

# New linked macrocyclic systems. Interaction of palladium(II) and platinum(II) with tri-linked N<sub>2</sub>S<sub>2</sub>-donor macrocycles and their single-ring analogues

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Palladium(II) and platinum(II) complexes of ligands incorporating three linked, 16-membered, N<sub>2</sub>S<sub>2</sub>-donor macrocycles, together with their single-ring analogues have been synthesised. The former complexes are of the form [M<sub>3</sub>L](PF<sub>6</sub>)<sub>6</sub> (where M = Pd or Pt, and L is a linked three-ring macrocyclic species incorporating a 1,3,5-‘tribenzyl’ or a phloroglucinol core). The X-ray structure determination of the single ring species [PdL](PF<sub>6</sub>)<sub>2</sub> (where L is a single N-benzylated derivative of the N<sub>2</sub>S<sub>2</sub>-donor macrocycle) showed that the palladium is coordinated to all four donor atoms of the macrocycle in a ‘square planar’ manner. The electrospray mass spectra of the tri-linked metal-containing species show a series of multiply charged ions resulting from the loss of hexafluorophosphate counter ions and hydrogens, and corresponding to [M – nPF<sub>6</sub>]<sup>n+</sup> and [M – nPF<sub>6</sub> – mH]<sup>(n – m)+</sup>. Expansion of individual charged peaks revealed the expected wide mass range resulting from the presence of three metal ions, each of which possesses a number of isotopes. Spectrophotometric titrations confirm that 3 : 1 (metal : ligand) stoichiometries occur for the complexes of these tri-linked ligands in acetonitrile.

## Introduction

Over the past decade or so there has been increased interest in larger molecular entities incorporating macrocycles as structural elements. While there is now a considerable number of linked macrocyclic systems incorporating two macrocyclic rings,<sup>1</sup> systems incorporating three or more rings are considerably less common. Gokel and co-workers<sup>2</sup> have reported linearly-linked tris-macrocyclic species based on aza crowns. More recently, there have also been reports of the synthesis of new tri-linked tetraazacycloalkane macrocycles together with their binding to a restricted number of metal ions.<sup>3</sup> The N<sub>3</sub>[9]ane macrocyclic ring has also been incorporated into dendritic arrangements by Beer and Gao.<sup>4</sup>

Systems incorporating di-linked N<sub>2</sub>S<sub>2</sub>-macrocycles have been reported.<sup>5,6</sup> The introduction of thioether donors into macrocyclic systems is expected to favour binding towards ‘softer’ metals such as palladium(II) and platinum(II);<sup>7</sup> complexes of monomeric N<sub>2</sub>S<sub>2</sub>-donor macrocyclic ligands of these metals have been investigated in previous studies.<sup>8–11</sup>

We now report the results of an investigation of the interaction of palladium(II) and platinum(II) with **1** and **2** containing three linked N<sub>2</sub>S<sub>2</sub>-donor macrocycles. For comparison, the interaction of these metal ions with the corresponding single ring species **3** and **4** is also reported.

## Experimental section

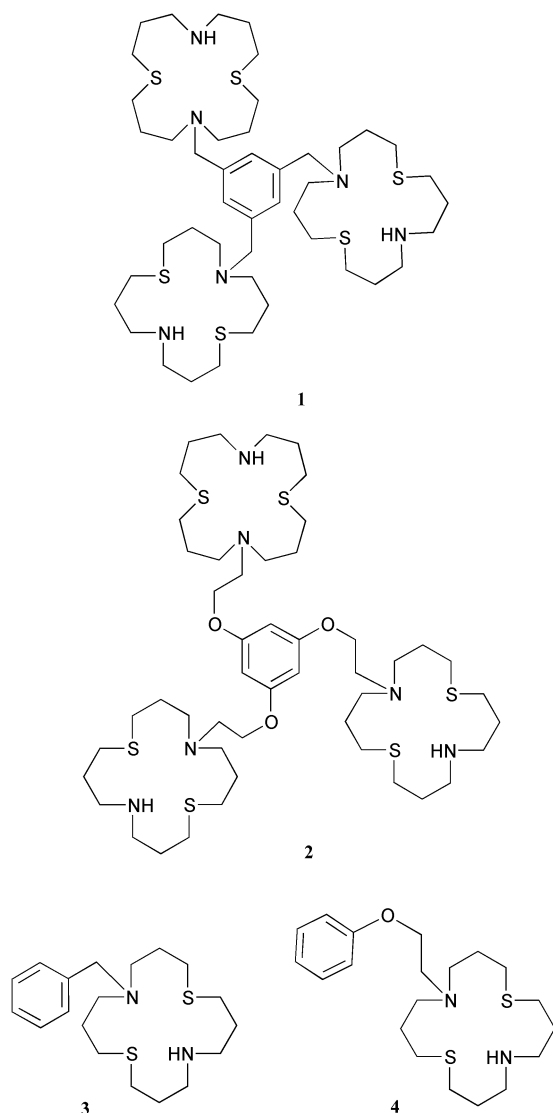
### Materials

Where available, all reagents were of analytical grade. Bis(benzonitrile)dichloroplatinum(II)<sup>12</sup> was synthesised by the

published procedure. 5-Benzyl-1,9-dithia-5,13-diazacyclohexadecane **3**, 5-*tert*-butoxycarbonyl-1,9-dithia-13-chloroacetyl-5,13-diazacyclohexadecane, 1,3,5-tris[2-(1,9-dithia-5,13-diazacyclohexadec-5-yl)ethoxy]benzene **2** and 1,3,5-tris[2-(1,9-dithia-5,13-diazacyclohexadec-5-yl)methyl]benzene **1** were synthesised as described elsewhere.<sup>13</sup>

### Physical methods

NMR spectra were recorded on a Bruker AC-200 spectrometer;  $\delta_{\text{H}}$  values are relative to TMS. Liquid secondary-ion mass spectra (LSIMS) were obtained on a Kraytos M25RFA spectrometer. Electrospray ionisation mass spectra (ESIMS) were obtained on Bruker BioApex 47e (high resolution) and Finnigan Mat LCQ (low resolution) spectrometers using acetonitrile solutions. Masses (HR) quoted for the metal complexes correspond to the mono-isotopic peak of the most abundant metal isotope (<sup>106</sup>Pd or <sup>195</sup>Pt) of the identified species. Spectrophotometric ‘batch-wise’ titrations were performed employing acetonitrile as solvent. An aliquot (3 cm<sup>3</sup>) of MCl<sub>2</sub> solution (M = Pd, 1.50 × 10<sup>−4</sup> mol dm<sup>−3</sup>; M = Pt, 1.51 × 10<sup>−4</sup> mol dm<sup>−3</sup>) and the appropriate number of 5.5 μL additions of ligand (L) solution (L = **1**, 1.96 × 10<sup>−3</sup> mol dm<sup>−3</sup>; L = **2**, 2.06 × 10<sup>−3</sup> mol dm<sup>−3</sup>) were added to a volumetric flask and the solution made up to 5 cm<sup>3</sup>. In this manner, a constant final metal ion concentration was maintained. These solutions were left for seven days to ensure that equilibrium had been established, after which time the spectra were recorded (no further absorbance change occurred on leaving the solutions for an additional two weeks). Spectra were recorded using a Varian Cary 5E UV/VIS/NIR spectrometer at λ = 270 nm for [M<sub>3</sub>L](PF<sub>6</sub>)<sub>6</sub> (M = Pd, L = **1** or **2**) and λ = 230 nm for (M = Pt, L = **1** or **2**).



### Structure determination

A unique single-counter diffractometer data set was measured at *ca.* 295 K (monochromatic Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å,  $2\theta/\theta$  scan mode,  $2\theta_{\max} = 60^\circ$ ) yielding 7957 independent reflections, 6948 with  $I > 2\sigma(I)$  being used in the full-matrix, least squares refinement after Gaussian absorption correction, refining anisotropic thermal parameter forms for the non-hydrogen atoms,  $(x, y, z, U_{\text{iso}})_H$  being constrained at estimated values. One of the anions was modelled as rotationally disordered about an F–P– axis, component site occupancies refining to 0.867(2) and complement. Conventional residuals  $R$ ,  $R_w$  on  $|F|$  at convergence were 0.044, 0.052, statistical reflection weights being derivative of  $\sigma^2(I) = (\sigma^2(I_{\text{diff}}) + 0.0004\sigma(I_{\text{diff}}))$ . Pertinent results are given below and in Fig. 1 and Table 1. Neutral atom complex scattering factors were employed within the Xtal 3.4 program system.<sup>14</sup> Crystal data:  $C_{19}H_{32}F_{12}N_2P_2PdS_2$ ,  $M = 749.0$ , monoclinic, space group  $P2_1/c$  ( $C_{2h}^5$ , no. 14),  $a = 8.712(3)$ ,  $b = 9.094(2)$ ,  $c = 34.48(2)$  Å,  $\beta = 92.00(4)^\circ$ ,  $V = 2730$  Å<sup>3</sup>,  $D_C$  ( $Z = 4$ ) =  $1.822$  g cm<sup>−3</sup>,  $\mu_{\text{Mo}}$  =  $10.5$  cm<sup>−1</sup>, specimen:  $0.75 \times 0.65 \times 0.65$  mm,  $A_{\text{min,max}}^* = 1.76, 1.89$ ,  $|\Delta\rho_{\text{max}}| = 1.32(4)$  e Å<sup>−3</sup>.

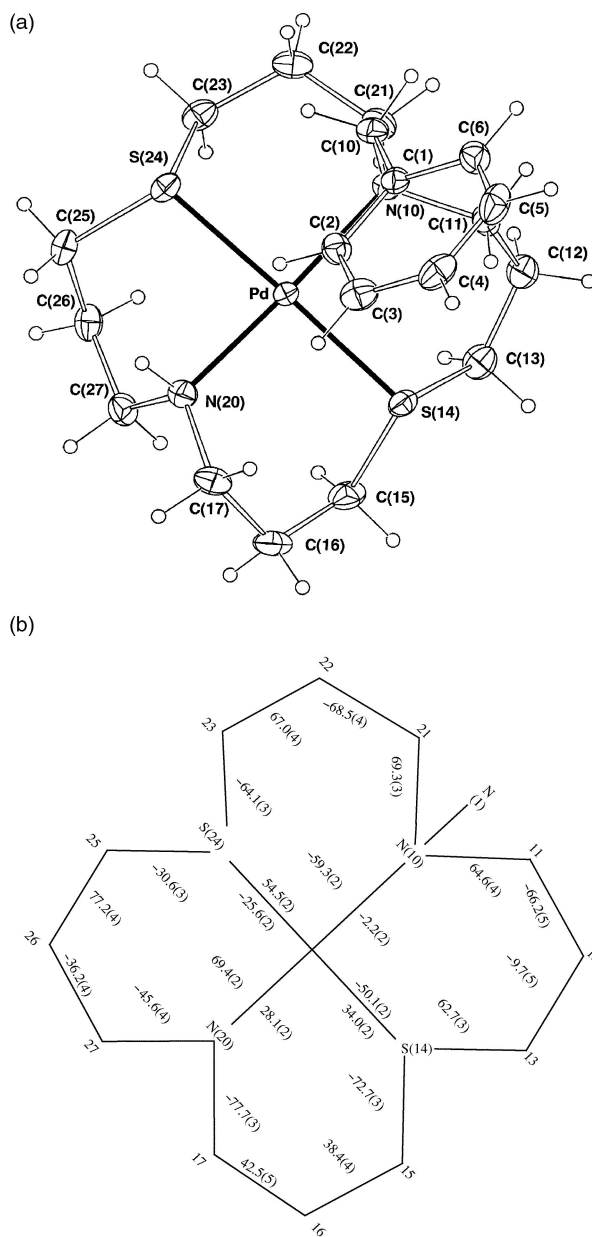
CCDC reference number 165073.

See <http://www.rsc.org/suppdata/dt/b1/b104492n/> for crystallographic data in CIF or other electronic format.

### Syntheses

#### 2-(1,9-Dithia-5,13-diazacyclohexadec-5-yl)ethoxybenzene 4.

(a) Cesium carbonate (2.28 g, 7.0 mmol) was suspended in a solution of 5-*tert*-butoxycarbonyl-1,9-dithia-13-chloroacetyl-



**Fig. 1** (a) The cation, projected normal to the coordination plane showing 20% probability amplitude displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. (b) Torsion angles within the chelate rings of the macrocycle ( $^\circ$ ).

**Table 1** Selected bond lengths (Å) and angles ( $^\circ$ )

Atoms	Parameter	Atoms	Parameter
Pd–N(10)	2.113(4)	Pd–S(14)	2.320(1)
Pd–N(20)	2.075(3)	Pd–S(24)	2.319(1)
N(10)–Pd–N(20)	173.9(1)	N(10)–Pd–S(24)	90.18(8)
S(14)–Pd–S(24)	177.19(2)	N(20)–Pd–S(14)	90.90(8)
N(10)–Pd–S(14)	91.79(7)	N(20)–Pd–S(24)	87.33(8)
Pd–N(10)–C(11)	113.2(2)	Pd–N(20)–C(17)	114.8(2)
Pd–N(10)–C(21)	111.1(2)	Pd–N(20)–C(27)	117.8(2)
C(11)–N(10)–C(21)	107.3(2)	C(17)–N(20)–C(27)	112.8(3)
Pd–S(14)–C(13)	102.5(1)	Pd–S(24)–C(23)	101.8(1)
Pd–S(14)–C(15)	102.3(1)	Pd–S(24)–C(25)	105.8(1)
C(13)–C(14)–C(15)	98.2(2)	C(23)–S(24)–C(25)	101.3(2)

5,13-diazacyclohexadecane (2.71 g, 6.2 mmol) in dry DMF (20 cm<sup>3</sup>). Solid phenol (0.64 g, 6.8 mmol) was added and the reaction mixture stirred at 65  $^\circ$ C for 48 h. The DMF was removed *in vacuo* and the residue suspended in dichloromethane (100 cm<sup>3</sup>). The base was removed by filtration through Celite and the

solvent removed under reduced pressure. The crude mixture was purified by chromatography on silica gel (eluting with methanol–dichloromethane, 1 : 99) to give 5-*tert*-butoxycarbonyl-13-(2-phenoxyacetyl)-1,9-dithia-5,13-diazacyclohexadecane as a clear oil (1.91 g, 62%). MS (ESI) ( $M + H$ )<sup>+</sup> found 497.2500.  $C_{25}H_{40}N_2O_4S_2$  requires 497.2508;  $\delta_H$  (CDCl<sub>3</sub>, 300 MHz) *ca.* 6.9 (5 H, m, OPh), 4.69 (2 H, s, CH<sub>2</sub>OPh), 3.55, 3.49 (4 H, 2  $\times$  t, *J* 7.6, CH<sub>2</sub>NCOCH<sub>2</sub>), 3.35 (4 H, br m, CH<sub>2</sub>NBoc), 2.55 (4 H, t, *J* 6.7, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NCOCH<sub>2</sub>), 2.53 (4 H, t, *J* 5.9, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NBoc), 1.9–1.8 (8 H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 14.5 [9 H, s, (CH<sub>3</sub>)<sub>3</sub>O];  $\delta_C$  (CDCl<sub>3</sub>, 75 MHz) 167.9, 157.8, 155.5, 129.5, 121.5, 114.4, 79.4, 67.7, 47.5, 47.2, 45.8, 30.0, 29.8, 29.6, 29.2, 28.3, 27.3.

(b) 5-*tert*-Butoxycarbonyl-13-(2-phenoxyacetyl)-1,9-dithia-5,13-diazacyclohexadecane (0.23 g, 0.46 mmol) was dissolved in 1 : 2 hydrochloric acid–methanol (20 cm<sup>3</sup>) and stirred at room temperature for 1 h. The methanol was then removed under reduced pressure and the residue partitioned between 10% aqueous sodium hydroxide (100 cm<sup>3</sup>) and dichloromethane (100 cm<sup>3</sup>). The aqueous layer was extracted with dichloromethane (100 cm<sup>3</sup>  $\times$  2) and the combined organic layers dried (sodium sulfate) and evaporated under reduced pressure. The product was purified by chromatography on silica gel (eluting with methanol–dichloromethane, 1 : 49) to give 5-(2-phenoxyacetyl)-1,9-dithia-5,13-diazacyclohexadecane as a clear oil (0.17 g, 93%). MS (LSI) ( $M + H$ )<sup>+</sup>, found 397.1973.  $C_{20}H_{32}N_2O_2S_2$  requires 397.1983;  $\delta_H$  (CDCl<sub>3</sub>, 300 MHz) *ca.* 6.9 (5 H, m, OPh), 4.68 (2 H, s, CH<sub>2</sub>OPh), 3.51, 3.48 (4 H, 2  $\times$  t, *J* 7.7, CH<sub>2</sub>NCO), 2.74–2.53 (12 H, m, CH<sub>2</sub>SCH<sub>2</sub>, CH<sub>2</sub>NH), 1.95 (4 H, m, CH<sub>2</sub>CH<sub>2</sub>NCO), 1.78 (4 H, quin, *J* 6.5, CH<sub>2</sub>CH<sub>2</sub>NH);  $\delta_C$  (CDCl<sub>3</sub>, 75 MHz) 167.5, 157.5, 129.3, 121.3, 114.2, 76.4, 67.4, 47.1, 47.0, 45.3, 29.5, 29.4, 29.0, 28.9, 28.5, 26.8.

(c) 5-(2-Phenoxyacetyl)-1,9-dithia-5,13-diazacyclohexadecane (2.08 g, 5.25 mmol) was dissolved in dry tetrahydrofuran (100 cm<sup>3</sup>). A 2.0 mol dm<sup>−3</sup> solution of a borane–dimethyl sulfide complex in tetrahydrofuran (13 cm<sup>3</sup>, 26 mmol) was added to the reaction flask and the solution refluxed for 4 h. The solution was allowed to cool to room temperature and the excess borane destroyed by careful addition of methanol. The tetrahydrofuran was removed under reduced pressure and the residue hydrolysed in refluxing methanol–water–concentrated hydrochloric acid (40 : 10 : 4; 54 cm<sup>3</sup>) for 1 h. The methanol was removed under reduced pressure and the resulting solution partitioned between 10% aqueous sodium hydroxide (200 cm<sup>3</sup>) and dichloromethane (200 cm<sup>3</sup>). The aqueous layer was extracted twice further with dichloromethane (200 cm<sup>3</sup>  $\times$  2) and the combined organic layers dried (sodium sulfate) and evaporated under reduced pressure. Purification by chromatography on silica gel (eluting with methanol–dichloromethane, 1 : 40 with 1% saturated NH<sub>3</sub> solution) gave 2-(1,9-dithia-5,13-diazacyclohexadec-5-yl)ethoxybenzene **4** as a clear oil (1.04 g, 52%). MS (LSI) ( $M + H$ )<sup>+</sup> found 383.2187.  $C_{20}H_{34}N_2O_2S_2$  requires 383.2191;  $\delta_H$  (CDCl<sub>3</sub>, 300 MHz) *ca.* 6.9 (5 H, m, OPh), 4.02 (2 H, t, *J* 6.0, CH<sub>2</sub>OPh), 2.84 (2 H, t, *J* 6.0, NCH<sub>2</sub>CH<sub>2</sub>OPh), 2.74 (4 H, t, *J* 7.0, CH<sub>2</sub>NH), 2.65 (4 H, t, *J* 7.2, CH<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>O), 2.61 (8 H, t, *J* 7.1, CH<sub>2</sub>SCH<sub>2</sub>), 1.78 (8 H, quin, *J*  $\approx$  7, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N);  $\delta_C$  (CDCl<sub>3</sub>, 75 MHz) 158.7, 129.4, 120.6, 114.4, 66.3, 53.4, 53.3, 47.2, 29.8, 29.7, 28.9, 27.8.

**5-Benzyl-1,9-dithia-5,13-diazacyclohexadecaneplatinum(II) hexafluorophosphate [PtL](PF<sub>6</sub>)<sub>2</sub> (L = 3).** A solution of bis(benzonitrile)dichloroplatinum(II) (0.043 g, 0.09 mmol) in acetonitrile (2 cm<sup>3</sup>) was added to a solution of ammonium hexafluorophosphate (0.059 g, 0.36 mmol) in acetonitrile (2 cm<sup>3</sup>). The solution was heated to boiling and **3** (0.032 g, 0.09 mmol) in dichloromethane (3 cm<sup>3</sup>) was added. The solution was refluxed for 24 h. The solution was allowed to cool, filtered, and the solvent removed under vacuum. The residue was dissolved in acetone (3 cm<sup>3</sup>), and propan-2-ol (1 cm<sup>3</sup>) was added. Slow evaporation of the solvent mixture at room temperature to a

volume of *ca.* 1 cm<sup>3</sup> resulted in the formation of a colourless crystalline product which was filtered off, washed with propan-2-ol and diethyl ether then dried under vacuum to give [PtL](PF<sub>6</sub>)<sub>2</sub> (L = 3) (0.045 g, 60%); (Found: C, 27.38; H, 3.86; N 3.31. Calc. for C<sub>19</sub>H<sub>32</sub>F<sub>12</sub>N<sub>2</sub>PtS<sub>2</sub>: C, 27.24; H, 3.85; N, 3.34%). MS(ESI) ( $M - PF_6$ )<sup>+</sup> found 692.1293. C<sub>19</sub>H<sub>32</sub>F<sub>6</sub>N<sub>2</sub>PPtS<sub>2</sub> requires, 692.1271; MS (+ESI); *m/z* = 692.1 ([ $M - PF_6$ ]<sup>+</sup>, [C<sub>19</sub>H<sub>32</sub>F<sub>6</sub>N<sub>2</sub>PPtS<sub>2</sub>]<sup>+</sup>), 546.2 ([ $M - 2PF_6 - H$ ]<sup>+</sup>, [C<sub>19</sub>H<sub>31</sub>N<sub>2</sub>PtS<sub>2</sub>]<sup>+</sup>), 455.1 ([ $M - 2PF_6 - H - C_7H_7$ ]<sup>+</sup>, [C<sub>12</sub>H<sub>24</sub>N<sub>2</sub>PtS<sub>2</sub>]<sup>+</sup>), 273.6 ([ $M - 2PF_6$ ]<sup>2+</sup>, [C<sub>19</sub>H<sub>32</sub>N<sub>2</sub>PtS<sub>2</sub>]<sup>2+</sup>);  $\delta_H$  (acetone-*d*<sub>6</sub>, 200 MHz) 8.16–8.12 (2H, m, *o*-Ph), 7.53–7.49 (3H, m, *m*-,*p*-Ph), 4.37 (2H, s, PhCH<sub>2</sub>), 3.64–2.61 (16H, br m, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 2.61–2.34 (8H, br, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N).

**5-Benzyl-1,9-dithia-5,13-diazacyclohexadecanepalladium(II) hexafluorophosphate [PdL](PF<sub>6</sub>)<sub>2</sub> (L = 3).** A suspension of palladium(II) chloride (0.032 g, 0.18 mmol) in acetonitrile (5 cm<sup>3</sup>) was heated to boiling to yield an orange solution of Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub>. Ammonium hexafluorophosphate (0.116 g, 0.71 mmol) in acetonitrile (2 cm<sup>3</sup>) was added to the solution followed by **3** (0.063 g, 0.18 mmol) in acetonitrile (2 cm<sup>3</sup>). The reaction solution was heated at reflux for 30 min. The reaction mixture was allowed to cool, filtered and the filtrate evaporated to dryness under vacuum. The residue was dissolved in acetone (5 cm<sup>3</sup>) then propan-2-ol (2 cm<sup>3</sup>) was added. Slow evaporation of the solvent mixture at room temperature to a volume of *ca.* 2 cm<sup>3</sup> resulted in the formation of the product as an orange crystalline solid which was filtered off, washed with propan-2-ol and diethyl ether, then dried under vacuum to give [PdL](PF<sub>6</sub>)<sub>2</sub> (L = 3) (0.077 g, 57%); (Found: C, 30.43; H, 4.27; N 3.71. Calc for C<sub>19</sub>H<sub>32</sub>F<sub>12</sub>N<sub>2</sub>PdS<sub>2</sub>: C, 30.47; H, 4.31; N, 3.74%). MS (ESI) ( $M - PF_6$ )<sup>+</sup> found 603.0651. C<sub>19</sub>H<sub>32</sub>F<sub>12</sub>N<sub>2</sub>PdS<sub>2</sub> requires 603.0680; MS (+ESI); *m/z* = 603.1 ([ $M - PF_6$ ]<sup>+</sup>, [C<sub>19</sub>H<sub>32</sub>F<sub>6</sub>N<sub>2</sub>PPdS<sub>2</sub>]<sup>+</sup>), 457.1 ([ $M - 2PF_6 - H$ ]<sup>+</sup>, [C<sub>19</sub>H<sub>31</sub>N<sub>2</sub>PdS<sub>2</sub>]<sup>+</sup>), 366.1 ([ $M - 2PF_6 - H - C_7H_7$ ]<sup>+</sup>, [C<sub>12</sub>H<sub>24</sub>N<sub>2</sub>PdS<sub>2</sub>]<sup>+</sup>), 229.1 ([ $M - 2PF_6$ ]<sup>2+</sup>, [C<sub>19</sub>H<sub>32</sub>N<sub>2</sub>PdS<sub>2</sub>]<sup>2+</sup>);  $\delta_H$  (CD<sub>3</sub>CN, 200 MHz) 8.02–7.95 (2H, m, *o*-Ph), 7.61–7.57 (3H, m, *m*-,*p*-Ph), 3.90 (2H, s, PhCH<sub>2</sub>), 3.35–2.56 (16H, br m, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 2.38–2.14 (8H, br, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N).

**2-(1,9-Dithia-5,13-diazacyclohexadec-5-yl)ethoxybenzene-platinum(II) hexafluorophosphate [PtL](PF<sub>6</sub>)<sub>2</sub> (L = 4).** Bis(benzonitrile)dichloroplatinum(II) (0.041 g, 0.09 mmol) in acetonitrile (5 cm<sup>3</sup>) was heated to boiling and **4** (0.033 g, 0.09 mmol) in dichloromethane (2 cm<sup>3</sup>) was then added. The reaction solution was heated under reflux for a further 24 h. The solution was then allowed to cool, filtered, and the solvent removed under vacuum. The residue was dissolved in acetonitrile (3 cm<sup>3</sup>), and a solution of ammonium hexafluorophosphate (0.059 g, 0.36 mmol) in methanol (1 cm<sup>3</sup>) was added. The solvent was removed under vacuum and the residue then dissolved in acetone. This solution was filtered and propan-2-ol (1 cm<sup>3</sup>) was added to the filtrate. Slow evaporation of the solvent mixture at room temperature to a volume of *ca.* 1 cm<sup>3</sup> resulted in the formation of the product as a colourless crystalline solid. This was filtered, washed with propan-2-ol and diethyl ether and dried under vacuum to give [PtL](PF<sub>6</sub>)<sub>2</sub> (L = 4) (0.055 g, 70%); (Found: C, 28.02; H, 4.27; N 3.24. Calc. for C<sub>20</sub>H<sub>34</sub>F<sub>12</sub>N<sub>2</sub>OPtS<sub>2</sub>: C, 27.69; H, 3.95; N, 3.23%). MS (ESI) ( $M - PF_6$ )<sup>+</sup> found 722.1390. C<sub>20</sub>H<sub>34</sub>F<sub>12</sub>N<sub>2</sub>OPtS<sub>2</sub> requires 722.1376; MS (+ESI); *m/z* = 722.1 ([ $M - PF_6$ ]<sup>+</sup>, [C<sub>20</sub>H<sub>34</sub>F<sub>6</sub>N<sub>2</sub>OPPtS<sub>2</sub>]<sup>+</sup>), 576.2 ([ $M - 2PF_6 - H$ ]<sup>+</sup>, [C<sub>20</sub>H<sub>33</sub>N<sub>2</sub>OPtS<sub>2</sub>]<sup>+</sup>), 288.6 ([ $M - 2PF_6$ ]<sup>2+</sup>, [C<sub>20</sub>H<sub>34</sub>N<sub>2</sub>OPtS<sub>2</sub>]<sup>2+</sup>);  $\delta_H$  (CD<sub>3</sub>CN, 200 MHz) 7.40–7.32 (2H, m, *o*-Ph), 7.06–6.99 (3H, m, *m*-,*p*-Ph), 4.66 (2H, br, OCH<sub>2</sub>CH<sub>2</sub>N), 3.42 (2H, br, OCH<sub>2</sub>CH<sub>2</sub>N), 3.30–2.66 (16H, br m, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 2.37–2.14 (8H, br, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N).

**2-(1,9-Dithia-5,13-diazacyclohexadec-5-yl)ethoxybenzene-palladium(II) hexafluorophosphate [PdL](PF<sub>6</sub>)<sub>2</sub> (L = 4).** To

**Table 2** Electrospray mass spectral data<sup>a</sup> of the trimers [M<sub>3</sub>L](PF<sub>6</sub>)<sub>6</sub> where M = Pt, Pd

Ion	[Pt <sub>3</sub> L](PF <sub>6</sub> ) <sub>6</sub> (L = 1)	[Pd <sub>3</sub> L](PF <sub>6</sub> ) <sub>6</sub> (L = 1)	[Pt <sub>3</sub> L](PF <sub>6</sub> ) <sub>6</sub> (L = 2)	[Pd <sub>3</sub> L](PF <sub>6</sub> ) <sub>6</sub> (L = 2)
[M – 2PF <sub>6</sub> – H] <sup>+</sup>	—	—	—	1888.7
[M – 3PF <sub>6</sub> – 2H] <sup>+</sup>	—	—	—	1741.0
[M – 4PF <sub>6</sub> – 3H] <sup>+</sup>	—	—	—	—
[M – 5PF <sub>6</sub> – 4H] <sup>+</sup>	—	—	—	—
[M – 6PF <sub>6</sub> – 5H] <sup>+</sup>	—	—	—	—
[M – 2PF <sub>6</sub> ] <sup>2+</sup>	1032.6	899.0	1077.9	944.8
[M – 3PF <sub>6</sub> – H] <sup>2+</sup>	959.7	826.1	1005.0	871.9
[M – 4PF <sub>6</sub> – 2H] <sup>2+</sup>	886.4	753.1	932.0	798.9
[M – 5PF <sub>6</sub> – 3H] <sup>2+</sup>	813.1	680.1	859.1	725.5
[M – 6PF <sub>6</sub> – 4H] <sup>2+</sup>	—	607.1	—	652.5
[M – 3PF <sub>6</sub> ] <sup>3+</sup>	639.7	551.0	670.3	581.6
[M – 4PF <sub>6</sub> – H] <sup>3+</sup>	591.5	502.4	621.7	532.2
[M – 5PF <sub>6</sub> – 2H] <sup>3+</sup>	542.3	—	572.5	484.2
[M – 6PF <sub>6</sub> – 3H] <sup>3+</sup>	494.5	405.1	524.4	435.3
[M – 4PF <sub>6</sub> ] <sup>4+</sup>	—	—	466.5	399.9
[M – 5PF <sub>6</sub> – H] <sup>4+</sup>	—	—	430.1	363.7
[M – 6PF <sub>6</sub> – 2H] <sup>4+</sup>	—	304.1	—	326.8
[M – 5PF <sub>6</sub> ] <sup>5+</sup>	—	—	344.0	290.9
[M – 6PF <sub>6</sub> – H] <sup>5+</sup>	—	243.4	—	—

<sup>a</sup> Samples were run on a mass spectrometer with a mass range of  $m/z = 0$ –2000, hence any (singly charged) species with  $m/z > 2000$  were not able to be observed.

palladium(II) diacetate (0.018 g, 0.08 mmol) in dichloromethane (5 cm<sup>3</sup>) was added **4** (0.029 g, 0.08 mmol) in dichloromethane (5 cm<sup>3</sup>). The solution was heated under reflux for 1 h. On cooling the solution, the solvent was removed under vacuum and the glassy orange residue was dissolved in methanol (3 cm<sup>3</sup>). This solution was added to a large excess of ammonium hexafluorophosphate in methanol (1 cm<sup>3</sup>) and water (1 cm<sup>3</sup>). Acetone (3 cm<sup>3</sup>) was added to this solution; slow evaporation of the solvent at room temperature resulted in the precipitation of the product as an orange crystalline solid. This was filtered off, washed with propan-2-ol and diethyl ether, then dried under vacuum to give [PdL](PF<sub>6</sub>)<sub>2</sub> (L = **4**) (0.043 g, 69%); (Found: C, 30.84; H, 4.78; N 3.61. Calc. for C<sub>20</sub>H<sub>34</sub>F<sub>12</sub>N<sub>2</sub>O<sub>2</sub>PdS<sub>2</sub>: C, 30.84; H, 4.40; N, 3.60%). MS (ESI) (M – PF<sub>6</sub>)<sup>+</sup> found 633.0787. C<sub>20</sub>H<sub>34</sub>F<sub>12</sub>N<sub>2</sub>O<sub>2</sub>PdS<sub>2</sub> requires 633.0787; MS (+ESI):  $m/z = 633.1$  ([M – PF<sub>6</sub>]<sup>+</sup>, [C<sub>20</sub>H<sub>34</sub>F<sub>6</sub>N<sub>2</sub>OPdS<sub>2</sub>]<sup>+</sup>), 487.1 ([M – 2PF<sub>6</sub> – H]<sup>+</sup>, [C<sub>20</sub>H<sub>33</sub>N<sub>2</sub>OPdS<sub>2</sub>]<sup>+</sup>), 224.1 ([M – 2PF<sub>6</sub>]<sup>2+</sup>, [C<sub>20</sub>H<sub>34</sub>N<sub>2</sub>OPdS<sub>2</sub>]<sup>2+</sup>);  $\delta_H$  (acetone-*d*<sub>6</sub>, 200 MHz) 7.38–7.30 (2H, m, *o*-Ph), 7.11–6.98 (3H, m, *m*-,*p*-Ph), 4.79 (2H, tr, OCH<sub>2</sub>CH<sub>2</sub>N), 3.61 (2H, br, OCH<sub>2</sub>CH<sub>2</sub>N), 3.38–2.76 (16H, br m, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 2.56–2.35 (8H, br, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N).

**1,3,5-Tris[2-(1,9-dithia-5,13-diazacyclohexadec-5-yl)ethoxy]-benzenetriplatinum(II) hexafluorophosphate [Pt<sub>3</sub>L](PF<sub>6</sub>)<sub>6</sub> (L = 2).** Bis(benzonitrile)dichloroplatinum(II) (0.037 g, 0.09 mmol) in acetonitrile (6 cm<sup>3</sup>) was added to ammonium hexafluorophosphate (0.103 g, 0.63 mmol) in acetonitrile (2 cm<sup>3</sup>). The solution was heated to boiling and **3** (0.026 g, 0.03 mmol) in dichloromethane (3 cm<sup>3</sup>) was added. The reaction solution was refluxed for 24 h. The solution was cooled, filtered, and the solvent removed under vacuum. The residue was washed with water to remove excess NH<sub>4</sub>PF<sub>6</sub> and then dissolved in acetone (6 cm<sup>3</sup>), propan-2-ol (1 cm<sup>3</sup>) and water (1 cm<sup>3</sup>) was then added. Slow evaporation of the solvent mixture at room temperature to a volume of ca. 2 cm<sup>3</sup> resulted in the formation of the product as a white powder. This was filtered off, washed with propan-2-ol and diethyl ether, then dried under vacuum to give [Pt<sub>3</sub>L](PF<sub>6</sub>)<sub>6</sub> (L = 2) (0.038 g, 60%). MS (ESI) (M – 2PF<sub>6</sub>)<sup>2+</sup> found 1077.6496. C<sub>48</sub>H<sub>90</sub>F<sub>36</sub>N<sub>6</sub>O<sub>3</sub>P<sub>6</sub>Pt<sub>3</sub>S<sub>6</sub> requires 1077.6441; detailed MS (+ESI) assignments are given in Table 2;  $\delta_H$  (CD<sub>3</sub>CN, 200 MHz) 6.36 (3H, br, Ph), 4.64 (6H, br, OCH<sub>2</sub>CH<sub>2</sub>N), 3.47 (6H, br, OCH<sub>2</sub>CH<sub>2</sub>N), 3.40–2.79 (48H, br m, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 2.34–2.11 (24H, br, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N).

**1,3,5-Tris[2-(1,9-dithia-5,13-diazacyclohexadec-5-yl)ethoxy]-benzenetriplatinum(II) hexafluorophosphate [Pd<sub>3</sub>L](PF<sub>6</sub>)<sub>6</sub> (L = 2).** To palladium(II) diacetate (0.017 g, 0.09 mmol) in dichloromethane (5 cm<sup>3</sup>) was added **2** (0.025 g, 0.03 mmol) in dichloromethane (1 cm<sup>3</sup>). The reaction was heated under reflux for 30 min. The solvent was then removed under vacuum to yield a glassy orange residue which was dissolved in methanol (3 cm<sup>3</sup>). To this solution was added a large excess of ammonium hexafluorophosphate in methanol (3 cm<sup>3</sup>). The resulting orange precipitate was filtered off and dissolved in acetone (3 cm<sup>3</sup>). This solution was filtered. Addition of trifluoroethanol (1 cm<sup>3</sup>) and slow evaporation of the solvent at room temperature resulted in the formation of the product as an orange powder. This was filtered off, washed with propan-2-ol and diethyl ether, then dried under vacuum to give [Pd<sub>3</sub>L](PF<sub>6</sub>)<sub>6</sub> (L = 2) (0.029 g, 53%). MS (ESI) (M – 2PF<sub>6</sub>)<sup>2+</sup> found 945.0530. C<sub>48</sub>H<sub>90</sub>F<sub>36</sub>N<sub>6</sub>O<sub>3</sub>P<sub>6</sub>Pd<sub>3</sub>S<sub>6</sub> requires 945.0540; detailed MS (+ESI) assignments are given in Table 2;  $\delta_H$  (acetone-*d*<sub>6</sub>, 200 MHz) 6.41 (3H, br, Ph), 4.67 (6H, br, OCH<sub>2</sub>CH<sub>2</sub>N), 3.61 (6H, br, OCH<sub>2</sub>CH<sub>2</sub>N), 3.50–2.83 (48H, br m, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 2.50–2.38 (24H, br, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N).

**1,3,5-Tris[1,9-dithia-5,13-diazacyclohexadec-5-yl)methyl]-benzenetriplatinum(II) hexafluorophosphate [Pt<sub>3</sub>L](PF<sub>6</sub>)<sub>6</sub> (L = 1).** This was obtained as a white solid by a similar procedure to that described for [Pt<sub>3</sub>L](PF<sub>6</sub>)<sub>6</sub> (L = 2) using **1** (0.014 g, 0.02 mmol), bis(benzonitrile)dichloroplatinum(II) (0.022 g, 0.05 mmol), ammonium hexafluorophosphate (0.061 g, 0.37 mmol) in acetonitrile (5 cm<sup>3</sup>) and acetonitrile (2 cm<sup>3</sup>) to give [Pt<sub>3</sub>L](PF<sub>6</sub>)<sub>6</sub> (L = 1) (0.014 g, 38%). MS (ESI) (M – 2PF<sub>6</sub>)<sup>2+</sup> found 1032.6282. C<sub>45</sub>H<sub>84</sub>F<sub>36</sub>N<sub>6</sub>P<sub>6</sub>Pt<sub>3</sub>S<sub>6</sub> requires 1032.6260; detailed MS (+ESI) assignments are given in Table 2;  $\delta_H$  (CD<sub>3</sub>CN, 200 MHz) 7.81 (3H, br, Ph), 4.55–4.22 (6H, br, PhCH<sub>2</sub>), 3.30–2.75 (48H, br m, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 2.42–2.08 (24H, br, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N).

**1,3,5-Tris[1,9-dithia-5,13-diazacyclohexadec-5-yl)methyl]-benzenetriplatinum(II) hexafluorophosphate [Pd<sub>3</sub>L](PF<sub>6</sub>)<sub>6</sub> (L = 1).** This was obtained as an orange solid by a similar procedure to that described for [Pd<sub>3</sub>L](PF<sub>6</sub>)<sub>6</sub> (L = 2) using **1** (0.018 g, 0.02 mmol), palladium(II) diacetate (0.013 g, 0.06 mmol) and dichloromethane (6 cm<sup>3</sup>) and subsequent addition of excess ammonium hexafluorophosphate in methanol (3 cm<sup>3</sup>) to give [Pd<sub>3</sub>L](PF<sub>6</sub>)<sub>6</sub> (L = 1) (0.027 g, 65%). MS (ESI) (M – 2PF<sub>6</sub>)<sup>2+</sup> found 899.0391. C<sub>45</sub>H<sub>84</sub>F<sub>36</sub>N<sub>6</sub>P<sub>6</sub>Pd<sub>3</sub>S<sub>6</sub> requires 899.0387;

detailed MS (+ESI) assignments are given in Table 2;  $\delta_{\text{H}}$  ( $\text{CD}_3\text{CN}$ , 200 MHz) 7.71 (3H, br, Ph), 4.34 (6H, br,  $\text{PhCH}_2$ ), 3.25–2.52 (48H, br m,  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{N}$ ), 2.39–2.04 (24H, br,  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{N}$ ).

## Results and discussion

### Metal complex synthesis

Complexes of type  $[\text{ML}](\text{PF}_6)_2$  ( $\text{M} = \text{Pd}$  or  $\text{Pt}$ ,  $\text{L} = \mathbf{3}$  or  $\mathbf{4}$ ) and  $[\text{M}_3\text{L}](\text{PF}_6)_6$  ( $\text{M} = \text{Pd}$  or  $\text{Pt}$ ,  $\text{L} = \mathbf{1}$  or  $\mathbf{2}$ ) were isolated. The palladium(II) complexes were prepared from either  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  [formed *in situ* from palladium(II) chloride and acetonitrile] in the presence of excess hexafluorophosphate, or from palladium(II) acetate followed by addition of excess ammonium hexafluorophosphate. The bis-benzonitrile complex of platinum(II) chloride in the presence of an excess of hexafluorophosphate was used for the synthesis of the corresponding platinum(II) complexes.

Other than chemical shift differences, the  $^1\text{H}$  NMR spectra of corresponding palladium and platinum complexes are essentially identical. While consistent with the expected structures, the respective spectra contain aliphatic regions that are characterised by overlapping resonances, with there being a tendency for these resonances to be broadened. Such broadening may reflect the presence of molecular motion which is somewhat slow on the NMR timescale. The existence of two or more isomeric species in solution is also a possibility. With respect to the latter, thioether sulfur stereocentres have been well documented to be capable of thermodynamically controlled pyramidal inversion in solution<sup>15–18</sup> with, for example, the barriers for inversion typically lying in the range 50–70  $\text{kJ mol}^{-1}$  for thioether–palladium systems.<sup>19</sup> McCrindle *et al.*<sup>8</sup> have observed the presence of two major isomers for the palladium and platinum complexes of the  $\text{N}_2\text{S}_2$  macrocycle 3,3,7,7,11,11,15,15-octamethyl-1,9-dithia-5,13-diazacyclohexadecane (incorporating the same 16-membered macrocyclic core as used in this study but with two methyl substituents on the central methylene carbon in each link between donor atoms). It was shown in this study that there are five main configurations predicted for the coordinated ligand; these depend on the orientations of the sulfur lone pairs and NH protons with respect to the ring plane (assuming a square-planar coordination geometry). Of these five, two were found to predominate.

### X-Ray structure determination

While suitable crystals for X-ray structure determination of the complexes of the tri-linked ligand species proved elusive, the room-temperature single crystal X-ray structure of the single-ring complex,  $[\text{Pd}(\text{L})](\text{PF}_6)_2$  ( $\text{L} = \mathbf{3}$ ), was obtained. The results are consistent with the stoichiometry and connectivity as given above, one formula unit, comprising cation and two hexafluorophosphate anions (one disordered), devoid of crystallographic symmetry, comprising the asymmetric unit of the structure. The structure confirms that a single isomer is present in the solid state (Fig. 1). Selected bond lengths and angles are listed in Table 1. The geometry about the ‘planar’, four-coordinate metal atom is slightly puckered; for the  $\text{N}_2\text{S}_2$  plane,  $\chi^2 = 3.5 \times 10^3$ , deviations  $\delta\text{N}(10,20)$  are 0.111(3), 0.138(3),  $\delta\text{S}(14,24) = 0.018(1) (\times 2)$  with  $\delta\text{Pd}$  0.024(1) Å. A significant difference in the pair of Pd–N distances may be ascribable to differences in nitrogen quaternization, but may also be associated with differences in associated chelate ring conformations. Pd–S distances are very similar to those found in the structures of two palladium complexes of the related octa-methylated macrocyclic derivative mentioned above. The first of these<sup>8</sup> has a Pd–S distance of 2.307(1) Å and consists of an array with crystallographic *i* symmetry, obviously with pairs of obligate equal Pd–S, Pd–N distances whereas the second<sup>9</sup> contains Pd–S 2.290(5)–2.297(6), [ave. 2.294(3) Å]. The present array

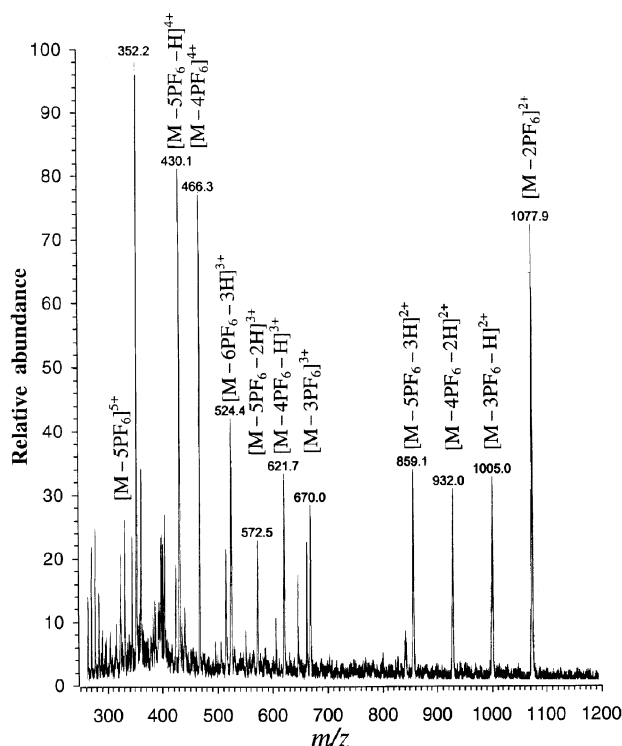


Fig. 2 Mass spectrum of  $[\text{Pt}_3\text{L}](\text{PF}_6)_6$  ( $\text{L} = \mathbf{2}$ ).

resembles the second structure<sup>9</sup> in that the N pendants (H, bz) and sulfur lone pairs all lie to the same side of the macrocycle, one of the *ortho*-phenyl hydrogens possibly agostic with the palladium  $[\text{H}(2) \cdots \text{Pd}$  (2.70 Å)] [see Fig. 1]. The ring conformations of the octa-methylated derivatives are diverse; these of the above first structure<sup>8</sup> (in which the NH hydrogens are necessarily to either side of the ring) are all chairs, whereas those of the second—containing two independent  $[\text{PdL}]^{2+}$  cations<sup>9</sup>—are 2 : 2 and 1 : 3 chair : (twisted) boat, the chairs being adjacent in the 2 : 2 cation of the pair found in that structure. The present array is of the 1 : 3 combination, with the ring containing C(21–23) the ‘chair’.

### Mass spectral studies

The present single ring species yielded electrospray mass spectra in which peaks corresponding to  $[\text{M} - \text{PF}_6]^+$ ,  $[\text{M} - 2\text{PF}_6 - \text{H}]^+$  and  $[\text{M} - 2\text{PF}_6]^{2+}$  were prominent. The mass spectra of the corresponding tri-linked species were more complex but were still readily interpreted in terms of fragmentation patterns involving a range of species of type  $[\text{M} - n\text{PF}_6]^{n+}$  and  $[\text{M} - n\text{PF}_6 - m\text{H}]^{(n-m)+}$ . Most of the possible ion fragments of this type (up to the 5+ ions) were observed. The spectrum of  $\text{Pt}_3\text{L}(\text{PF}_6)_6$  ( $\text{L} = \mathbf{2}$ ) is shown in Fig. 2, with the assignments for the observed fragments for this and the other trinuclear species given in Table 2. Groups of similarly charged ions are observed; for example, the cluster of dipositive ions shows consecutive loss of hexafluorophosphate along with hydrogen and moves from  $[\text{M} - 2\text{PF}_6]^{2+}$  at  $m/z$  1077.9 to  $[\text{M} - 5\text{PF}_6 - 3\text{H}]^{2+}$  at  $m/z$  859.1. Expansion of the peaks corresponding to  $[\text{M} - n\text{X}]^{n+}$  (where  $n = 2$ –5) clearly shows peak separations from 0.5 to 0.2 as the charge on the ions increases from 2+ to 5+. As additional characterisation, the spectrum of the  $[\text{M} - 2\text{PF}_6]^{2+}$  ion was also successfully simulated; this confirmed the expected complex pattern produced by the several isotopes of platinum and also the fact that there are three metals present in the system. A similar overall result was also obtained for the other trinuclear platinum species  $[\text{Pt}_3\text{L}](\text{PF}_6)_6$  ( $\text{L} = \mathbf{1}$ ). The palladium complexes  $[\text{Pd}_3\text{L}](\text{PF}_6)_6$  ( $\text{L} = \mathbf{1}$  and  $\mathbf{2}$ ) also showed similar behaviour. It was demonstrated that individual ions of the type discussed above can be further fragmented using MS–MS

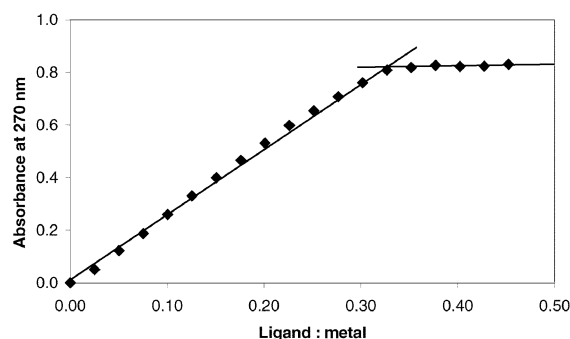


Fig. 3 Spectrophotometric titration curve for the addition of **2** to palladium(II) chloride in acetonitrile.

experiments. For example, in the spectrum of  $M = [Pd_3L](PF_6)_6$  ( $L = 2$ ), the  $[M - 2PF_6]^{2+}$  ion ( $m/z = 944.8$ ) under suitable MS–MS conditions was shown to lose additional  $PF_6^-$  counter ions. Under conditions where full fragmentation was induced, this ion disappeared from the overall spectrum with the generation of a series of dipositive fragments of type  $[M - 3PF_6 - H]^{2+}$  ( $m/z = 871.3$ ),  $[M - 4PF_6 - 2H]^{2+}$  ( $m/z = 797.8$ ),  $[M - 5PF_6 - 3H]^{2+}$  ( $m/z = 725.5$ ) and  $[M - 6PF_6 - 4H]^{2+}$  ( $m/z = 652.5$ ). It appears that the molecules  $[M_3L](PF_6)_6$  ( $M = Pd, Pt$ ;  $L = 1, 2$ ) lose 1–5  $PF_6$  counter ions, to generate the 1+ to 5+ species, and then that these undergo subsequent fragmentation by loss of additional counter ions accompanied in each case by loss of hydrogen. In the many MS–MS experiments carried out, in no case did a species of a specific charge give rise to a species of a higher charge. In addition, no species were observed corresponding to the incorporation of less than three metal ions, providing confirmatory evidence that all three metal-binding sites are occupied in these complexes.

#### Spectrophotometric titrations

Spectrophotometric titrations were employed to follow palladium(II) and platinum(II) binding by the tri-linked ligands **1** and **2**. The addition of **2** in acetonitrile to palladium(II) chloride in acetonitrile was characterised by the build up of a shoulder at 270 nm, the change in absorbance at this wavelength was used to derive the plot shown in Fig. 3. The latter shows a sharp ligand to metal endpoint of 1 : 3, consistent with the formation of the expected trinuclear complex species. Similarly sharp 1 : 3 ligand to metal end-points were obtained for the remaining titrations involving palladium and/or platinum chloride and **1** and **2**.

#### Concluding remarks

We have shown that the palladium(II) and platinum(II) chemistry of the tri-linked species **1** and **2** parallels that of the related single ring macrocycles **3** and **4**. For the complexes of the former ligands, the mass spectral and spectrophotometric results confirm that a metal ion is bound to each of the linked macrocyclic rings, spaced by the central tribenzyl or phloroglucinol hubs. The X-ray crystal structure of  $[PdL](PF_6)_2$  ( $L = 3$ ) confirms that the palladium is coordinated in the anticipated square planar manner.

The above results provide a basis for extending the investigation to a study of the palladium and platinum complexes of larger (dendritic) systems composed of the present tri-linked

frameworks to which additional  $N_2S_2$ -donor macrocyclic units have been appended. An investigation of this type is currently in progress and the results of this study will be presented in due course.

#### Acknowledgements

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