

# Self-assembly of 2:2 and 3:3 metallamacrocyclic complexes of platinum(II) with symmetrical, bipodal $N',N',N''N''$ -tetraalkyl- $N,N''$ -phenylenedicarbonylbis(thiourea)

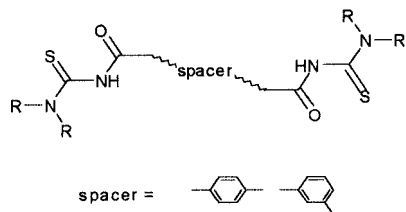
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Bipodal  $N',N',N''N''$ -tetraalkyl- $N,N''$ -phenylenedicarbonylbis(thiourea) readily 'self-assemble into'  $Pt_2L_2$  and  $Pt_3L_3$  metallamacrocyclic complexes depending on whether the  $S,O$  chelating moieties are *meta* or *para* relative to each other in the ligand. Thus treatment of  $PtCl_4^{2-}$  with one equivalent of 3,3,3',3'-tetra(*n*-butyl)-1,1'-terephthaloylbis(thiourea),  $\{H_2L^1\}_2$ , leads to the exclusive formation of the *cis*- $[Pt(L^1-S,O)]_3$  complex, while 3,3,3',3'-tetraethyl-1,1'-isophthaloylbis(thiourea),  $\{H_2L^2\}_2$ , yields only the *cis*- $[Pt(L^2-S,O)]_2$  complex. The *cis*- $[Pt(L^1-S,O)]_3$  complex forms extremely friable crystals, necessitating X-ray data collection in mother-liquor, the lattice of which was found to contain chloroform, water and ethanol molecules as 'guests'. By contrast, the sparingly soluble diethyl-substituted  $Pt_2L_2$  complex does not include solvent molecules in the crystal lattice.

The pronounced affinity of  $N$ -aroyl- $N',N'$ -dialkylthioureas as ligands for the 'softer' transition metal ions is well known,<sup>1</sup> and in recent years these deceptively simple ligands have attracted renewed interest in view of their selective co-ordination of the platinum group metals (PGMs). Of particular interest is the analytical utility of these ligands which are useful in the solvent extraction<sup>2</sup> and high-performance chromatographic separation of the PGMs,<sup>3</sup> as well as in the pre-concentration and determination of palladium at ultra-trace levels in various matrices.<sup>4</sup> As part of our interest in the synthesis of new ligands for the PGMs based on the  $RC(O)NHC(S)N(R')_2$  motif, as well as the elucidation of the fundamental co-ordination chemistry of such ligands toward  $Pt(II)$  and  $Pd(II)$ ,<sup>5</sup> we have prepared a series of symmetrical bipodal ligands of the general structure shown below, and explored their co-ordination of  $Pt(II)$ , with a view to preparing new metallamacrocyclic complexes. A survey of the published literature reveals only two reports of similar ligands and their co-ordination to some transition metals: Hoyer *et al.*<sup>5</sup> reported the crystal structure of a  $Ni_3L_3$  complex ( $L = 3,3,3',3'$ -tetraethyl-1,1'-terephthaloylbis(thioureaato) anion) as well as some less well characterized complexes of  $Cu(II)$ ,  $Zn(II)$ ,  $Hg(II)$  and  $Pd(II)$ , the latter three being reported as polymeric  $(ML)_n$  complexes of low solubility. König *et al.*<sup>6</sup> prepared some  $Ni(II)$ ,  $Cu(II)$ ,  $Pd(II)$  and  $Pt(II)$  complexes with a series of 3,3,3',3'-tetraalkyl-1,1'-alkanedicarbonylbis(thiourea) ligands but no structural details are available. Only in the case of 3,3,3',3'-tetraethyl-1,1'-adipoylbis(thiourea) were complexes with stoichiometry  $Pd_3L_3$  and  $Pt(H_2L)Cl_2$  reported.



By exploiting the overwhelming tendency of the  $RC(O)NHC(S)N(R')_2$  moiety (with loss of a proton), to form stable planar *cis*-chelates of  $Pt(II)$ ,<sup>7</sup> it should be possible to assemble a variety

of metallamacrocycles. In the case of the ligands 3,3,3',3'-tetra(*n*-butyl)-1,1'-terephthaloylbis(thiourea),  $\{H_2L^1\}_2$ , and 3,3,3',3'-tetraethyl-1,1'-isophthaloylbis(thiourea),  $\{H_2L^2\}_2$ , derived from terephthalic and isophthalic acids respectively, consideration of models suggests that these ligands are ideal for the self-assembly of new metallamacrocyclic complexes. Thus for the  $\{H_2L^2\}_2$  ligand, models suggest that only 2:2 and 6:6 complexes appear favorable, while for the  $\{H_2L^1\}_2$  ligand only a 3:3 complex appears easily conceivable as shown schematically below.

We here report the facile preparation and crystal structures of the first example of a 2:2 *cis*- $[Pt(L^2-S,O)]_2$  complex **1**, as well as that of the 3:3 *cis*- $[Pt(L^1-S,O)]_3$  **2** metallamacrocyclic complex, shown in Fig. 1 and 2 respectively. These complexes are formed in high yield (89% **2** and 96% **1**) showing that these metallamacrocycles are the exclusive product obtained from the treatment of  $PtCl_4^{2-}$  with one mole-equivalent of the bipodal ligand.

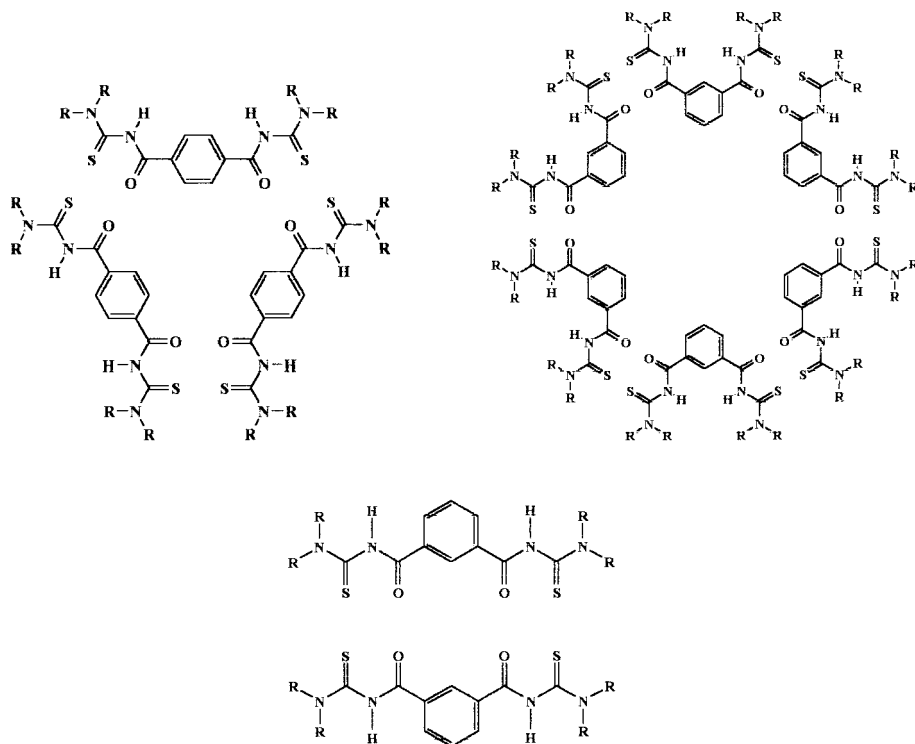
## Experimental

### Preparative methods

The ligands 3,3,3',3'-tetra(*n*-butyl)-1,1'-terephthaloylbis(thiourea)  $\{H_2L^1\}_2$  and 3,3,3',3'-tetraethyl-1,1'-isophthaloylbis(thiourea)  $\{H_2L^2\}_2$  were prepared according to the method of Douglass and Dains,<sup>8</sup> and were purified by recrystallization from chloroform-ethanol mixtures. All reagents were commercially available and were used without further purification.

<sup>1</sup>H and <sup>195</sup>Pt NMR spectra were recorded in 5 mm tubes in  $CDCl_3$  solution using a Varian Unity-400 spectrometer operating at 400 and 85.85 MHz respectively. <sup>1</sup>H spectra were recorded at 25 °C, while <sup>195</sup>Pt chemical shifts were measured at 30 °C relative to the usual reference of external  $H_2PtCl_6$  [500 mg in 1 cm<sup>3</sup> 30% (v/v)  $D_2O$ -1 M HCl].<sup>9</sup>

**3,3,3',3'-Tetra(*n*-butyl)-1,1'-terephthaloylbis(thiourea),  $\{H_2L^1\}_2$ .** Yield 96%, mp 154–155 °C. Found: C, 61.82; H, 8.47; N, 11.23; S, 12.68.  $C_{26}H_{42}N_4O_2S_2$  requires C, 61.61; H, 8.37; N, 11.06; S, 12.65%. <sup>1</sup>H NMR (200 MHz,  $CDCl_3$ ):  $\delta$  0.96 (t + t, 12H), 1.20–1.50 (m, 8H), 1.60–1.88 (m, 8H), 3.51 (t, 4H), 3.96 (t, 4H), 7.91 (s, 4H), 8.47 (br s, 2H).



**3,3,3',3'-Tetraethyl-1,1'-isophthaloylbis(thiourea),  $\{H_2L^2\}_2$ .** Yield 87%, mp 136–138 °C. Found: C, 54.93; H, 6.76; N, 14.40; S, 16.44.  $C_{18}H_{26}N_4O_2S_2$  requires C, 54.78; H, 6.65; N, 14.20; S, 16.25%.  $^1H$  NMR (200 MHz,  $CDCl_3$ ):  $\delta$  1.29 (t, 6H), 1.33 (t, 6H), 3.58 (q, 4H), 4.00 (q, 4H), 7.50 (t, 1H), 7.96 (d, 2H), 8.26 (s, 1H), 9.29 (s, 2H).

H, 4.09; N, 9.61; S, 11.16.  $C_{36}H_{48}N_8O_4S_4Pt_2$  requires C, 36.79; H, 4.12; N, 9.54; S, 10.91%.  $^1H$  (400 MHz,  $CDCl_3$ ):  $\delta$  1.27–1.36 (t + t, 24H), 3.75–3.87 (q + q, 16H), 7.35 (t, 2H), 8.39–8.41 (d + d, 4H), 9.31 (s, 2H).

***cis*-[Pt(L<sup>1</sup>-S,O)]<sub>3</sub> **2**.** A 0.5 mmol portion of ligand  $\{H_2L^1\}_2$  (254 mg) was dissolved in 30 ml acetonitrile to which 2.0 mmol (165 mg) sodium acetate dissolved in 10 ml water was added. A 0.5 mmol portion of  $K_2PtCl_4$  dissolved in 10 ml water, mixed with 10 ml acetonitrile, was added dropwise to the ligand solution over a period of *ca.* 30 minutes. The mixture was stirred at room temperature for a further 3 hours before being diluted with 60 ml water and kept at 4 °C overnight. The fine yellow precipitate which formed was recovered by centrifugation and washed with ethanol. The complex *cis*-[Pt(L<sup>1</sup>-S,O)]<sub>3</sub> was recrystallised from a 3 : 1 mixture of chloroform and ethanol, from which suitable crystals were also grown. The crystals obtained rapidly disintegrated out of the mother liquor, but after drying in vacuum at 60 °C, yield an analytically pure substance. Yield  $\approx$  96%, mp 350 °C (decomp.). Found (for dried complex): C, 44.80; H, 5.85; N, 8.10; S, 9.05.  $C_{78}H_{120}N_{12}O_6S_6Pt_3$  requires C, 44.61; H, 5.77; N, 8.01; S, 9.16%.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  0.91–0.99 (t + t, 36H), 1.30–1.41 (m, 24H), 1.64–1.80 (m + m, 24H), 3.65–3.78 (t + t, 24H), 8.31 (br s, 12H).  $^{195}Pt$  NMR:  $\delta$  -2719, sharp singlet (85.85 MHz,  $CDCl_3$ , external ref.  $H_2PtCl_6$ ).

#### Crystal structure determination and refinement

Crystals were mounted on a thin glass fibre using fast setting cyanoacrylate glue (**1**) or in a Lindemann capillary (**2**). Data were collected on a Nonius Kappa CCD diffractometer using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.7107$  Å) with a detector to crystal distance of 35 mm (**1**) and 25 mm (**2**). A total of either 360 or 200 oscillation frames were recorded, each of width 1° in  $\varphi$ , followed by 95 or 37 frames of 1° width in  $\omega$  (with  $\kappa \neq 0$ ). Crystals were indexed from the first ten frames using the DENZO package<sup>10</sup> and positional data were refined along with diffractometer constants to give the final cell parameters. Integration and scaling (DENZO, Scalepack<sup>10</sup>) resulted in unique data sets corrected for Lorentz-polarisation effects and for the effects of crystal decay and absorption by a combination of averaging of equivalent reflections and an overall volume and scaling correction. Crystallographic data are recorded in Table 1. The structures were solved using SHELXS-97<sup>11</sup> and developed *via* alternating least squares cycles and Fourier difference synthesis (SHELXL-97<sup>11</sup>) with the aid of the program RES2INS.<sup>12</sup> In **1**, all non-hydrogen atoms were modeled anisotropically, while in **2**, the non-hydrogen atoms of the platinum complex, with the exception of those of the *tert*-butyl carbons, were modeled anisotropically. The chloroform, ethanol and water molecules in **2** displayed high thermal motion and were modeled isotropically. Hydrogen atoms were assigned an isotropic thermal parameter 1.2 times that of the parent atom (1.5 times for terminal atoms) and allowed to 'ride'.

CCDC reference number 186/1604.

See <http://www.rsc.org/suppdata/dt/1999/3157/> for crystallographic files in .cif format.

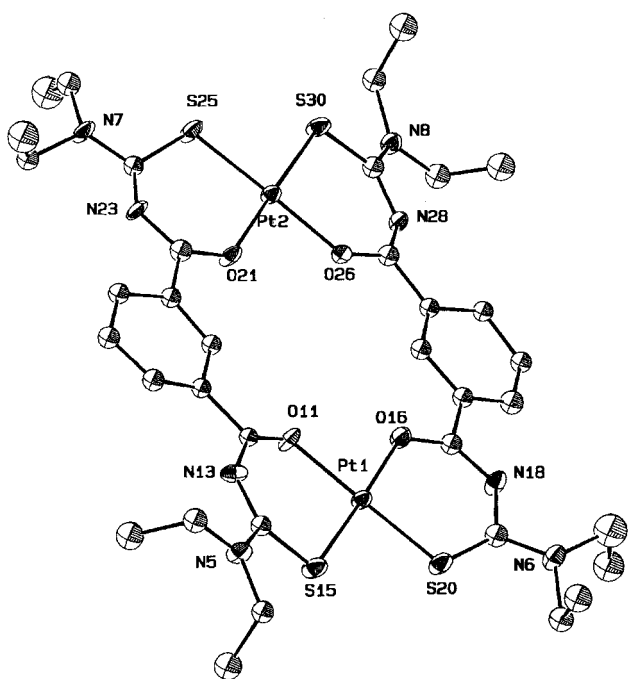
#### Results and discussion

The  $^1H$  NMR spectra of the sparingly soluble *cis*-[Pt(L<sup>2</sup>-S,O)]<sub>2</sub> **1**, and very soluble *cis*-[Pt(L<sup>1</sup>-S,O)]<sub>3</sub> **2** in  $CDCl_3$ , suggest com-

***cis*-[Pt(L<sup>2</sup>-S,O)]<sub>2</sub> **1**.** A 0.5 mmol portion of ligand  $\{H_2L^2\}_2$  (197.3 mg) was dissolved in 30 ml acetonitrile to which 2.0 mmol (165 mg) sodium acetate dissolved in 10 ml water was added. A 0.5 mmol portion of  $K_2PtCl_4$  dissolved in 10 ml water, mixed with 10 ml acetonitrile, was added dropwise to the ligand solution over a period of *ca.* 30 minutes. The mixture was stirred at room temperature for a further 3 hours before being diluted with 60 ml water and kept at 4 °C overnight. The fine yellow precipitate which formed was recovered by centrifugation and washed with ethanol. The sparingly soluble complex *cis*-[Pt(L<sup>2</sup>-S,O)]<sub>2</sub> was recrystallised from chloroform and dried in vacuum at 60 °C. (Yield  $\approx$  89%, mp > 350 °C (decomp.)). Found C, 37.15;

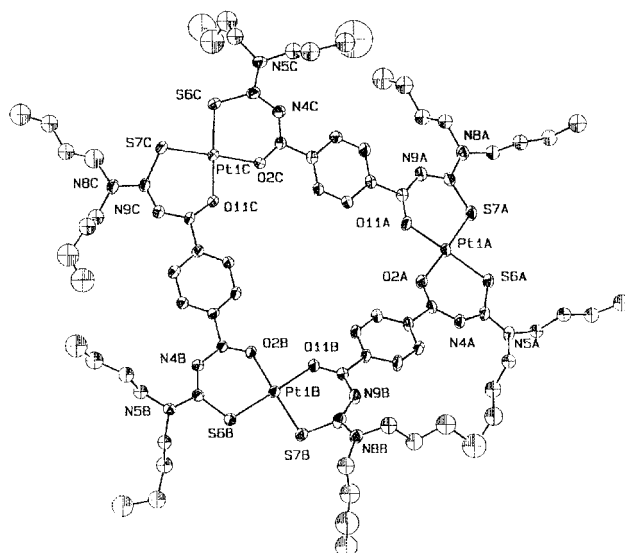
**Table 1** Crystallographic data of complexes **1** and **2**

	<b>1</b>	<b>2</b>
Molecular formula	C <sub>36</sub> H <sub>48</sub> N <sub>8</sub> O <sub>4</sub> Pt <sub>2</sub> S <sub>4</sub>	C <sub>78</sub> H <sub>120</sub> N <sub>12</sub> O <sub>6</sub> Pt <sub>3</sub> S <sub>6</sub> ·2CHCl <sub>3</sub> ·CH <sub>3</sub> CH <sub>2</sub> OH·2H <sub>2</sub> O
<i>M</i>	1175.24	2420.41
<i>T</i> /K	293	293
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	8.3986(2)	17.611(1)
<i>b</i> /Å	9.7283(3)	23.293(2)
<i>c</i> /Å	13.0248(4)	26.033(1)
<i>α</i> /°	80.512(2)	
<i>β</i> /°	82.187(3)	94.261(2)
<i>γ</i> /°	84.719(2)	
<i>V</i> /Å <sup>3</sup>	1037.24(5)	10650(1)
<i>μ</i> /mm <sup>-1</sup>	6.986	4.253
Reflections collected/unique	7930/4227	25105/25105
Final <i>R</i> 1, <i>wR</i> 2 [ <i>I</i> > 2σ <i>I</i> ]	0.0197, 0.0494	0.0617, 0.1713
(all data)	0.0222, 0.0512	0.0934, 0.1972



**Fig. 1** The molecular structure of *cis*-[Pt(L<sup>2</sup>-S,O)]<sub>2</sub> with selected bond lengths (Å) and angles (°) within the co-ordination sphere of the Pt(II) atoms: Pt(1)–O(16) 2.032(12), Pt(1)–O(11) 2.066(10), Pt(1)–S(20) 2.219(5), Pt(1)–S(15) 2.236(5), Pt(2)–O(26) 2.009(11), Pt(2)–O(21) 2.044(11), Pt(2)–S(25) 2.230(5), Pt(2)–S(30) 2.234(4); O(16)–Pt(1)–O(11) 83.5(5), O(16)–Pt(1)–S(20) 95.6(3), O(11)–Pt(1)–S(20) 179.0(4), O(16)–Pt(1)–S(15) 177.0(4), O(11)–Pt(1)–S(15) 94.3(4), S(20)–Pt(1)–S(15) 86.55(18), O(26)–Pt(2)–O(21) 84.9(4), O(26)–Pt(2)–S(25) 176.6(4), O(21)–Pt(2)–S(25) 95.0(3), O(26)–Pt(2)–S(30) 94.0(3), O(21)–Pt(2)–S(30) 178.6(4), S(25)–Pt(2)–S(30) 86.14(18). Atoms are drawn at the 30% probability level.

plexes of high symmetry. Moreover the magnetic equivalence and significant downfield shift (0.40 ppm in the complex with respect to the unbound ligand {H<sub>2</sub>L<sup>2</sup>}) of the resonances due to the aromatic 4H atoms of the terephthaloyl moiety of **2**, together with the sharp single <sup>195</sup>Pt resonance at δ –2719 implies that **2** has a 1 : 1 M : L stoichiometry with the Pt atom in a *cis*-(S,O) type co-ordination sphere, consistent with all previously observed mononuclear complexes with this geometry, which show <sup>195</sup>Pt resonances in the region δ –2719 ± 40.<sup>7b,13</sup> Unfortunately complex **1** was too insoluble to obtain a <sup>195</sup>Pt spectrum in a reasonable time. Nevertheless the simplicity and symmetry of the <sup>1</sup>H spectrum of this complex in CDCl<sub>3</sub> suggests a very similar mode of co-ordination to that of complex **2**. Moreover the considerable downfield displacement of 1.05 ppm of the H(2) proton (δ 9.31) in **1**, compared to the unbound



**Fig. 2** The molecular structure of *cis*-[Pt(L<sup>1</sup>-S,O)]<sub>3</sub> with selected bond lengths (Å) and angles (°): Pt(1A)–O(2A) 2.024(7), Pt(1A)–O(11A) 2.3031(6), Pt(1A)–S(7A) 2.240(3), Pt(1A)–S(6A) 2.240(3), Pt(1B)–O(2B) 2.026(6), Pt(1B)–O(11B) 2.048(6), Pt(1B)–S(6B) 2.230(3), Pt(1B)–S(7B) 2.239(3), Pt(1C)–O(11C) 2.025(7), Pt(1C)–O(2C) 2.031(6), Pt(1C)–S(6C) 2.228(3), Pt(1C)–S(7C) 2.229(3); O(2A)–Pt(1A)–O(11A) 82.7(3), O(2A)–Pt(1A)–S(7A) 177.4(2), O(11A)–Pt(1A)–S(7A) 94.9(2), O(2A)–Pt(1A)–S(6A) 87.56(10), O(2A)–Pt(1B)–O(11B) 82.6(3), O(2B)–Pt(1B)–S(6B) 94.93(19), O(11B)–Pt(1B)–S(6B), O(2B)–Pt(1B)–S(7B) 177.6(2), O(11B)–Pt(1B)–S(7B) 95.0(2), S(6B)–Pt(1B)–S(7B) 87.43(10), O(11C)–Pt(1C)–O(2C) 83.3(3), O(11C)–Pt(1C)–S(6C) 178.8(2), O(2C)–Pt(1C)–S(6C) 95.6(2), O(11C)–Pt(1C)–S(7C) 95.12(19), O(2C)–Pt(1C)–S(7C) 177.6(2), S(6C)–Pt(1C)–S(7C) 85.96(10). Atoms are drawn at the 30% probability level.

ligand {H<sub>2</sub>L<sup>1</sup>}<sub>2</sub> (δ 8.26), is noteworthy, presumably resulting from a significant chemical shift anisotropy effect on this proton, something which is consistent only with a planar, cyclic complex structure.

Inspection of the molecular structures of **1** (Fig. 1) and **2** (Fig. 2), shows these complexes to be approximately planar 2 : 2 and 3 : 3 metallamacrocyclic assemblies respectively, with the aromatic rings of the isophthaloyl and terephthaloyl moieties essentially coplanar with the co-ordination sphere of the Pt(II) atoms. In the case of **2** however, the macrocyclic ring is somewhat twisted as may be seen from the non-bonded torsion angles through the oxygen atoms: in **1** the angle O11–O16–O26–O21 is 0.5(8)° while in **2** the three torsion angles O2A–O11A–O2C–O11C, O2C–O11C–O2B–O11B and O2B–O11B–O2A–O11A are –16.1(5), 8.6(5) and 22.7(5)° respectively. Similarly the non-bonded torsion angle describing the orientation of the aromatic rings show that **2** is more twisted than **1**:

in **1** C41–C43–C33–C31 is 0.2(9)° while in **2** the angles C3A1–C3A4–C3B1–C3B4, C3B1–C3B4–C3C1–C3C4, C3C1–C3C4–C3A1–C3A4 are –24.5(6), 13.9(6) and –1.0(6)°.

The co-ordination sphere of each Pt(II) atom in both **1** and **2** is also distorted from ideal square planarity as exemplified by the significant deviation from 90° of the S–Pt–S and O–Pt–O bond angles: in **1** these are O11–Pt1–O16 (83.5(5)°) and S15–Pt1–S20 (86.6(2)°) and in **2** O2A–Pt1A–O11A (82.7(3)°) and S7A–Pt1A–S6A (87.6(1)°). Deviations from 180° are also seen: in **1** O11–Pt1–S20 is 179.0(4)° and O16–Pt1–S15 is 177.0(4)° while in **2** O2A–Pt1A–S7A is 177.4(2)° and O11A–Pt1A–S6A is 177.6(2)° (similar distortions pertain to the co-ordination spheres of the other Pt atoms). Evidently both metallamacrocycles are somewhat strained, causing a buckling of the assembly from perfect planarity, something which is most evident in the case of the 3:3 complex, **2**.

In general the average of the most important Pt–S and Pt–O bond distances are as expected, ranging from 2.219(5)–2.240(3) Å and 2.028(2)–2.037(6) Å respectively, thus not differing substantially from the corresponding bond lengths of the simple mononuclear *cis*-bis(*N*-benzoyl-*N'*,*N'*-di(*n*-butyl)thioureato)-platinum(II) complex.<sup>7b</sup> Other important bond lengths and angles are given with Fig. 1 and 2.

Interestingly, while the crystals of **1** are quite stable in the dry state, those of **2**, grown from a mixture of chloroform and ethanol, were found to be extremely friable in air, disintegrating almost immediately once removed from the mother-liquor. This necessitated the X-ray data collection of the latter crystals sealed in mother-liquor in a Lindeman capillary. Evidently, the crystal lattice of **2** acts as a host to two molecules of chloroform, one molecule of ethanol and two molecules of water per *cis*-[Pt(L<sup>1</sup>-S,O)]<sub>3</sub> moiety, so that this substance in crystalline form should more properly be formulated *cis*-[Pt(L<sup>1</sup>-S,O)]<sub>3</sub>·2*n*CHCl<sub>3</sub>·*m*CH<sub>3</sub>CH<sub>2</sub>OH·2*p*H<sub>2</sub>O. Unfortunately, possibly due to the instability of the crystal, there is a degree of crystallographic disorder in this structure, which hampered our ability to locate *all* solvent guest molecules. Nevertheless at least two molecules of CHCl<sub>3</sub> were clearly located and could be included in the refined model, along with one ethanol and two molecules of water. The crystals of **2** were also found to be too unstable for thermogravimetric analysis to enable a more accurate estimate of the total number of guest molecules per host platinum complex. On the other hand, drying of the crystals of **2** under vacuum yields an analytically pure complex with high melting point (decomp. >350 °C). Nevertheless, the inclusion of chloroform, ethanol and water molecules into the lattice of crystals of **2** could independently be confirmed in the <sup>1</sup>H NMR spectrum of intact crystals, which were rapidly rinsed and dissolved in CD<sub>2</sub>Cl<sub>2</sub>. Apart from a single resonance due to the magnetically equivalent H-atoms of the terephthaloyl moiety (*s*, δ = 8.36) and a set of resonances due to the *n*-butyl moieties, the <sup>1</sup>H NMR spectrum also shows a characteristic CHCl<sub>3</sub> (*s*, δ 7.34) and CH<sub>3</sub>CH<sub>2</sub>OH (*t*, δ 1.21; *q*, δ 3.67) and H<sub>2</sub>O (*br s*, δ 1.56) resonances; the resonance integrals show two molecules of CHCl<sub>3</sub> per molecule of CH<sub>3</sub>CH<sub>2</sub>OH in the lattice; the absolute number of solvent molecules per complex molecule **2** could not more accurately be estimated in this way, because of the extreme instability of these solvated crystals.

While molecules of **1** are capable of packing quite closely in layers parallel to [110] (Fig. 3), molecules of **2** have longer, more flexible side chains and are evidently not able to pack as closely. Instead, pockets are formed in which solvent molecule(s) are trapped. The metallamacrocycles pack in layers parallel to [011], as shown schematically in Fig. 4, in which the 3:3 macrocycle is represented by a shaded triangle formed by the 3 Pt atoms. The chloroform, ethanol and water molecules modeled are drawn with van der Waals radii. The packing of this structure appears to be stabilized by hydrogen bonds between the oxygen atoms of the ethanol and water molecules [O(2J)<sub>ethanol</sub>···O(1L)<sub>water</sub> is 2.548 Å (*via* 1 + *x*, 1 + *y*, *z*); O(2J)<sub>ethanol</sub>···O(1K)<sub>water</sub> is

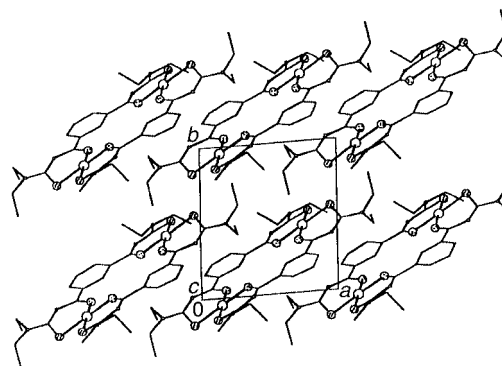


Fig. 3 Packing diagram for the 2:2 complex *cis*-[Pt(L<sup>2</sup>-S,O)]<sub>2</sub>, showing relatively close packing of the dimers.

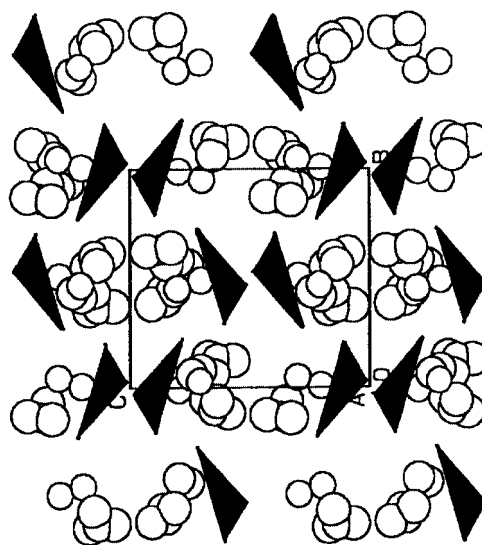


Fig. 4 Packing diagram for *cis*-[Pt(L<sup>1</sup>-S,O)]<sub>3</sub> with the 3:3 complex represented as shaded triangles in the lattice, and showing the solvent molecules chloroform, ethanol and water modeled, drawn with van der Waals radii.

3.081 Å (*via* 1 + *x*, 1 + *y*, *z*) and O(1K)<sub>water</sub>···O(1L)<sub>water</sub> is 2.668 Å].

In conclusion it is clear that for these bipodal ligands, the position of substitution of the chelating moieties in the benzene rings (1,4 *vs.* 1,3), as well as the strong *cis*-S,O co-ordination preference of the *N*-aroyl-*N'*,*N'*-dialkylthiourea moiety to platinum(II) and other d<sup>8</sup> metal ions, pre-determines (or these molecular components can be regarded as being “pre-programmed” according to Lehn<sup>14</sup>) the resultant structures of the complexes which are formed according to the simple models presented in the scheme above. These relatively rigid, bipodal ligands, thus represent an interesting new class of molecules with which to design metallamacrocycles in order to assemble new supramolecular structures. We are actively pursuing this tantalizing possibility of preparing even larger metallamacrocyclic complexes, as well as 3-dimensional assemblies of such complexes.

## Acknowledgements

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