FULL PAPER

Dalton
www.rsc.org/dalton

Reactions of halogens with Pt(II) complexes of *N*-alkyl- and *N*,*N*-dialkyl-*N*′-benzoylthioureas: oxidative addition and formation of an I_2 inclusion compound

Arjan N. Westra,[a] Susan A. Bourne,[b] Catharine Esterhuysen[a] and Klaus R. Koch*[a]

[a] *Department of Chemistry and Polymer Science, University of Stellenbosch, Private Bag X1, Matieland, 7602, South Africa. E-mail: krk@sun.ac.za; Fax: +27-(0)21-8083342; Tel: +27-(0)21-8083020*

[b] *Department of Chemistry, University of Cape Town, PB Rondebosch, Cape Town, 7701, South Africa*

Received 11th March 2005, Accepted 4th May 2005
First published as an Advance Article on the web 18th May 2005

The treatment of *cis*-[Pt^{II}(**L$^{1a/b}$**-***S***,***O***)$_2$] complexes of *N*,*N*-diethyl- (**HL^{1a}**) and *N*,*N*-di(n-butyl)-*N*'-benzoylthiourea (**HL^{1b}**) with I_2 or Br_2 in chloroform, leads to rapid oxidative addition to yield several geometric isomers of [Pt^{IV}(**L**-***S***,***O***)$_2$X$_2$] (X = I, Br); the reactions can be monitored by ^{195}Pt NMR and UV-visible spectrophotometry. The products *cis*-[Pt^{IV}(**L^{1a}**-***S***,***O***)$_2$I$_2$] **6** and *cis*-[Pt^{IV}(**L^{1a}**-***S***,***O***)$_2$Br$_2$] **7**, which have been isolated and structurally characterized, are the first-reported crystal structures of complexes of Pt(IV) with this class of ligand. Molecules of **6** pack such that the I–Pt–I axes are essentially aligned, with unusually close nearest-neighbour iodide contacts (3.553(1) Å). These short I · · · I intermolecular interactions lead to infinite chains of weakly connected molecules in crystals of the compound. No such interactions are evident in the corresponding crystals of **7**. Reaction of the Pt(II) complex of *N*-propyl-*N*'-benzoylthiourea (**H$_2$L^{2a}**) *cis*-/*trans*-[Pt^{II}(**H$_2$L^{2a}**-***S***)$_2$Br$_2$] with Br_2 also results in oxidative addition, to yield *trans*-Pt^{IV}(**H$_2$L^{2a}**-***S***)$_2$Br$_4$ **9**. By contrast, treatment of *cis*-/*trans*-[Pt^{II}(**H$_2$L^{2a}**-***S***)$_2$I$_2$] with I_2 does not lead to an oxidative addition product, yielding instead an interesting iodine inclusion compound of Pt^{II}, *trans*-[Pt^{II}(**H$_2$L^{2a}**-***S***)$_2$I$_2$]·I$_2$ **8**. In **8**, short intermolecular I · · · I distances of 3.453(1) Å between I_2 and coordinated iodide ions in *trans*-[Pt^{II}(**H$_2$L^{2a}**-***S***)$_2$I$_2$] molecules, result in infinite chains of weakly linked *trans*-[Pt^{II}(**H$_2$L^{2a}**-***S***)$_2$I$_2$] · · · I$_2$ groups in the lattice. However, the empirically estimated bond order of 0.75 for the included I_2 molecules does not support the possible existence of discrete tetraiodide ions (I_4^{2-}) in the lattice of compound **8**.

Introduction

Ligands of the type *N*,*N*-dialkyl-*N*′-aroyl(acyl)thiourea (**HL^1**; R^1_2NC(S)NHC(O)R^2, R^1 = alkyl, R^2 = alkyl or aryl) are known to form stable, neutral coordination compounds with a variety of transition metal ions,[1] a number of which have been structurally characterized; for example, Co(III),[2] Ni(II),[3] Cu(II),[4] Zn(II),[5] Ru(III),[6] Rh(III),[7,8] Pd(II),[9] Ag(I),[10] Cd(II),[5] Re(I),[11] Pt(II),[8,12] and Hg(II).[13] These ligands show a pronounced affinity for coordination to the platinum group metals (PGMs),[14] which allows for their potential application in the solvent extraction, preconcentration, separation and trace determination of the PGMs.[14,15] We have studied the complexation of **HL^1**, as well as the analogous *N*-alkyl-*N*′-aroyl(acyl)thioureas (**H$_2$L^2**; R^1NHC(S)NHC(O)R^2, R^1 = alkyl, R^2 = alkyl or aryl), to Pd(II), Rh(III) and particularly Pt(II) with the aim of fully understanding the fundamental coordination chemistry of these complexes, and with a view to developing practically useful analytical and process chemical applications for these ligands.[8,16]

The molecules **HL^1** and **H$_2$L^2** are easily synthesised in high yields in a two-step, ‘one-pot’ procedure,[17] and readily coordinate to Pt(II).[8,18] An intramolecular hydrogen bond between the thiourea RNHC(S)-moiety and the carbonyl *O*-atom in **H$_2$L^2** generally leads to coordination of such ligands with PtX$_4^{2-}$ (X = I, Br, Cl) *via* the *S*-atom only, resulting in mixtures of *cis*- and *trans*-[Pt^{II}(**H$_2$L^2**-***S***)$_2$X$_2$] (X = I, Br, Cl).[19,20] On the other hand, **HL^1** ligands generally coordinate to Pt(II) *via* both the *S*- and *O*-atoms with loss of a thioamidic proton, forming predominantly *cis*-[Pt^{II}(**L^1**-***S***,***O***)$_2$] complexes, several of which have been structurally characterized,[8,12,21] with only a single authenticated *trans* complex of Pt^{II} having been reported to date.[22] Recently we discovered that the *cis*-[M(**L^1**-***S***,***O***)$_2$] (M = Pt(II), Pd(II)) complexes undergo photochemically induced *cis*–*trans* isomerization.[23]

We have found that extraction of Pt(II) into chloroform containing excess **HL^1** from an acidic aqueous (HCl) source phase containing only PtCl$_4^{2-}$, leads to at least three major species in the organic phase, *viz.* [Pt^{II}(**L^1**-***S***,***O***)(**HL^1**-***S***)Cl], *cis*-[Pt^{II}(**HL^1**-***S***)$_2$Cl$_2$] and *trans*-[Pt^{II}(**HL^1**-***S***)$_2$Cl$_2$], *i.e.* protonated analogues of the well-known *cis*-[Pt^{II}(**L^1**-***S***,***O***)$_2$].[24] Moreover extraction experiments with Pt(IV) using an excess of **HL^1** (PtCl$_6^{2-}$ being the predominant species present in strongly acidic refining-process solutions[25]) results in a significantly more complicated distribution of both Pt^{II} and Pt^{IV} complex species in the organic phase, arising *inter alia* from redox reactions between Pt(IV) and the ligand.[24]

To date, very little is known about the coordination of **HL^1** or **H$_2$L^2** to Pt(IV), and no conclusions could be drawn regarding the nature of the extracted Pt(IV) species present in the extraction mixtures. Initial attempts to synthesise Pt(IV) complexes of *N*,*N*-diethyl-*N*′-benzoylthiourea (**HL^{1a}**) directly, by reacting PtCl$_6^{2-}$ with this ligand under various conditions and in various media, resulted in the isolation of predominantly the Pt(II) complex, *cis*-[Pt^{II}(**L^{1a}**-***S***,***O***)$_2$] **1**, evidently due to redox reactions between Pt(IV) and the ligand. The reduction of Pt(IV) by **HL^{1a}** is not unexpected since several investigations into anti-cancer drugs have revealed that many sulfur-containing biomolecules act as reducing agents, reducing antitumour-active Pt(IV) drugs to their Pt(II) analogues.[26] We have thus explored an alternative strategy to the synthesis of Pt(IV) complexes with these ligands, by means of oxidative addition of molecular halogens to the corresponding Pt(II) complexes. Many square-planar Pt(II) complexes can be oxidised to the octahedral Pt(IV) compounds by addition of I_2, Br_2 or Cl_2.[27,28]

We here report the facile synthesis of the first Pt(IV) complexes of *N*,*N*-diethyl-*N*′-benzoylthiourea (**HL^{1a}**), *N*,*N*-di(n-butyl)-*N*′-benzoylthiourea (**HL^{1b}**) and *N*-propyl-*N*′-benzoylthiourea (**H$_2$L^{2a}**) by direct oxidation of *cis*-[Pt^{II}(**L^{1a}**-***S***,***O***)$_2$] **1**,

DOI: 10.1039/b503653d

cis-[Pt^{II}(**L^{1b}**-***S***,***O***)$_2$] **2** and *cis*- and *trans*-[Pt^{II}(**H$_2$L^{2a}**-***S***)$_2$Br$_2$] **3** with elemental halogens (I$_2$, Br$_2$) in organic solvents. Whereas treatment of **1** and **2** with I$_2$ or Br$_2$, and **3** with Br$_2$, leads to simple oxidative addition of the halogens, treatment of *cis*- and *trans*-[Pt^{II}(**H$_2$L^{2a}**-***S***)$_2$I$_2$] **4** with I$_2$ does *not* result in oxidative addition, but in the formation of an interesting iodine inclusion compound, *trans*-[Pt^{II}(**H$_2$L^{2a}**-***S***)$_2$I$_2$]·I$_2$.

Results and discussion

Oxidative addition of I$_2$ and Br$_2$ to *cis*-[Pt^{II}(L^{1a}-*S*,*O*)$_2$] 1 and *cis*-[Pt^{II}(L^{1b}-*S*,*O*)$_2$] 2

^{195}Pt NMR spectroscopic as well as UV-visible spectrophotometric experiments revealed that the oxidative addition reaction is rapid in chloroform, and can readily be monitored by 'titrating' chloroform solutions of *cis*-[Pt^{II}(**L^{1a}**-***S***,***O***)$_2$] **1** or *cis*-[Pt^{II}(**L^{1b}**-***S***,***O***)$_2$] **2** with appropriate quantities of halogen. Fig. 1a shows the reaction of I$_2$ with compound **1** as monitored by UV-visible spectrophotometry; the spectra display two isosbestic points indicating the occurrence of at least two predominant species in solution. Fig. 1b shows the corresponding ^{195}Pt NMR spectra obtained by treatment of *cis*-[Pt^{II}(**L^{1a}**-***S***,***O***)$_2$] **1** in CDCl$_3$ with small quantities of I$_2$ (s), up to a mole ratio I$_2$: Pt of 1 : 1, directly in an NMR tube at room temperature. Addition of I$_2$ results in the diminution of the ^{195}Pt NMR peak of complex **1** ($\delta_{Pt\ 1} = -2719$ ppm), and the appearance of a major and several minor peaks of varying intensities to lower field: $\delta_{Pt} = -2422$ ppm (70% by relative peak intensity at mole ratio Pt : I$_2$ of 1 : 1), −2325 ppm (9%), −2160 ppm (18%), −2114 ppm (2%), −2076 ppm (1%). Similar treatment of compound **2** with a sub-stoichiometric quantity of Br$_2$ (l), results in the appearance of a comparable distribution of ^{195}Pt resonances ($\delta_{Pt} = -1320$ ppm (82% by relative product peak intensities), −1230 ppm (6%), −1087 ppm (9%), −1037 ppm (2%), −1005 ppm (1%)), and diminution of the peak corresponding to complex **2** ($\delta_{Pt\ 2} = -2713$ ppm). Since generally it is found that ^{195}Pt NMR shifts of Pt(IV) complexes appear significantly more downfield relative to Pt(II) complexes,[29,30] the downfield shift in the ^{195}Pt peaks suggests oxidative addition of I$_2$ or Br$_2$, resulting in one predominant Pt(IV) species in addition to several minor species in solution.

Treatment of **1** in chloroform with stoichiometric quantities of I$_2$ (s) or Br$_2$ (l), led to the isolation and characterization by single crystal X-ray diffraction of *cis*-bis(*N*,*N*-diethyl-*N′*-benzoylthioureato)diiodoplatinum(IV), **6** (Fig. 2), and *cis*-bis(*N*,*N*-diethyl-*N′*-benzoylthioureato)dibromoplatinum(IV), **7** (Fig. 3), respectively, confirming the expected oxidative addition of the halogens to Pt(II) in **1**. Complexes **6** and **7** are to our knowledge, the first authenticated Pt(IV) complexes with *N*,*N*-dialkyl-*N′*-aroyl(acyl)thiourea ligands.

Crystal and molecular structure of *cis*-bis(*N*,*N*-diethyl-*N′*-benzoylthioureato)diiodoplatinum(IV) 6

The crystal structure of **6** (Fig. 2, Table 1) shows that in the dominant product (confirmed by ^{195}Pt NMR) of oxidative addition of I$_2$ to **1**, the thiourea ligands (**L^{1a}**) remain coordinated

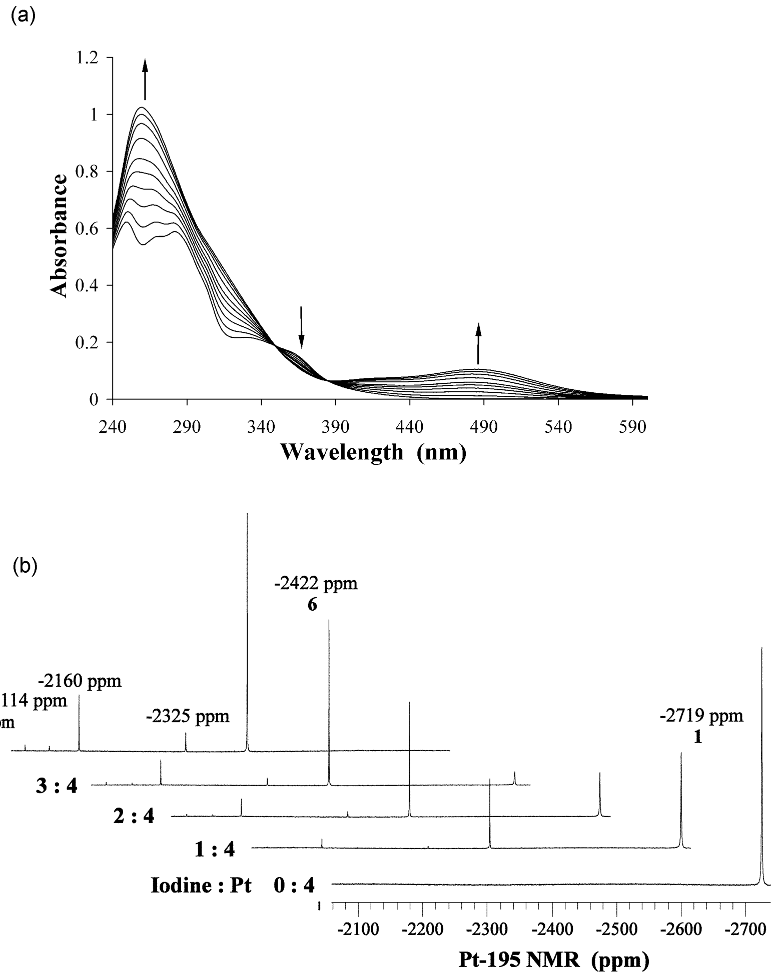

Fig. 1 (a) Distribution of UV-visible spectra obtained by 'titration' of *cis*-[Pt^{II}(**L^{1a}**-***S***,***O***)$_2$] **1** (9.17 × 10^{-6} mol in 100 cm^3 CHCl$_3$) with small volumes of 0.15 M I$_2$ in chloroform, to equimolarity (the arrows indicate changes in absorbance with increase of I$_2$ added). (b) ^{195}Pt NMR spectra obtained by 'titration' of *cis*-[Pt^{II}(**L^{1a}**-***S***,***O***)$_2$] **1** (9.96 × 10^{-5} mol in 0.7 cm^3 CDCl$_3$) with small quantities of I$_2$ to a mole ratio of 1 : 1.

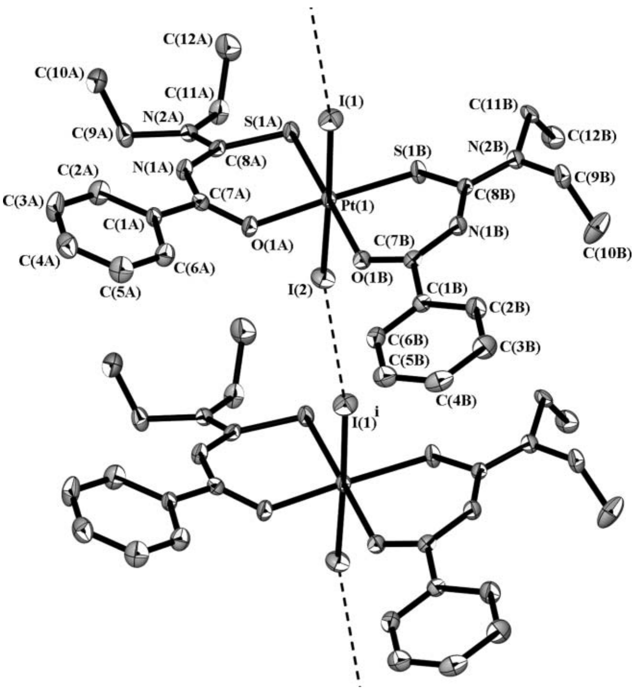

Fig. 2 The molecular structure of *cis*-bis(*N*,*N*-diethyl-*N*′-benzoylthioureato)diiodoplatinum(IV) **6** with atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. Unusually short nearest-neighbour iodide distances (I(2) $\cdots$ I(1^i), 3.553(1) Å; symmetry code: (i) $x - 1, y, z$) suggest intermolecular I $\cdots$ I interactions. Selected bond lengths and angles are given in Table 1.

in a *cis*-*S*,*O* fashion to the Pt(IV) centre, with the iodide ligands *trans* in the octahedral complex.

The Pt–I bond lengths (2.674(1)/2.676(1) Å) and the I–Pt–I bond angle (178.2(1)°) compare well with values reported for the Pt(IV) complex *trans*-Pt(acac)$_2$I$_2$ (acac = acetylacetonate) in which the iodide ligands are similarly coordinated axially to the planar Pt(acac)$_2$ moiety (Pt–I, 2.667(1) Å; I–Pt–I, 180.0°).[31] A particularly interesting feature of complex **6**, is the short intermolecular I $\cdots$ I contact between adjacent molecules as a result of their alignment in the crystal lattice. The molecules pack such that their I–Pt–I axes are essentially parallel (*trans*-Pt–I bonds are directed nearly along the *a* axis) but slightly off-centre relative to each other (Pt(1)–I(2) $\cdots$ I (1^i), 163.75(1)°; symmetry code: (i) $x - 1, y, z$), with intermolecular distances between nearest-neighbour iodide ligands of 3.553(1) Å. These intermolecular I $\cdots$ I distances are considerably shorter than the sum of the van der Waals radii for two iodine atoms (4.20 Å [32]), and are only slightly longer than the range of distances (3.3 to 3.5 Å) found for covalent bond formation in polyiodide anions.[33,34] These intermolecular interactions seem to be only slightly 'weaker' than those in crystalline I$_2$, for which intermolecular I $\cdots$ I distances are 3.496(6) Å.[35] Octahedral *trans*-Pt(IV)-iodo compounds with intermolecular I $\cdots$ I distances shorter than twice the van der Waals radius of iodine have been reported; for example in *trans*-Pt(acac)$_2$I$_2$,[31] [*cis*-Pt(ethylamine)I$_4$][36] and [Pt(*o*-diaminobenzene)I$_3$].[37] In these compounds, the intermolecular I $\cdots$ I distances lie in the range 3.48–3.56 Å.

In compound **6**, the Pt–S bond lengths (2.283(1)/2.281(1) Å) and the Pt–O bond lengths (2.058(2)/2.055(3) Å) are longer than in the platinum(II) complex **1** (Pt–S: 2.231(2)/2.233(2) Å; Pt–O: 2.018(5)/2.023(6) Å).[12] The Pt(IV) complexes might be expected to have shorter Pt–S and Pt–O bond lengths, but the observed elongation of these bonds can probably be ascribed to the presence of the bulky iodide ligands in the octahedral coordination sphere. Complex **6** crystallizes in a $P\bar{1}$ space group. The atoms Pt(1)/S(1A)/O(1A)/S(1B)/O(1B) lie in a plane (a maximum deviation of 0.003(1) Å from a least-squares plane through these atoms is calculated for O(1B)), but the two ligands coordinated to the metal centre do not lie in this coordination plane. Ligand B is twisted significantly out of the Pt^{IV}S$_2$O$_2$ plane, while ligand A is twisted through the coordination plane with the ethyl end-groups below and the phenyl group above the plane. The chains of weakly connected molecules, which result from the intermolecular I $\cdots$ I interactions, pack such that adjacent chains appear to slot into one another with molecules inverted, the phenyl groups of one chain overlaying amine *N*-atoms of an adjacent chain, and *vice versa*.

Crystal and molecular structure of *cis*-bis(*N*,*N*-diethyl-*N*′-benzoylthioureato)dibromoplatinum(IV) 7

The major product of the oxidative addition of Br$_2$ to **1** crystallizes in the *C*2/*c* space group with two independent half molecules, denoted A and B, in the asymmetric unit. In both structures A and B the thiourea ligands (**L^{1a}**) remain *cis*-*S*,*O* coordinated to the metal centre, with the bromide ligands *trans* in the resulting complex (component A is shown in Fig. 3, see Table 1). A two-fold axis of symmetry lies in the coordination plane, through the metal centre and between the thiourea ligands

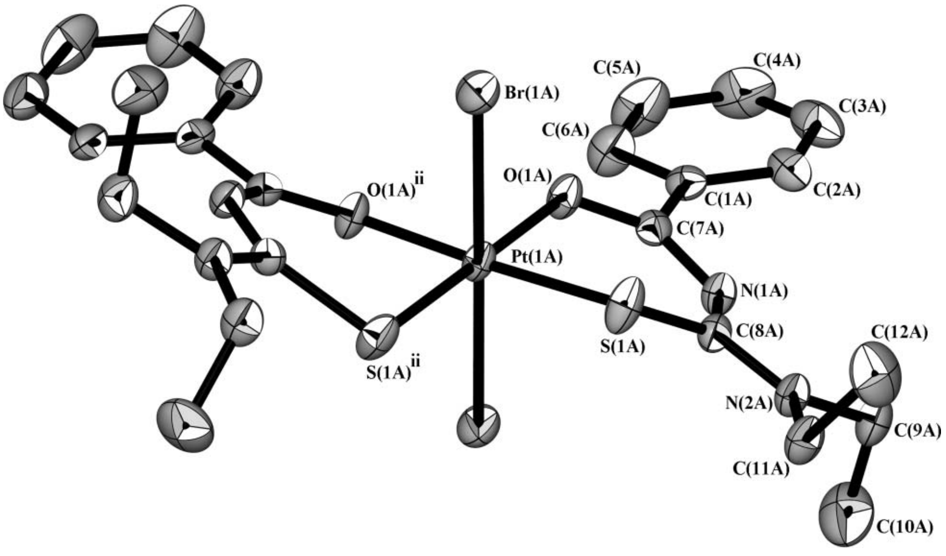

Fig. 3 Compound **7**, *cis*-bis(*N*,*N*-diethyl-*N*′-benzoylthioureato)dibromoplatinum(IV), crystallizes with two independent half molecules (denoted A and B) in the asymmetric unit; the molecular structure of component A is shown with atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. Selected bond lengths and angles are given in Table 1.

Table 1 Selected bond lengths (Å) and angles (°) for compounds **6, 7, 8** and **9**

	6		**7**		**8**	**9**	
	Ligand A	Ligand B	Structure A	Structure B		Ligand A	Ligand B
Pt(1)–S(1)	2.283(1)	2.281(1)	2.280(1)	2.280(1)	2.308(1)	2.378(1)	2.372(1)
S(1)–C(8)	1.737(4)	1.742(4)	1.744(4)	1.745(4)	1.700(3)	1.722(4)	1.721(4)
C(8)–N(1)	1.345(4)	1.340(4)	1.347(4)	1.346(4)	1.381(3)	1.366(4)	1.373(5)
N(1)–C(7)	1.307(5)	1.325(4)	1.316(4)	1.313(4)	1.387(3)	1.395(5)	1.390(5)
C(7)–O(1)	1.277(4)	1.276(5)	1.283(4)	1.269(4)	1.222(3)	1.221(5)	1.229(4)
O(1)–Pt(1)	2.058(2)	2.055(3)	2.044(2)	2.043(3)			
C(8)–N(2)	1.334(5)	1.324(4)	1.329(4)	1.339(4)	1.315(3)	1.313(5)	1.310(5)
Pt(1)–S(1)–C(8)	104.1(1)	104.6(1)	103.3(1)	104.8(1)	111.1(1)	114.4(1)	115.2(1)
S(1)–C(8)–N(1)	127.0(3)	128.1(3)	128.5(3)	130.1(3)	121.9(2)	122.5(3)	122.9(3)
C(8)–N(1)C–(7)	128.1(3)	128.8(4)	126.6(3)	128.0(3)	126.2(2)	126.0(3)	127.0(3)
N(1)–C(7)–O(1)	129.9(4)	130.3(4)	131.0(3)	130.8(3)	121.1(3)	120.9(3)	120.8(3)
C(7)–O(1)–Pt(1)	125.4(2)	126.2(2)	125.1(2)	127.4(2)			
N(1)–C(8)–N(2)	115.8(3)	115.1(4)	115.7(3)	115.2(3)	118.8(2)	119.0(3)	118.6(3)
O(1)–Pt(1)–S(1)	95.56(8)	93.24(8)	91.89(7)	94.73(8)			
6							
Pt(1)–I(1)	2.676(1)	I(1)–Pt(1)–I(2)	178.2(1)	S(1A)–Pt(1)–O(1B)	179.5(1)	O(1A)–Pt(1)–I(1)	87.83(8)
Pt(1)–I(2)	2.674(1)	O(1B)–Pt(1)–I(1)	89.80(8)	S(1A)–Pt(1)–I(1)	90.31(4)	S(1B)–Pt(1)–I(1)	92.06(4)
7							
Pt(1A)–Br(1A)	2.460(1)	Br(1A)–Pt(1A)–Br(1A^{ii})	177.4(1)	Br(1B)–Pt(1B)–Br(1B^{ii})	178.1(1)	S(1A)–Pt(1A)–O(1A^{ii})	177.3(1)
Pt(1B)–Br(1B)	2.462(1)	S(1B)–Pt(1B)–O(1B^{ii})	177.3(1)	O(1A)–Pt(1A)–Br(1A)	89.11(8)	O(1B)–Pt(1B)–Br(1B)	88.55(9)
		S(1A)–Pt(1A)–Br(1A)	92.65(3)	S(1B)–Pt(1B)–Br(1B)	90.56(4)		
8							
Pt(1)–I(1)	2.597(1)	I(1)–Pt(1)–I(1^{iii})	180	I(1^{iii}) · · · I(2)	3.453(1)	I(2)–I(2^{iv})	2.768(1)
9							
Pt(1)–Br(1)	2.468(1)	Pt(1)–Br(2)	2.472(1)	Pt(1)–Br(3)	2.467(1)	Pt(1)–Br(4)	2.477(1)
Br(1)–Pt(1)–Br(2)	179.7(1)	Br(3)–Pt(1)–Br(4)	179.6(1)	S(1A)–Pt(1)–S(1B)	179.5(3)	Br(1)–Pt(1)–S(1A)	91.59(3)
Br(2)–Pt(1)–Br(3)	90.84(2)	98.29(3)	92.24(3)	Br(3)–Pt(1)–S(1B)	97.86(3)	Br(2)–Pt(1)–S(1B)	92.24(3)
Br(1)–Pt(1)–Br(4)	91.09(2)					Br(4)–Pt(1)–S(1A)	98.29(3)

Symmetry codes: (ii) $1 - x, y, 3/2 - z$; (iii) $1 - x, 1 - y, -z$; (iv) $2 - x, 2 - y, -z$.

in A and B. The Pt–Br bond lengths (2.460(1)/2.462(1) Å) and Br–Pt–Br bond angles (177.4(1)/178.1(1)°) compare well with corresponding values for *trans*-$\mathrm{Pt(acac)_2Br_2}$ (Pt–Br, 2.451(2) Å; Br–Pt–Br, 180.0°[38]).

The coordinating atoms Pt(1)/S(1)/O(1)/S(1$^{\mathrm{ii}}$)/O(1$^{\mathrm{ii}}$) (symmetry code: (ii) $1 - x, y, {}^3/_2 - z$) in both structures A and B are planar, with maximum deviations from these plane of 0.033(2) Å for O(1) in A and 0.012(2) Å for O(1) in B. The ethyl end-groups extend from, and the phenyl groups are bent or twisted out of, planes defined by the atoms S(1)/C(8)/N(2)/N(1)/C(7)/O(1). The chelating ligands are, however, twisted significantly out of the Pt(1)/S(1)/O(1)/S(1$^{\mathrm{ii}}$)/O(1$^{\mathrm{ii}}$) coordination planes, giving the structures distinctly puckered shapes when viewed side-on along the two-fold axes, as illustrated in Fig. 3. This puckering is more pronounced for one of the molecules in the asymmetric unit than for the other. The angle between least squares planes through the coordinating *S*- and *O*-atoms (coordination plane), and the atoms S(1)/C(8)/N(2)/N(1)/C(7)/O(1) (ligand plane) is 33.78(14)° for structure A (Fig. 3) and 18.80(10)° for structure B. The two molecules are orientated at 65.68(7)° with respect to each other and appear to slot into one another along the two-fold axes.

The Pt–S bond lengths in **6** and **7** are very similar (2.282(1)/2.281(1) Å and 2.280(1)/2.280(1) Å respectively), but longer than in **1** (2.231(2)/2.233(2) Å[12]), while the Pt–O bond lengths for **1, 6**, and **7** are respectively 2.018(5)/2.023(6) Å, 2.058(2)/2.055(3) Å, and 2.044(2)/2.043(3) Å.[12] One of the ethyl chains in structure B is disordered over two positions; the alternative chains are labelled C(11B)–C(12B) (sof refined to 74%) and C(11C)–C(12C) (sof refined to 26%). There are no other significant intermolecular contacts in this structure.

Crystal and molecular structure of the inclusion compound *trans*-bis(*N*-benzoyl-*N*'-propylthiourea-κ*S*)diiodoplatinum(II) diiodine 8

The invariable UV-visible spectra obtained by 'titration' with $\mathrm{I_2}$ of **4** (*cis-/trans*-bis(*N*-benzoyl-*N*'-propylthiourea-κ*S*)diiodoplatinum(II) mixture, *cis* : *trans* isomer ratio 5 : 95[18]) in chloroform at room temperature, suggested that **4** is apparently *not* oxidized by $\mathrm{I_2}$ to any significant extent under these conditions. 'Titration' experiments with higher reagent concentrations, examined by ^{195}Pt NMR spectroscopy (δ_{Pt}(*cis*-$[\mathrm{Pt^{II}}(\mathbf{H_2L^{2a}}\text{-}\boldsymbol{S})_2\mathrm{I_2}]$) = −4693 ppm, δ_{Pt}(*trans*-$[\mathrm{Pt^{II}}(\mathbf{H_2L^{2a}}\text{-}\boldsymbol{S})_2\mathrm{I_2}]$) = −4870 ppm[18]), resulted in a dark precipitate forming during the 'titration' prior to its completion, although careful examination of the ^{195}Pt spectrum did indicate the emergence of two very low intensity peaks at −4934 ppm and −5082 ppm with the addition of increasing quantities of $\mathrm{I_2}$. Oxidative addition of $\mathrm{I_2}$ to **4** might be expected to result in only *cis*-$[\mathrm{Pt^{IV}}(\mathbf{H_2L^{2a}}\text{-}\boldsymbol{S})_2\mathrm{I_4}]$ and *trans*-$[\mathrm{Pt^{IV}}(\mathbf{H_2L^{2a}}\text{-}\boldsymbol{S})_2\mathrm{I_4}]$ in solution, so that it is tempting to assign the two small ^{195}Pt peaks to these complexes. The ^{195}Pt chemical shift of Pt(IV) species might however be expected somewhat downfield of the corresponding Pt(II) complexes,[30] so that unambiguous assignment of the low intensity peaks at −4934 ppm and −5082 ppm has not yet been possible.

Interestingly, careful recrystallization of the precipitate formed during the $\mathrm{I_2}$ 'titration' allowed the isolation and characterization of compound **8** which is actually an $\mathrm{I_2}$ inclusion compound of *trans*-$[\mathrm{Pt^{II}}(\mathbf{H_2L^{2a}}\text{-}\boldsymbol{S})_2\mathrm{I_2}]$, as determined by X-ray diffraction (Fig. 4).

A survey of the literature shows that treatment of Pt(II) compounds with $\mathrm{I_2}$ need not necessarily always lead to oxidative addition. Reactions of platinum(II) complexes of, for example, Group 15 donor ligands with iodine can give Pt(IV)-iodides (*e.g.* $[\mathrm{Pt(4,7\text{-}Ph_2phen)I_4}]$,[39] and [*cis*-Pt(ethylamine)$\mathrm{I_4}$][36]), but may also leave the metal centre un-oxidised (leading reportedly to Pt(II) poly-iodides as in the case of $[\mathrm{Pt(1,2\text{-}dimethylimidazole)_4}](\mathrm{I_3})_2$[40]).

The crystal structure of *trans*-bis(*N*-benzoyl-*N*'-propylthiourea-κ*S*)diiodoplatinum(II) diiodine (*trans*-$[\mathrm{Pt^{II}}(\mathbf{H_2L^{2a}}\text{-}\boldsymbol{S})_2\mathrm{I_2}]\cdot\mathrm{I_2}$) reveals that the *trans*-$[\mathrm{Pt^{II}}(\mathbf{H_2L^{2a}}\text{-}\boldsymbol{S})_2\mathrm{I_2}]$ molecules alternate with $\mathrm{I_2}$ molecules diagonally to the *a*-, *b*-axes, in the *ab*-plane (Fig. 4 and 5). Nearest-neighbour I(1$^{\mathrm{iii}}$)···I(2) distances at 3.453(1) Å are considerably shorter than the sum of the van der Waals radii for two iodine atoms (4.20 Å[32]), and connote the occurrence of intermolecular I···I interactions in the structure, resulting in infinite zigzag chains of weakly linked *trans*-$[\mathrm{Pt^{II}}(\mathbf{H_2L^{2a}}\text{-}\boldsymbol{S})_2\mathrm{I_2}]$···$\mathrm{I_2}$ groups. Moreover, interatomic distances of 3.771(1) Å are found between iodide ligands of *trans*-$[\mathrm{Pt^{II}}(\mathbf{H_2L^{2a}}\text{-}\boldsymbol{S})_2\mathrm{I_2}]$ molecules in adjacent chains (I(1)···I(1$^{\mathrm{v}}$); symmetry code: (v) $2 - x, 2 - y, -z$; Fig. 6); these distances indicate the possible occurrence of further intermolecular I···I interactions in the structure, connecting the chains to form sheets, or layers, of weakly linked molecules.

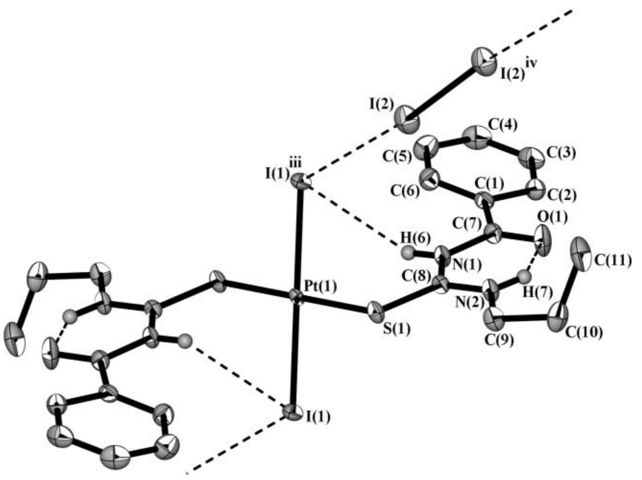

Fig. 4 Molecular structure of *trans*-bis(*N*-benzoyl-*N*′-propylthiourea-κ*S*)diiodoplatinum(II) diiodine **8**, with atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level; H(6) and H(7) are shown as small spheres of arbitrary radius, and the H atoms not involved in hydrogen bonding have been omitted for clarity. Molecular iodine is included in the structure at short nearest-neighbour I(1$^{\mathrm{iii}}$)···I(2) distances (3.453(1) Å; symmetry code: (iii) $1 - x, 1 - y, -z$), indicative of intermolecular I···I interaction. Selected bond lengths and angles are given in Tables 1 and 2.

The product crystallizes in a $P\bar{1}$ space group with the Pt(II) ion located at an inversion centre, which ensures that the coordinated Pt*S*$_2$I$_2$ moiety is strictly planar. The potentially bidentate thiourea ligands in **8** remain bound to Pt(II) *via* the sulfur atom only, with the carbonyl *O*-atom locked into a six-membered O–C–N–C–N–H ring by means of an intramolecular N(2)–H(7)···O(1) hydrogen bond (Fig. 4, Table 2), similar to that reported for *trans*-bis(*N*-benzoyl-*N*′-propylthiourea-κ*S*)diiodoplatinum(II).[20] The maximum deviation from a least-squares plane through the carbonyl-thiourea atoms N(2)/C(8)/S(1)/N(1)/C(7)/O(1) in **8** is 0.057(2) Å for O(1), while the maximum deviation from a plane through the –NC(S)NC(O)– moiety in pure *trans*-$[\mathrm{Pt^{II}}(\mathbf{H_2L^{2a}}\text{-}\boldsymbol{S})_2\mathrm{I_2}]$ is 0.013(2) Å for the carbonyl carbon.[20] The torsion angles of −16.4(4)° for N(1)–C(7)–C(1)–C(6) and −63.1(4)° for N(2)–C(9)–C(10)–C(11) in the *trans*-$[\mathrm{Pt^{II}}(\mathbf{H_2L^{2a}}\text{-}\boldsymbol{S})_2\mathrm{I_2}]$ molecule of **8** illustrate that the thiourea ligands are more distorted in **8** than those in pure *trans*-bis(*N*-benzoyl-*N*′-propylthiourea-κ*S*)diiodoplatinum(II), for which the corresponding torsion angles are −8.4(4)° and −178.4(4)° respectively. The central carbonyl-thiourea moiety (N(2)/C(8)/S(1)/N(1)/C(7)/O(1)) in compound **8** is tilted at an angle of 68.03(6)° to the Pt*S*$_2$I$_2$ coordination plane. This angle allows for the interatomic distance between N(1) and I(1$^{\mathrm{iii}}$) of 3.652(3) Å (symmetry code: (iii) $1 - x, 1 - y, -z$), a distance which is practically identical to the sum of the van der Waals radii for N···I contacts (*ca.* 3.65 Å[32]) suggesting possible weak intramolecular N(1)–H(6)···I(1$^{\mathrm{iii}}$) hydrogen bonding (Table 2). The increased steric hindrance which results from the tilted thiourea

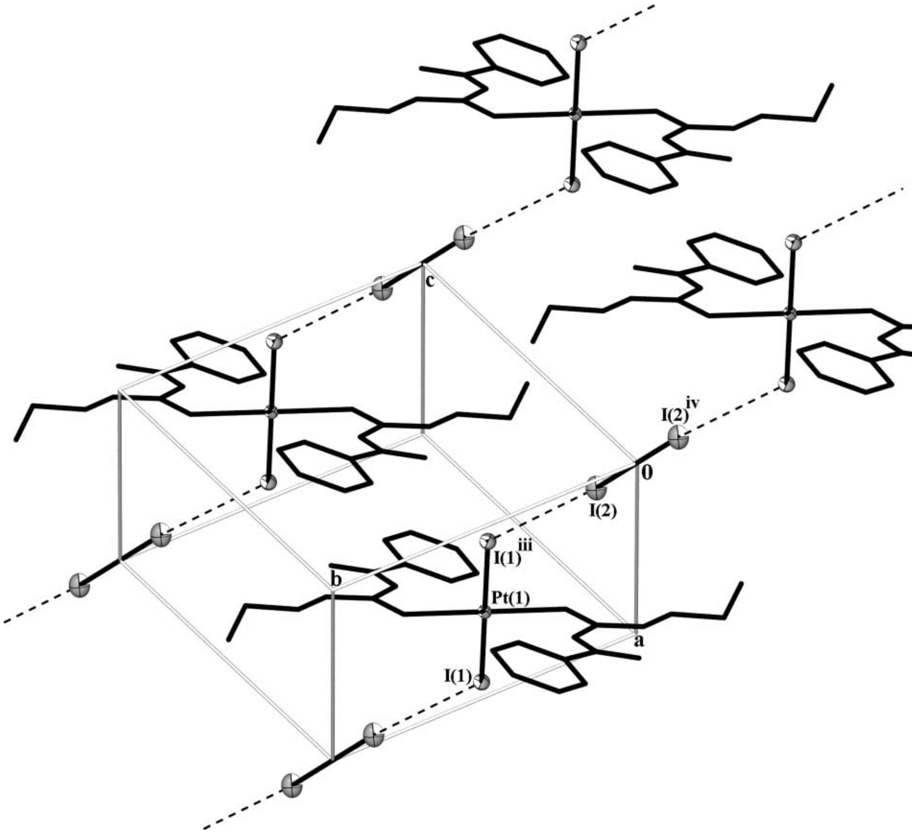

Fig. 5 In compound **8** molecules of *trans*-[Pt^{II}(**H$_2$L^{2a}-*S***)$_2$I$_2$] alternate with I$_2$ diagonally to the *a*- and *b*-axes in the *ab*-plane (the unit cell is shown), leading to infinite zigzag chains of weakly linked *trans*-[Pt^{II}(**H$_2$L^{2a}-*S***)$_2$I$_2$] · · · I$_2$ groups. Only Pt and I atoms are shown by displacement ellipsoids (50% probability), while the remainder of the structure is shown in wireframe style for clarity; H atoms have been omitted.

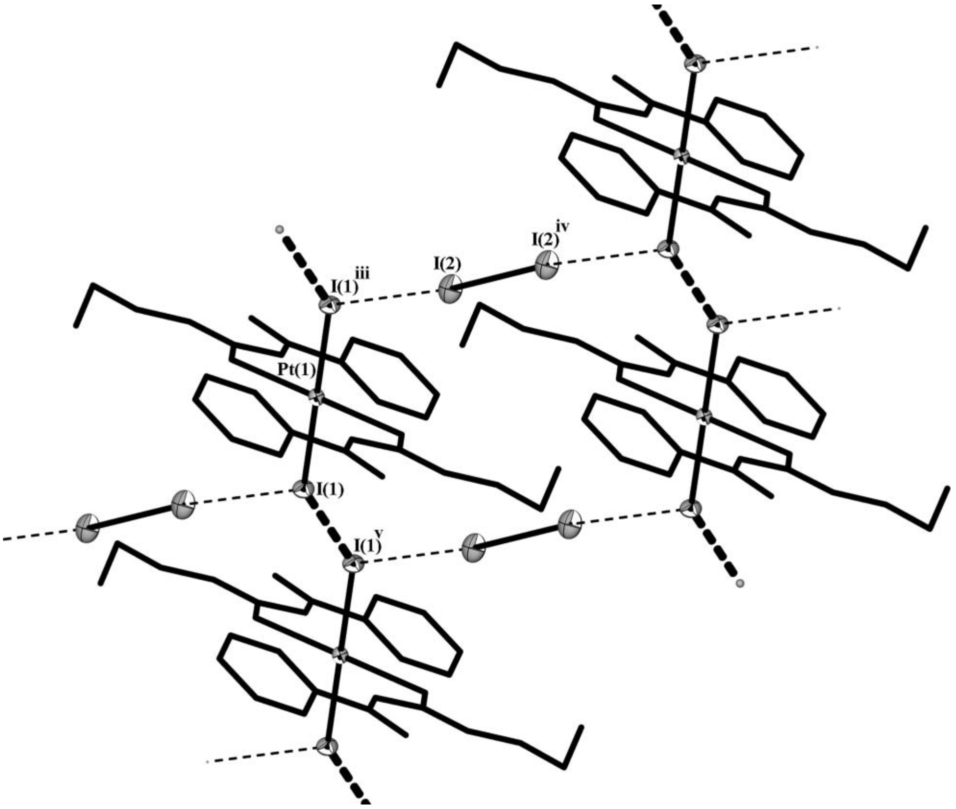

Fig. 6 Distances between iodide ligands of *trans*-[Pt^{II}(**H$_2$L^{2a}-*S***)$_2$I$_2$] molecules in adjacent chains (bold fragmented bonds, I(1) · · · I(1^v), 3.771(1) Å; symmetry code: (v) $2 - x$, $1 - y$, $-z$) indicate the occurrence of intermolecular I · · · I interactions which connect the *trans*-[Pt^{II}(**H$_2$L^{2a}-*S***)$_2$I$_2$] · · · I$_2$ chains into sheets of weakly linked molecules. Only Pt and I atoms are shown by displacement ellipsoids (50% probability), while the remainder of the structure is shown in wireframe style for clarity; H atoms have been omitted.

Table 2 Hydrogen-bonding geometry (Å, °) for structures **8** and **9**

Donor–H · · · Acceptor	Donor–H	H · · · Acceptor	Donor · · · Acceptor	Donor–H · · · Acceptor
8				
N(2)–H(7) · · · O(1)	0.88	1.92	2.608(3)	133.5
N(1)–H(6) · · · I(1^{iii})	0.88	3.11	3.652(3)	122.3
9				
N(2A)–H(7A) · · · O(1A)	0.88	2.003	2.635(4)	127.6
N(2B)–H(7B) · · · O(1B)	0.88	1.934	2.622(4)	133.9
N(1A)–H(6A) · · · Br(1)	0.88	2.638	3.500(3)	153.8
N(1A)–H(6A) · · · Br(4)	0.88	2.854	3.199(3)	105.2
N(1B)–H(6B) · · · Br(2)	0.88	2.635	3.418(3)	148.1
N(1B)–H(6B) · · · Br(3)	0.88	2.763	3.258(3)	117.0
N(2A)–H(7A) · · · O(1B^{vii})	0.88	2.522	3.272(4)	143.6

Symmetry codes: (iii) $1 - x, 1 - y, -z$; (vii) $x - 1/2, 1/2 - y, 1/2 + z$.

ligand, leads to the enlargement of the S(1)–Pt(1)–I(1^{iii}) angle to 92.68(3)°, leaving the Pt(II) centre with a slightly distorted square-planar coordination geometry. Similar N–H · · · I interactions were also observed in *trans*-bis(*N*-benzoyl-*N*'-propylthiourea-κ*S*)diiodoplatinum(II).[20] The Pt–I bond distance (2.597(1) Å) and the Pt–S bond distance (2.308(1) Å) in **8** are only slightly shorter than the corresponding distances in *trans*-bis(*N*-benzoyl-*N*'-propylthiourea-κ*S*)diiodoplatinum(II) (2.617(2) Å and 2.315(6) Å respectively[20]), and are also comparable to those determined for *trans*-bis(*N*,*N*-di(*n*-butyl)-*N*'-benzoylthiourea)diiodoplatinum(II) (2.608(2) Å and 2.294(3) Å respectively).[41]

Iodine inclusion compounds with Pt-iodide complexes, which lead to arrays of four iodine atoms in the structure (Pt–**I** · · · **I–I** · · · **I**–Pt) similar to **8**, have been reported (*e.g.*, [Pt^{IV}(1,10-phen)$I_4 \cdot I_2$], [(Pt^{IV}(1,10-phen)$I_4)_2 \cdot I_2$],[42] and [$Pt^{III}_2(Me_2CHCS)_4I_2 \cdot I_2$][43]). In fact the I_4 array is a common feature in several metal iodide–iodine structures,[34] but *trans*-[Pt^{II}(**H_2L^{2a}**-***S***)$_2I_2$]·I_2 is, to our knowledge, the first such structure reported for Pt(II).[44] In the previously reported Pt structures,[42,43] the I_4-arrays are linear or slightly bent, with the distance between 'inner' iodine atoms (**I–I**, 2.739–2.759 Å) somewhat longer than that found in crystalline iodine (2.715(6) Å[35]) and the 'outer' distances (**I** · · · **I**, 3.288–3.518 Å) in a range which suggest weaker I · · · I interactions. The elongation of the central I–I bond occurs as a result of donation of electron density from the iodide ligands into the I_2 LUMO, an antibonding σ* orbital, leading to net bond order decrease.[45] The 'inner' distance in the symmetrical, slightly bent I_4-array of **8** (I(2)–I(2^{iv}), 2.768(1) Å; I(1^{iii}) · · · I(2)–I(2^{iv}), 174.49(2)°; symmetry code: (iii) $1 - x, 1 - y, -z$; (iv) $2 - x, 2 - y, -z$) is just longer than that found in the reported structures, while the 'outer' distances (I(1^{iii}) · · · I(2), 3.453(1) Å) lie within the range of previously reported values.[42,43]

The I_4-array in metal iodide–iodine structures has sometimes alternatively been considered to be a polyiodide (I_4^{2-}); for example in [Pt(1,10-phen)$I_4 \cdot I_2$],[42] [$Cu(C_9H_{13}N_5)I_2 \cdot I_2$],[46] [Pd(*cis*-$Ph_2PCHCHPPh_2)I_4$][47] and [$(NH_4)_2[(AuI_4)(AuI_2(\mu_2\text{-}I_4))]$].[48] Svensson *et al.*[34] however caution that in these cases, the characterization of the array as an I_4^{2-} ion is questionable and that the notation is only a formal one, since the terminal iodides of the I_4-arrays in metal iodide–iodine structures are more weakly bound than in 'pure' tetraiodides (*e.g.* in [$Ni\{(CH_3)_2SO\}_6]I_4$[49] and [$V(MeCN)_6][I_4]$[50]), and should thus more appropriately be seen as a part of the metal ion complex. Deplano *et al.*[45] have proposed an empirical criterion to determine whether or not iodine atom arrays in structures may be considered as discrete polyiodide entities; the 'building blocks' of the iodine arrays are accepted to be I^- ions and/or I_3^- ions with I_2 molecules. The criterion is based on the value of the bond order (n) of an I_2 'building block' in the array. The bond order, n, is calculated as a function of the I_2 bond lengthening, which results from the donor–acceptor interactions between the I^- (and/or I_3^-) and I_2 'building blocks', using the equation: $d = d_o - c \log n$ (where d and d_o are the I–I bond distances in coordinated, or interacting, and free I_2 respectively, and c is an empirical constant, 0.85 Å). For values of $n > 0.6$, the arrays are considered non-discrete, weakly interacting adducts of I^- (and/or I_3^-) and I_2, but if $n \sim 0.5$ the iodine atoms in the array may be described as being covalently bonded to give discrete polyiodide entities. The bond order for the 'inner' bond in the I_4-array of **8** (I(2)–I(2^{iv})) is 0.75 ($d = 2.768$ Å; bond distance of I_2 in the gas phase, *i.e.* d_o, is 2.662 Å[51]), and hence the array cannot be described as a discrete I_4^{2-} polyanion. Instead, the 4-atom iodine array should be seen as arising from van der Waals interactions between iodide ligands of *trans*-[Pt^{II}(**H_2L^{2a}**-***S***)$_2I_2$] and I_2 molecules, leading to the zigzag $^1_\infty$[· · · I–I · · · I–Pt–I · · · I–I · · ·] chains[34] in the solid form of compound **8**.

Oxidative addition of Br_2 to *cis-/trans*-[Pt^{II}(H_2L^{2a}-*S*)$_2Br_2$] 3

Treatment of **3** (*cis-/trans*-bis(*N*-benzoyl-*N*'-propylthiourea-κ*S*)dibromoplatinum(II) mixture, *cis* : *trans* isomer ratio 42 : 58[18]) in chloroform with a stoichiometric quantity of Br_2 (l), results, in contrast to the formation of **8** above, in oxidative addition of the halogen and formation of compound **9**, *trans*-bis(*N*-benzoyl-*N*'-propylthiourea-κ*S*)tetrabromoplatinum(IV), as shown in Fig. 7. A ^{195}Pt NMR spectrum of the pre-recrystallization mixture shows two peaks, one major signal at −2440 ppm, assigned to **9** based on relative resonance intensities, and one at −2426 ppm, most likely due to *cis*-bis(*N*-benzoyl-*N*'-propylthiourea-κ*S*)tetrabromoplatinum(IV). If this assignment is correct, the ^{195}Pt chemical shift of *trans*-[Pt^{IV}(**H_2L^2**-***S***)$_2Br_4$] occurs upfield to that of the *cis* isomer. This is in contrast to the relative shift positions of the Pt(II) precursors (δ_{Pt}(*cis*-[Pt^{II}(**H_2L^{2a}**-***S***)$_2Br_2$]) = −3693 ppm, δ_{Pt}(*trans*-[Pt^{II}(**H_2L^{2a}**-***S***)$_2Br_2$]) = −3678 ppm[18]), but is consistent with the results obtained for [Pt^{IV}(**L^{1a}**-***S***,***O***)$_2X_2$] (X = I, Br) in the present study in which the shifts for the *trans*-halide isomers appear farthest upfield in the distribution of Pt(IV) product peaks. Crystals of *cis*-[Pt^{IV}(**H_2L^{2a}**-***S***)$_2Br_4$] suitable for structure determination, could not be obtained.

Crystal and molecular structure of *trans*-bis(*N*-benzoyl-*N*-propylthiourea-κ*S*)tetrabromoplatinum(IV) 9

The octahedral six-coordinate environment of the Pt centre in compound **9** (Fig. 7, see Table 1) confirms oxidative addition of bromine to *trans*-[Pt^{II}(**H_2L^{2a}**-***S***)$_2Br_2$]. Recrystallization from a toluene/dichloromethane mixture, led to inclusion of one toluene solvent guest molecule per *trans*-[Pt^{IV}(**H_2L^{2a}**-***S***)$_2Br_4$] molecule. This product crystallizes in a $P2_1/n$ space group, with an inversion centre at the origin of the chosen unit cell.

The four bromide ligands and the Pt(IV) centre lie in a plane (a maximum deviation of only 0.007(1) Å is calculated for Br(3) and Br(4)), with Pt–Br bond distances

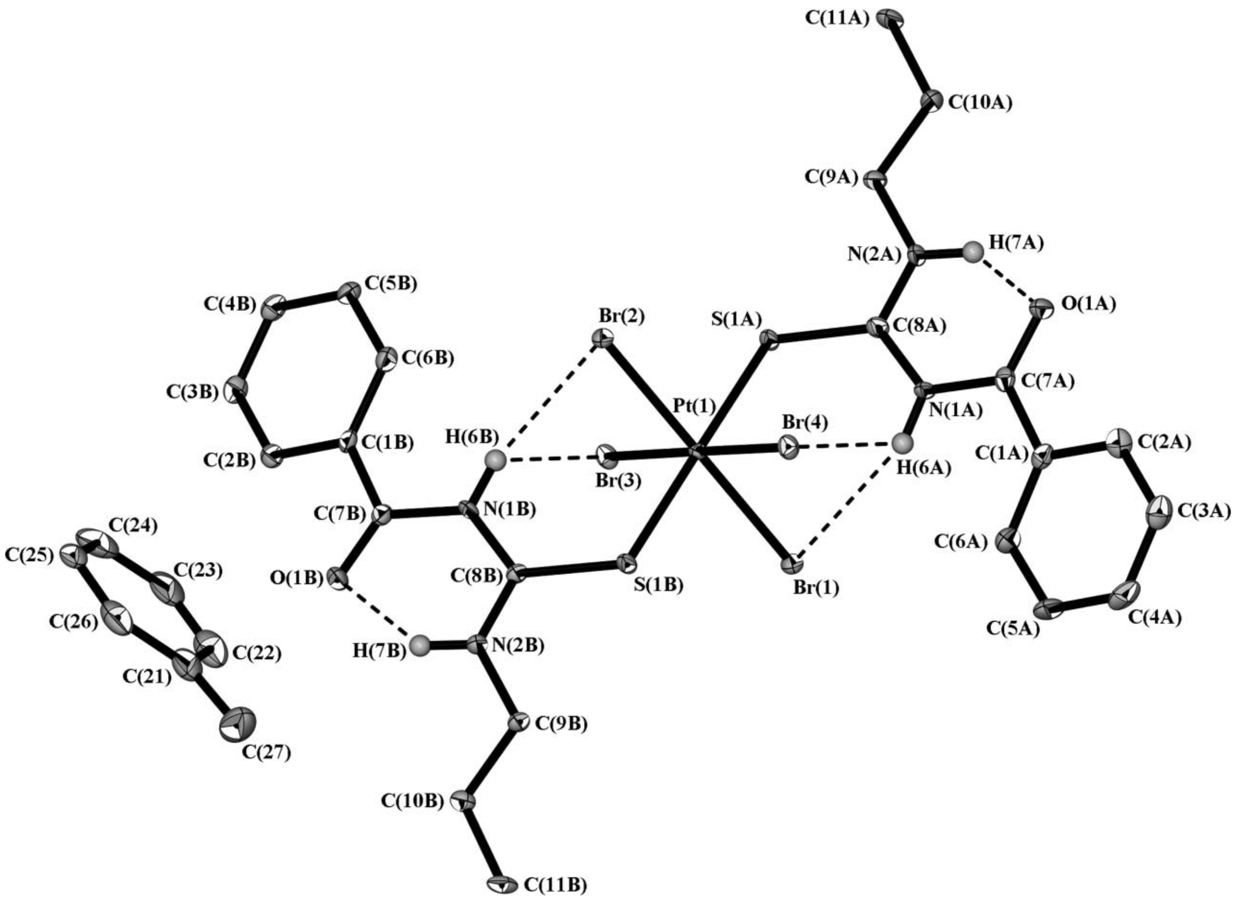

Fig. 7 Molecular structure of *trans*-bis(*N*-benzoyl-*N′*-propylthiourea-κ*S*)tetrabromoplatinum(IV) **9**, with atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level; H(6A), H(7A), H(6B) and H(7B) are shown as small spheres of arbitrary radius, and the H atoms not involved in hydrogen bonding have been omitted for clarity. One toluene solvent guest molecule per *trans*-[Pt^{IV}($\mathbf{H_2L^{2a}}$-***S***)$_2$Br$_4$] molecule was located in the model refinement. Selected bond lengths and angles are given in Table 1. N–H · · · O and N–H · · · Br intramolecular hydrogen bonding is illustrated, with details given in Table 2.

varying only slightly in the range 2.467–2.477 Å. These distances are only slightly longer than the Pt–Br bond lengths in *cis*-[Pt^{IV}($\mathbf{L^{1a}}$-***S***,***O***)$_2$Br$_2$] **7** (see Table 1), but are longer than the Pt–Br distances in *trans*-bis(*N*-benzoyl-*N′*-propylthiourea-κ*S*)dibromoplatinum(II) (*trans*-[Pt^{II}($\mathbf{H_2L^{2a}}$-***S***)$_2$Br$_2$]; Pt–Br, 2.440(4) Å[20]) despite the higher oxidation state of the platinum ion in **9**, possibly as a result of the steric requirements in the octahedral coordination sphere. The Pt–S bond distances in **9** (Pt(1)–S(1A), 2.378(1) Å; Pt(1)–S(1B), 2.372(1) Å) are also considerably longer than those in *trans*-[Pt^{II}($\mathbf{H_2L^{2a}}$-***S***)$_2$Br$_2$] (Pt–S, 2.305(8) Å). In both compounds **9** and *trans*-[Pt^{II}($\mathbf{H_2L^{2a}}$-***S***)$_2$Br$_2$] the thiourea ligands are monodentately *S*-bound to the metal, resulting in longer Pt–S bond lengths than in *cis*-[Pt^{IV}($\mathbf{L^{1a}}$-***S***,***O***)$_2$Br$_2$] **7**, which has the thiourea ligands chelated *via S*- and *O*-atoms. The intramolecular N–H · · · O hydrogen bonds (propylamine side) observed in *trans*-bis(*N*-benzoyl-*N*'-propylthiourea-κ*S*)dibromoplatinum(II),[20] are also evident in the thiourea ligands of *trans*-[Pt^{IV}($\mathbf{H_2L^{2a}}$-***S***)$_2$Br$_4$] (N(2A)–H(7A) · · · O(1A) and N(2B)–H(7B) · · · O(1B), Table 2); these interactions lock the carbonyl oxygen atoms into six-membered O–C–N–C–N–H rings, thereby resulting in the monodentate *S*-coordination of the ligands. The two *S*-donor ligands however assume different conformations (denoted A and B in Fig. 7) in the Pt(IV) compound **9**, and are more distorted than in the Pt(II) complex in which the two thiourea ligands are related by an inversion centre located at the Pt(II) ion.[20] The N(2A)/C(8A)/S(1A)/N(1A)/C(7A)/O(1A) moiety of ligand A in **9** is tilted at an angle of 63.96(6)° to the Pt(1)/S(1A)/Br(1)/S(1B)/Br(2) coordination plane (maximum deviation from the coordination plane is 0.003(1) Å for Br(1)), which results in interatomic N(1A) · · · Br(1) and N(1A) · · · Br(4) distances of 3.500(3) Å and 3.199(3) Å respectively (Table 2). The central carbonyl-thiourea moiety of ligand B is tilted at 55.63(6)° to the coordination plane, leading to N(1B) · · · Br(2) and N(1B) · · · Br(3) distances of 3.418(4) Å and 3.259(3) Å respectively (Table 2). All these N · · · Br distances are shorter than, or practically identical to, the sum of the van der Waals radii for N · · · Br contact (3.45 Å[32]). This suggests that the N(1A)–H(6A) group in ligand A acts as a donor for intramolecular hydrogen bonds to Br(1) and Br(4), and that the N(1B)–H(6B) group in ligand B similarly acts as hydrogen bond donor to Br(2) and Br(3) (Table 2). Such interactions account for the distortions from ideal octahedral geometry, leading to the larger than 90° bond angles for the coordination sphere of the Pt(IV) centre (see Table 1).

In crystals of compound **9**, molecules of *trans*-bis(*N*-benzoyl-*N*'-propylthiourea-κ*S*)tetrabromoplatinum(IV) may be paired, with molecules of a pair oriented with their Br(1) atoms pointing toward each other (the orientations are related by an inversion centre). Furthermore, the pairs of molecules can have two different orientations with the orientations related by a two-fold screw axis or an n-glide plane normal to the *b*-axis. The Br(1)–Pt(1)–Br(2) axes of a pair of molecules (Br(1)–Pt(1)–Br(2) 179.7(1)°) are essentially parallel but slightly off-centre (Pt(1)–Br(1) · · · Br(1^{vi}) 170.6(1)°; symmetry code: (vi) $-x$, $1 - y$, $1 - z$), with nearest-neighbour Br(1) · · · Br(1^{vi}) distances of 3.396(1) Å. This intermolecular Br(1) · · · Br(1^{vi}) distance is considerably shorter than twice the van der Waals radius of bromine (3.90 Å[32]), and suggests the possible occurrence of Br · · · Br intermolecular interactions between molecules of a pair. Moreover, intermolecular N(2A)–H(7A) · · · O(1B^{vii}) hydrogen bonds (symmetry code: (vii) $x - 1/2$, $1/2 - y$, $1/2 + z$;

Table 2) exist between adjacent molecules which have orientations related by the n-glide plane normal to the *b*-axis, resulting in a complicated network of intermolecular Br(1) · · · Br(1^{vi}) and N(2A)–H(7A) · · · O(1B^{vii}) interactions in the solid. A search in the Cambridge Structural Database[44] revealed that only a limited number of Pt(IV)-bromo complexes with intermolecular Br · · · Br distances shorter than twice the van der Waals radius of bromine have been synthesized and structurally characterized; examples are [Pt(2-pyridyldiphenylphosphine oxide)Br_4],[52] *trans*-[Pt(acac)$_2$Br$_2$],[38] [Pt(ethylenediamine)Br_4].[53] In these complexes the intermolecular Br · · · Br distances lie in the range of 3.46–3.54 Å.

Oxidative addition with Cl_2

Attempts to isolate well defined single products from the oxidative addition of Cl_2 to **1** (*cis*-[Pt^{II}(**L^{1a}**-***S***,***O***)$_2$]) or **5** (*cis-/trans*-[Pt^{II}(**H$_2$L^{2a}**-***S***)$_2$Cl$_2$] mixture) were unsuccessful, partly due to the difficulty in controlling the reaction with gaseous Cl_2. Experiments in which Cl_2 (g) was bubbled through solutions of **1** in chloroform for several minutes resulted in mixtures from which droplets containing $PtCl_6^{2-}$ separated, indicating destructive oxidation of **1** which is not surprising in view of the higher oxidative strength of Cl_2. Efforts at more controlled addition of Cl_2 (g) yielded solutions of which the ^{195}Pt NMR show several peaks in the range −500 to −1000 ppm, suggesting several Pt(IV)-chloro complexes, but crystals could not be isolated from these mixtures. The successful electrochemical synthesis of *trans*-[Pt^{IV}(acac)$_2$X$_2$] (X = Cl, Br) by controlled electrolytic oxidation of Pt^{II}(acac)$_2$ in the presence of chloride or bromide in dichloromethane as solvent,[54] prompted us to attempt this method for the synthesis of Pt(IV)-chloro complexes of **HL^{1a}** and **H$_2$L^{2a}**. Although ^{195}Pt NMR spectra of the resulting electrolysis solutions exhibit a complicated distribution of peaks in the range of 0 to −1000 ppm, we have not, to date, been able to isolate crystals from these solutions either. Efforts to establish the structures of Pt(IV)-chloro complexes of **HL^1** and **H$_2$L^2** ligands are still underway.

Conclusions

Dihalogen molecules undergo facile oxidative addition to Pt(II) complexes of **HL^1** and **H$_2$L^2**, under moderate conditions resulting in *inter alia* Pt(IV) complexes of these ligands. Mechanistically this oxidative addition is possibly initiated by an end-on interaction of X_2 (X = Cl, Br, I) with the metal centre;[28] a useful model for this initial stage of oxidative addition of molecular halogens to transition metal centres is given by the isolated η^1-I$_2$ Pt(II) adduct formed by the reaction of I_2 with [PtI(C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6)].[55] The X–X bond is presumably cleaved in an S$_N$2-type process, forming a cationic five-coordinate Pt(IV) intermediate and X$^-$, followed by attack of the anion to produce a neutral Pt(IV)(X$_2$) product, and subsequent isomerization. Reaction with iodine, however, need not necessarily lead to oxidative addition, but may result in the incorporation of I_2 within the crystal lattice;[55] iodine can be oxidatively added to *cis*-[Pt^{II}(**L^{1a}**-***S***,***O***)$_2$] **1**, but forms an iodine inclusion compound with *trans*-[Pt^{II}(**H$_2$L^{2a}**-***S***)$_2$I$_2$] **4**. This difference in reaction of compounds **1** and **4** towards iodine, suggests that these two Pt(II) compounds have markedly different redox potentials; electrochemical investigations of the Pt(II) and available Pt(IV) complexes of **HL^1** and **H$_2$L^2**, are currently in progress.

Experimental

Methods and instruments

The ligands *N*,*N*-diethyl-*N*′-benzoylthiourea (**HL^{1a}**), *N*,*N*-di(n-butyl)-*N*′-benzoylthiourea (**HL^{1b}**) and *N*-propyl-*N*′-benzoylthiourea (**H$_2$L^{2a}**) were synthesized and recrystallized according to a method described by Douglass *et al.*[17] The Pt^{II} complexes of **HL^{1a}**, *cis*-[Pt^{II}(**L^{1a}**-***S***,***O***)$_2$] **1**, and **HL^{1b}**, *cis*-[Pt^{II}(**L^{1b}**-***S***,***O***)$_2$] **2**, and the Pt^{II} complexes of **H$_2$L^{2a}**, *cis-/trans*-[Pt^{II}(**H$_2$L^{2a}**-***S***)$_2$X$_2$] (X = Br, I or Cl; **3, 4, 5** respectively), were synthesized and purified as previously reported.[8,18] All reagents and solvents were commercially available, and all were used without further purification except for the acetone used in ligand synthesis, which was distilled before use. ^{1}H and ^{13}C NMR spectra (25 °C) were recorded in chloroform-d using either a Varian INOVA 600 MHz spectrometer operating at 600 or 151 MHz respectively, or a Varian VXR 300 MHz spectrometer operating at 300 or 76 MHz respectively. ^{195}Pt NMR spectra (30 °C) were recorded in chloroform-d using the Varian INOVA 600 MHz spectrometer operating at 128 MHz. ^{1}H chemical shifts are quoted relative to the residual $CDCl_3$ solvent resonance at 7.26 ppm, and ^{13}C chemical shifts relative to the $CDCl_3$ triplet. All ^{195}Pt chemical shifts are quoted relative to external H_2PtCl_6 (500 mg ml^{-1} in 30% v/v D$_2$O/1 M HCl), and are estimated to be accurate to ±4 ppm. UV-visible spectrophotometric experiments were carried out on an Agilent 8453E UV-visible spectrophotometer (Agilent Technologies). Melting points were determined using an Electrothermal IA9000 Digital Melting Point Apparatus. Elemental analyses were performed using a Carlo Erba EA 1108 elemental analyser in the microanalytical laboratory of the University of Cape Town. Thin layer chromatography was performed on Alugram® Sil G/UV$_{254}$ aluminium sheets (Marchery-Nagel).

Preparative methods

cis*-Bis(*N*,*N*-diethyl-*N*′-benzoylthioureato)diiodoplatinum(IV), *cis*-[Pt^{IV}(L^{1a}-*S*,*O*)$_2$I$_2$] 6.** 0.394 mmol (262 mg) of *cis*-[Pt^{II}(**L^{1a}**-S***,***O***)$_2$] was dissolved in 3 cm^3 of chloroform and treated with a stoichiometric 100 mg of solid I_2. Crystals of *cis*-bis(*N*,*N*-diethyl-*N*′-benzoylthioureato)diiodoplatinum(IV) **6** were obtained by diffusion crystallization with pentane, and analysed. Mp: 154–157 °C. Found: C, 31.4; H, 3.0; N, 6.3; S, 6.8. $C_{24}H_{30}N_4S_2O_2PtI_2$ requires: C, 31.3; H, 3.3; N, 6.1; S, 7.0%. δ_H(600 MHz; solvent $CDCl_3$): 8.25 (4H, d, C_6H_5), 7.52 (2H, t, C_6H_5), 7.44 (4H, t, C_6H_5), 3.93 (4H, q, 2CH$_2$), 3.89 (4H, q, 2CH$_2$), 1.42 (6H, t, 2CH$_3$), 1.38 (6H, t, 2CH$_3$). δ_C(151 MHz; solvent $CDCl_3$): 171.23 (C(O)), 167.43 (C(S)), 136.27–128.06 (C_6H_5), 47.54 (2CH$_2$), 46.95 (2CH$_2$), 13.46 (2CH$_3$), 13.26 (2CH$_3$). δ_{Pt}(128 MHz; solvent $CDCl_3$): −2420 (s). TLC (silica gel, $CHCl_3$): $R_f = 0.95$.

0.394 mmol (262 mg) of *cis*-[Pt^{II}(**L^{1a}**-***S***,***O***)$_2$] was dissolved in 3 cm^3 of chloroform and treated stoichiometrically with 20.3 µl of Br_2 (3.1 g ml^{-1}) using a gastight syringe. Crystals of *cis*-bis(*N*,*N*-diethyl-*N*′-benzoylthioureato)dibromoplatinum(IV) **7** were obtained by diffusion crystallization with pentane, and analysed. Mp: 177–180 °C. Found: C, 35.1; H, 3.4; N, 6.9; S, 7.8. $C_{24}H_{30}N_4S_2O_2PtBr_2$ requires: C, 34.9; H, 3.7; N, 6.8; S, 7.8%. δ_H(600 MHz; solvent $CDCl_3$): 8.27 (4H, d, C_6H_5), 7.53 (2H, t, C_6H_5), 7.43 (4H, t, C_6H_5), 3.92 (4H, q, 2CH$_2$), 3.89 (4H, q, 2CH$_2$), 1.42 (6H, t, 2CH$_3$), 1.36 (6H, t, 2CH$_3$). δ_C(151 MHz; solvent $CDCl_3$): 171.17 (C(O)), 166.82 (C(S)), 136.39–128.06 (C_6H_5), 47.80 (2CH$_2$), 46.99 (2CH$_2$), 13.43 (2CH$_3$), 13.17 (2CH$_3$). δ_{Pt}(128 MHz; solvent $CDCl_3$): −1322 (s). TLC (silica gel, $CHCl_3$): $R_f = 0.92$.

***trans*-Bis(*N*-benzoyl-*N*’-propylthiourea-κ*S*)diiodoplatinum(II) diiodine, *trans*-[Pt^{II}(H$_2$L^{2a}-*S*)$_2$I$_2$]·I$_2$ 8.** The addition of 28.3 mg of solid I_2 to 0.111 mmol (99.5 mg) of a mixture of *cis*- and *trans*-bis(*N*-benzoyl-*N*’-propylthiourea-κ*S*)diiodoplatinum(II) (*cis* : *trans* isomer ratio of 5 : 95[18]) dissolved in 0.7 cm^3 of chloroform, led to the formation of a dark purple precipitate. Careful dissolution of the precipitate in dichloromethane, and diffusion crystallization with pentane, allowed the isolation of crystals of *trans*-bis(*N*-benzoyl-*N*’-propylthiourea-κ*S*)diiodoplatinum(II) diiodine **8**. Mp: 153–155 °C. Found: C, 23.2; H, 2.1; N, 4.9; S, 5.5. $C_{22}H_{28}N_4S_2O_2PtI_4$ requires: C, 23.1; H, 2.5; N, 4.9; S, 5.6%.

Table 3 Crystal and structure refinement data for compounds **6, 7, 8** and **9**

	cis-$[\mathrm{Pt^{IV}}(\mathbf{L^{1a}}\text{-}\boldsymbol{S,O})_2\mathrm{I}_2]$ **6**	*cis*-$[\mathrm{Pt^{IV}}(\mathbf{L^{1a}}\text{-}\boldsymbol{S,O})_2\mathrm{Br}_2]$ **7**	*trans*-$[\mathrm{Pt^{II}}(\mathrm{H}_2\mathbf{L^{2a}}\text{-}\boldsymbol{S})_2\mathrm{I}_2]\cdot\mathrm{I}_2$ **8**	$\{$*trans*-$[\mathrm{Pt^{IV}}(\mathrm{H}_2\mathbf{L^{2a}}\text{-}\boldsymbol{S})_2\mathrm{Br}_4]\}(\mathrm{C_7H_8})$ **9**
Molecular formula	$C_{24}H_{30}I_2N_4O_2PtS_2$	$C_{24}H_{30}Br_2N_4O_2PtS_2$	$C_{22}H_{28}I_4N_4O_2PtS_2$	$C_{29}H_{36}Br_4N_4O_2PtS_2$
Formula weight	919.53	825.55	1147.29	1051.47
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P2_1/n$
a/Å	8.810(2)	26.321(5)	8.513(2)	13.568(4)
b/Å	10.920(2)	15.743(3)	9.400(2)	13.739(4)
c/Å	16.228(2)	18.693(4)	10.064(2)	18.962(6)
α/°	74.23(3)	90	77.00(3)	90
β/°	78.50(3)	130.64(3)	80.70(3)	103.34(1)
γ/°	75.76(3)	90	86.19(3)	90
V/Å^3	1441.7(6)	5878(3)	773.9(3)	3439(2)
μ/mm^{-1}	7.181	7.663	8.683	8.881
Z	2	8	1	4
T/K	193(2)	193(2)	193(2)	100(2)
Reflections collected/unique	14013/7598 [R(int) = 0.0363]	14663/7786 [R(int) = 0.0394]	21068/3020 [R(int) = 0.0254]	34743/6745 [R(int) = 0.0442]
Goodness-of-fit	0.959	1.012	1.048	1.040
Final R [$I > 2\sigma(I)$] (all data)	0.0564	0.0592	0.0158	0.0326
$wR2$ [$I \geq 2\sigma(I)$] (all data)	0.0608	0.0681	0.0314	0.0639
Largest remaining feature in electron density map: max, min/e Å^3	1.32 (1.66 Å from H(14A)), −0.95 (0.83 Å from Pt(1))	1.35 (1.19 Å from Pt(1A)), −0.98 (0.84 Å from Pt(1A))	0.93 (0.78 Å from I(2)), −0.93 (0.75 Å from I(2))	1.80 (1.43 Å from H(21)), −0.50 (1.09 Å from Pt(1))

***trans*-Bis(*N*-benzoyl-*N*'-propylthiourea-κ*S*)tetrabromoplatinum(IV), *trans*-$[\mathrm{Pt^{IV}}(\mathbf{H_2L^{2a}}\text{-}\boldsymbol{S})_2\mathrm{Br}_4]$ 9.** 0.196 mmol (156 mg) of a mixture of *cis*- and *trans*-bis(*N*-benzoyl-*N*′-propylthiourea-κ*S*)dibromoplatinum(II) (*cis* : *trans* isomer ratio of 42 : 58[18]) was dissolved in 3 cm^3 of dichloromethane and stoichiometrically treated with 10.1 μl of Br_2 (3.1 g ml^{-1}) using a gastight syringe. Good quality crystals of *trans*-bis(*N*-benzoyl-*N*′-propylthiourea-κ*S*)tetrabromoplatinum(IV) **9** were obtained by slow evaporation from a toluene/dichloromethane solvent mixture. Crystals of *cis*-$[\mathrm{Pt^{IV}}(\mathbf{H_2L^{2a}}\text{-}\boldsymbol{S})_2\mathrm{Br}_4]$ suitable for structure determination could not be obtained. The recrystallized product, a mixture of *cis*- and *trans*-isomers, shows two melting points; mp: 183–187 and 196–198 °C. Found: C, 27.9; H, 2.6; N, 5.9; S, 7.3. $C_{22}H_{28}N_4S_2O_2PtBr_4$ requires C, 27.6; H, 3.0; N, 5.9; S, 6.7%. δ_H(600 MHz; solvent $CDCl_3$; based on relative peak intensities): 11.65 (1H, s, H(6)), 11.16 (1H, s, H(7)), 8.26 (4H, d, C_6H_5), 7.63 (2H, t, C_6H_5), 7.51 (4H, t, C_6H_5), 3.82 (4H, $2CH_2$), 1.88 (4H, $2CH_2$), 1.10 (6H, $2CH_3$). δ_C(151 MHz; solvent $CDCl_3$; based on relative peak intensities): 174.92 (C(S)), 169.62 (C(O)), 134.63–129.21 (C_6H_5), 48.27 ($2CH_2$), 22.10 ($2CH_2$), 11.56 ($2CH_3$). δ_{Pt}(128 MHz; solvent $CDCl_3$; based on relative peak intensities): −2440 (s).

Crystallography and structure refinement

Suitable crystals were mounted on a thin glass fiber and data were collected either on a Nonius Kappa CCD or Bruker-Nonius SMART Apex diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å). The structures were solved using SHELXS-97 and refined using SHELXL-97[56] with the aid of the interface program X-SEED.[57] Peaks of electron density in the Fourier map for compound **7** indicated that one of the ethyl chains in structure B is disordered over two positions. The disorder alternatives are labelled C(11B)–C(12B) and C(11C)–C(12C), and C–C distances have been constrained to reasonable values using the SADI command in SHELXL. In each structure all non-hydrogen atoms were modelled anisotropically, with the exception of C(11C) in compound **7**. Hydrogen atoms were placed in geometrically calculated positions, with C–H = 0.99 (for –CH_2–), 0.98 (for –CH_3), or 0.95 Å (for phenyl), and N–H = 0.88 Å. These were refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}$(parent) (for –CH_2–, phenyl, and N–H) or $1.5U_{eq}$(parent) (for –CH_3). Crystal structure interpretation was performed with the aid of the programs PLATON[58] and MERCURY.[59] Relevant crystallographic data is shown in Table 3, and selected bond lengths and angles for structures are presented in Tables 1 and 2.

CCDC reference numbers 213425, 213426, 266047 and 266048.

See http://www.rsc.org/suppdata/dt/b5/b503653d/ for crystallographic data in CIF or other electronic format.

Acknowledgements

Financial support from the University of Stellenbosch, the NRF, (GUN 2046827), THRIP (project 2921) and Angloplatinum Ltd., is gratefully acknowledged.

References

1 L. Beyer, E. Hoyer, H. Hartman and J. Liebscher, *Z. Chem.*, 1981, **21**, 81; P. Mühl, K. Gloe, F. Dietze, E. Hoyer and L. Beyer, *Z. Chem.*, 1986, **26**, 81–94.

2 L. Beyer, R. Richter and O. Seidelmann, *J. Prakt. Chem./Chem.-Ztg.*, 1999, **341**, 704.

3 G. Binzet, U. Florke, N. Kulcu and H. Arslan, *Acta Crystallogr., Sect. E*, 2003, **59**, m705–m706; R. del Campo, J. J. Criado, E. Garcia, M. R. Hermosa, A. Jimenez-Sanchez, J. L. Manzano, E. Monte, E. Rodriguez-Fernandez and F. Sanz, *J. Inorg. Biochem.*, 2002, **89**, 74–82.

4 R. Flores-Centurion, R. Richter, J. Angulo-Comejo and L. Beyer, *Bol. Soc. Quim. Peru*, 1999, **65**, 211.

5 M. Reinel, R. Richter and R. Kirmse, *Z. Anorg. Allg. Chem.*, 2002, **628**, 41–44.

6 J. Sieler, R. Richter, E. Hoyer, L. Beyer, O. Lindqvist and L. Andersen, *Z. Anorg. Allg. Chem.*, 1990, **580**, 167–174.

7 W. Bensch and M. Schuster, *Z. Anorg. Allg. Chem.*, 1992, **615**, 93–96.

8 A. N. Mautjana, J. D. S. Miller, A. Gie, S. A. Bourne and K. R. Koch, *Dalton Trans.*, 2003, 1952–1960.

9 M. Dominguez, E. Antico, L. Beyer, A. Aguirre, S. Garcia-Granda and V. Salvado, *Polyhedron*, 2002, **21**, 1429–1437.

10 R. Richter, F. Dietze, S. Schmidt, E. Hoyer, W. Poll and D. Mootz, *Z. Anorg. Allg. Chem.*, 1997, **623**, 135–140.

11 U. Abram, S. Abram, R. Alberto and R. Schibli, *Inorg. Chim. Acta*, 1996, **248**, 193–202.

12 C. Sacht, M. Datt, S. Otto and A. Roodt, *J. Chem. Soc., Dalton Trans.*, 2000, 727–733.

13 R. Richter, J. Sieler, L. Beyer, O. Lindqvist and L. Andersen, *Z. Anorg. Allg. Chem.*, 1985, **522**, 171–183.

14 K.-H. König, M. Schuster, B. Steinbrech, G. Schneeweis and R. Schlodder, *Fresenius' Z. Anal. Chem.*, 1985, **321**, 457–460; P. Vest, M. Schuster and K. H. König, *Fresenius' Z. Anal. Chem.*, 1989, **335**, 759–763.

15 K.-H. König, M. Schuster, G. Schneeweis and B. Steinbrech, *Fresenius' Z. Anal. Chem.*, 1984, **319**, 66–69; M. Merdivan, A. Gungor, S. Savasci and R. S. Aygun, *Talanta*, 2000, **53**, 141–146; M. Schuster, B. Kugler and K. H. Koenig, *Fresenius' J. Anal. Chem.*, 1990, **338**, 717–720; M. Schuster and M. Sandor, *Fresenius' J. Anal. Chem.*, 1996, **356**, 326–330; M. Schuster and M. Schwarzer, *Anal. Chim. Acta*, 1996, **328**, 1–11.

16 K. R. Koch, *Coord. Chem. Rev.*, 2001, **216–217**, 473–488.

17 I. B. Douglass and F. B. Dains, *J. Am. Chem. Soc.*, 1934, **56**, 719–721.

18 K. R. Koch, Y. Wang and A. Coetzee, *J. Chem. Soc., Dalton Trans.*, 1999, 1013–1016.

19 S. Bourne and K. R. Koch, *J. Chem. Soc., Dalton Trans.*, 1993, 2071–2072.

20 A. N. Westra, C. Esterhuysen and K. R. Koch, *Acta Crystallogr., Sect. C*, 2004, **60**, m395–m398.

21 A. Irving, K. R. Koch and M. Matoetoe, *Inorg. Chim. Acta*, 1993, **206**, 193–199.

22 K. R. Koch, J. du Toit, M. R. Caira and C. Sacht, *J. Chem. Soc., Dalton Trans.*, 1994, 785–786.

23 D. Hanekom, J. M. McKenzie, N. M. Derix and K. R. Koch, *Chem. Commun.*, 2005, 767–769.

24 A. N. Westra, J. D. C. Miller and K. R. Koch, in *International Solvent Extraction Conference, ISEC 2002*, ed. P. M. C. K. C. Sole, J. S. Preston and D. J. Robinson, South African Institute of Mining and Metallurgy, Johannesburg, 2002, pp. 327–334.

25 R. I. Edwards, A. J. Bird and G. J. Berfeld, in *Gmelin Handbook of Inorganic Chemistry, Platinum Supplement*, Springer-Verlag, Berlin, 8th edn., 1986.

26 T. Shi, J. Berglund and L. I. Elding, *J. Chem. Soc., Dalton Trans.*, 1997, 2073–2077.

27 J. J. Zuckerman and J. D. Atwood, in *Inorganic Reactions and Methods, Formation of bonds to transition and inner-transition metals*, Wiley-VCH, New York, 1998.

28 L. M. Rendina and R. J. Puddephatt, *Chem. Rev.*, 1997, **97**, 1735–1754.

29 J. J. Pesek and W. R. Mason, *J. Magn. Reson.*, 1977, **25**, 519–529.

30 P. S. Pregosin, *Coord. Chem. Rev.*, 1982, **44**, 247–291.

31 P. M. Cook, L. F. Dahl, D. Hopgood and R. A. Jenkins, *J. Chem. Soc., Dalton Trans.*, 1973, 294–301.

32 J. E. Huheey, E. A. Keiter and R. L. Keiter, in *Inorganic Chemistry: Principles of Structure and Reactivity*, Harper-Collins, New York, 4th edn., 1993.

33 F. A. Cotton and G. Wilkinson, in *Advanced Inorganic Chemistry*, Wiley-Interscience, New York, 5th edn., 1988.

34 P. H. Svensson and L. Kloo, *Chem. Rev.*, 2003, **103**, 1649–1684.

35 F. van Bolhuis, P. B. Koster and T. Migchelsen, *Acta Crystallogr.*, 1967, **23**, 90–91.

36 G. Thiele, O. F. Danzeisen, H. W. Rotter and M. Goanta, *J. Mol. Struct.*, 1999, **482–483**, 93–102.

37 O. F. Danzeisen, M. Goanta, H. W. Rotter and G. Thiele, *Inorg. Chim. Acta*, 1999, **287**, 218–222.

38 D. Rickert and W. Preetz, *Z. Naturforsch.*, 1996, **51**, 1400–1406.

39 F. P. Fanizzi, G. Natile, M. Lanfranchi, A. Tiripicchio, F. Laschi and P. Zanello, *Inorg. Chem.*, 1996, **35**, 3173–3182.

40 H.-J. Korte, B. Krebs, C. G. van Kralingen, A. T. M. Marcelis and J. Reedijk, *Inorg. Chim. Acta*, 1981, **52**, 61–67.

41 K. R. Koch and S. Bourne, *J. Mol. Struct.*, 1998, **441**, 11–16.

42 K. D. Buse, H. J. Keller and H. Pritzkow, *Inorg. Chem.*, 1977, **16**, 1072–1076.

43 C. Bellitto, M. Bonamico, G. Dessy, V. Fares and A. Flamini, *J. Chem. Soc., Dalton Trans.*, 1986, 595–601.

44 F. H. Allen, *Acta Crystallogr., Sect. B*, 2002, **58**, 380–388.

45 P. Deplano, J. R. Ferraro, M. L. Mercuri and E. F. Trogu, *Coord. Chem. Rev.*, 1999, **188**, 71–95.

46 M. F. Belicchi, G. G. Fava and C. Pelizzi, *Acta Crystallogr., Sect. B*, 1981, **37**, 924–926.

47 L. R. Gray, D. J. Gulliver, W. Levason and M. Webster, *Inorg. Chem.*, 1983, **22**, 2362–2366.

48 E. Schulz Lang and J. Strahle, *Z. Anorg. Allg. Chem.*, 1996, **622**, 981–984.

49 D.-L. Long, H.-M. Hu, J.-T. Chen and J.-S. Huang, *Acta Crystallogr., Sect. C*, 1999, **55**, 339–341.

50 P. B. Hitchcock, D. L. Hughes, G. J. Leigh, J. R. Saers, J. Desouza, C. J. Mcgarry and L. F. Larkworthy, *J. Chem. Soc., Dalton Trans.*, 1994, **24**, 3683–3687.

51 I. L. Karle, *J. Chem. Phys.*, 1955, **23**, 1739.

52 F. E. Wood, M. M. Olmstead, J. P. Farr and A. L. Balch, *Inorg. Chim. Acta*, 1985, **97**, 77–83.

53 K. Hindmarsh, D. A. House and M. M. Turnbull, *Inorg. Chim. Acta*, 1997, **257**, 11–18.

54 A. Grabowski and W. Preetz, *Z. Anorg. Allg. Chem.*, 1987, **544**, 95–100.

55 R. A. Gossage, A. D. Ryabov, A. L. Spek, D. J. Stufkens, J. A. M. van Beek, R. van Eldik and G. van Koten, *J. Am. Chem. Soc.*, 1999, **121**, 2488–2497.

56 G. M. Sheldrick, *SHELXS-97 and SHELXL-97, Programs for the Solution and Refinement of Crystal Structures*, University of Göttingen, Germany, 1997.

57 L. J. Barbour, *J. Supramol. Chem.*, 2003, **1**, 189.

58 A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, University of Utrecht, Netherlands, 1999.

59 I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. McCabe, J. Pearson and R. Taylor, *Acta Crystallogr., Sect. B*, 2002, **58**, 389–397.