].

Reaction of $PtCl_2$ or $K_2[PtCl_4]$ with two molar equivalents of ($\mathbf{1}$) gives, on addition of NH_4PF_6, the complex $[Pt(\mathbf{1})_2](PF_6)_2$ in 70% yield. A single crystal *X*-ray structure[†] of the product shows two independent cations and four PF_6^- anions per asymmetric unit of the monoclinic cell. Views of



[†] *Crystal data* for $[Pt(\mathbf{1})_2](PF_6)_2$: $C_{12}H_{24}PtS_6{}^{2+}2PF_6{}^-$ monoclinic, $P2_1$, a = 11.848(4), b = 17.817(6), c = 11.750(11) Å, β = 98.06(4)°, U = 2456 Å^3, $D_{calc.}$ = 1.77 g cm^{-3}, Z = 4; 3515 data measured to θ = 22.5°, refinement based on 2721 data with $F \geqslant 6\sigma(F)$. At convergence, R,R_w = 0.044, 0.048 respectively for 354 parameters. Reflections with $h + l = 2n$ were much stronger than others, indicating that the two independent Pt atoms are related by a pseudo B-centring. Approximate positions derived from a Patterson synthesis were used as input to D.I.R.D.I.F.[6] which fixed both the origin and the enantiomorph of the structure, and two subsequent rounds located the other 64 non-hydrogen atoms in the structure. The data were corrected for absorption using D.I.F.A.B.S.,[7] hydrogen atoms were included in calculated positions, and Pt, P, and S atoms were refined anisotropically.[8] At convergence, the difference map showed no feature above 0.7 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.

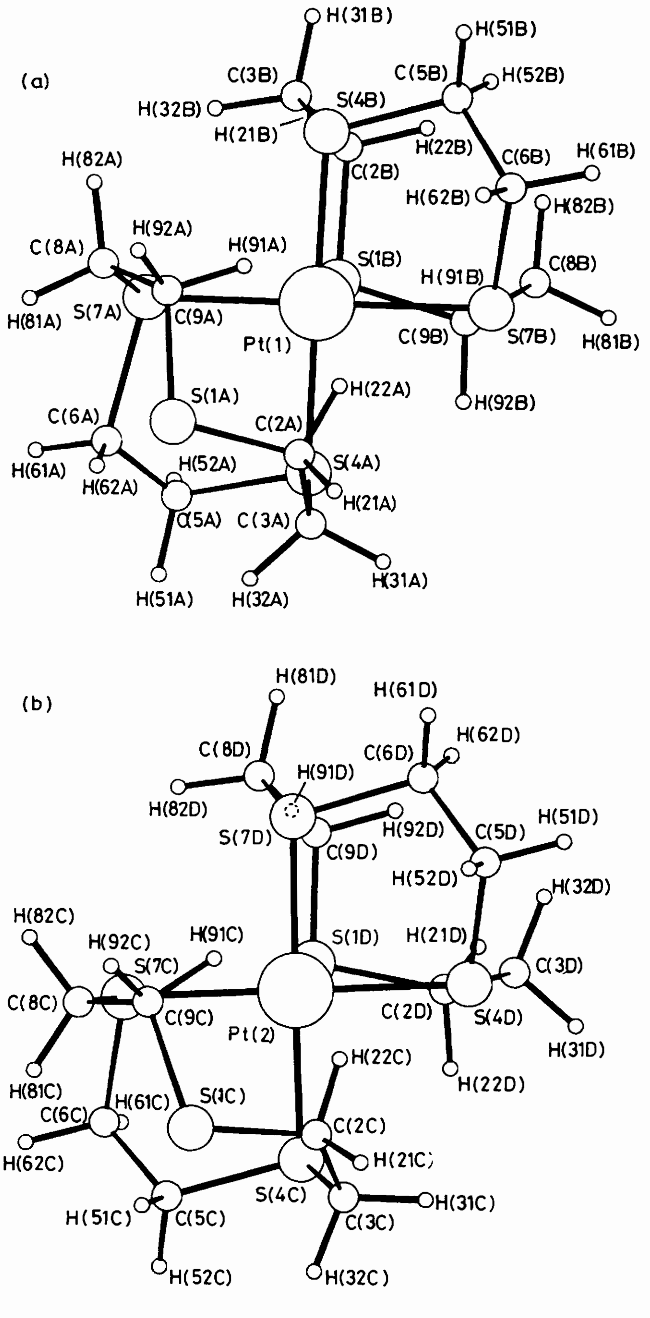


Figure 1. Single crystal *X*-ray structure of $[Pt(\mathbf{1})_2]^{2+}$ with numbering scheme adopted.

the two independent cations are shown in Figure 1. In both cases the Pt atoms are co-ordinated by four sulphur atoms from two ligands in a square plane (Pt–S = 2.25—2.30 Å; ∠SPtS = 88.1—91.5°). An elongated square pyramidal co-ordination is achieved in both cases by the third sulphur donor in one of the macrocycles co-ordinating apically (Pt–S′ = 2.88, 2.93 Å; ∠SPtS′ = 84.0—97.2°). The final sulphur atom is not co-ordinated with S · · · Pt = 4.04, 4.18 Å. This unusual stereochemistry around platinum(II) contrasts markedly with that observed for the 1,4,7-triazacyclononane analogue which is centrosymmetric with two dangling nitrogen donors and a square planar metal centre.[9]

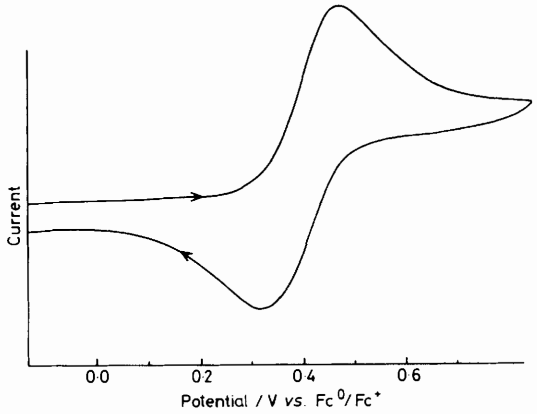


Figure 2. Cyclic voltammogram of $[Pt(\mathbf{1})_2](PF_6)_2$ in MeCN (0.1 M $Bu^n_4NPF_6$) at 20 °C at platinum electrodes. Scan rate = 100 mV s^{-1}. Fc = ferrocene.

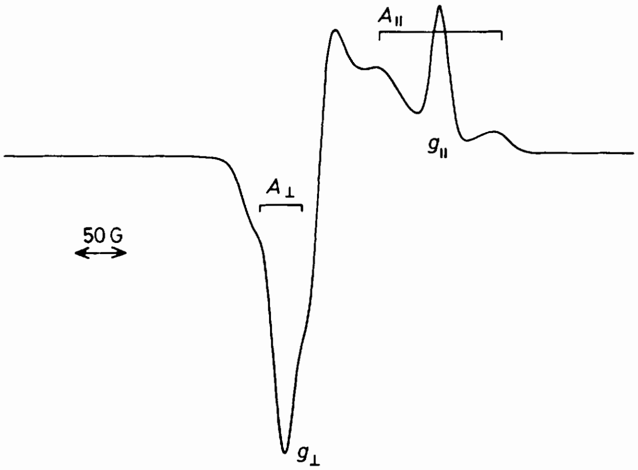


Figure 3. E.s.r. spectrum of $[Pt(\mathbf{1})_2]^{3+}$ at 77 K in MeCN glass. (1 G = 10^{-4} T.)

Cyclic voltammetry of $[Pt(\mathbf{1})_2](PF_6)_2$ in MeCN (0.1 M $Bu^n_4NPF_6$) shows a one electron oxidation E_{pa} = +0.46 V, with a return wave at E_{pc} = +0.315 V *vs.* Fc^0/Fc^+, ΔE_p = 145 mV, I_{pa}/I_{pc} = 1.0 at a scan rate of 100 mV s^{-1} (Figure 2). Oxidation of the metal-free ligand (**1**), and of the complex cation $[Ni(\mathbf{1})_2]^{2+}$ occurs near +1.0 V[10] suggesting that the oxidation of $[Pt(\mathbf{1})_2]^{2+}$ might be occurring predominantly at the metal centre. Controlled potential electrolysis of $[Pt(\mathbf{1})_2]^{2+}$ ($\lambda_{max.}$ = 432 nm, ε = 95 $dm^3\,mol^{-1}\,cm^{-1}$) at +0.5 V under N_2 (20 °C, MeCN) affords a stable oxidised product ($\lambda_{max.}$ = 401 nm, ε = 3500 $dm^3\,mol^{-1}\,cm^{-1}$), the e.s.r. spectrum (77 K, MeCN glass) of which shows an anisotropic signal with $g_{\perp}$ = 2.044, $g_{\parallel}$ = 1.987 with coupling to ^{195}Pt (33.8%), $A_{\perp}$ = 30 G, $A_{\parallel}$ = 85 G (1 G = 10^{-4} T) (Figure 3). A similar e.s.r. spectrum has been reported previously for $[Pt(diamsar)]^{3+}$, prepared by γ-radiolysis of the platinum(IV) tetracation at 77 K, and assigned to a transient, octahedral platinum(III) species.[5] The co-ordination geometry of $[Pt(\mathbf{1})_2]^{3+}$ is likely therefore to be distorted octahedral with the trithia macrocycles adapting to the stereochemical and electronic requirements of d^7 platinum(III) and positive charge being delocalised onto the thia donors.

The importance of the ability of (**1**) to adjust its mode of co-ordination in response to the oxidation state of the metal is reflected by the relative stability of the platinum(III) product, and by the oxidative inactivity of the related homoleptic species $[Pt(L)]^{2+}$ (L = 1,4,8,11-tetrathiacyclotetradecane,[11] 1,4,7,10,13,16-hexathiacyclo-octadecane[12]). The inactivity of the hexathia ligand to stabilise the higher valent state may reflect the inability of the two unbound sulphur donor atoms in the complex cation to complete octahedral or pyramidal co-ordination around the metal centre,[12] while for the tetrathia complex, co-ordination is restricted to square planarity. Interestingly, Wieghardt and coworkers have shown[9] that platinum(IV) can be readily stabilised using the corresponding triaza ligand system; this clearly reflects the electronic differences between poly-aza and -thia donors and suggests that homoleptic sulphur macrocycles may indeed be useful ligands for selective metal redox activation and control. The stabilisation of related d^7 palladium(III) and rhodium(II) species has also been achieved using (**1**), while work on the corresponding iridium(II) system is in progress.

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