Platinum(II) Mixed Ligand Complexes with Thiourea Derivatives, Dimethyl Sulphoxide and Chloride: Syntheses, Molecular Structures, and ESCA Data

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Abstract. The platinum(II) mixed ligand complexes [PtCl($L^{1\text{-}6}$)(dmso)] with six differently substituted thiourea derivatives HL, $R_2NC(S)NHC(O)R'$ (R = Et, R′ = *p*-O_2N-Ph: HL^1; R = Ph, R′ = *p*-O_2N-Ph: HL^2; R = R′ = Ph: HL^3; R = Et, R′ = *o*-Cl-Ph: HL^4; R_2N = $EtOC(O)N(CH_2CH_2)_2N$, R′ = Ph: HL^5) and $Et_2NC(S)N{=}CNH$-*1*-Naph (HL^6), as well as the bis(benzoylthioureato-$\kappa O,\kappa S$)-platinum(II) complexes [Pt($L^{1,2}$)$_2$] have been synthesized and characterized by elemental analysis, IR, FAB(+)-MS, ^{1}H-NMR, ^{13}C-NMR, as well as X-ray structure analysis ([PtCl(L^1)(dmso)] and [PtCl($L^{3,4}$)(dmso)]) and ESCA ([PtCl($L^{1,2}$)(dmso)] and [Pt($L^{1,2}$)$_2$]). The mixed ligand complexes [PtCl(L)(dmso)] have a nearly square-planar coordination at the platinum atoms. After deprotonation, the thiourea derivatives coordinate bidentately via O and S, DMSO bonds monodentately to the Pt^{II} atom via S atom in a *cis* arrangement with respect to the thiocarbonyl sulphur atom. The Pt−S-bonds to the DMSO are significant shorter than those to the thiocarbonyl-S atom. In comparison with the unsubstituted case, electron withdrawing substituents at the phenyl group of the benzoyl moiety of the thioureate (*p*-NO_2, *o*-Cl) cause a significant elongation of the Pt−S(dmso)-bond trans arranged to the benzoyl-O−Pt-bond. The ESCA data confirm the found coordination and bonding conditions. The Pt $4f_{7/2}$ electron binding energies of the complexes [PtCl($L^{1,2}$)(dmso)] are higher than those of the bis(benzoylthioureato)-complexes [Pt($L^{1,2}$)$_2$]. This may indicate a withdrawal of electron density from platinum(II) caused by the DMSO ligands.

Keywords: Platinum; Thiourea; DMSO; Crystal structure; ESCA

Platin(II)-Gemischtliganden-Komplexe mit Thioharnstoffderivaten, Dimethylsulfoxid und Chlorid: Synthesen, Molekülstrukturen und ESCA-Daten

Inhaltsübersicht. Es wurden die Platin(II)-Gemischtliganden-Komplexe [PtCl($L^{1\text{-}6}$)(dmso)] mit sechs unterschiedlich substituierten Thioharnstoffderivaten HL, $R_2NC(S)NHC(O)R'$ (R = Et, R′ = *p*-O_2N-Ph: HL^1; R = Ph, R′ = *p*-O_2N-Ph: HL^2; R = R′ = Ph: HL^3; R = Et, R′ = *o*-Cl-Ph: HL^4; R_2N = $EtOC(O)N(CH_2CH_2)_2N$, R′ = Ph: HL^5) und $Et_2NC(S)N{=}CNH$-*1*-Naph (HL^6), sowie die Bis(benzoylthioureato-$\kappa O,\kappa S$)-platin(II)-Komplexe [Pt($L^{1,2}$)$_2$] dargestellt und mittels Elementaranalyse, IR, FAB(+)-MS, ^{1}H-NMR, ^{13}C-NMR, sowie Röntgenkristallstrukturanalyse ([PtCl(L^1)(dmso)] und [PtCl($L^{3,4}$)(dmso)]) und ESCA ([PtCl($L^{1,2}$)(dmso)] und [Pt($L^{1,2}$)$_2$]) charakterisiert. Die Gemischtliganden-Komplexe [PtCl(L)(dmso)] weisen eine nahezu quadratisch-planare Koordination an den Platinatomen auf. Die Thioharnstoffderivate koordinieren nach Deprotonierung bidentat über O und S, DMSO bindet monodentat über S in *cis*-Anordnung zum Thiocarbonyl-Schwefelatom an das Pt^{II}-Atom. Die Pt−S-Bindungen zum DMSO sind dabei deutlich kürzer als jene zum Thiocarbonyl-S-Atom. Elektronenziehende Substituenten an der Phenylgruppe des Benzoylteils des Thioureats (*p*-NO_2, *o*-Cl) führen zu einer signifikanten Verlängerung der zur Benzoyl-O−Pt-Bindung *trans*-ständigen Pt−S(dmso)-Bindung im Vergleich zum unsubstituierten Fall. Die ESCA-Daten bestätigen die gefundenen Koordinations- und Bindungsverhältnisse. Die im Vergleich zu den Bis(benzoylthioureato)-Komplexen [Pt($L^{1,2}$)$_2$] erhöhten Pt $4f_{7/2}$-Elektronenbindungsenergien der Komplexe [PtCl($L^{1,2}$)(dmso)] deuten auf einen möglichen Abzug von Elektronendichte vom Platin(II)-Atom durch die DMSO-Liganden hin.

Introduction

Cis-platinum complexes are very important neoplasic agents [1]. The aim of the research is to find out compounds with a spectrum of action different from that of cisplatin. In this context platinum complexes with ligands of gradual leaving tendencies are of special interest because the therapeutical efficacy is determined by substitution intermediates produced in the organism. Recently, we showed the cancerostatic efficacy of related *cis*-bis(acylthioureato)platinum(II) chelates [2]. This fact motivated us to synthesize and characterize some new *cis*-platinum(II) complexes with the title ligands. Furthermore, the ligands we used *per se* have bioactivity, thus there is a hope of synergistic effects.

Sacht and co-workers recently described platinum(II) complexes − also related to the acylthioureato complexes studied long-standingly in our group − and investigated

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them for interactions with DNA [3−6]. Furthermore, metal complexes with dimethyl sulphoxide (DMSO) as ligands are interesting for us because such complexes in our group have been the object of earlier preparative and kinetic investigations about the building and the substitution reactions in solution, namely in the case of classical *Werner* type complexes of cobalt(III) [7, 8]. We herein present the syntheses, as well as the characterization of the ligands and platinum(II) complexes by elemental analysis, IR, FAB(+)-mass, ^{1}H-NMR and ^{13}C-NMR spectroscopy. Especially comparative ESCA data are used in order to reveal the bonding and structural situation. The X-ray structures of the complexes **1**, **3** and **4** are also reported. The synthesized complexes will be tested for their cancerostatic efficacy in a further study.

Results and Discussion

Synthesis

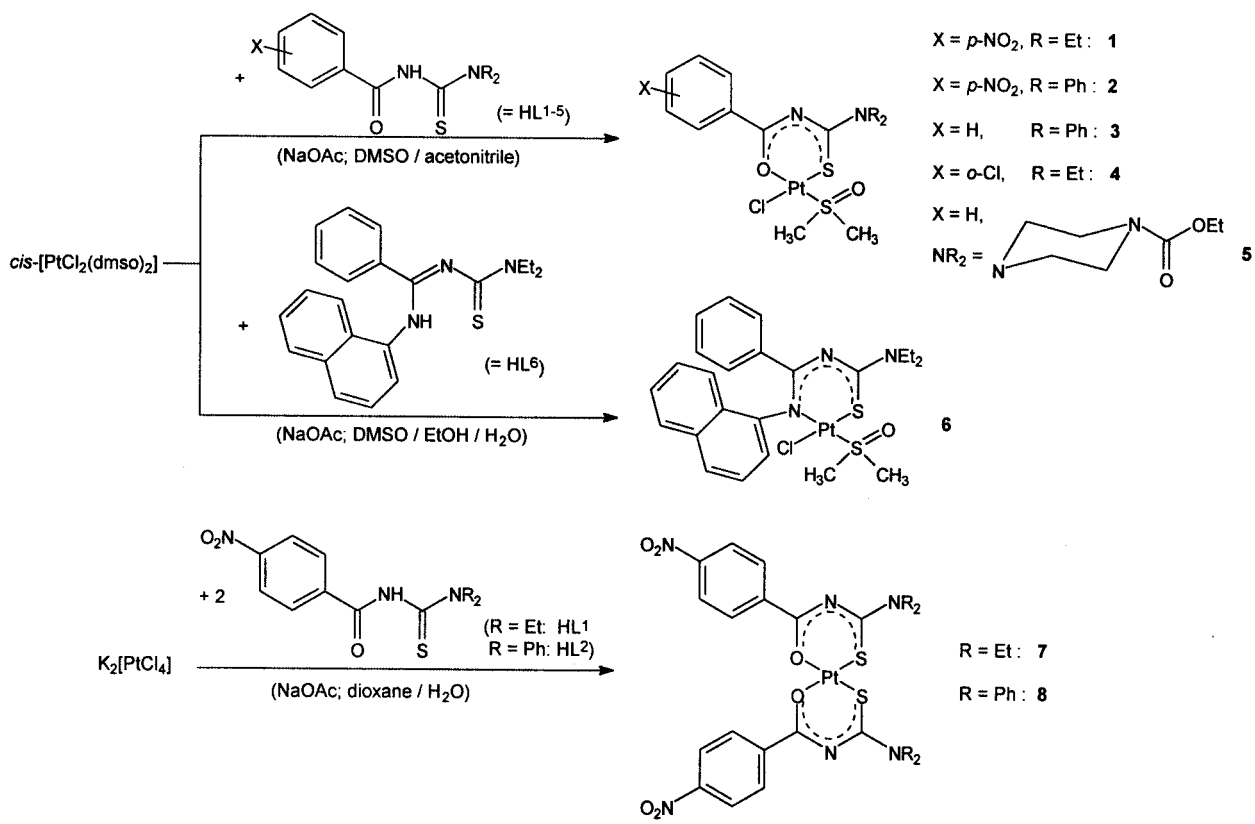
Scheme 1 shows the pathways for the syntheses of the platinum(II) complexes **1**-**8**. Compounds **1**-**5** were obtained by reaction of *cis*-dichloro-bis(dimethylsulphoxide)-platinum(II) by reaction with the bidentate ligands HL$^{1\text{-}5}$ in a DMSO-acetonitrile-mixture, compound **6** by treatment with *N*-(diethylaminothiocarbonyl)-*N*′-1-naphthylbenzamidine (HL^6) in a DMSO-ethanol-water-mixture. The bis-thioureato-$\kappa O,\kappa S$ platinum(II) complexes **7** and **8** were synthesized from $K_2[PtCl_4]$ and HL^{1,2} in dioxane/water in the molar metal/ligand ratio of 1 : 2. Sodium acetate as proton acceptor was added in all cases.

The platinum complexes were isolated in yields of 40-60 % as yellow or orange solids. They were washed with water and ethanol and dried in vacuo. Recrystallization from dichloromethane gave crystals suitable for X-ray diffraction for **1**, **3** and **4**. The elemental analysis, FAB(+)-mass-, ^{1}H-NMR-, and IR- spectra data proving the structures presented here are given in experimental part.

Molecular structures

The molecular structures of the complexes *cis*-[PtCl(L)(dmso)] **1, 3** and **4** with the atom numbering scheme for all non-hydrogen atoms are shown in the figures 1, 2 and 3, respectively. Selected bond lengths and angles are given in Table 1.

All three complexes have a nearly square-planar coordination at the platinum atoms indicated by the angles between the planes through Pt1S1O1 and Pt1S2Cl1: 3.9(1) and 4.0(1)° for **1** and 1.9(1)° for **3** and **4**. The platinum(II) ion is coordinated to a chelate ligand and two monodentate groups, namely DMSO and chloride. The structural determinations of these complexes confirm that the chelate ligand is bonded bidentately to platinum atom through the sulphur and oxygen donor atoms while the sulphoxide ligand is coordinated to platinum atom via the sulphur atom



Scheme 1

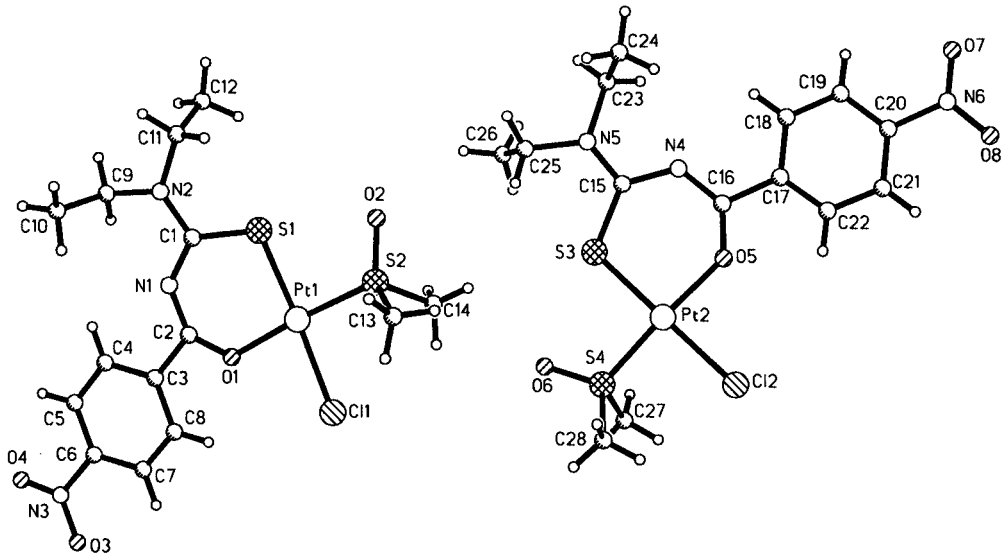


Figure 1 Molecular structure of {chloro-[*N*-(*p*-nitrobenzoyl)-*N*′,*N*′-diethyl-thioureato-$\kappa O,\kappa$S]-dimethylsulphoxide-κS}-platinum(II) (**1**)

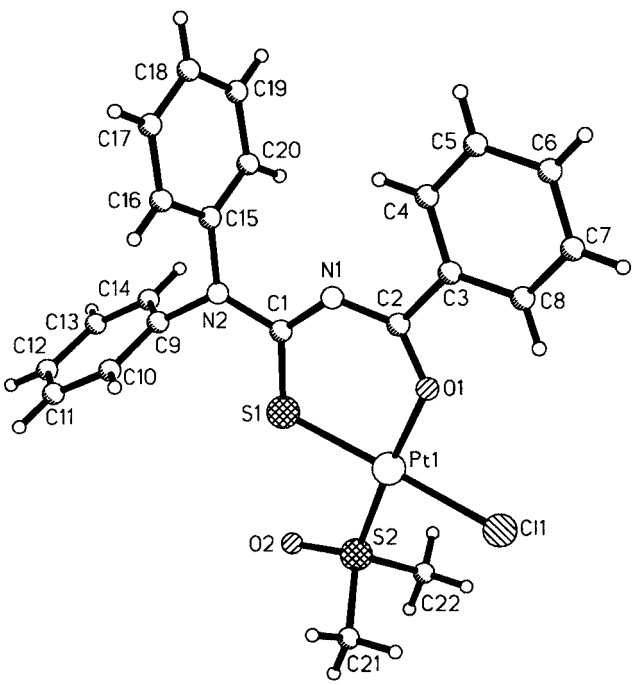


Figure 2 Molecular structure of [chloro-(*N*-benzoyl-*N*′,*N*′-diphenyl-thioureato-$\kappa O,\kappa$S)-dimethylsulphoxide-κS]-platinum(II) (**3**)

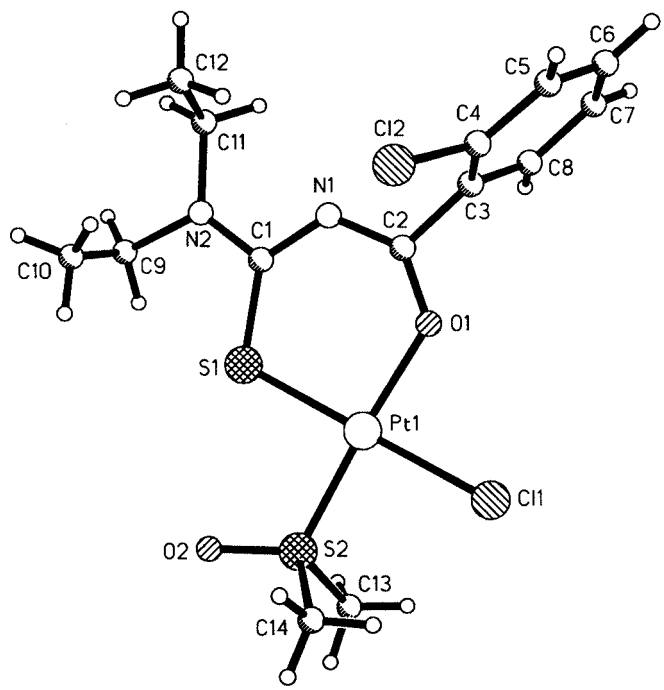


Figure 3 Molecular structure of {chloro-[*N*-(*o*-chlorbenzoyl)-*N*′,*N*′-diethyl-thioureato-$\kappa O,\kappa$S]-dimethylsulphoxide-κS}-platinum(II) (**4**)

in a *cis* arrangement with respect to the sulphur atom of the acylthiourea as reported in related platinum(II) complexes, too [4, 5]. The bond lengths involving platinum fall within the expected ranges. The Pt1−S1 bonds (2.255-2.259 Å) are significantly longer than the Pt1−S2 bonds to the DMSO ligand (2.188-2.199 Å). The Pt1−O1 bonds (2.010-2.011 Å) and the Pt1−Cl1 bonds (2.328-2.332 Å) also agree well with the structures of other complexes of this type [4, 5].

By comparison with the structures of the free ligands HL^2 [2] and HL^4 [9], the thiocarbonyl bonds (S1−C1: 1.736 (average), 1.736(5) and 1.725(6) Å) and carbonyl bonds (O1−C2: 1.278 (average), 1.281(6) and 1.270(7) Å) for **1**, **3** and **4**, respectively, are longer than in the ligands (S1−C1: 1.664(2) and 1.658(2) Å , O1−C2: 1.209(3) and 1.218(2) Å). Furthermore, the two contiguous C−N bonds in the chelate rings (N1−C1: 1.377 (average), 1.329(6) and 1.356(7) Å, N1−C2: 1.303 (average), 1.308(6) and 1.330(7) Å), for **1**, **3** and **4**, respectively) are shorter compared with the corresponding bonds of the ligands (N1−C1: 1.391(3) and 1.428(2) Å, N1−C2: 1.389(3) and 1.360(2) Å). In all three structures the N1−C1 bonds in the

Table 1 Selected bond lengths/Å and angles/° for **1**, **3** and **4**.

	1		**3**	**4**
	molecule a	molecule b		
Bond lengths				
Pt1−S1	2.262(3)	2.252(3)	2.259(1)	2.255(2)
Pt1−O1	2.015(8)	2.005(7)	2.011(3)	2.010(4)
S1−C1	1.734(12)	1.738(12)	1.736(5)	1.725(6)
O1−C2	1.274(15)	1.282(14)	1.281(6)	1.270(7)
N1−C1	1.376(15)	1.378(14)	1.329(6)	1.356(7)
N1−C2	1.276(16)	1.330(16)	1.308(6)	1.330(7)
N2−C1	1.323(17)	1.258(16)	1.361(6)	1.367(9)
Pt1−S2	2.200(3)	2.189(3)	2.188(1)	2.199(1)
S2−O2	1.467(9)	1.449(10)	1.456(4)	1.467(4)
Pt1−Cl1	2.330(4)	2.334(4)	2.328(1)	2.328(1)
Bond angles				
S1−Pt1−O1	93.6(3)	93.5(3)	94.27(10)	93.98(12)
S1−Pt1−S2	90.1(1)	89.7(1)	89.69(5)	89.98(5)
S2−Pt1−Cl1	91.0(1)	91.4(1)	90.48(5)	90.75(5)
O1−Pt1−Cl1	85.4(3)	85.6(3)	85.56(10)	85.31(12)
S1−Pt1−Cl1	176.7(1)	177.4(1)	178.05(5)	179.17(5)
S2−Pt−O1	175.6(3)	175.5(3)	176.04(10)	175.63(13)
Pt1−S1−C1	108.4(5)	109.3(4)	106.9(2)	108.3(2)
Pt1−O1−C2	129.6(8)	130.5(8)	130.3(3)	130.0(3)
C1−N1−C2	126.8(11)	125.7(10)	127.1(4)	125.6(5)
S1−C1−N1	128.1(11)	127.8(10)	130.9(4)	130.0(4)
O1−C2−N1	132.4(11)	130.5(11)	130.1(5)	131.1(5)

thiourea fragment are longer than the N1−C2 bonds in the acyl fragment of the chelate ring, in general agreement with other platinum(II) complexes of the investigated type [4, 5] and also with the structures of several bis(*N*-acylthioureato) complexes [2, 4, 9−15]. These results confirm the decrease of the bond orders of the thiocarbonyl and carbonyl groups upon complexation and indicate the presence of an extensive delocalization of π electron density in the chelate ring of the platinum(II) sulphoxide complexes. This is also confirmed by IR, FAB(+)-mass and ^{1}H-NMR spectroscopy.

As can be seen in Table 1, the Pt−S2(sulphoxide) bonds for the complexes **1** and **4** (2.195 (average) and 2.199(1) Å, respectively) with substituted phenyl rings are slightly longer than in the complex **3** (2.188(1) Å) and in *cis*-[PtCl(L)(dmso)] (HL = *N*,*N*-diethyl-*N*′-benzoylthiourea) (2.189(1) Å [5]) with unsubstituted phenyl rings. This fact indicates that the presence of the substituent groups (*p*-NO_2 and *o*-Cl) in the benzoyl fragment seems to elongate the Pt−S2(sulphoxide) bonds.

The phenyl rings of the acylthiourea ligands form different angles with the chelate rings: 7.3(7) and 8.6(10)° for **1** (*p*-nitrophenyl), 6.0(6)° for **3** (phenyl) and 80.5(5)° for **4** (*o*-chlorophenyl).

No significant intermolecular interactions are observed in **1**, **3** and **4**.

ESCA spectra

Table 2 shows the electron binding energies (eV) of the complexes **1** and **2** (with DMSO as one ligand), the ligands HL^1, HL^2 and the *cis*-bis(benzoyl-thioureato)-platinum(II) complexes **7** and **8**. The values of HL^1, HL^2, **7** and **8** are presented here for comparative purposes. The electron binding energies were acquired from photoelectron spectra of core levels. Information obtained concerns binding situation and structure.

The electron binding energies confirm the proposed coordination patterns for the DMSO complexes **1** and **2** and also for the bis complexes **7** and **8**. This is proved by the N 1s, S $2p_{3/2}$ and Pt $4f_{7/2}$ signals in the spectra of compounds under investigation.

N 1s electron binding energies. At the complex formation occurs deprotonation of one nitrogen atom in the ligands

Table 2 Binding energies/eV, (half-widths/eV / concentrations (atom percent)) of the inner shell levels of the photoelectron spectra.

	C1s	**N1s**	**O1s**	**S2p$_{3/2}$**	**Pt 4f$_{7/2}$**
HL^1	285.0 (1.8/39.33) 285.8 (1.8/15.58) 287.8 (1.8/7.18)	400.0 (1.7/10.45) 405.9 (1.7/5.51)	531.5 (1.6/6.37) 533.0 (1.6/9.89) 535.5 (1.6/0.94)	161.7 (1.5/4.45) 167.7 (1.2/0.30)*	
7	285.0 (1.8/41.27) 285.7 (1.8/14.11) 287.3 (1.8/8.57) 289.5 (1.8/0.90)	398.4 (1.7/4.45) 399.8 (1.7/3.84) 406.0 (1.7/4.66)	532.2 (1.7/10.00) 533.3 (1.7/6.45) 535.3 (1.7/0.53)	162.8 (1.5/3.37)	72.8 (1.6/1.85)
1[a)]	285.0 (1.8/31.98) 285.7 (1.8/18.47) 287.6 (1.8/6.00)	398.8 (1.8/3.90) 400.1 (1.8/4.63) 406.1 (1.8/3.16)	532.0 (1.8/9.95) 533.2 (1.8/6.78)	163.4 (1.8/4.83) 167.1 (1.8/3.20)	73.4 (1.8/3.90)
HL^2	284.6 (1.7/46.58) 285.5 (1.7/20.59) 287.9 (1.7/3.79)	400.2 (1.7/7.93) 405.9 (1.7/4.40)	531.6 (1.7/4.73) 532.9 (1.7/8.07) 535.6 (1.7/0.57)	161.9 (1.6/3.16) 168.4 (1.5/0.18)*	
8	284.6 (1.7/58.29) 285.5 (1.7/7.58) 287.2 (1.7/4.99)	398.3 (1.7/4.15) 400.0 (1.7/2.89) 405.8 (1.7/3.98)	532.2 (1.8/9.71) 533.3 (1.8/4.02) 535.1 (1.8/0.42)	162.7 (1.5/2.63)	72.6 (1.5/1.34)
2[b)]	284.6 (1.8/42.95) 285.4 (1.8/20.12) 287.1 (1.8/3.32) 288.7 (1.8/2.41)	398.6 (1.8/1.99) 400.2 (1.8/1.80) 406.0 (2.0/2.03)	532.1 (1.8/12.26) 533.4 (1.8/6.28)	163.1 (1.9/1.90) 166.9 (1.4/1.50)	73.2 (1.7/1.70)

* slight contamination on the surface. **1**[a)]: Cl2p$_{3/2}$ 198.4 eV (1.7/3.2); **2**[b)]: Cl2p$_{3/2}$ 198.3 eV (1.5/1.74).

HL^1 and HL^2 containing the thiourea unit. This is indicated by a shift of the N 1s signal of the complex in comparison with the thiourea ligand. The results indicate a decrease of the N 1s binding energy comparing the signals of the ligand HL^1 and its platinum (II) complexes **7** and **1** from 400.0 eV (HL^1) to 398.4 eV (**7**) and 398.8 eV (**1**). The second series of comparison with the ligand HL^2 and its platinum complexes **8** and **2** leads to analogous changes of the N 1s signals from 400.2 eV (HL^2) to 398.3 eV (**8**) and 398.6 eV (**2**). The nitrogen atoms of the $-NEt_2$ and $-NPh_2$ groups in the complexes **7** (399.8 eV) and **1** (400.1 eV) as well as **8** (400.0 eV) and **2** (400.2 eV) in comparison with the corresponding ligands HL^1 (400.0 eV) and HL^2 (400.2 eV), as expected, have nearly unchanged values. The N 1s signal from the NO_2 group likewise remains constant: HL^1 (405.9 eV); **7** (406.0 eV); **1** (406.1 eV) and HL^2 (405.9 eV); **8** (405.8 eV); **2** (406.0 eV).

S $2p_{3/2}$ binding energies. A dative bond of the thioureato sulphur atom is indicated for the complexes **1** (163.4 eV) and **7** (162.8 eV) as well as **2** (163.1 eV) and **8** (162.7 eV) by the increase of the S $2p_{3/2}$ electron binding energy in comparison with the non complexed ligands 161.7 eV (HL^1) and 161.9 eV (HL^2). Thereby it is to be stated that the S $2p_{3/2}$ binding energies of the respective metal coordinated thioureato sulphur atom in the DMSO complexes are significant higher than in the respective bis-complexes (**1** compared with **7** by 0.6 eV; **2** compared with **8** by 0.4 eV). This means an increased electron donor influence of the respective sulphur atom related to the platinum central atom in the DMSO coordinated complexes. The electron binding energy of the metal coordinated DMSO sulphur atom is considerable higher than that in the thioureato ligands (**1**: 167.1 eV, **2**: 166.9 eV).

Pt $4f_{7/2}$electron binding energies. In view of the comparatively increased donor power of the sulphur atom in the DMSO complexes, surprisingly, the Pt $4f_{7/2}$ signals of **1** (73.4 eV) and **2** (73.2 eV) in comparison to the bis-complexes **7** (72.8 eV) and **8** (72.6 eV) are increased in each case by 0.6 eV, i. e. the electrons are tighter bound at the platinum atom. Obviously, this is consistent with the assumption that DMSO is able to take up electron density from the platinum(II) which on its part compensates this deficiency by the thiourea sulphur atom.

The Cl $2p_{3/2}$ signals with the binding energies (198.4 eV for **1** and 198.3 eV for **2**) prove the behaviour of the chlorine atoms as chloro (chloride) ligands.

Also the intensities of the individual components and the derived concentrations (atom-%) using sensitivity factors are, after rounding, in accordance with the composition of the samples (see Table 2).

Experimental

General

Potassium tetrachloroplatinate(II) was purchased from Merck, Darmstadt. The complex *cis*-$[PtCl_2(dmso)_2]$ was prepared according to a reported method [16]. All other chemicals and solvents (Aldrich) were analytical grade and used as supplied, except acetone which was distilled before use. Elemental analyses were determined on a Fisons-Carlo Erba 1108 elemental microanalyser. Melting points were determined on a Boetius melting-point apparatus. IR spectra were recorded as KBr discs in the range 4000-400 cm^{-1} on a Bruker FT-IR IFS 55 Equinox spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded on a Bruker advance DRX 300 spectrometer at 300 K using $CDCl_3$ as solvent. FAB(+) mass spectra were obtained on a ZAB-HSQ (V.G. Analytical Ltd.) spectrometer (matrix: 3-NBA).

Table 3 Crystal data and details of structure determination for **1**, **3** and **4**.

	1	**3**	**4**
Empirical formula	$C_{14}H_{20}O_4N_3S_2ClPt$	$C_{22}H_{21}O_2N_2S_2ClPt$	$C_{14}H_{20}O_2N_2S_2Cl_2Pt$
M_r /g mol^{-1}	588.99	640.07	578.43
Crystal habit, color	yellow prisms	yellow prisms	yellow prisms
Crystal system	triclinic	trigonal	monoclinic
Space group	$P\bar{1}$ (No. 2)	$R\bar{3}$ (No. 148)	$P2_1/c$ (No. 14)
a / Å	7.143(1)	34.949(7)	9.963(2)
b / Å	10.193(2)	34.949(7)	10.190(2)
c / Å	28.237(6)	9.935(3)	18.439(4)
α / °	88.024(4)		
β / °	83.717(4)		99.331(4)
γ / °	74.871(4)		
V / $Å^3$	1972.6(7)	10509(4)	1847.2(8)
Z; F(000)	4; 1136	18; 5580	4; 1112
ρ(calc.) /g cm^{-3}	1.983	1.820	2.080
Crystal size /mm	0.06 x 0.25 x 0.25	0.04 x 0.08 x 0.26	0.13 x 0.50 x 0.55
Absorption coeff. μ/mm^{-1}	7.484	6.322	8.120
2θ range /°	4.1−58.6	4.0−58.3	4.1−58.5
Measured reflections	12872	22383	11277
Unique reflections	9145	5875	4548
Observed reflections(I> 2σ (I))	7439	4132	4345
Refined parameters	459	273	241
wR_2 (unique refl.)	0.1655	0.0647	0.1226
R_1 (observed refl.)	0.0675	0.0395	0.0432
Goodness-of-fit on F^2	1.199	1.009	1.109
Largest difference peak and hole/e $Å^{-3}$	6.15/−2.28	2.51/−0.61	3.33/−3.90

Crystal structure determination

The data for the crystal structure determinations were collected on a Siemens CCD Smart Diffractometer (MoK_α radiation, λ = 0.71073 Å, graphite monochromator, T = 218(2) K).

The intensities were corrected for Lorentz and polarization effects and for absorption using SADABS. The structures were solved by direct methods and refined by least-squares procedures [17]. The positions of all hydrogen atoms were calculated geometrically and taken into account with isotropic temperature factors 1.2 times higher than U_{eq} of the parent C atoms. In spite of the fact that the crystals of **1** were not of good quality we included the results in this paper because the structure is well defined and is of acceptable accuracy.

Some details of crystal data and structure determination are given in Table 3.

Further details of the crystal structure determinations are available on request from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK, on quoting the depositing numbers CCDC-218079 (**1**), CCDC-218080 (**3**) and CCDC-218081 (**4**), the names of the authors, and the journal citation.

ESCA spectra

The ESCA spectra were recorded using the photoelectron spectrometer VG (Vacuum Generators) ESCALAB 220i XL by excitation with Al Kα radiation (U = 12 kV, I = 20 mA). The vacuum during the measurements was $3 \cdot 10^{-8}$ Torr. The powder samples were grinded onto double-sided adhesive carbon tape. To account for charging the binding energies were related to the main component of the carbon 1s peak (285.0 eV for sample series HL^1/**7**/**1** sp^3 carbon], 284.6 eV for sample series HL^2/**8**/**2** sp^2 carbon]). The analyser pass energy was for the single spectra 10 eV. Curve fitting was performed using the program "UNIFIT for WINDOWS" [18]. The single components were approximated with Gaussian-Lorentzian fractions (Voigt curves).

Synthesis and characterization of the ligands

The ligands $HL^{1\text{-}4}$ and HL^6 were synthesized following literature procedures: HL^1 [19, 20], HL^2, HL^3 [2, 19], HL^4 [9, 19], HL^6 [21, 22].

N-(4-ethoxycarbonyl-piperazin-1-yl-thiocarbonyl)benzamide, HL^5: A solution of 10 mmol (1.5 mL) 4-ethoxycarbonyl-piperazine in 20 mL acetone was added drop by drop to a solution of 10 mmol (1.35 mL) benzoylisothiocyanate in 20 mL acetone and kept refluxed for two hours. Then the mixture was stirred for 24 hours at room temperature, followed by filtration and evaporation. Thus a greasy mass was obtained and digested with ether yielding a colourless precipitation which was washed with ethanol, dried in vacuo and recrystallized from dichloromethane. Yield: 2.19 g (68 %). Melting point: 135-137 °C. $C_{15}H_{19}O_3N_3S$ (321.4 g/mol)-calc.: C 56.06; H 5.96; N 13.07; S 9.98 %; found: C 55.9; H 5.74; N 13.1; S 9.89 %.

IR (KBr, cm^{-1}): ν(NH) 3284 (m); ν(COO) 1701 (vs); ν(C=O) 1671 (vs); ν(C=S) 1225 (s). **MS** (FAB^+) m/z 322.1 (M^+, 100 %). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ 1.28 (t, 3H, CH_3); 3.20 (br, 4H, CH_{2pip}); 3.67 (t, 4H, CH_{2pip}); 4.19 (q, 2H, CH_2); 7.50 (dd, 2H, *m*-Ph); 7.61 (t, 1H, *p*-Ph); 7.87 (d, 2H, *o*-Ph); 8.56 (s, 1H, N*H*). **^{13}C-NMR** (75.45 MHz, $CDCl_3$): δ 14.8 (CH_3); 40.7 43.5 62.0 (CH_2); 127.1 (*C*OO); 127.9 129.1 130.2 133.3 (Ph); 163.4 (*C*O); 179.9 (*C*S).

*General procedure for the synthesis of the platinum(II) complexes **1-6**:*

0.25 mmol of the ligand ($HL^{1\text{-}6}$) dissolved in 10 mL DMSO/acetonitrile (1:1 v/v) were added drop by drop to a solution of 0.25 mmol *cis*-$[PtCl_2(dmso)_2]$ in 50 mL, for **1-5**, DMSO/acetonitrile (1:1 v/v) and, for **6**, DMSO/ethanol/water (1:1:1 v/v/v). 2mL of a aqueous solution of 0.25 mmol sodium acetate was added. The reaction mixture was stirred at room temperature for 48 h followed by the reduction of the volume to the half. After addition of 70 mL water, the complexes **1-6** precipitated as yellow solids which were washed with water and ethanol and dried in vacuo.

*{Chloro-[N-(p-nitrobenzoyl)-N′,N′-diethylthioureato-κO,κS]-dimethylsulphoxide-κS}-platinum(II), (**1**)*

Yellow prisms. Yield: 0.089 g (61 %). Mp.: 182-184 °C. $C_{14}H_{20}O_4N_3S_2ClPt$ (588.99 g/mol);calc.: C 28.5; H 3.4; N 7.1; S 10.9 %; found: C 28.0; H 3.4; N 7.2; S 11.3 %.

IR (KBr, cm^{-1}): ν(C=O) 1638 (m); ν(C=S) 1251 (m); ν(S=O) 1157 (m). **MS** (FAB^+) m/z 589 (M^+, 100 %). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ 1.32 (t, 3H, CH_3); 1.38 (t, 3H, CH_3); 3.62 (s, 6H, SCH_3); 3.86 (m, 4H, CH_2); 8.23 (d, 2H, *o*-Ph); 8.34 (d, 2H, *m*-Ph). **^{13}C-NMR** (75.45 MHz, $CDCl_3$): δ 12.2 13.1 (CH_3); 46.5 46.6 (CH_2); 47.7 (SCH_3); 123.3 130.7 141.5 149.9 (Ph); 166.8 (*C*O); 167.6 (*C*S).

*{Chloro-[N-(p-nitrobenzoyl)-N′,N′-diphenylthioureato-κO,κS]-dimethylsulphoxide-κS}-platinum(II), (**2**)*

Yellow prisms. Yield: 0.09 g (62 %). Mp.: 142-145 °C. $C_{22}H_{20}O_4N_3S_2ClPt$ (684.58 g/mol); calc.: C 50.7; H 3.0; N 8.9; S 6.7 %; found: C 50.3; H 3.2; N 8.6; S 6.4 %.

IR (KBr, cm^{-1}): ν(C=O) 1640 (m); ν(C=S) 1257 (m); ν(S=O) 1163 (m). **MS** (FAB^+) m/z 685 ($[M + H]^+$, 100 %). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ 3.57 (s, 6H, SCH_3); 7.46 (m, 10H, Ph); 7.90 (d, 2H, Ph); 8.06 (d, 2H, Ph). **^{13}C-NMR** (75.45 MHz, $CDCl_3$): δ 46.6 (SCH_3); 123.2 127.6 127.7 129.4 131.1 143.8 (Ph); 168.11 (*C*O); 173.5 (*C*S).

*[Chloro-(N-benzoyl-N′,N′-diphenyl-thioureato-κO,κS)-dimethylsulphoxide-κS]-platinum(II), (**3**)*

Pale yellow prisms. Yield: 0.109 g (68 %). Mp. 238-240 °C(dec.). $C_{22}H_{21}O_2N_2S_2ClPt$ (640.07 g/mol); calc.: C 41.3; H 3.3; N 4.4; S 10.0 %; found: C 40.9; H 3.4; N 4.5; S 10.1 %.

IR (KBr, cm^{-1}): ν(C=O) 1620 (m); ν(C=S) 1255 (m); ν(S=O) 1141 (m). **MS** (FAB^+) m/z 640 (M^+, 100 %). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ 3.56 (s, 6H, SCH_3); 7.22-7.37 (m, 10H, Ph); 7.42 (d, 2H, Ph); 7.70 (d, 1H, Ph); 7.80 (d, 2H, Ph). **^{13}C-NMR** (75.45 MHz, $CDCl_3$): δ 46.6 (SCH_3); 128.1 129.6 130.4 132.6 134.0 134.8 (Ph); 164.1 (*C*O); 171.1 (*C*S).

*{Chloro-[N-(o-chlor-benzoyl)-N′,N′-diethylthioureato-κO,κS]-dimethylsulphoxide-κS}-platinum(II), (**4**)*

Yellow prisms. Yield: 0.087 g (60 %). Mp.: 157-159 °C. $C_{14}H_{20}O_2N_2S_2Cl_2Pt$ (578.43 g/mol); calc.: C 29.07; H 3.49; N 4.84; S 11.09; Cl 12.26 %; found: C 30.02; H 3.26; N 4.71; S 10.69; Cl 11.98 %.

IR (KBr, cm^{-1}): ν(C=O) 1528 (w); ν(C=S) 1245 (m); ν(S=O) 1149 (s). **MS** (FAB^+) m/z 579 ($[M + H]^+$, 100 %). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ 1.32

(m, 6H, CH_3); 3.61 (s, 6H, SCH_3); 3.98 (m, 4H, CH_2); 7.85 (d, 1H, *o*-Ph); 7.43 (t, 1H, *p*-Ph); 7.25 (m, 2H, *m*-Ph).

*{Chloro-[N-(4-ethoxycarbonyl-piperazin-1-yl-thiocarbonyl)benzamidato-κO,κS]-dimethylsulphoxide-κS}-platinum(II), (**5**)*

Yellow solid. Yield: 100 mg (60.4 %). Mp.: 180-185 °C. $C_{17}H_{24}O_4N_3S_2ClPt$ (629.05 g/mol), calc.: C 32.46; H 3.85; N 6.68; S 10.19; Cl 5.64 %; found: C 32.2; H 3.91; N 6.88; S 10.39; Cl 5.75 %.

IR (KBr, cm^{-1}): ν(COO) 1698 (s); ν(C=O) 1645 (w,sh); ν(C=S) 1234 (m); ν(S=O) 1128 (s); ν(Pt-Cl) 325 (m), 311 (m). **MS** (FAB^+) m/z 629 (M^+, 100 %). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ 1.24 (t, 3H, CH_3); 3.58 (br, 8H, CH_{2pip}); 3.63 (br, 6H, SCH_3); 4.09 (q, 2H, CH_2); 7.50 (t, 2H, *m*-Ph); 7.68 (t, 1H, *p*-Ph); 8.12 (d, 2H, *o*-Ph). **^{13}C-NMR** (75.45 MHz, $CDCl_3$): δ 14.5 (CH_3); 40.8 60.9 (CH_2); 128.4 129.4 132.6 134.6 (Ph).

*{Chloro-[N-diethylaminothiocarbonyl)-N′-1-naphthylbenzamidinato-κN,κS]-dimethylsulphoxide-κS}-platinum(II), (**6**)*

Yellow prisms. Yield: 0.078 g (46 %). Mp.: 175-178 °C; $C_{24}H_{28}ON_3S_2ClPt$ (669.16 g/mol); calc.: C 43.08; H 4.22; N 6.28; S 9.58; Cl 5.29 %; found: C 42.02; H 3.98; N 6.51; S 10.39; Cl 5.58 %.

IR (KBr, cm^{-1}): ν(C=O) 1625 (m); ν(C=S) 1259 (m); ν(S=O) 1139 (m). **MS** (FAB^+) m/z 669 (M^+, 100 %); 633.2 (M^+ −Cl, 64 %). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ 1.37 (m, 6H, CH_3); 3.61 (s, 6H, SCH_3); 3.73 (m, 2H, CH_2); 4.01 (m, 2H, CH_2); 7.14-7.55 (m, 6H, Arom); 7.75- 8.76 (m, 6H, Arom).

*Bis[N-(para-nitrobenzoyl)-N′,N′-(diethylamino)-thioureato−κO, κS]-platinum(II), (**7**)*

To a solution of HL^1 (0.141 g, 0.50 mmol) in dioxane (40 mL) was added dropwise a solution of $K_2[PtCl_4]$ (0.1038 g, 0.25 mmol) in water (20 mL), followed by sodium acetate (0.041 g, 0.5 mmol) in water (2 mL), and stirred for 2 h at 60 °C. Then the mixture was stirred for 24 h at room temperature. The yellow precipitate was collected by filtration, washed several times with small portions of water, cold ethanol and dried in vacuo. Recrystallization of the yellow solid was carried out from hot acetone.

Orange prisms. Mp.: 252-254 °C; Yield: 0.113 g (60 %). $C_{24}H_{28}O_6N_6S_2Pt$ (755.08 g/mol). calc.: C 38.1; H 3.7; N 11.0; S 8.5 %; found: C 38.6; H 4.0; N 10.9; S 8.1 %.

IR (KBr, cm^{-1}): ν(C=O) 1640 (m), ν(C=S) 1220 (w). **MS** (FAB^+) m/z 756 ([M + H]$^+$, 100 %). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ 1.34 (m, 12H, CH_3); 3.82 (m, 8H, CH_2); 8.29 (d, 4H, *o*-Ph); 8.38 (d, 4H, *m*-Ph). **^{13}C-NMR** (75.45 MHz, $CDCl_3$): δ 12.7 (CH_3); 46.9 (CH_2); 123.4 130.06 143.4 145.5 (Ph); 166.0 (*C*O); 167.3 (*C*S).

*Bis[N-(para-nitrobenzoyl)-N′,N′-diphenyl-thioureato-κO, κS]-platinum(II), (**8**)*

A similar procedure to **7** was carried out using HL^2 (0.189 g, 0.50 mmol) and $K_2[PtCl_4]$ (0.1038 g, 0.25 mmol) and stirring at room temperature for 2 days.

Yellow solid. Mp.: 283-285 °C; Yield: 0.19 g (80 %). $C_{40}H_{28}O_6N_6S_2Pt$ (947.89 g/mol). calc.: C 50.68; H 2.96; N 8.87; S 6.76 %; found: C 50.3; H 3.05; N 8.54; S 6.38 %.

IR (KBr, cm^{-1}): ν(C=O) 1640 (m), ν(C=S) 1220 (w). **MS** (FAB^+; matrix: 3-NBA) m/z 948 (M^+, 100 %). **^{1}H-NMR** (300 MHz, $CDCl_3$) : δ 7.41 (m, 20H, Ph); 7.93 (d, 4H, Ph); 8.13 (d, 4H, Ph).

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