DALTON
FULL PAPER

Platinum(II) and palladium(II) complexes of *N*-benzoyl-*N′*-propylthiourea (H_2L): synthesis and geometric isomer distribution of $[M(H_2L\text{-}S)_2X_2]$ ($M = Pt^{II}$ or Pd^{II}; $X = Cl^-$, Br^- or I^-); crystal structure of *trans*-$[Pd(H_2L\text{-}S)_2Br_2]$

Klaus R. Koch,* Yali Wang and Anita Coetzee

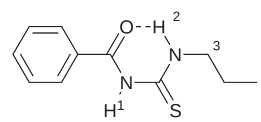
Department of Chemistry, University of Cape Town, P Bag Rondebosch, Cape Town, 7701, RSA

Received 7th December 1998, Accepted 27th January 1999

A systematic study of the synthesis and *cis*/*trans* isomer distribution for simple $[M(H_2L\text{-}S)_2X_2]$ complexes ($M = Pt^{II}$ or Pd^{II}; X = Cl, Br or I; H_2L = *N*-benzoyl-*N′*-propylthiourea) has shown that the pure *cis*-$[Pt(H_2L\text{-}S)_2Cl_2]$ complex is obtained prior to recrystallization. The *cis*-$[Pt(H_2L\text{-}S)_2Cl_2]$ complex undergoes facile isomerization in a variety of organic solvents, the equilibrium *cis*/*trans* distribution of which depends on solvent polarity. The corresponding bromo- and iodo-complexes of Pt^{II} tend toward mainly the *trans* isomers, as do the corresponding palladium(II) complexes. The crystal structure of *trans*-$[Pd(H_2L\text{-}S)_2Br_2]$ has been determined which is the first example of a palladium(II) complex in which the potentially chelating ligand is bound through the S atom only.

We have become interested in the co-ordination chemistry of a group of deceptively simple ligands based on the *N*-alkyl-*N′*-aroyl- (H_2L) and *N,N*-dialkyl-*N′*-aroylthioureas (HL), in view of their selective co-ordination of the platinum group metals.[1] Of particular interest is the potential utility of these ligands in the analytical chemistry of the platinum group metals (PGMs) such as for example the chromatographic separation and determination of the PGMs at trace level,[2,3] as well as the on-line preconcentration of Pd^{II} followed by its determination at ultra-trace level by means of electrothermal atomic absorption spectroscopy.[4] We, and others, have previously shown that the co-ordination of the *N,N*-dialkyl-*N′*-aroylthioureas usually leads to very stable bidentate-S,O co-ordination to Pd^{II},[5] Pt^{II}[6] and Rh^{III}.[7] On the other hand the co-ordination chemistry of *N*-alkyl-*N′*-aroylthioureas is strongly influenced by an intramolecular hydrogen-bond between the carbonyl atom of the aroyl moiety and the thiourea NH group, resulting in co-ordination through the S atom of the ligand.[8] Despite the analytical utility of these ligands, there is relatively little detailed information in the literature concerning the synthesis and structure of complexes of Pt^{II} and Pd^{II} with *N*-alkyl-*N′*-aroylthioureas. Of interest in the case of d^8 metal ions are the factors which determine the distribution of *cis*/*trans* isomers of complexes of Pt^{II}/Pd^{II} of for example *N*-benzoyl-*N′*-propylthiourea. Recently we characterized the *cis*-$[Pt(H_2L\text{-}S)_2Cl_2]$ complex by means of X-ray diffraction,[8] and reported that the corresponding *trans* isomer coexists in chloroform solution in *cis*:*trans* mole ratio of 67:33 at 25 °C. As part of our continuing interest in elucidating the fundamental co-ordination chemistry of *N*-alkyl-*N′*-aroylthioureas of the PGMs, we here report a systematic study of the synthesis of $[M(H_2L\text{-}S)X_2]$ complexes ($M = Pt^{II}$ or Pd^{II}; X = Cl, Br or I; H_2L = *N*-benzoyl-*N′*-propylthiourea) with reference to determining the distribution of *cis*/*trans* isomers in the solid state, as well as in various solvents.

We report the crystal structure of *trans*-$[Pd(H_2L\text{-}S)_2Br_2]$, the first example of H_2L co-ordinated to Pd^{II} only through the S atom is this manner. For the purposes of this contribution, we have adopted an arbitrary numbering scheme for the *N*-benzoyl-*N′*-propylthiourea ligand which is consistent with that used in the crystal structure of *trans*-$[Pd(H_2L\text{-}S)_2Br_2]$.



Experimental

Preparative methods

N-Benzoyl-*N′*-propylthiourea was prepared as previously described[8] and purified by recrystallization from chloroform–ethanol mixtures.

$[M(H_2L\text{-}S)_2X_2]$ ($M = Pt^{II}$ or Pd^{II}; $X = Cl^-$, Br^- or I^-) complexes. These complexes were prepared according to the following standardized procedure from commercially available $K_2[PtCl_4]$ and $K_2[PdCl_4]$ or $PdCl_2$, which were used without further purification. The complexes were characterized by means of melting points (measured using a Reichert Thermovar microscope), elemental (C, H, and N) analysis, IR and NMR spectroscopy.

$[Pt(H_2L\text{-}S)_2Cl_2]$. A 0.25 mmol portion (103.8 mg) of $K_2[PtCl_4]$ dissolved in 30 cm^3 of a 1:2 (v/v) mixture of 1 M HCl–1,4-dioxane or acetonitrile was added dropwise to 30 cm^3 of a well stirred solution containing 0.50 mmol H_2L (111.2 mg) in the same solvent, at the desired temperature (25, 60, 85 ± 2 °C), using a water-jacketed dropping funnel over a period of 5–15 min. The bright yellow mixture was then stirred at the desired temperature for a fixed time interval (Table 1). On cooling, 200 cm^3 cold water were added to complete the precipitation of the complex, which was collected in high yield by centrifugation, washed with cold water and ethanol, followed by drying at 60 °C under vacuum. If desired (see below), the complex was recrystallized from mixtures of chloroform and ethanol, with minimum losses followed by drying (Found: C, 37.24; H, 4.01; N, 7.71. $C_{22}H_{28}Cl_2N_4O_2PtS_2$ requires C, 37.18; H, 3.97; N, 7.88%).

$[Pt(H_2L\text{-}S)_2Br_2]$ and $[Pt(H_2L\text{-}S)_2I_2]$. The dibromo- and diiodo-complexes were prepared by an identical procedure to that for the dichloro-complexes, except that the corresponding $[PtBr_4]^{2-}$ and $[PtI_4]^{2-}$ anions were generated *in situ* by addition of a 25 fold molar excess of NaBr or NaI to the solution of

Table 1 Conditions of synthesis and physical properties of recrystallized $[Pt(H_2L\text{-}S)_2Cl_2]$ complexes prepared by a standardized procedure

X	t/h	T/°C	Reaction medium (0.01 M HX + solvent)	Yield (%)	Mp[a]/°C	^{1}H NMR shifts (δ)[b] cis-N(1)H	trans-N(1)H	cis:trans Ratio (%)[c] (not equilibrium)
Cl	1	25	1,4-Dioxane	77	154–158, 162–165	11.80	11.55	74:26
	6	25	1,4-Dioxane	87	152–153, 158–160	11.80	11.55	75:25
	17	25	1,4-Dioxane	94	153–155, 160–163	11.80	11.56	75:25
	1	60	1,4-Dioxane	84	154–155, 165–168	11.80	11.55	75:25
	1	85	Acetonitrile	82	154–155, 165–169	11.80	11.56	75:25
Br	1	25	1,4-Dioxane	69	162–164, 174–178	11.49	11.31	40:60
	6	25	1,4-Dioxane	84	161–164, 176–179	11.49	11.31	42:58
	1	60	1,4-Dioxane	62	161–164, 175–178	11.50	11.32	42:58
	1	85	Acetonitrile	71	163–166, 175–178	11.50	11.32	42:58
I	1	25	1,4-Dioxane	82	172–173, 196–199	11.36	10.99	8:92
	6	25	1,4-Dioxane	75	172–173, 196–198	11.36	10.99	6:94
	1	60	1,4-Dioxane	84	172–173, 195–197	11.36	10.99	5:95
	1	85	Acetonitrile	81	171–173, 196–197	11.36	10.99	8:92

[a] For two distinct crystals. [b] Measured at 25 °C within 2 min of dissolution in $CDCl_3$. [c] Estimated from the resonance integrals of the N(1)H signals in solution described in footnote *b*; for the chloro-complexes the equilibrium distribution is different in this solvent.

$K_2[PtCl_4]$ and substituting the 1 M HCl by 10% (v/v) HBr or HI, allowing this mixture to stir for 1 h prior to addition to the solution of ligand, and proceeding as before (Found: C, 33.30; H, 3.50; N, 6.97. $C_{22}H_{28}Br_2N_4O_2PtS_2$ requires C, 33.05; H, 3.53; N, 7.01. Found: C, 29.75; H, 3.14; N, 6.26. $C_{22}H_{28}I_2N_4O_2PtS_2$ requires C, 29.57; H, 3.16; N, 6.27%).

$[Pd(H_2L\text{-}S)_2Cl_2]$ and $[Pd(H_2L\text{-}S)_2Br_2]$. These complexes were prepared by means of an identical method to that for the platinum(II) complexes described above, using $K_2[PdCl_4]$ or $PdCl_2$ as the source of Pd^{II} (Found: C, 42.89; H, 4.61; N, 9.16. $C_{22}H_{28}Cl_2N_4O_2PdS_2$ requires C, 42.49; H, 4.54; N, 9.01. Found: C, 37.51; H, 4.00; N, 7.85. $C_{22}H_{28}Br_2N_4O_2PdS_2$ requires C, 37.17; H, 3.97; N, 7.88%). Yields and other pertinent analytical data are given in Table 1.

NMR and IR spectroscopy

The ^{1}H and ^{195}Pt NMR spectra were recorded in 5 mm tubes in $CDCl_3$ solution using a Varian Unity-400 spectrometer operating at 400 and 85.85 MHz respectively; ^{1}H spectra were recorded at 25 °C, while ^{195}Pt chemical shifts were measured at 30 °C relative to the usual reference of external H_2PtCl_6 [500 mg in 1 cm^3 30% (v/v) D_2O–1 M HCl].[9] Infrared spectra were recorded using a Perkin-Elmer 983 dispersive spectrometer, as freshly prepared Nujol mulls between polyethylene plates.

Crystal structure determination and refinement

Crystals of *trans*-$[Pd(H_2L\text{-}S)_2Br_2]$ of dimensions 0.30 × 0.25 × 0.25 mm, crystallizing in the triclinic system, were chosen for analysis. Data were collected at 173(2) K on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å). A Lorentz-polarization correction was applied to the data, as well as an empirical absorption correction.[10] The structure was solved by direct methods[11] and refined using full-matrix least squares[12] on F^2. Non-hydrogen atoms were treated anisotropically while hydrogen atoms were placed in geometrically calculated positions and linked to common thermal parameters. Pertinent crystal and structure refinement data are given in Table 3.

CCDC reference number 186/1333.

See http://www.rsc.org/suppdata/dt/1999/1013/ for crystallographic files in .cif format.

Results and discussion

A standardized procedure for the synthesis of $[M(H_2L\text{-}S)_2X_2]$ (M = Pt^{II} or Pd^{II}) was adopted, consisting of the dropwise addition of the metal salt MX_4^{2-} dissolved in a 1:1 mixture of 0.1 M HX (X = Cl, Br or I) and 1,4-dioxane or acetonitrile over a 15 min period to a well stirred solution of the required amount of H_2L (L:M mole ratio 2:1) at a predetermined temperature. The reactions were carried out at fixed temperatures of 25, 60 and 85 °C for various reaction times of 1, 6 and 17 h, respectively. In general, the complex precipitates during the reaction and high yields of analytically pure complex $[M(H_2L\text{-}S)_2X_2]$ were obtained. These data are summarized in Table 1.

$[Pt(H_2L)_2X_2]$ (X = Cl^-, Br^- or I^-) complexes

The recrystallized (chloroform–ethanol), analytically pure $[Pt(H_2L\text{-}S)_2Cl_2]$ complex shows two distinct melting points at 154–158 and 165–169 °C irrespective of the solvent mixture, temperature and reaction time used during the synthesis, suggesting that isomerism takes place during the recrystallization process. Moreover, the ^{1}H NMR spectrum of a fresh solution of the recrystallized $[Pt(H_2L\text{-}S)_2Cl_2]$ complex (acquired within 2 min of dissolution) shows this to be a two component mixture consisting of *cis*:*trans* isomers in the ratio of *ca.* 75%:25% (Table 1). We have shown recently that the *cis*/*trans* isomer distribution of bis(*N*-benzoyl-*N′*-propylthioureato)dichloroplatinum(II) can conveniently be determined by means of ^{1}H and ^{195}Pt NMR spectroscopy.[8] Thus in the ^{1}H NMR spectrum of *cis*-bis(*N*-benzoyl-*N′*-propylthioureato)dichloroplatinum(II) (characterized by X-ray diffraction) the ^{1}H resonances of N(1)H and N(2)H appear at δ 11.80 ± 0.03 and 11.15 ± 0.03 [partially resolved triplet ^3J(H2-H3) ≈ 13 Hz] respectively, with δ(^{195}Pt) at −3231 ± 2. The corresponding chemical shifts for the *trans* isomer occur at δ(^{1}H) 11.55 ± 0.03, 11.11 ± 0.03 and δ(^{195}Pt) −3052 ± 2 respectively.

To test the possibility that isomerization occurs during the recrystallization of $[Pt(H_2L\text{-}S)_2Cl_2]$, we examined the ^{1}H NMR spectrum of a freshly made $CDCl_3$ solution (25 °C) of an *unrecrystallized*, but analytically pure, sample of $[Pt(H_2L\text{-}S)_2Cl_2]$ (mp 154–157 °C). The infrared spectrum of this solid confirms the *cis* configuration, since only two strong ν(Pt–Cl) stretching bands at 304 and 321 cm^{-1} are observed, consistent with literature values for mononuclear *cis* complexes.[13] The ^{1}H NMR spectrum acquired within 2 min of dissolution of unrecrystallized $[Pt(H_2L\text{-}S)_2Cl_2]$ shows only one set of N(1)H and N(2)H resonances corresponding to the *cis*-$[Pt(H_2L\text{-}S)_2Cl_2]$ complex as shown by the first spectrum in the array in Fig. 1. On standing in $CDCl_3$ solution (at 25 °C) an additional set of ^{1}H resonances appears in the spectrum over time, corresponding to the *trans* isomer, the system reaching an equilibrium distribution after 3–4 h, as shown by the partial ^{1}H NMR spectrum as a function of time in Fig. 1. From these spectra an equilibrium

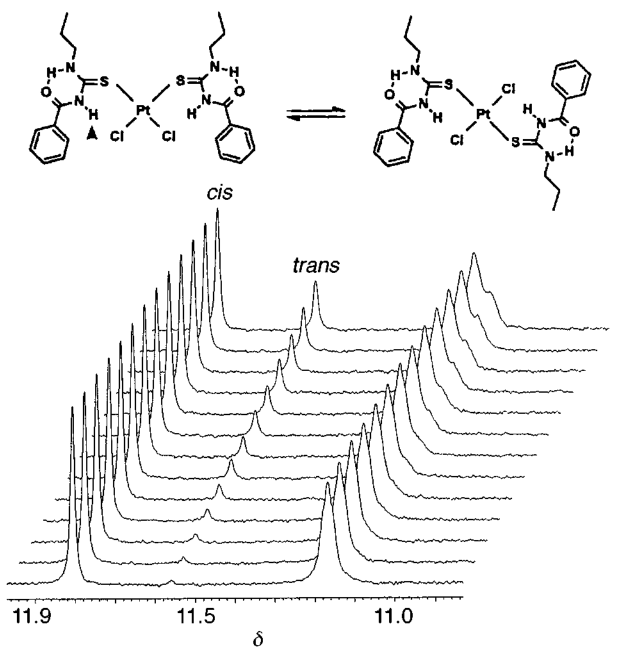


Fig. 1 Portion of the ^{1}H NMR spectrum of a freshly dissolved sample of unrecrystallized *cis*-[Pt(H_2L-*S*)$_2$$Cl_2$] in $CDCl_3$ at 25 °C as a function of time. The first spectrum in the array was recorded 1.9 min after dissolution, while the last spectrum was recorded *ca.* 24 h later, at steady state. The isomerization of *cis* to *trans* is clearly evident.

constant,† K = {*trans*-[Pt(H_2L-*S*)$_2$$Cl_2$]/*cis*-[Pt($H_2$L-*S*)$_2$$Cl_2$]} defined for the system *cis*-[Pt(H_2L-*S*)$_2$$Cl_2$] $\rightleftharpoons$ *trans*-[Pt(H_2-L-*S*)$_2$$Cl_2$] can easily be estimated from the relative resonance integrals of the *cis* and *trans* N(1)H resonances; in $CDCl_3$ solution we find $K = 0.47 \pm 0.02$ at 25 °C. Several repeated preparations of [Pt(H_2L-*S*)$_2$$Cl_2$] under different conditions of temperature, reaction time and solvent composition confirm that *all unrecrysallized* samples have essentially the pure *cis* configuration, but *on dissolution* undergo facile isomerization.

Table 2 shows the measured equilibrium isomer distribution constants of [Pt(H_2L-*S*)$_2$$Cl_2$] in a number of deuteriated solvents of differing polarity at 25 °C. It is clear that an inverse correlation between K and the relative permittivity, D, of the solvent [14] is observed. The *cis* isomer is favored in solvents of highest polarity, while in benzene-d_6 with lowest D in this series the *trans* isomer predominates; these trends are similar to observations made for [Pd(PR_3)$_2$$Cl_2$] by Jenkins and Shaw [15] and Redfield and Nelson [16] some years ago. An interesting, if poorly understood aspect of the *cis*/*trans* isomerization of [Pt(H_2L-*S*)$_2$$Cl_2$] is that the rate of equilibration also depends on the nature of the solvents. Qualitatively, we find that the relative rates of isomerization are *greatest* in benzene-d_6 (lowest D), the process being complete within the time of preparing a solution and recording a ^{1}H NMR spectrum (<2 min), while it takes more than 24 h to reach equilibrium in CD_3NO_2 (highest D). We are currently studying the kinetics of isomerism of [Pt(H_2L-*S*)$_2$$Cl_2$] in more detail, the results of which will be published elsewhere.

As might be expected, substitution of the Cl^- by Br^- or I^- ions is likely to significantly affect the K values of isomer distribution in [Pt(H_2L-*S*)$_2$$X_2$], in view of the increasing *trans* effect in the order Cl < Br < I.[17] Results in Table 1 essentially confirm this expectation, showing that the *trans* complex is strongly favored in the order I > Br > Cl. By contrast to [Pt(H_2L-*S*)$_2$$Cl_2$]

† The attainment of an equilibrium distribution is confirmed by the invariance of the respective resonance integrals for these complexes for at least 72 h at 25 °C. In determining the K values by means of ^{1}H NMR spectroscopy care was taken to ensure that the system was fully relaxed and that resonance integrals accurately reflected the concentrations of the *cis*/*trans* isomers.

Table 2 Measured equilibrium values for the *cis*-[Pt(H_2L-*S*)$_2$-Cl_2] $\rightleftharpoons$ *trans*-[Pt(H_2L-*S*)$_2$$Cl_2$] system in various solvents at 25 °C as a function of solvent polarity

Solvent	Relative permittivity, D	Equilibrium constant, K
Nitromethane-d_3	38.6	0.16
Dimethylformamide-d_7	36.7	0.23
Acetone-d_6	20.5	0.28
Tetrahydrofuran-d_8	7.39	0.39
Chloroform-d_3	4.7	0.47
Benzene-d_6	2.27	0.88

however, the isomer distribution in $CDCl_3$ found for [Pt(H_2L-*S*)$_2$$Br_2$] and [Pt($H_2$L-*S*)$_2$$I_2$] remains invariant irrespective of whether these complexes are recrystallized or not. In the case of [Pt(H_2L-*S*)$_2$$Br_2$] we find a distribution of *ca.* 42% *cis* : 68% *trans* (mp 161–166 and 175–179 °C), while for the [Pt(H_2L-*S*)$_2$$I_2$] complexes the distribution is *ca.* 5% *cis* and 95% *trans* (mp 171–173 and 195–199 °C). Evidently the dibromo- and diiodo-complexes in $CDCl_3$ appear to reach an equilibrium isomer distribution ($K = 1.41 \pm 0.06$ and 15.4 ± 3.8, respectively) during the synthesis in the water–dioxane/acetonitrile phase, whereas the dichloro-complexes undergo facile isomerization in various solvents at room temperature (Table 2). These various assignments are independently confirmed by the ^{195}Pt NMR resonances of the dibromo- and diiodo-complexes, which show ^{195}Pt resonances at δ −3693, −3678 and −4693, −4870 for the *cis*- and *trans*-[Pt(H_2L-*S*)$_2$$Br_2$] or [Pt($H_2$L-*S*)$_2$$I_2$] complexes respectively. The ^{195}Pt shift assignments are based on the relative resonance intensities of these signals, which mirror those of the corresponding ^{1}H NMR spectra. Moreover the ^{195}Pt chemical shift of *trans*-[Pt(H_2L-*S*)$_2$$I_2$] is *upfield* relative to the *cis* isomer, in contrast to the corresponding dichloro- and dibromo-complexes, which is consistent with similar trends generally found in other uncharged mononuclear platinum(II) complexes involving two halide ions and two uncharged ligands.[9]

[Pd(H_2L-*S*)$_2$$X_2$] (X = Cl^- or Br^-) complexes

It was only possible to prepare the dichloro and dibromo [Pd(H_2L-*S*)$_2$$X_2$] complexes by a similar synthetic method as used for the corresponding platinum(II) analogues. Moreover the isomer distribution observed for the palladium(II) complexes differs substantially from that observed for the corresponding platinum(II) complexes. The unrecrystallized, pure [Pd(H_2L-*S*)$_2$$Cl_2$] complex is presumed to be a single isomer, in view of the sharp melting point (149–152 °C). However, from the ^{1}H NMR spectrum of a fresh $CDCl_3$ solution of unrecrystallized [Pd(H_2L-*S*)$_2$$Cl_2$], it appears that *trans*-[Pd(H_2L-*S*)$_2$$Cl_2$] predominates with a equilibrium constant $K = 2.33$ at 25 °C [assignment is based on the relative resonance integral ratio of the N(1)H peaks at δ 12.18 to 11.62 which are assigned to the *cis* and *trans* complexes respectively, by comparison with the corresponding platinum(II) complexes]. Moreover, the ^{1}H NMR spectra of the palladium(II) complexes remain invariant for 24 h, suggesting that the isomer distribution rapidly reaches equilibrium on dissolution of the substance. By contrast to the platinum(II) complexes, the intramolecular hydrogen-bonded N(2)H resonances of *cis*-[Pd(H_2L-*S*)$_2$$Cl_2$] ($\delta$ 11.39) and *trans*-[Pd(H_2L-*S*)$_2$$Cl_2$] ($\delta$ 11.26) are substantially broadened so that the ^3J coupling between the α-CH_2 moiety of the propyl group is unresolved, something which might cast doubt on the unambiguous assignment of *cis* and *trans* configuration of these isomers.

Substitution of the Cl^- ion by the Br^- ion leads to the formation of the pure *trans*-[Pd(H_2L-*S*)$_2$$Br_2$] complex (mp 176–178 °C), for which the ^{1}H N(1)H resonance appears at δ 11.17, the N(2)H resonance being just visible as a shoulder of the latter peak. There is no evidence of any *cis* isomer in $CDCl_3$,

Table 3 Crystal and structure refinement data for *trans*-bis(*N*-benzoyl-*N'*-propylthioureato)dibromopalladium(II)

Empirical formula	$C_{22}H_{28}Br_2N_4O_2PdS_2$
Formula weight	710.84
T/K	293(2) K
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	8.768(1)
b/Å	8.9525(9)
c/Å	9.8668(8)
α/°	104.034(8)
β/°	113.016(8)
γ/°	99.226(9)
U/Å^3	662.7(1)
μ/mm^{-1}	3.849
Z	1
Independent reflections	1744 [R(int) = 0.0137]
Goodness of fit on F^2	1.093
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0254, 0.0724
(all data)	0.0306, 0.0739

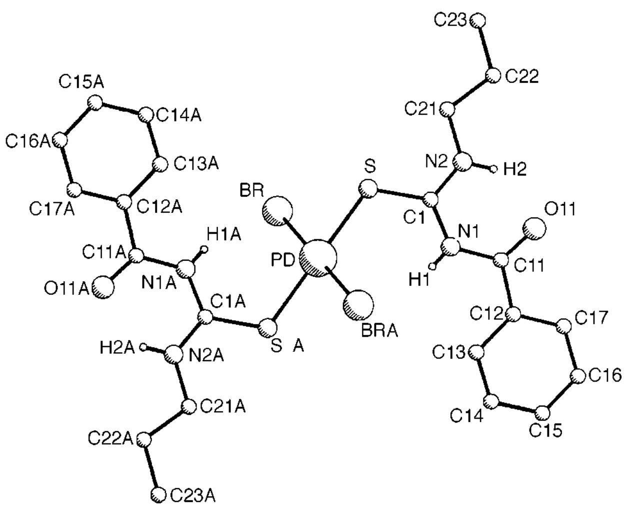


Fig. 2 The molecular structure of *trans*-[Pd(H_2L-*S*)$_2$Br$_2$], with the numbering scheme used. Only those hydrogen atoms involved in intramolecular hydrogen bonding are shown (see text). Selected bond lengths and angles: Pd–S 2.3164(10), Pd–Br 2.4415(5), S–C(1) 1.689(4), N(1)–C(11) 1.379(5), N(2)–C(21) 1.315(5), N(2)–C(21) 1.460(5) and C(11)–O(11) 1.220(5) Å; S(A)–Pd–S 180, S(A)–Pd–Br 94.54(3) and S–Pd–Br 85.46(3)°.

nor does the ^{1}H NMR spectrum change with time. The *trans* stereochemistry of this complex, and thus by inference of the corresponding dichloro-complexes, was confirmed by the crystal structure of [Pd(H_2L-*S*)$_2$Br$_2$] described below.

Crystal structure of *trans*-bis(*N*-benzoyl-*N'*-propylthioureato)-dibromopalladium(II)

The structure of the *trans*-[Pd(H_2L-*S*)$_2$Br$_2$] complex is shown in Fig. 2, while the crystal and structure refinement data, are given in Table 3. Inspection of the structure shows the expected square-planar co-ordination with two ligands H_2L bonded through the S atom with Pd–S 2.316(1) Å. The bond lengths Pd–Br are 2.442(1) Å, while the bond angles S(A)–Pd–Br 94.54(3) and S–Pd–Br 85.46(3)° deviate significantly from 90°, the distortion presumably being induced by the two weak hydrogen bonds between N1(H) ··· Br(A) [and N1A(H) ··· Br] at 3.294 Å (van der Waals radii N–Br ≈ 3.45 Å). Similar weak N(H) ··· Cl hydrogen bonds, and the resultant mild distortion of bond angles from 90°, have previously been observed for the *cis*-bis(*N*-benzoyl-*N'*-propylthioureato)dichloroplatinum(II) complex.[8] An additional hydrogen bond between the N(2)H and the carbonyl oxygen atom (O11) of the co-ordinated ligand at 2.601(4) Å effectively locks the ring C1–N1–C11–O11–H2–N2 into a planar structure, the atoms of this ring deviating from planarity by not more than 0.026 Å. The structure, bond lengths and angles of the co-ordinated H_2L in *trans*-[Pd(H_2L-*S*)$_2$Br$_2$] are remarkably similar to that of the unbound ligand,[18] as well as that of the co-ordinated ligand in the corresponding *cis*-platinum complex.[8] This mode of co-ordination of *N*-benzoyl-*N'*-alkylthiourea once again highlights the importance and relative stability of the intramolecular hydrogen bond between the thiourea NH moiety and the carbonyl oxygen atom of these ligands in determining the preferred mode of S atom co-ordination.

Conclusion

From our studies some interesting and fairly significant conclusions can be drawn which have relevance to the synthesis of simple mononuclear complexes of Pt^{II} and Pd^{II} with *N*-benzoyl-*N'*-propylthiourea and related ligands. In the case of Pt^{II} only the pure *cis*-[Pt(H_2L-*S*)$_2$Cl$_2$] complex is obtained by our method of synthesis; this complex undergoes relatively rapid partial isomerization in solution to yield a *cis*/*trans* distribution which is dependent on solvent polarity. In contrast the corresponding palladium(II) complexes are predominantly *trans*, and appear to have reached an equilibrium *cis*/*trans* distribution on dissolution, something consistent with the greater lability of palladium(II) complexes in general. The corresponding bromo- and iodo-complexes of Pt^{II} and Pd^{II} are mainly *trans*, as illustrated by the crystal structure of the *trans*-[Pd(H_2L-*S*)$_2$Br$_2$] complex.

Acknowledgements

We thank the University of Cape Town and the Foundation for Research Development for financial assistance. The loan of platinum and palladium salts from Johnson Matthey plc is gratefully acknowledged.

References

1 K. R. Koch, C. Sacht, T. Grimmbacher and S. Bourne, *S. Afr. J. Chem.*, 1995, **48**, 71
2 K.-H. König, M. Schuster, B. Steinbrech, G. Schneeweis and R. Schlodder, *Fresenius Z. Anal. Chem.*, 1985, **321**, 457; M. Schuster, *Fresenius Z. Anal. Chem.*, 1986, **324**, 127.
3 M. Schuster, *Fresenius Z. Anal. Chem.*, 1992, **342**, 791.
4 M. Schwarzer and M. Schuster, *Anal. Chim. Acta*, 1996, **328**, 1.
5 G. Fitzl, L. Beyer, R. Sieler, R. Richter, J. Kaiser and E. Hoyer, *Z. Anorg. Allg. Chem.*, 1977, **433**, 237.
6 K. R. Koch, A. Irving and M. Matoetoe, *Inorg. Chim. Acta*, 1993, **206**, 193.
7 W. Bensch and M. Schuster, *Z. Anorg. Allg. Chem.*, 1992, **615**, 93.
8 K. R. Koch and S. Bourne, *J. Chem. Soc., Dalton Trans.*, 1993, 2071.
9 P. S. Pregosin, *Coord. Chem. Rev.*, 1982, **44**, 247.
10 A. T. C. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
11 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
12 G. M. Sheldrick, SHELXL 97, Suite of programs for crystal structure determinations, 1997.
13 D. M. Adams and J. B. Cornell, *J. Chem. Soc. A*, 1967, 884.
14 J. Burgess, *Metal Ions in Solution*, Ellis Horwood, Chichester, 1978, p. 32.
15 J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 1966, 770.
16 D. A. Redfield and J. H. Nelson, *Inorg. Chem.*, 1973, **12**, 15.
17 J. E. Huheey, *Inorganic Chemistry*, 2nd edn., Harper & Row, London, 1978, p. 491.
18 A. Drago, Yu Shepelev, F. Fajardo, F. Alvarez and R. Pomes, *Acta Crystallogr., Sect. C*, 1989, **45**, 1192.

Paper 8/09543D