DALTON
FULL PAPER

Synthesis, characterisation and coordination chemistry of novel chiral *N*,*N*-dialkyl-*N*′-menthyloxycarbonylthioureas. Crystal and molecular structures of *N*,*N*-diethyl-*N*′-(−)-(3*R*)-menthyloxycarbonylthiourea and *cis*-(S,S)-[Pt(L)Cl(DMSO)] [where HL = *N*-(+)-(3*R*)-menthyloxycarbonyl-*N*′-morpholinothiourea or *N*-benzoyl-*N*′,*N*′-diethylthiourea]

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Received 19th September 2000, Accepted 27th October 2000
First published as an Advance Article on the web 4th December 2000

The novel ligands *N*,*N*-diethyl-*N*′-(−)-(3*R*)-menthyloxycarbonylthiourea (HL^3), *N*,*N*-diethyl-*N*′-(+)-(3*R*)-menthyloxycarbonylthiourea (HL^4), *N*-(−)-(3*R*)-menthyloxycarbonyl-*N*′-morpholinothiourea (HL^5) and *N*-(+)-(3*R*)-menthyloxycarbonyl-*N*′-morpholinothiourea (HL^6) have been prepared and characterised. The molecular structure of HL^3 has been confirmed by X-ray crystallography. The reaction of these *N*,*N*-disubstituted-*N*′-menthyloxycarbonylthiourea ligands with *cis*-$[PtCl_2(DMSO)_2]$ in the presence of sodium acetate yields geometric isomers of the resultant [Pt(L)Cl(DMSO)] complexes, that is the DMSO is sulfur bonded to the platinum in either a *cis*-(S,S) or *trans*-(S,S) arrangement with respect to the sulfur donor atom of the chelated ligand. This is in contrast to the complexation reaction of *cis*-$[PtCl_2(DMSO)_2]$ with *N*-benzoyl-*N*′,*N*′-diethylthiourea (HL^1) or *N*-benzoyl-*N*′-morpholinothiourea (HL^2) which yields only one [Pt(L)Cl(DMSO)] complex in which the DMSO is in a *cis*-(S,S) arrangement with respect to the sulfur donor atom of the chelated ligand. The molecular structures of *cis*-(S,S)-[Pt(L)Cl(DMSO)], where L = $(L^1)^-$ or $(L^6)^-$, have been determined by X-ray crystallography. The difference in the coordination chemistry of the acylthiourea and alkoxycarbonylthiourea ligands has been examined further by treating the [Pt(L)Cl(DMSO)] complexes with PPh_3 to give the corresponding mono- and bis-(phosphine) complexes, $[Pt(L)Cl(PPh_3)]$ and $[Pt(L)(PPh_3)_2]^+$. The ^{31}P NMR studies of these complexes reveal that the alkoxycarbonylthiourea ligands bind less strongly than the acylthiourea ligands, which is consistent with the crystallographic studies. The weaker binding properties of the alkoxycarbonylthiourea ligands might be a possible explanation for the observed geometric isomerisation of the complexes and that the mechanism could involve a chelate ring opening step.

Introduction

We are currently investigating the design and synthesis of a novel series of platinum(II) complexes, of the type [Pt(L)-Cl(RR′SO)] (where L = O,S chelate), for potential use as chemotherapeutic agents.[1,2] Our approach has been to prepare complexes that are not structurally analogous to cisplatin [Pt-$(NH_3)_2Cl_2$] in an attempt to develop new platinum(II)-based antitumour drugs that will hopefully overcome its major drawbacks. We have, to date, focused on the use of the oxygen–sulfur acylthiourea, $RCONHCSN(R')_2$, chelate ligand systems.[1,2] Interest in these ligands was prompted by their versatility in that one can readily vary the functional groups R and R′ to give a wide range of different ligand systems with different physical and chemical properties. We have since extended these studies to include the alkoxycarbonylthioureas, $ROCONHCSN(R')_2$, the only difference between the two ligand systems being the O atom between the R and carbonyl groups. While the coordination chemistry of acylthiourea ligands with platinum(II) is fairly well established,[3] the corresponding complexation behaviour of alkoxycarbonylthiourea ligands has, to the best of our knowledge, hardly been explored.

Since platinum(II) forms 4-coordinate square planar complexes it is only possible to prepare chiral platinum(II) complexes using chiral ligands. Hence further interest in the alkoxycarbonylthiourea ligand systems stems from the fact that we could prepare chiral ligands from optically pure alkoxycarbonyl chloride precursors, such as menthyloxycarbonyl chlorides. Interest in preparing chiral platinum(II) metal-based drugs is motivated by the fact that enzymes and other natural binding sites recognise substrates with a particular chirality to generate a variety of biological functions. Although chirality is not a prerequisite for biological activity, when bioactive molecules contain a stereogenic centre large differences are usually observed in the activities of the individual enantiomers. This is a general phenomenon and applies to all bioactive substances, including metal-based drugs. For example, different activities have been observed for isomeric platinum(II) complexes, and this difference could be ascribed to the chiral recognition between the active platinum(II) species and their final target, DNA.[4,5]

The anionic ligands or leaving groups in the platinum complexes also have considerable influence on antitumour activities, and are believed to play important roles in drug metabolism. Unsymmetrical sulfoxides are chiral, and therefore special regard has to be paid not only to the chiralities of the carrier ligands but also to those of the sulfoxide leaving groups. The effect of the chirality of the leaving group has recently been reported by Farrell *et al.*; they noted that for a series of complexes of the type $[Pt(diamine)Cl(RR'SO)]^+$

DOI: 10.1039/b007589m

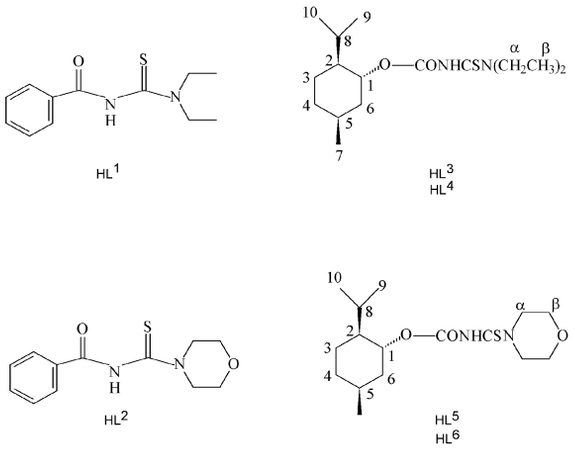

Fig. 1 Structural formulae of ligands. The atom numbering scheme adopted for NMR assignments is also given.

enhanced biological activity was observed when RR′SO = (*S*)-methyl (*p*-tolyl) sulfoxide (*S*-MTSO).[5]

To this end we have synthesized the chiral carrier ligands, *N*,*N*-diethyl-*N*′-(−)-(3*R*)-menthyloxycarbonylthiourea, *N*,*N*-diethyl-*N*′-(+)-(3*R*)-menthyloxycarbonylthiourea, *N*-(−)-(3*R*)-menthyloxycarbonyl-*N*′-morpholinothiourea and *N*-(+)-(3*R*)-menthyloxycarbonyl-*N*′-morpholinothiourea (Fig. 1) and their corresponding platinum(II) complexes, [Pt(L)Cl(RR′SO)], where RR′SO = DMSO or *S*-MTSO. To the best of our knowledge the synthesis and characterisation of these chiral ligands and their corresponding platinum(II) complexes are being reported for the first time. A comparison of the coordination chemistry of these novel ligands to that of the *N*,*N*-disubstituted-*N*′-benzoylthioureas is also presented.

Experimental

Materials and physical methods

Diethylamine, morpholine and acetone were dried over 4 Å molecular sieve and freshly distilled before use. All other reagents were commercial grade and used as received. The complexes *cis*-[$PtCl_2(DMSO)_2$] and *cis*-[$PtCl_2$(*S*-MTSO)$_2$] were prepared according to a literature procedure.[6] IR spectra were obtained as KBr disks on a Perkin-Elmer FT-IR Spectrum 2000, between 4000 and 250 cm^{-1}, ^1H, ^{13}C, ^{31}P and ^{195}Pt NMR spectra on a Bruker 400AMX Spectrometer at 30 ± 1 °C. All samples were prepared using deuteriated solvents purchased from Aldrich Chemical Company, and 5 mm NMR tubes were used throughout. Chemical shifts for ^1H NMR are reported in parts per million (ppm) relative to the centre line of the solvent proton resonance of known shifts relative to TMS, those for ^{31}P NMR relative to an external standard (85% H_3PO_4) and ^{195}Pt shifts relative to the external standard H_2PtCl_6 [500 mg in 1 ml 30% (v/v) D_2O–HCl (1 M)]. Melting points were determined using a Reichert hot-stage microscope and are uncorrected. Elemental analyses were carried out at the microanalytical unit at the University of Cape Town, South Africa. Thin-layer chromatography was performed on silica sheets $60F_{254}$ (Merck, Darmstadt). The optical rotations of chiral ligands were determined using a Perkin-Elmer 141 Polarimeter, with dry acetone as solvent. High performance liquid chromatography was performed with a Spectro-Physics P100 isocratic pump, Whatman Partisil 10 column (NP), Waters 401 Differential Refractometer and Rikadenki chart recorder (5 mm min^{-1}; 10 mV).

Preparation of ligands

The synthesis and full characterisation of the ligands HL^1 and HL^2 have recently been reported.[1,2] The ligands $HL^{3–6}$ were prepared using a modified method of Douglass and Dains.[7] To dry potassium thiocyanate (9.53 mmol) in dry acetone (50 ml) was added dropwise an equimolar amount of menthyl chloroformate (9.57 mmol). The solution was refluxed under nitrogen for 2 hours. The amine (9.58 mmol) was then added dropwise to the cooled reaction mixture and the solution refluxed for 2 hours then cooled to room temperature. KCl was removed by filtration and the filtrate concentrated to half the volume under reduced pressure. Water (100 ml) was added whereupon a yellow oil formed. The aqueous layer was decanted and the oil extracted into diethyl ether (40 ml). The aqueous layer was extracted twice with ether (40 ml) and the ether fractions were combined, dried over anhydrous $MgSO_4$ and evaporated to dryness under reduced pressure to yield a yellow oil. The oil was dissolved in a small volume of ethanol and the solution placed in a freezer. Colourless crystals were collected by filtration, washed with water, ethanol and dried *in vacuo* over silica gel. The ligands were fully characterised and the experimental data are summarised in Tables 1 and 2. Recrystallisation of HL^3 **1** from EtOH yielded crystals suitable for X-ray analysis.

Platinum sulfoxide complexes

[Pt(L^3)Cl(DMSO)] and [Pt(L^4)Cl(DMSO)]. A solution of the respective ligand (0.48 mmol) in acetonitrile (10 ml) was added dropwise to a solution of *cis*-[$PtCl_2(DMSO)_2$] (0.48 mmol) in acetonitrile–DMSO (6 ml, 1:1 v/v), followed by sodium acetate (0.74 mmol) in water (1.5 ml), and stirred for 3 days at room temperature. Water (100 ml) was then added to the bright yellow solution whereupon a yellow oil formed. The mixture was placed in a refrigerator (4 °C) overnight. The yellow oil was extracted into ether (40 ml), dried over $MgSO_4$ and evaporated to dryness under reduced pressure to yield a yellow precipitate. The complexes were fully characterised and the experimental data are summarised in Tables 5 and 6.

[Pt(L^5)Cl(DMSO)] and [Pt(L^6)Cl(DMSO)] 2. A solution of the respective ligand (0.47 mmol) in acetonitrile (10 ml) was added dropwise to a solution of *cis*-[$PtCl_2(DMSO)_2$] (0.47 mmol) in acetonitrile–DMSO (6 ml, 1:1 v/v), followed by sodium acetate (0.72 mmol) in water (1.5 ml), and stirred for 3 days at room temperature. After a few hours a yellow precipitate was observed. Water (100 ml) was then added and the mixture placed in a refrigerator (4 °C) overnight. The yellow precipitate was collected by filtration, washed with water, ethanol, and dried *in vacuo* over silica gel. The complexes were fully characterised and the experimental data are given in Tables 5 and 6. Slow evaporation of a solution of [Pt(L^6)-Cl(DMSO)] **2** in benzene–hexane yielded crystals suitable for X-ray crystallography.

[Pt(L^3)Cl(*S*-MTSO)]. A solution of HL^3 (0.115 g, 0.364 mmol) in acetonitrile (10 ml) was added dropwise to a solution of *cis*-[$PtCl_2$(*S*-MTSO)$_2$] (0.209 g, 0.364 mmol) in acetonitrile (6 ml), followed by sodium acetate (0.045 g, 0.546 mmol) in water (1.5 ml), and stirred for 3 days at room temperature. Water (100 ml) was then added to the orange solution whereupon a fine yellow precipitate formed. This mixture was placed in a refrigerator (4 °C) for a week. The precipitate was extracted into $CHCl_3$ (40 ml), dried over $MgSO_4$ and evaporated to dryness under reduced pressure to yield a brown oil. The oil was dissolved in ethanol and placed in a freezer for several days. The resultant yellow precipitate was collected by filtration, washed with water, ethanol and dried *in vacuo* over silica gel. The complex was fully characterised and the experimental data are summarised in Tables 5 and 6.

***cis*-(S,S)-[Pt(L^1)Cl(DMSO)] 3 and *cis*-(S,S)-[Pt(L^2)Cl-(DMSO)].** The preparation and full characterisation of these

Table 1 Analytical data for *N*,*N*-diethyl-*N*′-menthyloxycarbonylthiourea and *N*-menthyloxycarbonyl-*N*′-morpholinothiourea ligands

Ligand	mp/°C	Yield (%)	α_{25}^{D}/°	Analytical data (% C/H/N/S)[a]	IR ν(NH)	IR δ(NH) + ν(C=O)	IR ν(C=O) + δ(NH)
HL[3]	88–90	26	−42.4	60.6; 10.3; 9.0; 9.8 (61.1; 9.6; 8.9; 10.2)	3179	1536	1737
HL[4]	89–90	32	+36.5	61.0; 10.3; 9.1; 10.2 (61.1; 9.6; 8.9; 10.2)	3179	1536	1737
HL[5]	128–130	42	−45.8	58.9; 8.8; 8.55; 9.3 (58.5; 8.6; 8.5; 9.8)	3209	1540	1737
HL[6]	127–129	42	+45.4	59.0; 8.9; 8.4; 9.1 (58.5; 8.6; 8.5; 9.8)	3209	1540	1737

[a] Required values are given in parentheses.

Table 2 Selected ^{1}H NMR data for the *N*,*N*-diethyl-*N*′-menthyloxycarbonylthiourea and *N*-menthyloxycarbonyl-*N*′-morpholinothiourea ligands

Compound	H^1	H^2	H^3	H^4	H^5	H^6	H^7	H^8	H^9	H^{10}	H_α	H_β	H_{NH}
HL[3]	4.575	1.341	1.676 1.030	1.676 0.854	1.466	2.038 1.030	0.906	1.898	0.783	0.894	3.639	1.274	6.998
HL[4]	4.575	1.341	1.676 1.030	1.676 0.854	1.466	2.038 1.030	0.906	1.898	0.783	0.894	3.639	1.274	6.998
HL[5]	4.557	1.349	1.671 1.024	1.671 0.837	1.460	2.002 1.024	0.894	1.868	0.760	0.894	3.785	3.785	7.346
HL[6]	4.557	1.349	1.671 1.024	1.671 0.837	1.460	2.002 1.024	0.894	1.868	0.760	0.894	3.785	3.785	7.346

complexes have recently been reported.[1,2] Recrystallisation of **3** from chloroform–hexane yielded crystals suitable for X-ray crystallography.

Phosphine studies

The phosphine studies were carried out by adding stoichiometric amounts of triphenylphosphine to a solution of the [Pt(L)Cl(DMSO)] (where L = L^1, L^2, L^4, or L^6) complex (5–10 mg) in $CDCl_3$ in an NMR tube. The mixture was shaken vigorously and then the ^{1}H and ^{31}P NMR spectra were recorded. The ^{31}P NMR data for the [Pt(L)Cl(PPh_3)] and [Pt(L)(PPh_3)$_2$]$^+$ complexes are given in Tables 9 and 10, respectively.

Crystal structure determinations

The three dimensional intensity data were collected on a Syntex P-1 for HL[3] **1** and those for *cis*-(S,S)-[Pt(L^6)Cl(DMSO)] **2** and *cis*-(S,S)-[Pt(L^1)Cl(DMSO)] **3** on a Bruker SMART CCD diffractometer. All reflections were corrected for Lorentz and polarisation effects. Data reduction was performed using PROFIT[8] for **1** and SHELXTL[9] for **2**, while absorption corrections for **2** and **3** were done using SADABS.[10] The structure of HL[3] was solved by the direct method and those of **2** and **3** by Patterson and successive Fourier synthesis (SHELXS 97[11] and SHELXL 97[12]). The crystal of HL[3] was covered with Canada Balsam after signs of decay were detected, hence a data reduction was done to eliminate weak reflections and identical reflections were merged. All hydrogen atoms were included in calculated positions with fixed isotropic thermal parameters except for the amine hydrogens of HL[3] that were detected from the Fourier map. All the relevant structural details and refinement parameters are given in Table 3. The molecular graphics were produced using ORTEP.[13]

CCDC reference number 186/2253.

See http://www.rsc.org/suppdata/dt/b0/b007589m/ for crystallographic files in .cif format.

Results and discussion

Ligand synthesis and characterisation

The *N*,*N*-disubstituted *N*′-menthyloxycarbonylthiourea ligands (HL[3-6]), as shown in Fig. 1, were prepared using a modified method of Douglass and Dains.[7] The synthesis involves reaction of menthyl chloroformate with potassium thiocyanate followed by condensation with the appropriate secondary amine. The ligands were characterised using infrared (IR) and ^{1}H NMR spectroscopy, polarimetry and elemental analysis. The analytical data, principal infrared bands and ^{1}H NMR data are summarised in Tables 1 and 2. The assignments of the ^{1}H NMR spectra were accomplished using 2-D ^{1}H and ^{13}C-{^{1}H} NMR and HMQC (heteronuclear multiple quantum correlation) experiments. The elemental analyses, IR and ^{1}H NMR data are consistent with the proposed structures and the structure of HL[3] has been confirmed by X-ray crystallography.

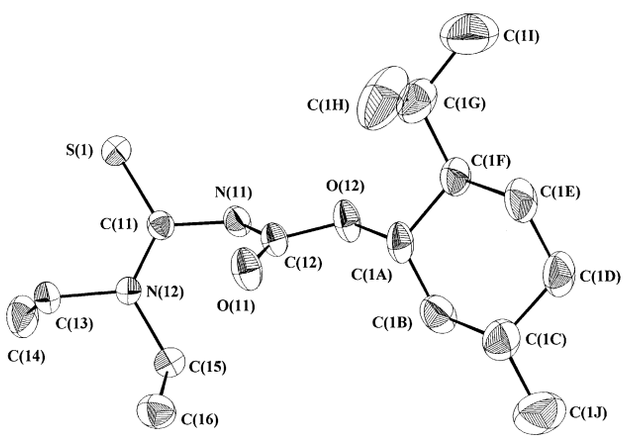

Fig. 2 Molecular structure showing the atom numbering scheme and displacement ellipsoids (30% probability) for molecule 1 of *N*,*N*-diethyl-*N*′-(−)-(3*R*)-menthyloxycarbonylthiourea **1**. Hydrogen atoms have been omitted for clarity.

Crystal structure of *N*,*N*-diethyl-*N*′-(−)-(3*R*)-menthyloxycarbonylthiourea (HL[3])

The structure of HL[3] consists of two discrete molecules per asymmetric unit, thus four chemically equivalent molecules in the unit cell. The structure of molecule 1, together with the atom numbering scheme, is given in Fig. 2. The conformations of the two molecules differ as illustrated in Fig. 3, wherein the two molecules are superimposed on one another. Relevant bond lengths and angles are given in Table 4, and it is clear

Table 3 Crystal data and structure refinement for compounds **1**, **2** and **3**

	1	**2**	**3**
Empirical formula	$C_{32}H_{60}N_4O_4S_2$	$C_{18}H_{35}ClN_2O_4PtS_2$	$C_{14}H_{21}ClN_2O_2PtS_2$
Formula weight	628.96	638.14	543.99
T/K	293(2)	293(2)	293(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1$	$P2_12_12_1$	$P\bar{1}$
a/Å	8.889(2)	9.8964(6)	8.7436(4)
b/Å	13.207(3)	13.2721(8)	10.0717(5)
c/Å	16.911(3)	18.0016(11)	11.5723(6)
α/°	90	90	76.263(10)
β/°	100.51(3)	90	89.207(10)
γ/°	90	90	68.205(10)
V/Å^3	1952.0(7)	2364.4(2)	916.05(8)
Z	2	4	2
μ/mm^{-1}	0.172	6.249	8.039
Reflections collected	2910	15355	9904
Independent reflections	2770	5462	4433
R_{int}	0.031	0.0369	0.0365
Final R, R_w indices [$I > 2\sigma(I)$]	0.0385, 0.0925	0.0296, 0.0535	0.0299, 0.0725
Absolute structure parameter[14]	0.18(11)	0.013(6)	

Table 4 Selected bond lengths (Å), angles (°) and torsion angles (°) for the ligands in compounds **1**, **2** and **3**

	1			
	Molecule 1	Molecule 2	**2**	**3**
S(1)–C(11)	1.677(4)	1.673(4)	1.734(5)	1.735(4)
O(11)–C(12)	1.200(5)	1.186(5)	1.254(5)	1.271(5)
O(12)–C(12)	1.333(5)	1.343(5)	1.329(5)	
O(12)–C(1A)	1.463(5)	1.458(4)	1.464(5)	
N(11)–C(11)	1.399(5)	1.396(5)	1.345(6)	1.348(5)
N(11)–C(12)	1.370(5)	1.382(5)	1.309(5)	1.312(6)
N(12)–C(11)	1.329(6)	1.326(6)	1.343(6)	1.335(5)
C(12)–O(12)–C(1A)	117.2(3)	117.1(3)	120.1(3)	
C(12)–N(11)–C(11)	125.6(4)	122.3(3)	125.0(4)	127.3(4)
N(12)–C(11)–N(11)	116.8(4)	117.5(4)	114.8(4)	113.8(4)
N(12)–C(11)–S(1)	124.6(3)	124.0(3)	115.3(4)	117.4(3)
N(11)–C(11)–S(1)	118.5(3)	118.5(3)	129.8(4)	128.8(3)
O(11)–C(12)–N(11)	125.3(4)	126.4(4)	132.6(4)	130.3(4)
O(11)–C(12)–O(12)	126.0(4)	126.0(4)	115.7(4)	
N(11)–C(12)–O(12)	108.7(4)	107.7(3)	111.7(4)	
O(11)–C(12)–O(12)–C(1A)	4.7(7)	3.3(6)		
C(1G)–C(1F)–C(1A)–O(12)	59.2(5)	58.8(5)		
O(11)–C(12)–C(11)–S(1)	115.0(4)	−109.3(4)		
C(13)–N(12)–C(11)–N(11)	173.9(3)	19.5(6)		
C(15)–N(12)–C(11)–N(11)	−19.7(6)	−171.5(3)		

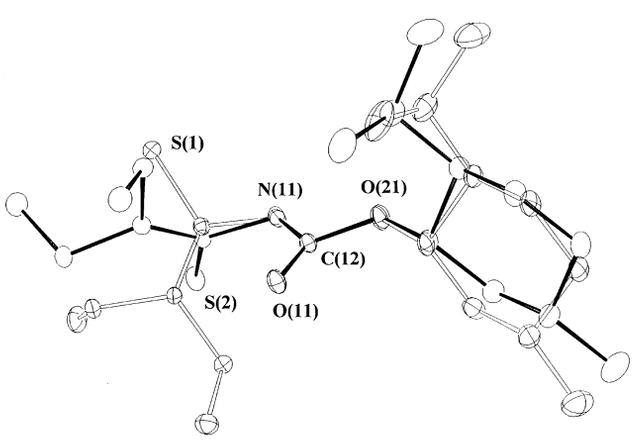

Fig. 3 Molecular structures of molecules 1 and 2 of *N*,*N*-diethyl-*N*′-(−)-(3*R*)-menthyloxycarbonylthiourea superimposed. Molecule 2 is numbered with the first digit referring to the number of the molecule and the second to the number of the atom. Hydrogen atoms have been omitted for clarity.

that most of the bond distances, angles and torsion angles for molecules 1 and 2 of compound **1** are essentially the same. The largest difference concerns the orientation of the sulfur [S(1) and S(2)] and carbonyl groups [C(12)–O(11) and C(22)–O(21)] with respect to one another, as illustrated by the torsion angles O(11)–C(12)–C(11)–S(1) and O(21)–C(22)–C(21)–S(2) of 115.0(4) and −109.3(4) °, respectively.

The C–N bond lengths range from 1.326(6) to 1.399(5) Å and are shorter than the average single C–N bond length of 1.479 Å, thus showing varying degrees of double bond character. The partial double bond character of the C(11)–N(12) bond is further manifested by the magnetic inequivalence of the methylene protons adjacent to the nitrogen atom of the diethylamino moiety.

Synthesis of [Pt(L)Cl(RR′SO)] complexes

Dimethyl sulfoxide complexes were prepared using all four alkoxycarbonylthiourea ligands, while the complex with an unsymmetrical sulfoxide (*S*-MTSO) was prepared using *N*,*N*-diethyl-*N*′-(−)-(3*R*)-menthyloxycarbonylthiourea only. The

Table 5 Analytical data for platinum(II) sulfoxide complexes

Complex	mp/°C	Yield (%)	Analytical data (% C/H/N/S)[a]	ν(SO)/cm^{-1}
[Pt(L^3)Cl(DMSO)]	72–75	29	35.1; 5.8; 4.5; 10.25 (34.75; 5.7; 4.5; 10.3)	1142
[Pt(L^4)Cl(DMSO)]	74–80	64	35.1; 5.8; 4.5; 10.5 (34.75; 5.7; 4.5; 10.3)	1142
[Pt(L^5)Cl(DMSO)]	200–(decomp.)	75	34.2; 5.3; 4.6; 10.0 (34.0; 5.2; 4.4; 10.1)	1154
[Pt(L^6)Cl(DMSO)]	200–(decomp.)	80	34.3; 5.2; 4.5; 9.95 (34.0; 5.2; 4.4; 10.1)	1154
[Pt(L^3)Cl(*S*-MTSO)]	170–171	48	41.1; 6.1; 4.0; 9.1 (41.3; 5.6; 4.0; 9.2)	1138

[a] Required values are given in parentheses.

complexes were prepared in a two step synthesis according to eqns. (1) and (2), where HL represents the alkoxycarbonylthiourea ligands.

$$K_2PtCl_4 + 3\ RR'SO \longrightarrow cis\text{-}[PtCl_2(RR'SO)_2] \quad (1)$$

$$cis\text{-}[PtCl_2(RR'SO)_2] + HL \xrightarrow{NaOAc} [Pt(L)Cl(RR'SO)] \quad (2)$$

Characterisation of complexes

All the complexes were fully characterised by elemental analysis, IR and ^{1}H, ^{195}Pt NMR spectroscopy. The elemental analyses, principal infrared bands, ^{1}H and ^{195}Pt NMR data are given in Tables 5 and 6.

The strong IR band in the region 1130–1154 cm^{-1} is assigned to the ν(SO) stretching frequency. The ν(SO) peak is shifted to a higher wavenumber upon complexation compared to the corresponding vibration of the unbound sulfoxide ν(SO) 1055 cm^{-1}, and is indicative of sulfur bonded sulfoxide.[6] Upon complexation of the alkoxycarbonylthiourea ligands the N–H stretching vibrations disappear and the ligand ν(CO) peak shifts to higher wavenumbers. Such a shift is also expected for the C=S stretch vibration, but this could not be assigned unambiguously.

In the ^{1}H NMR spectra for the complexes two proton resonances for the methyl protons of the sulfoxide ligand are observed in the region δ 3.6–3.4. These are shifted 1 ppm downfield relative to the "free" sulfoxide ligand and are thus typical for sulfur bonded sulfoxides.[6] Moreover, the signals due to the methyl protons of the sulfoxide, in cases where there were no overlapping peaks, show a ^{195}Pt satellite doublet with ^3J(PtH) of about 23 Hz, due to vicinal coupling with the platinum centre, ^{195}Pt (33.7%, $I = \frac{1}{2}$), the same order of magnitude as found for sulfur bonded sulfoxide complexes.[6] The presence of two resonances for the sulfoxide ligand was unexpected as it suggested that there are two sulfur-bonded sulfoxide species present in solution, which is a phenomenon not observed for the corresponding complexes with acylthiourea ligands.[1,2] Attempts were made to separate the two species by normal phase (NP)-HPLC [1 : 1 v/v EtOAc–hexane] and although two HPLC peaks were obtained with relative peak heights of 1.66 : 1 respectively the ^{1}H NMR spectra of the two fractions were identical to the original spectrum with two sulfoxide resonances, suggesting that the separated species re-equilibrated to give both species in solution. Using ^{195}Pt NMR spectroscopy it was possible to establish that the two species in solution were geometric isomers, that is with the sulfoxide ligand in a *trans*-(S,S) and *cis*-(S,S) arrangement with respect to the sulfur donor atom of the chelated ligand. This is notably different to the complexation reaction of *cis*-[PtCl$_2$(RR′SO)$_2$] with acylthiourea ligands which yields a single complex with the sulfoxide ligand in a *cis*-(S,S) arrangement with respect to the sulfur donor atom of the chelated ligand.

It is well known that the ^{195}Pt chemical shift is sensitive to the coordination sphere of the metal centre and it is generally accepted that the chemical shifts of *cis* isomers are upfield relative to those of *trans*.[15] For all the alkoxycarbonylthiourea complexes prepared two ^{195}Pt signals were observed at

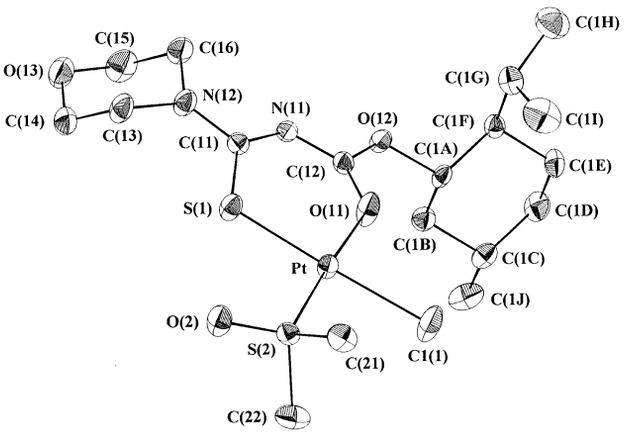

Fig. 4 Molecular structure of *cis*-(S,S)-[Pt(L^6)Cl(DMSO)] **2**, showing the atom numbering scheme and displacement ellipsoids (30% probability). Hydrogen atoms have been omitted for clarity.

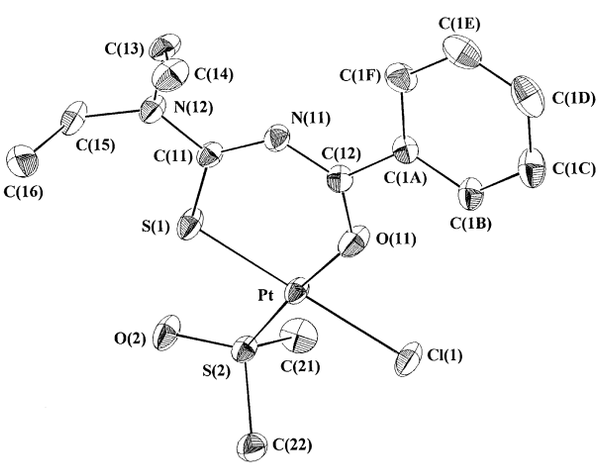

Fig. 5 Molecular structure of *cis*-(S,S)-[Pt(L^1)Cl(DMSO)] **3**. Details as in Fig. 4.

equilibrium with an approximate *cis*-(S,S) : *trans*-(S,S) ratio of 1 : 2 (Table 6), the *cis*-(S,S) and *trans*-(S,S) isomers being the complexes with the sulfoxide ligand in a *cis* and *trans* arrangement with respect to the sulfur donor atom of the chelated ligand, respectively. The *trans* isomer is the thermodynamically favoured isomer in $CDCl_3$, for all the complexes prepared, which is in contrast to what is found for the acylthiourea complexes. The polarity of the solvent appears to have a marginal effect on the *cis*/*trans* equilibrium.

Crystal structures of *cis*-(S,S)-[Pt(L^6)Cl(DMSO)] and *cis*-(S,S)-[Pt(L^1)Cl(DMSO)]

The crystal and molecular structures of *cis*-(S,S)-[Pt(L^6)-Cl(DMSO)] **2** and *cis*-(S,S)-[Pt(L^1)Cl(DMSO)] **3** are shown in Figs. 4 and 5 respectively, together with the atom numbering scheme, while selected bond lengths and angles are given in Tables 4, 7 and 8.

Table 6 ^{1}H and ^{195}Pt NMR data for platinum(II) sulfoxide complexes

Complex	H^1	H^2	H^3	H^4	H^5	H^6	H^7	H^8	H^9	H^{10}	H_α	H_β	H_{Sme}	H_{SAr}	^{195}Pt
[Pt(L^3)Cl(DMSO)]	4.572	1.265	1.640	1.640	1.419	2.061	0.864	2.061	0.747[a]	0.864	3.604	1.265	3.557[a]		−3282[a]
			1.015	0.864		1.015			0.742[b]			1.172	3.402[b]		−3239[b]
[Pt(L^4)Cl(DMSO)]	4.572	1.265	1.640	1.640	1.419	2.061	0.864	2.061	0.747[a]	0.864	3.604	1.265	3.557[a]		−3281[a]
			1.015	0.864		1.015			0.742[b]			1.172	3.402[b]		−3239[b]
[Pt(L^5)Cl(DMSO)]	4.603[a]	1.437	1.645	1.645	1.437	2.086	0.891	1.938	0.772[a]	0.865	3.693	3.971	3.566[a]		−3281[a]
	4.511[b]		1.041	0.825		1.041			0.735[b]				3.411[b]		−3227[b]
[Pt(L^6)Cl(DMSO)]	4.603[b]	1.437	1.645	1.645	1.437	2.086	0.891	1.938	0.772[a]	0.865	3.693	3.971	3.566[a]		−3281[a]
	4.511[b]		1.041	0.825		1.041			0.735[b]				3.411[b]		−3227[b]
[Pt(L^3)Cl(*S*-MTSO)]	4.558	1.311	1.623	1.623	1.420	2.058	0.921	2.158	0.749	0.905	3.428	1.251	3.675[a]	7.989	−3299[a]
			1.000	0.870		1.000							3.518[b]	7.337	−3248[b]
														2.434	

[a] *cis*-(*S*,*S*) isomer. [b] *trans*-(*S*,*S*) isomer.

Table 7 Coordination polyhedron (distances in Å, angles in °) for complexes **2** and **3**

	2	**3**
Pt(1)–O(11)	2.018(3)	2.010(3)
Pt(1)–S(2)	2.1839(12)	2.1885(10)
Pt(1)–S(1)	2.2595(13)	2.2586(11)
Pt(1)–Cl(1)	2.3276(14)	2.3337(11)
S(1)–C(11)	1.734(5)	1.735(4)
S(2)–O(2)	1.457(4)	1.462(3)
S(2)–C(21)	1.752(5)	1.764(5)
S(2)–C(22)	1.775(5)	1.759(5)
O(11)–Pt(1)–S(2)	176.40(11)	175.38(10)
O(11)–Pt(1)–S(1)	92.66(10)	93.75(10)
S(2)–Pt(1)–S(1)	90.71(4)	90.87(4)
O(11)–Pt(1)–Cl(1)	86.00(10)	84.94(10)
S(2)–Pt(1)–Cl(1)	90.66(5)	90.44(4)
S(1)–Pt(1)–Cl(1)	178.15(6)	178.64(4)
O(2)–S(2)–Pt(1)	117.16(14)	119.13(15)
C(21)–S(2)–Pt(1)	111.26(19)	110.36(18)
C(22)–S(2)–Pt(1)	109.1(2)	109.2(2)
O(2)–S(2)–C(21)	108.4(3)	107.4(2)
O(2)–S(2)–C(22)	108.5(3)	108.2(3)
C(21)–S(2)–C(22)	101.1(3)	101.0(3)

The bond lengths and angles all fall within the expected limits.[1] Both the Pt–Cl and the Pt–S=O bond lengths in complex **2**, 2.3276(14) and 2.1839(12) Å, are however statistically significantly shorter than in **3**, that is 2.3337(11) and 2.1885(10) Å, respectively. The opposite however holds (although not statistically significant, the tendency is observed) for the corresponding sulfur and oxygen donor atoms of the bidentate ligands as manifested in the Pt–S(1) and Pt–O(11) distances of 2.2595(13) and 2.018(3) Å in **2** *versus* 2.2586(11) and 2.010(3) Å for complex **3**, respectively. This implies that both the sulfur and oxygen donor atoms of ligand HL^1 have larger *trans* influences than the corresponding donor atoms in ligand HL^6. In general this implies further that the $(L^1)^-$ ligand as such is more strongly bonded than the $(L^6)^-$ moiety, which is in excellent agreement with what is observed from the NMR experiments described below. Small differences exist in the bond angles of the chelate in complexes **2** and **3**, but these may be due to packing effects and are thus not discussed further.

The Pt–MPSO bond length [2.192(3) Å] in complex **4** shows a tendency to slight elongation (although not statistically significant) compared to the Pt–DMSO bond length [2.1885(10) Å] in **3** (see Table 8). This is in agreement with the expected labilities of the coordinated sulfoxides, in which MPSO is more labile than DMSO.[5] The other bond distances of the chelate rings in **3** and **4** do not differ significantly.

However, the bond distances in ligand HL^3 and both the $(L^1)^-$ and $(L^6)^-$ moieties show significant differences. Substantial elongation of the S–C and C–O ligand fragments upon coordination to the platinum(II) centre (by as much as 0.06 Å in both cases) compared to the "free" ligand, is observed (Table 4). On the other hand, the C(11)–N(11) and C(2)–N(11) bonds are very similar in complexes **2** and **3** [1.345(6) *vs*. 1.348(5) and 1.309(5) *vs*. 1.312(6) Å respectively], and thus seem to be independent of the R and R′ groups of the ligand systems. However, these two bonds are significantly shortened (by 0.04–0.06 Å) compared to the corresponding ones [average 1.397(5) and 1.376(5) Å, respectively] in the "free" HL^3 ligand **1**, thus indicating substantial delocalisation of electrons within the chelate ring upon coordination.

Reactions with PPh_3

Further evidence for the difference in the coordination chemistry of the acylthiourea and alkoxycarbonylthiourea ligands was obtained by substitution of the bound sulfoxide by triphenylphosphine (PPh_3). ^{31}P NMR data for the monophos-

Table 8 Comparison of selected bond lengths (Å) of acylthiourea and alkoxycarbonylthiourea platinum(II) sulfoxide complexes

Complex	Pt–O	Pt–S	Pt–Cl	Pt–S=O	Reference
2 *cis*-(S,S)-[Pt(L^6)Cl(DMSO)]	2.018(3)	2.2595(13)	2.3276(14)	2.1839(12)	This work
3 *cis*-(S,S)-[Pt(L^1)Cl(DMSO)]	2.010(3)	2.2586(11)	2.3337(11)	2.1885(10)	This work
4 *cis*-(S,S)-[Pt(L^1)Cl(MPSO)]	2.016(9)	2.257(4)	2.334(3)	2.192(3)	1

Table 9 ^{31}P NMR data for [Pt(L)Cl(PPh_3)] complexes

Complex	δ^{31}P (^1J(PtP)/Hz)
cis-(P,S)-[Pt(L^1)Cl(PPh_3)]	8.137 (4040)
cis-(P,S)-[Pt(L^2)Cl(PPh_3)]	7.729 (4033)
cis-(P,S)-[Pt(L^4)Cl(PPh_3)]	8.001 (4181)
trans-(P,S)-[Pt(L^4)Cl(PPh_3)]	5.704 (3974)
cis-(P,S)-[Pt(L^6)Cl(PPh_3)]	7.769 (4189)
trans-(P,S)-[Pt(L^6)Cl(PPh_3)]	5.381 (3956)

Table 10 ^{31}P NMR data for [Pt(L)(PPh_3)$_2$]$^+$ complexes

	δ^{31}P (^1J(PtP)/Hz)		
Complex	*trans* sulfur	*trans* oxygen	^2J(PP)/Hz
[Pt(L^1)(PPh_3)$_2$]$^+$	21.912 (3088)	11.371 (3836)	26
[Pt(L^2)(PPh_3)$_2$]$^+$	22.249 (3129)	10.493 (3835)	25
[Pt(L^4)(PPh_3)$_2$]$^+$	22.010 (3064)	10.512 (3945)	24
[Pt(L^6)(PPh_3)$_2$]$^+$	Not present		—

phine and bis(phosphine) complexes are given in Tables 9 and 10, respectively. The phosphine complexes were prepared according to eqns. (3) and (4).

$$[PptCl(DMSO)(L)] + PPh_3 \longrightarrow [PtCl(L)(PPh_3)] + DMSO \quad (3)$$

$$[PtCl(DMSO)(L)] + 2\ PPh_3 \longrightarrow [Pt(L)(PPh_3)_2]^+ + DMSO + Cl \quad (4)$$

The substitution patterns of the chloride and dimethyl sulfoxide leaving groups were confirmed by ^{1}H NMR spectroscopy. Upon addition of 1 equivalent of PPh_3 to the platinum(II) sulfoxide complexes in $CDCl_3$ the proton resonance of the bound sulfoxide disappeared and a resonance peak due to free dimethyl sulfoxide was observed. This suggests that upon addition of one equivalent of PPh_3 the dimethyl sulfoxide ligand is displaced and further addition of PPh_3 results in exchange of the chloride ligand.

Monophosphine complexes. The ^{31}P NMR spectra for the complexes [Pt(L^1)Cl(PPh_3)] and [Pt(L^2)Cl(PPh_3)] each showed only one ^{31}P signal with ^1J(PtP) satellites of 4040 and 4033 Hz, respectively. On the other hand, two ^{31}P signals with ^1J(PtP) satellites were observed for the platinum complexes containing the alkoxycarbonylthiourea ligands $(L^4)^-$ and $(L^6)^-$, indicating that there are two monophosphine species present in solution. Likewise, these two species have, for convenience, been designated as *cis*-(P,S) and *trans*-(P,S) isomers, where *cis* refers to the complex with the phosphine ligand *cis* with respect to the sulfur donor atom of the chelate ligand. The signals could unequivocally be assigned to either the *cis*-(P,S) or *trans*-(P,S) isomers as it is well accepted for complexes of the type [$PtX_2(PR_3)_2$] that the *cis* isomers have significantly larger ^1J(PtP) coupling constants than those of the corresponding *trans* isomers.[16–18] It is clear from Table 9 that the platinum–phosphorus coupling constants for the *cis*-(P,S) isomers are larger than for the *trans*-(P,S) isomers, which is consistent with the greater *trans* influence of sulfur compared to oxygen. These results are also consistent with the work reported by Cavell *et al.* on platinum(II) complexes with monothio-β-diketone and phosphine ligands.[19]

Integration of the *cis*-(P,S)- and *trans*-(P,S)-[Pt(L^4)Cl(PPh_3)] signals gives rise to a *cis*:*trans* ratio of approximately 2:1. The opposite is observed for the sulfoxide complexes, where the *trans*-(S,S) isomers are favoured, and this could be due to the higher basicity and π-acceptor properties of PPh_3 compared to those of DMSO.

The ^1J(PtP) coupling constants for *cis*-(P,S)-[Pt(L^1)Cl(PPh_3)] and *cis*-(P,S)-[Pt(L^4)Cl(PPh_3)] are 4040 and 4181 Hz respectively. The increase of 141 Hz on going from an acylthiourea to alkoxycarbonylthiourea ligand suggests an increase in the Pt–P bond strength *trans* to the carbonyl oxygen donor atom of the alkoxycarbonylthiourea ligand. This implies that for the monophosphine complexes the acylthiourea carbonyl oxygen donor atom is relatively softer and therefore has a greater *trans* influence than the carbonyl oxygen donor atom of the alkoxycarbonylthiourea ligand, which is in agreement with the crystallographic data discussed above. Similar results were obtained for the morpholine containing complexes, except that the *cis*:*trans* ratio for the [Pt(L^6)Cl(PPh_3)] complex is 1:2. The inversion of the *cis*:*trans* ratio for the morpholine containing complexes is as yet not clearly understood.

Bis(phosphine) complexes. In the ^{31}P NMR spectrum of [Pt(L^1)(PPh_3)$_2$]$^+$ two doublets are observed at δ 21.912 and 11.371, with ^1J(PtP) coupling constants of 3088 and 3836 Hz, respectively. Similarly, two doublets are observed in the spectrum of [Pt(L^2)(PPh_3)$_2$]$^+$ at δ 22.249 and 10.493, with ^1J(PtP) coupling constants of 3129 and 3835 Hz, respectively. A significant difference between [Pt(L^1)(PPh_3)$_2$]$^+$ and [Pt(L^2)(PPh_3)$_2$]$^+$ is that while the former is stable in solution the latter is not, as manifested by the changes in the ^{31}P NMR spectrum of [Pt(L^2)(PPh_3)$_2$]$^+$ with time. After 12 hours the intensity of the doublets at δ 22.249 and 10.493 decreased dramatically and the solution only contained *ca.* 10% of the original complex. This decrease in intensity was accompanied by the appearance of singlets at δ 15.550 [^1J(PtP) 3674 Hz and *ca.* 21% abundance] and 7.720 [^1J(PtP) 4030 Hz and *ca.* 21% abundance], two singlets with no platinum satellites at δ 30.169 (*ca.* 12% abundance) and 44.582 (*ca.* 22% abundance), as well as two doublets at δ 12.553 and 20.096 [^2J(PP) 20 Hz; *ca.* 8% abundance] with unresolved platinum satellites. The signals at δ 7.720, 15.550 and 30.169 have been assigned as [Pt(L^2)Cl(PPh_3)], *cis*-[$PtCl_2(PPh_3)_2$] and triphenylphosphine oxide, respectively. The signals of *cis*-[$PtCl_2(PPh_3)_2$] and triphenylphosphine oxide were confirmed by recording the ^{31}P NMR spectra of the pure compounds. The signal at δ 44.582 appears to be due to the reaction between the deprotonated ligand and triphenylphosphine. The doublets at δ 20.096 and 12.553 have been tentatively assigned to the ring opened product [Pt(L^2-*S*)Cl(PPh_3)$_2$]$^+$, as the chemical shift positions and ^2J(PP) of 20 Hz correspond to the ring opened species of [Pt(L^6)(PPh_3)$_2$]$^+$ discussed below.

The reaction of [Pt(L^4)Cl(DMSO)] with two equivalents of PPh_3 yielded a ^{31}P NMR spectrum that consisted of three singlets (abundance) at δ 8.001 [^1J(PtP) 4181 Hz; *ca.* 11%], 5.704 (*ca.* 7%) and 15.562 (*ca.* 4%); ^1J(PtP) satellites for the signals at δ 5.704 and 15.562 could not be resolved due to overlapping peaks. Two sets of broad doublets were also observed at δ 22.010 and 10.512 [^1J(PtP) 3064 and 3945 Hz; 39%] and 15.562 and 8.855 [^1J(PtP) 3346 and 3512 Hz; 13%]. Based on the chemical shift positions and the ^1J(PtP) coupling constants observed for [Pt(L^1)(PPh_3)$_2$]$^+$, the doublets at δ 22.010 and 10.512 have been assigned to [Pt(L^4)(PPh_3)$_2$]$^+$. It is important to

note that the difference in the coupling constants for the one set of doublets (881 Hz) is far greater compared to that observed for the other set of signals (166 Hz). Since the ^1J(PtP) coupling is diagnostic of the *trans* ligand, this suggests that the difference in the *trans* influences of the two donor atoms *trans* to the phosphine ligands in the latter complex is much smaller than the difference in the *trans* influences of the oxygen and sulfur donor atoms in the chelated ligand. Moreover, the increase in the coupling constant from 3064 to 3346 Hz for the peak at δ 15.562 implies that a donor atom with a greater *trans* influence than oxygen has replaced the oxygen donor atom of the chelated ligand. These results suggest that ring opening has occurred and that the second set of doublets corresponds to a *cis*-[Pt(L^4-*S*)Cl(PPh_3)$_2$]$^+$ complex, where L^4-*S* represents the ring-opened ligand. The signals at δ 8.001 and 5.704 are the same as those products formed when one equivalent of PPh_3 is used and have been assigned to *cis*-(P,S)- and *trans*-(P,S)-[Pt(L^4)-Cl(PPh_3)], respectively. The singlet at δ 15.562 corresponds to *cis*-[$PtCl_2(PPh_3)_2$].

By contrast, the reaction of [Pt(L^6)Cl(DMSO)] with two equivalents of PPh_3 gave rise to a ^{31}P NMR spectrum that consisted of three singlets (abundance) at δ 7.766 [^1J(PtP) 4189 Hz; 13%], 5.381 [^1J(PtP) 3956 Hz; 16%] and 15.572 [^1J(PtP) 3673 Hz; 37%] and only one set of doublets at δ 20.083 and 12.971 [^1J(PtP) 3135 and 3477; ^2J(PP) 20 Hz; 15%]. Since the difference in the ^1J(PtP) coupling constants is 242 Hz, the set of doublets at δ 20.083 and 12.971 has been assigned to *cis*-[Pt(L^6-*S*)Cl-(PPh_3)$_2$]$^+$, where L^6-*S* represents the ring-opened ligand. The three singlets at δ 7.766, 5.381 and 15.572 have been assigned to *cis*-(P,S)- and *trans*-(P,S)-[Pt(L^6)Cl(PPh_3)] and *cis*-[$PtCl_2$-(PPh_3)$_2$], respectively. The signals due to [Pt(L^6)(PPh_3)$_2$]$^+$ were not detected in the spectrum, implying that this ligand, $(L^6)^-$, is weakly bound to the platinum(II) ion.

Conclusion

The phosphine studies highlight the difference in the coordination chemistry of the acylthiourea and alkoxycarbonylthiourea ligands illustrating that geometric isomers are formed when using the latter ligand systems and that these ligands bind less strongly to the platinum(II) ion. Moreover, the morpholine derivatives for both ligand systems appear to bind less tightly to the metal ion. These results are in agreement with the stability constant measurements reported by Beyer and co-workers which show that the Ni^{2+}, Zn^{2+} Cd^{2+} and Co^{2+} complexes of HL^1 are more stable than the corresponding complexes of HL^2.[20]

Further studies need to be carried out to establish the mechanism involved in the isomerisation of the alkoxycarbonylthiourea containing complexes. However, the weaker binding properties of these ligands might be a possible explanation for the observed geometric isomerisation of the complexes and that the mechanism could involve a chelate ring opening step.

Acknowledgements

We wish to thank Rhodes University, the University of the Free State and the National Research Foundation for financial support and Johnson Matthey for a generous loan of K_2PtCl_4.

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