

Intramolecular hydrogen-bond-directed coordination: *trans*-bis-(*N*-benzoyl-*N'*-propylthiourea- κ S)-diiodoplatinum(II) and *trans*-bis-(*N*-benzoyl-*N'*-propylthiourea- κ S)-dibromoplatinum(II)

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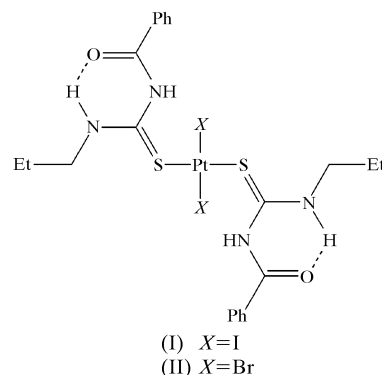
In the title compounds, *trans*-[PtI₂(C₁₁H₁₄N₂OS)₂], (I), and *trans*-[PtBr₂(C₁₁H₁₄N₂OS)₂], (II), respectively, intramolecular N—H···O (propylamine side) hydrogen bonds in the potentially bidentate thiourea ligands lock the carbonyl O atoms into six-membered rings, determining the *S*-monodentate mode of coordination of these ligands. Intramolecular N—H···X (*X* is I or Br) interactions (benzoylamine side) lead to slight distortions of the Pt^{II} coordination spheres from ideal square-planar geometry. The Pt^{II} ion is located on an inversion centre in both structures.

Comment

The compounds generally described as *N,N*-dialkyl- (*HL*¹) and *N*-alkyl-*N'*-aroylthioureas (*H₂L*²) have been found to display very different modes of coordination to Pt^{II} (Koch, 2001). *HL*¹ ligands [*R*¹NC(S)NHC(O)*R*², where *R*¹ = alkyl and *R*² = aryl] coordinate to this metal centre *via* both the S and O atoms with the loss of the thioamidic H atom, forming predominantly *cis* isomers, several of which have been structurally characterized (Irving *et al.*, 1993; Mautjana *et al.*, 2003; Sacht *et al.*, 2000). The structure of only one example of a *trans* complex has been reported to date (Koch *et al.*, 1994). *H₂L*² molecules [*R*¹NHC(S)NHC(O)*R*², where *R*¹ = alkyl and *R*² = aryl] coordinate to PtX₄²⁻ (*X* is I, Br or Cl) to form significant quantities of both *cis*- and *trans*-[PtX₂(*H₂L*²-S)₂] isomers (Koch *et al.*, 1999). In the only structurally characterized complex of Pt^{II} with an *H₂L*² ligand, namely *cis*-dichlorobis-(*N*-propyl-*N'*-benzoylthiourea)platinum(II) (Bourne & Koch, 1993), it was shown that the coordination of the ligand is directed by an intramolecular N—H···O hydrogen bond and occurs, without loss of an H atom, *via* the S atom only. No

structural data are available for a *trans* complex [Cambridge Structural Database (CSD), Version 5.25; Allen, 2002].

In the last decade, we have studied the coordination chemistry of these molecules with Pt^{II} and Pd^{II} as part of our interest in developing practically useful analytical and process-chemical applications for these compounds (Koch, 2001; Mautjana *et al.*, 2003). We present here the crystal structures of the title compounds, (I) and (II) (Figs. 1 and 2), the first two examples of *trans* complexes of Pt^{II} with an *N*-alkyl-*N'*-aroylthiourea ligand, *H₂L*².



Both compounds crystallize in space group *P* $\bar{1}$, with the Pt^{II} ion located on an inversion centre, but they are not isomorphous. Because of the inversion symmetry, both PtS₂X₂ moieties are strictly planar.

The molecular structures of (I) and (II) reveal that, despite the potentially bidentate nature of the ligand (*N*-benzoyl-*N'*-propylthiourea, *H₂L*^{2a}), only the S atom coordinates to the metal, while the carbonyl O atom is locked into an O/C/N/C/N/H ring by means of an intramolecular N2—H7···O1

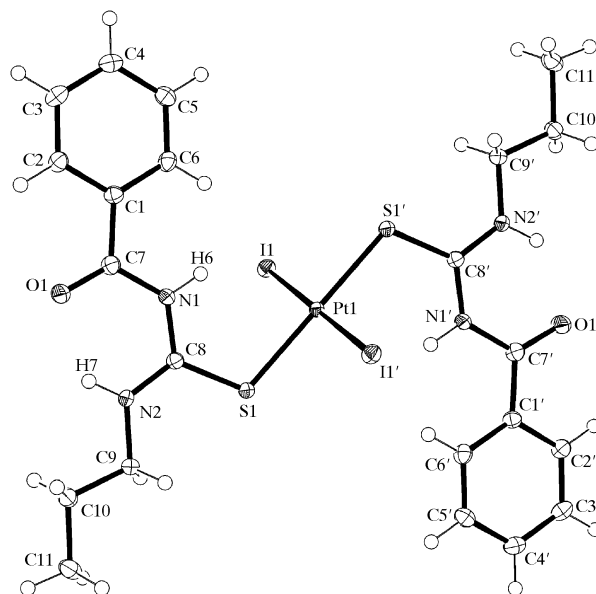


Figure 1

The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Atoms with primed labels are at the symmetry position (1 - *x*, -*y*, -*z*).

hydrogen bond (Tables 2 and 4), similar to that in the previously reported compounds *cis*-dichlorobis(*N*-propyl-*N'*-benzoylthiourea)platinum(II) (Bourne & Koch, 1993) and *trans*-dibromobis(*N*-propyl-*N'*-benzoylthiourea)palladium(II) (Koch *et al.*, 1999). The six-membered O1/C7/N1/C8/N2/H7 rings in both structures are virtually planar, with a maximum deviation from planarity of 0.013 (4) Å for atom N1 in (I) and of 0.05 (2) Å for atom H7 in (II).

The Pt–I and Pt–S bond lengths for (I) [2.617 (2) and 2.315 (6) Å, respectively] compare well with the corresponding distances in the previously reported *trans*-Pt^{II} complexes of *S*-donor ligands and iodide, [Pt{C₂H₅NHC(S)O–C₂H₅}₂I₂] [Pt–I = 2.610 (2) Å and Pt–S = 2.314 (4) Å; Bardi *et al.*, 1987], [Pt{(CH₃)₂S}₂I₂] [Pt–I = 2.604 (1) Å and Pt–S = 2.310 (2) Å; Löqvist *et al.*, 1996] and [Pt{(C₄H₉)₂NC(S)–NHC(O)Ph}₂I₂] [Pt–I = 2.608 (2) Å and Pt–S = 2.294 (3) Å; Koch & Bourne, 1998]. The Pt–Br and Pt–S bond distances in (II) [2.440 (4) and 2.305 (8) Å, respectively] are somewhat longer than the corresponding distances in *trans*-dibromobis(1,4-oxathian)platinum(II) [Pt–Br = 2.420 (1) Å and Pt–S = 2.281 (3) Å; Barnes *et al.*, 1977]. The latter is the only *trans*-Pt^{II} complex of *S*-donor ligands and Br[–] reported in the CSD.

The torsion angles in Tables 1 and 3 illustrate that there is no distortion of the thiourea ligands in compounds (I) and (II). The atoms of the central carbonyl–thiourea moieties, O1/C7/N1/C8/S1/N2, are nearly planar, with deviations of less than 0.04 Å for (I) and (II). The carbonyl–thiourea moiety (O1/C7/N1/C8/S1/N2) in (I) is tilted at an angle of 68.96 (3)° to the coordination plane, while the corresponding angle in (II) is 54.17 (7)°. These angles allow for the relatively short interatomic distances of 3.597 (2) Å between atoms N1 and I1 in (I),

and 3.289 (3) Å between atoms N1 and Br1 in (II). The sums of the van der Waals radii for the N···I and N···Br contacts are *ca* 3.65 and 3.45 Å, respectively (Huheey *et al.*, 1993), so the corresponding distances in (I) and (II) indicate intramolecular N1–H6···I1 and N1–H6···Br1 hydrogen bonds (Tables 2 and 4). Such interactions also account for the distortions of the coordination spheres of the Pt^{II} centres from ideal square-planar geometry, leading to angles slightly larger than 90° for S1–Pt1–I1 [92.03 (2)°] and S1–Pt1–Br1 [94.40 (3)°].

The intramolecular N–H···O hydrogen bond in (I) and (II) is also observed in the free ligand *N*-propyl-*N'*-benzoylthiourea, H₂L^{2a} (Dago *et al.*, 1989). Analogous intramolecular N–H···O interactions are a common phenomenon in related molecules which, as in H₂L^{2a}, feature a central carbonyl–thiourea moiety –NHC(S)NHC(O)–; examples include molecules such as *N*-(*n*-butyl)-*N'*-benzoylthiourea (Koch *et al.*, 1995), *N*-(2-pyridyl)-*N'*-benzoylthiourea (Kaminsky *et al.*, 2002), *N*-benzoylthiourea (Wagner *et al.*, 2003), *N*-(*p*-bromophenyl)-*N'*-benzoylthiourea (Yamin & Yusof, 2003), 3-(3-benzoylthioureido)propionic acid (Yusof & Yamin, 2003), *N*-benzoyl-*N'*-(2-hydroxyethyl)thiourea (Zhang, Xian *et al.*, 2003) and *N*-ethoxycarbonyl-*N'*-phenylthiourea (Zhang, Wei *et al.*, 2003).

In conclusion, for the H₂L² ligand, the relatively stable six-membered O/C/N/C/N/H hydrogen-bonded ring persists upon coordination to ‘softer’ transition metal ions, without the loss of an H atom. This is confirmed by the observations on (I) and (II) in this paper, and can be seen in several related structures, *e.g.* [[Cu{PhNHC(S)NHC(O)C₃H₅}₂Cl]₂] (Černak *et al.*, 1991), [Rh{C₃H₇NHC(S)NHC(O)Ph}(C₈H₁₂)Cl] (Cauzzi *et al.*, 1995), *trans*-[Pd{C₃H₇NHC(S)NHC(O)Ph}₂Br₂] (Koch *et al.*, 1999), [[Cu{C₅NH₄NHC(S)NHC(O)Ph}Cl₂]₂] (Li *et al.*, 2002), and [Cu{CH₃PhNHC(S)NHC(O)OC₂H₅}₂Cl] (Zhang, Xian & Wei, 2003).

Experimental

Reaction of PtX₄^{2–} (X is I, Br or Cl) with *N*-benzoyl-*N'*-propylthiourea (H₂L^{2a}) leads to isomer mixtures of *cis*- and *trans*-[PtX₂(H₂L^{2a}-S)₂] (X is I, Br or Cl), the equilibrium ratios of which were determined by ¹H NMR spectroscopy in a previous study to be 5:95, 42:58 and 68:32 for X = I, Br or Cl, respectively (Koch *et al.*, 1999). In the present study, the ligand H₂L^{2a} and complexes *cis*- and *trans*-[PtX₂(H₂L^{2a}-S)₂] (X is I or Br) were synthesized, recrystallized and characterized using the method previously reported by Koch *et al.* (1999). All reagents and solvents were commercially available and all were used without further purification, except for the acetone used in the ligand synthesis, which was distilled before use. ¹⁹⁵Pt NMR spectra of the products show resonances at δ_{Pt} –4846 and –4670 p.p.m. for *trans*- and *cis*-[PtI₂(H₂L^{2a}-S)₂], respectively, and at δ_{Pt} –3662 and –3681 p.p.m. for *trans*- and *cis*-[PtBr₂(H₂L^{2a}-S)₂], respectively, confirming the presence of both isomers. However, good quality crystals of only the dominant *trans* isomers could be isolated by recrystallization from chloroform–ethanol; suitable crystals of the *cis* complexes could not be obtained. The ¹⁹⁵Pt NMR spectra were recorded in CDCl₃ on a Varian INOVA 600 MHz spectrometer (128 MHz, 303 K); ¹⁹⁵Pt chemical shifts are quoted relative to external H₂PtCl₆ (500 mg ml^{–1} in 30% *v/v* D₂O–1 M HCl).

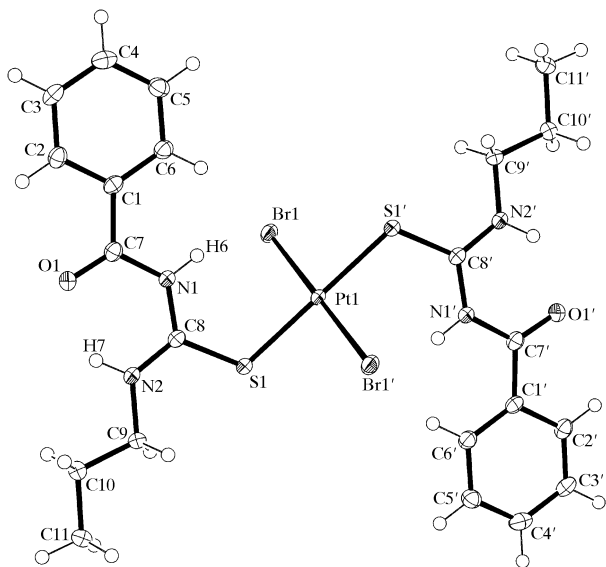


Figure 2
The molecular structure of (II), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Atoms with primed labels are at the symmetry position (1 – x, 1 – y, 1 – z).

Compound (I)*Crystal data*

[PtI₂(C₁₁H₁₄N₂OS)₂]
M_r = 893.49
 Triclinic, *P* $\bar{1}$
a = 7.3485 (4) Å
b = 10.2458 (6) Å
c = 10.5738 (6) Å
 α = 67.725 (1)°
 β = 74.742 (1)°
 γ = 70.468 (1)°
V = 685.76 (7) Å³
Z = 1

Data collection

Bruker SMART APEX CCD area-
 detector diffractometer
 ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2001)
T_{min} = 0.13, *T_{max}* = 0.28
 7162 measured reflections
 2682 independent reflections

Refinement

Refinement on *F*²
R(*F*) = 0.015
wR(*F*²) = 0.037
S = 1.06
 2682 reflections
 161 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

D_x = 2.164 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 7162
 reflections
 θ = 2–26°
 μ = 7.55 mm⁻¹
T = 100 (2) K
 Plate, brown
 0.30 × 0.24 × 0.17 mm

2673 reflections with *I* > 2 σ (*I*)
R_{int} = 0.019
 θ_{max} = 26.0°
h = -9 → 9
k = -12 → 12
l = -13 → 13

$w = 1/[\sigma^2(F_o^2) + (0.0174P)^2 + 0.2796P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.85 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.59 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 (Sheldrick, 1997)
 Extinction coefficient: 0.0036 (3)

Compound (II)*Crystal data*

[PtBr₂(C₁₁H₁₄N₂OS)₂]
M_r = 799.51
 Triclinic, *P* $\bar{1}$
a = 8.6641 (11) Å
b = 8.8178 (11) Å
c = 9.7472 (12) Å
 α = 104.609 (2)°
 β = 112.263 (2)°
 γ = 98.663 (2)°
V = 641.18 (14) Å³
Z = 1

Data collection

Bruker SMART APEX CCD area-
 detector diffractometer
 ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2001)
T_{min} = 0.14, *T_{max}* = 0.21
 6491 measured reflections
 2490 independent reflections

Refinement

Refinement on *F*²
R(*F*) = 0.024
wR(*F*²) = 0.060
S = 1.06
 2490 reflections
 160 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

D_x = 2.071 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 6491
 reflections
 θ = 2–26°
 μ = 8.78 mm⁻¹
T = 100 (2) K
 Prism, orange
 0.24 × 0.22 × 0.18 mm

2398 reflections with *I* > 2 σ (*I*)
R_{int} = 0.022
 θ_{max} = 26.0°
h = -10 → 10
k = -10 → 10
l = -12 → 12

$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 0.0891P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 2.68 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.20 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °) for (I).

Pt1—S1	2.3148 (6)	N1—C7	1.377 (3)
Pt1—I1	2.61667 (19)	N1—C8	1.380 (3)
S1—C8	1.701 (2)	N2—C8	1.314 (3)
O1—C7	1.226 (3)		
S1—Pt1—I1	92.033 (17)	O1—C7—N1	121.4 (2)
I1 ¹ —Pt1—I1	180.0	N2—C8—N1	118.8 (2)
C8—S1—Pt1	108.10 (8)	N2—C8—S1	120.49 (18)
C7—N1—C8	127.3 (2)		
C2—C1—C7—N1	172.2 (2)	C7—N1—C8—S1	-178.4 (2)
C7—N1—C8—N2	2.1 (4)	C8—N2—C9—C10	-170.2 (2)

Symmetry code: (i) 1 - *x*, -*y*, -*z*.**Table 2**

Hydrogen-bonding geometry (Å, °) for (I).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H7...O1	0.84 (3)	1.98 (3)	2.639 (3)	134 (2)
N1—H6...I1	0.80 (3)	3.06 (3)	3.600 (2)	127 (2)

Table 3

Selected geometric parameters (Å, °) for (II).

Pt1—S1	2.3046 (9)	N1—C8	1.372 (4)
Pt1—Br1	2.4407 (4)	N1—C7	1.389 (5)
S1—C8	1.702 (4)	N2—C8	1.313 (4)
O1—C7	1.220 (4)		
S1—Pt1—Br1	94.43 (3)	O1—C7—N1	121.5 (3)
Br1—Pt1—Br1 ¹	180.0	N2—C8—N1	119.0 (3)
C8—S1—Pt1	113.44 (13)	N2—C8—S1	119.2 (3)
C8—N1—C7	125.9 (3)		
C2—C1—C7—N1	179.6 (3)	C7—N1—C8—S1	-175.3 (3)
C7—N1—C8—N2	4.3 (5)	C8—N2—C9—C10	174.5 (3)

Symmetry code: (i) 1 - *x*, 1 - *y*, 1 - *z*.**Table 4**

Hydrogen-bonding geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H7...O1	0.83 (5)	1.95 (5)	2.603 (4)	135 (4)
N1—H6...Br1	0.78 (5)	2.62 (5)	3.290 (3)	145 (4)

H atoms involved in hydrogen bonding, *i.e.* those attached to N atoms, were located in a difference electron-density map and refined isotropically. All other H atoms were placed in geometrically calculated positions, with C—H = 0.99 (for CH₂ groups), 0.98 (for CH₃ groups) or 0.95 Å (for phenyl groups), and refined using a riding model, with *U*_{iso}(H) = 1.2*U*_{eq}(parent) (for CH₂ and phenyl groups) or 1.5*U*_{eq}(parent) (for CH₃ groups). In compound (II), the highest peak and deepest hole in the residual electron-density map, at distances of 0.91 and 0.99 Å, respectively, from atom Pt1, are unusually high, possibly due to residual absorption errors inherent in the use of empirical absorption corrections.

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 1999); software used to prepare material for publication: *X-SEED*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1636). Services for accessing these data are described at the back of the journal.

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