Deceptively simple Pt complexes of *N,N*-dialkyl-*N'*-benzoylthiourea: a ^{1}H, ^{13}C and ^{195}Pt NMR study of their acid–base chemistry in solution and the molecular structure of *cis*-bis(*N,N'*-di(n-butyl)-*N'*-benzoylthioureato)platinum(II)

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(Received September 15, 1992; revised November 30, 1992)

Abstract

N,N-Di(n-butyl)-*N'*-benzoylthiourea readily reacts with PtX_4^{2-} to yield neutral *cis*-$[PtL_2]$ complexes for $X=Cl^-$ and Br^-, while for $X=I^-$, the protonated *cis*-$[Pt(LH)_2]I_2$ complex is isolated. The crystal structure of *cis*-$[PtL_2]$ is reported. In chloroform solution, the neutral *cis*-$[PtL_2]$ complexes may readily be protonated to yield a distribution of *cis*-$[Pt(LH)L]^+$ and *cis*-$[Pt(LH)_2]^{2+}$ species which have been characterized by means of high resolution multinuclear NMR. Remarkably the ^{195}Pt chemical shift of the cationic species is strongly dependent on the nature of the uncoordinated anion (Cl^-, Br^-, I^-) present, suggesting tight ion-pair formation in solution.

Introduction

N,N'-Dialkyl-*N'*-benzoylthioureas have been found to be useful ligands for the potential determination of traces of the transition metals by means of normal phase chromatography [1]. More significantly these reagents have been shown to selectively extract several of the platinum group metals in the form of remarkably stable neutral metal chelates [2]. In view of the ease of synthesis and favourable properties of these ligands, we have investigated the potential determination of traces of Pt and Pd by means of solvent extraction into non-aqueous media, followed by high performance liquid chromatography [3]. We have found, however, that the chromatographic separation of metal chelates of Pt, Pd and Ni is complicated by the existence of several complex species in solution, depending on conditions. A survey of the literature shows that remarkably little has been published concerning the chemistry of these apparently simple complexes. Beyer and co-workers examined a series of neutral Ni(II), Cu(II), Co(II) and Pd(II) complexes [4–6], while the crystal structures of Hg(II) [7] and Ag(I) [8] have been reported. Recently a series of tris(*N,N'*-dialkyl-*N'*-benzoyl(oxo/thio)selenoureato)-cobalt(III) complexes have been examined by means of ^{59}Co NMR [9].

We here report a study of some Pt(II) complexes of *N,N*-di(n-butyl)-*N'*-benzoylthiourea (denoted hereafter LH for short) with reference to the structure and nature of these complexes in solution. To our knowledge all the well characterized transition metal complexes that have been reported are of the neutral ML_2 or ML_3 type. In the case of square planar $[PtL_2]$ complexes, it is obvious that both *cis* and *trans* configurations are possible, while the corresponding protonated *cis/trans*-$[Pt(LH)L]^+$ and $[Pt(LH_2)]^{2+}$ species may be postulated as shown in Scheme 1.

$$[PtCl_4]^{2-} + 2LH \longrightarrow cis/trans\text{-}[Pt(LH)_2]Cl_2 + 2Cl^-$$

$$[Pt(LH)_2]Cl_2 \longrightarrow [Pt(LH)L]Cl + HCl$$

$$[Pt(LH)L]Cl \longrightarrow \underset{\mathbf{I}}{[PtL_2]} + HCl$$

Scheme 1.

Experimental

Preparations of N,N-di(n-butyl)-N'-benzoylthiourea(LH)

This ligand was prepared according to the method of Douglass and Dains [10], in 70–90% yield. The crude product was recrystallized from ethanol/water mixtures to yield white crystals, m.p. 92–94 °C (lit. 93 °C [2]. *Anal.* Calc. for $C_{16}H_{24}N_2SO$: C, 65.7; H, 8.3; N, 9.6.

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Found: C, 65.9; H, 8.4; N, 9.8%, $m/e = 293$. δ^1H ($CDCl_3$): 0.89, 0.93 (6H, t, t), 1.29, 1.41 (4H, q, q), 1.65, 1.79 (4H, q, q), 3.39, 3.45 (2H, t, t), 7.50 (2H, d), 7.51 (2H, t), 7.91 (1H, d), 10.58 (1H, s) ppm. As a result of restricted rotation about the C–N thioamide bond, the butyl fragments are non-equivalent.

Preparation of platinum complexes

In general the Pt complexes were prepared as follows. 20–40 cm^3 of a hot (70 °C) solution of water containing 1.01 mmol K_2PtCl_4 (Johnson Matthey) were added dropwise to a solution containing 2 mmol LH in 60 cm^3 (1 + 1) ethanol/water at 70 °C, over 10–15 min. The mixture was stirred for 1 h after reagents had been mixed followed by cooling in ice. The bright yellow precipitate was collected by centrifugation, washed with cold water and dried at 60 °C under vacuum. Essentially quantitative yields were obtained. Recrystallization from chloroform–ethanol mixtures gave bright yellow crystals, m.p. 164–166 °C. *Anal.* Calc. for $C_{32}H_{46}N_4S_2O_2Pt$: C, 49.4; H, 6.0; N, 7.2. Found: C, 48.9; H, 5.9; N, 6.8%. δ ^{1}H ($CDCl_3$): 0.92, 0.97 (12H, t, t), 1.34, 1.39 (8H, q, q), 1.64, 1.74 (8H, q, q), 3.67, 3.77 (8H, q, q), 7.40 (4H, dt), 7.44 (4H, d), 8.24 (2H, d) ppm. As in the case of the ligand, the butyl fragments are non-equivalent, due to restricted C–N bond rotation.

The above procedure was repeated with various combinations of solvent mixtures consisting of 0.1–1 M HCl plus ethanol, as well as with K_2PtCl_4 solutions containing a 25 fold molar excess of NaCl, NaBr and NaI as shown in Table 1.

NMR spectroscopy

All ^{1}H, ^{13}C and ^{195}Pt NMR spectra were recorded in 5 mm tubes using a Varian VXR-200 spectrometer operating at 200.02, 50.32 and 42.925 MHz, respectively. ^{1}H and ^{13}C spectra were recorded at 25 °C, while ^{195}Pt spectra were obtained at 30 °C. ^{1}H and ^{13}C shifts are quoted relative to the residual chloroform-d solvent resonance at 7.25 and 77.0 ppm, respectively. ^{195}Pt spectra were recorded using 100 KHz spectral widths and 12 μs (80°) pulses with 1 s pulse delay. Between 2048 and 16 000 transients, with line broadening factor of 10–20 Hz, gave good spectra. All ^{195}Pt shifts are quoted relative to external H_2PtCl_6 (500 mg in 1 ml 30% (vol./vol.) D_2O/1 M HCl).

X-ray crystallography of bis(N,N-di(n-butyl)-N′-benzoylthioureato)platinum(II)

Crystals of compound **I** are triclinic, $P\bar{1}$, $a = 9.975(5)$, $b = 10.965(2)$, $c = 15.924(6)$ Å, $\alpha = 78.43(3)$, $\beta = 89.86(4)$, $\gamma = 83.97(3)°$, $V = 1696.5$ Å^3, $Z = 2$, $D_c = 1.52$ Mg m^{-3}, $F(000) = 784$, λ(Mo Kα) = 0.71069 Å, $\mu = 4.33$ mm^{-1}, room temperature.

Structure determination

Yellow parallepipeds suitable for single crystal X-ray diffraction were grown from chloroform. A specimen of dimensions 0.38 × 0.41 × 0.53 mm was used for the data collection. Lattice parameters were determined by least-squares fitting of the setting angles of 24 reflections with $16 \leqslant \theta \leqslant 17°$, automatically centred on a Enraf-Nonius CAD4 diffractometer. Intensities were collected with graphite monochromated Mo Kα radiation, $\lambda = 0.71069$ Å, in the $\omega/2\theta$ scan mode, scan width $(0.95 + 0.35 \tan \theta)°$, range of reflections $1 \leqslant \theta \leqslant 25°$. 6195 reflections were measured, 5053 unique with $F_0 > 4\sigma(F_0)$ were used in the refinement, with index range $h - 11/11$, $k - 13/13$, l 0/18. The data were corrected for background, scan speed, Lorentz and polarization factors and an empirical absorption correction [11] was applied; transmission factors were 0.85–0.99.

The structure was solved by Patterson and Fourier methods. Least-squares anisotropic refinement (based on F) was used for the positions of all non-hydrogen atoms. The positions of the hydrogen atoms were constrained to idealized positions, C–H = 0.96 Å, and refined isotropically. At convergence, $R_w = 0.037$, $w = 1/[\sigma^2(F_0) + 0.00465(F_0)^2]$, $S = 0.69$, $(\Delta/\sigma)_{max} < 0.01$, residual electron density was $-0.38 \leqslant \Delta\rho \leqslant +0.75$ e Å^{-3}. (Final atomic parameters are listed in Table 2.) Computer programs used: SHELX76 [12]; SHELX84[13]; PLUTO [14]; PARST [15]. All calculations were performed at the Computer Centre of the University of Cape Town on a Univac 1100/81 computer.

Results and discussion

The products obtained from the reaction of $PtCl_4^{2-}$ with LH (Pt:LH 1:2) in (1 + 1) water/ethanol mixtures at *c.* 70 °C depends *inter alia* on the HCl concentration of the aqueous phase and the presence of NaX (X = Cl, Br and I). Where the reaction medium consists of essentially neutral water/ethanol mixtures, the uncharged, yellow–orange [PtL_2] complexes are virtually quantitatively formed. Evidently complex formation results in the loss of the dissociable N–H proton of the ligand, forming the neutral [PtL_2] complex. Apart from conventional means of characterization, the high solubility of these complexes in chloroform renders ^{195}Pt NMR very useful in determining the distribution of species obtained under different conditions. Hence the ^{195}Pt NMR spectrum of unpurified [PtL_2] prepared in neutral water/ethanol solution consists of a single sharp resonance at −2723 ppm resulting from either the *cis* or *trans* complex (Fig. 1(a)). The stereochemistry of this complex has been unambiguously determined to be *cis*-[PtL_2] (**I**) by means of X-ray diffraction (see Fig. 3).

The ^{195}Pt NMR spectra of products obtained from an *acid* reaction medium (0.1–1 M HCl/ethanol mixtures) consist of at least three major resonances at −2723, −2960 and −3210 ppm, the relative intensities of which were found to depend on the initial acid concentration. The distribution of species present in unrecrystallized reaction products obtained from a variety of reaction conditions is summarized in Table 1. The ^{195}Pt resonances at −2960 and −3210 ppm are assigned to the protonated complexes *cis*-[Pt(LH)L]Cl and *cis*-[Pt(LH)$_2$]Cl$_2$, respectively (Fig. 1(b)). This assignment is based on the observation that addition of a slight excess of triethylamine directly to an NMR tube containing the above distribution of species, results in deprotonation to yield only the signal ascribed to **I** (Fig. 1(c)). These spectral changes are also mirrored in the ^{1}H and ^{13}C NMR spectra of these products. Thus the two N–H resonances at 11.27 and 11.14 ppm corresponding to the ^{195}Pt resonances at −2960 and −3210 ppm, respectively, vanish on addition of the triethylamine. Moreover the crude mixture of complexes isolated from acidic medium may conveniently be separated by means of thin layer chromatography (TLC) on silica gel using chloroform as eluent. The uncharged complex **I** has a high mobility (R_f = 0.8–0.9), allowing for ready separation from the protonated species which are more strongly retained on silica gel ([Pt(LH)L]Cl, R_f = 0.3–0.4 and [Pt(LH)$_2$]Cl$_2$, R_f = 0). Hence complex **I** has been separated from protonated species by means of preparative TLC, the pure product giving a single ^{195}Pt resonance at −2723 ppm, while the ^{195}Pt spectra of the less mobile fractions obtained from the preparative TLC separation show the presence of a small amount of the neutral **I**, in addition to the resonances assigned to *cis*-[Pt(LH)L]Cl and to *cis*-[Pt(LH$_2$)]Cl$_2$, suggesting a degree of dissociation in solution as postulated in Scheme 1.

TABLE 1. ^{195}Pt NMR data and assignments to species obtained under various preparative conditions

Reaction medium[a]	δ(^{195}Pt) (ppm)[b]	Assignment
H$_2$O/EtOH	−2723 (100%)	*cis*-[PtL$_2$] (**I**)
0.5–1 M HCl/EtOH	−2723 (12%)	**I**
	−2960 (74%)	*cis*-[Pt(LH)L]Cl (**II**)
	−3210 (14%)	*cis*-[Pt(LH)$_2$]Cl$_2$ (**III**)
1 M HCl/EtOH	−2723 (5%)	**I**
(+SnCl$_2$, Pt:Sn = 2.5)	−2960 (62%)	**II**
	−3000 (1%)	unknown
	−3210 (32%)	**III**
H$_2$O/EtOH	−2723 (96%)	**I**
(+25 mmol NaCl)	−3000 (4%)	unknown
(+25 mmol NaBr)	−2723 (92%)	**I**
	−3105 (8%)	unknown
(+25 mmol NaI)	−4771 (81%)	*cis*-[Pt(LH$_2$)$_2$]I$_2$ (**IV**)
	−3389 (19%)	*cis*-[Pt(LH)L]I (**V**)
[PtL$_2$] + conc. HCl	−3215 (>98%)	**III**
[PtL$_2$] + conc. HBr	−3630 (72%)	*cis*-[Pt(LH)$_2$]Br$_2$
	−3609 (28%)	*cis*-[Pt(LH)L]Br
[PtL$_2$] + conc. HI	−3389 (–)[c]	**V**
	−4771 (–)[c]	**IV**

[a] Prepared as described in 'Experimental'; addition of conc. acids directly into NMR tube, Pt complex concentration *c*. 100 mg/0.7 ml. [b] Shifts are estimated accurate to ±2 ppm and are quoted relative to external H$_2$PtCl$_6$ δ(^{195}Pt) = 0. Given in the parentheses are the relative intensities of ^{195}Pt resonances not corrected for T$_1$ effects. [c] Not determined.

An interesting aspect of these simple ML$_2$ complexes obtained from *N*,*N*-dialkyl-*N*′-benzoylthiourea and d^8 metal ions is that to the best of our knowledge, only the *cis* isomers have been isolated and well characterized [4–8], in keeping with our observations. Although it is reasonable to expect the *cis* configuration for square planar ML$_2$ complexes to be thermodynamically more stable in view of the relatively large *trans* influence of the polarizable sulfur donor atom, the corresponding *trans*-[PtL$_2$] complexes might be expected to be isolable (cf. *cis* and *trans* thiourea complexes in the Kurnakov test [16]). Furthermore the *cis*- and *trans*-[PtL$_2$X$_2$] complexes (where L = monodentate thiourea, X = Cl$^-$ and Br$^-$), have been reported and examined by ^{195}Pt NMR [17]. We thus attempted to prepare *trans*-[PtL$_2$] by examining the product distribution obtained by reaction

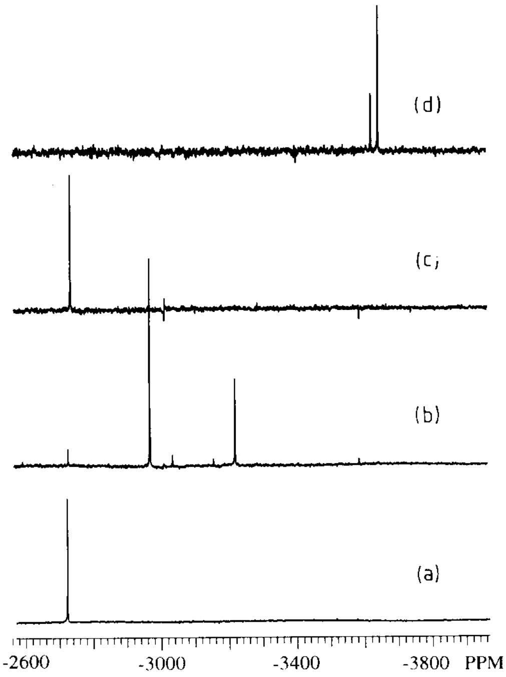


Fig. 1. ^{195}Pt NMR spectra at 30 °C: (a) pure *cis*-[PtL$_2$], (b) crude product prepared in 1 M HCl aqueous medium, (c) solution (b) with slight excess triethylamine, (d) solution (a) with conc. HBr added to NMR tube.

of PtX_4^{2-} ($X = Cl^-, Br^-, I^-$) with LH in neutral water/alcohol mixtures, expecting that the increasing *trans* effect in the order $I^- > Br^- > Cl^-$ might influence the distribution of species obtained (PtX_4^{2-} was prepared by equilibrating K_2PtCl_4 with a 25 fold molar excess of NaCl, NaBr and NaI). As is evident from Table 1, we find that in the presence of NaCl and NaBr, essentially only **I** is formed, while in the presence of NaI, the complex *cis*-$[Pt(LH)_2)]I_2$ is almost exclusively obtained (*Anal.* Found: C, 37.8; H, 4.2; N, 5.5. Calc. for $PtC_{32}H_{48}O_2N_4S_2I_2$: C, 37.19; H, 4.65; N, 5.42%). The ^{195}Pt spectrum of this complex shows a sharp single resonance at −4771 ppm in addition to a minor resonance at −3389 ppm assigned to *cis*-[Pt(LH)L]I, suggesting that in solution a degree of dissociation of the dication to yield the monocation *cis*-$[Pt(LH)L]^+$ occurs. The corresponding ^1H spectrum shows two N–H resonances at 10.08 and 10.24 ppm (81 and 19% relative intensity) corresponding to the *cis*-$[Pt(LH)_2]I_2$ and *cis*-[Pt(LH)L]I species, respectively. Addition of a slight excess of triethylamine to the NMR tube results in complete deprotonation of these complexes yielding ^{195}Pt and ^1H spectra consistent with only the **I** species in solution.

The protonation of **I** in chloroform solution may also be carried out by the addition of either some concentrated HCl, HBr or HI directly to a NMR tube. In the case of addition of HCl, a single ^{195}Pt resonance at −3215 ppm corresponding to *cis*-$[Pt(LH)_2]Cl_2$ results, while for HBr two resonances at −3609 and −3630 ppm (72 and 28% relative intensity) are obtained, which are assigned to *cis*-[Pt(LH)L]Br and *cis*-$[Pt(LH)_2]Br_2$, respectively. The latter assignments are supported by two N–H resonances at 10.72 and 10.48 ppm (73 and 27% intensity) in the corresponding ^1H spectrum of this solution. Addition of one drop of concentrated HI to a solution of **I** yields ^{195}Pt resonances at −3389 and −4771 ppm assigned to *cis*-[Pt(LH)L]I and *cis*-$[Pt(LH)_2L]I_2$, respectively. The species *cis*-[Pt(LH)L]I at $\delta(^{195}Pt) = -3389$ ppm may also be obtained by careful titration of a solution of authentic *cis*-$[Pt(LH)_2]I_2$ with triethylamine.

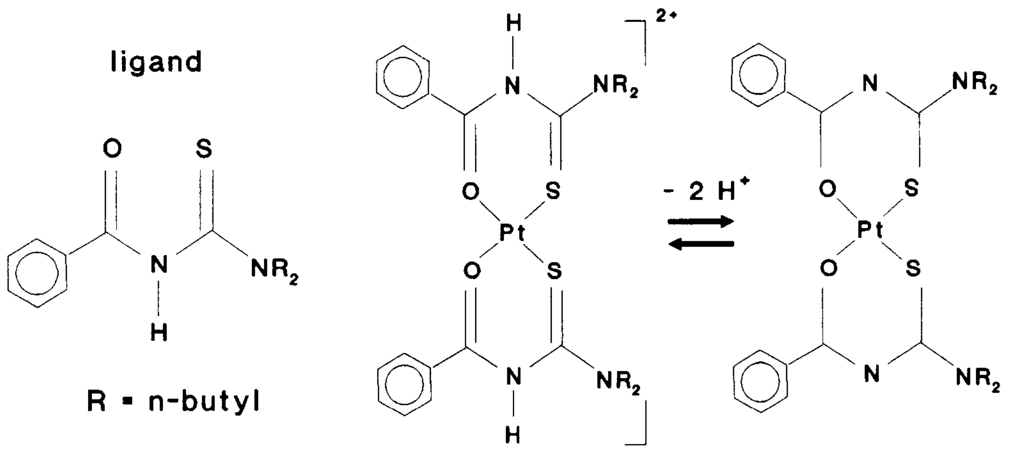
Additional support for the above assignments is obtained from the IR spectra of these complexes. In the case of *cis*-$[Pt(LH)_2]I_2$, the expected broad IR absorption assigned to the N–H amide stretching vibration at 3235 cm^{-1} is clearly visible in the solid state (Nujol mull) while no absorption is evident for **I** in the 3000–4000 cm^{-1} region. The sharp stretch at 1687 cm^{-1} assigned to the carbonyl stretch of the –CO–NH– moiety in the uncomplexed ligand, is present at 1695 cm^{-1} for *cis*-$[Pt(LH)_2]I_2$, while this vibrational band virtually disappears in the unprotonated **I** complex (weak shoulder at 1618 cm^{-1}). These observations are consistent with the expectation that the electron distribution in the six-membered chelate ring of *cis*-$[Pt(LH)_2]I_2$ resembles that of the uncomplexed ligand, while in the neutral **I** complex extensive electron delocalization may be postulated as illustrated in Scheme 2.

As is clear from Fig. 2 the ^{13}C shift values of thiocarbonyl and carbonyl carbon atoms support this view. Hence for the uncomplexed ligand the ^{13}C shifts of the thiocarbonyl and carbonyl atoms are 180.9 and 163.9 ppm, while in **I** these shieldings are nearly identical at 167.3 and 168.3 ppm, respectively. (The latter shieldings have been unambiguously assigned on the basis of ^{13}C enrichment techniques, as well as the observable $^2J(^{195}Pt–^{13}C) = 46$ Hz coupling to the thiocarbonyl carbon atom; we have published complete ^{13}C assignments for *cis*-$[ML_2]$ complexes (M = Pt(II) and Pd(II)) elsewhere [18].) Significantly, the corresponding ^{13}C shieldings for *cis*-$[Pt(LH)_2]I_2$, *cis*-$[Pt(LH)_2]Br_2$ and *cis*-$[Pt(LH)_2]Cl_2$ of the thiocarbonyl atoms are 175.2, 176.3, 177.2 ppm, while the carbonyl atoms resonate at 162.0, 162.8 and 162.9 ppm, respectively. These shifts indicate a close similarity of the local electronic distribution at these carbon atoms, between the uncomplexed ligand and the protonated *cis*-$[Pt(LH)_2]^{2+}$ cation in chloroform-d solution.

^{195}Pt chemical shifts

Inspection of the ^{195}Pt chemical shifts obtained for the protonated complexes *cis*-[Pt(LH)L]X and *cis*-$[Pt(LH)_2]X_2$ in chloroform-d solution, shows the shifts to depend significantly on the identity of the anion X. Thus the ^{195}Pt resonance moves upfield relative to the shift of the **I** species by 237, 886 and 666 ppm for the *cis*-[Pt(LH)L]X complexes, and by 487, 907 and 2048 ppm for the *cis*-$[Pt(LH)_2]X_2$ complexes in the order $Cl^- < Br^- < I^-$, respectively. Although it is well known that the ^{195}Pt chemical shift range is extremely large (> 12000 ppm) and that these shifts are highly sensitive to *inter alia* the nature of the donor atoms within the coordination sphere of the Pt atom, the temperature, solvent effects, as well as the oxidation state of the Pt [19, 20], the substantial effect of the apparently uncoordinated anion on the ^{195}Pt shift of the *cis*-$[Pt(LH)L]^+$ and *cis*-$[Pt(LH)_2]^{2+}$ cations deserves comment.

While the stepwise protonation of the neutral complex **I** evidently results in substantial upfield shifts, the influence of the halide anion on these shifts is unexpectedly large. When coordinated to the platinum atom, the 'heavy atom' effect, which is particularly evident for the halide ligands, has been explained in terms of a relativistic contribution to the resultant shielding of the metal nucleus [20]. In the present case, the large effect of the uncoordinated halide ions on the chemical shift of the ^{195}Pt resonance is unprecedented, and can only be understood in terms of struc-



Scheme 2.

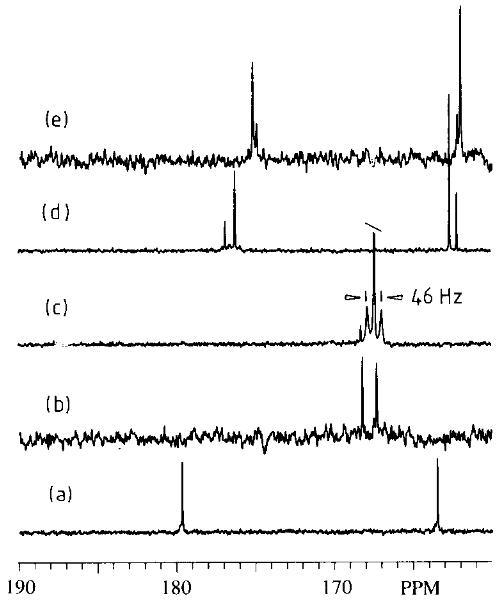


Fig. 2. Lowfield section of ^{13}C spectra of: (a) ligand, (b) *cis*-$[PtL_2]$, (c) 50% ^{13}C enriched (thiocarbonyl atom) *cis*-$[PtL_2]$ showing ^{2}J (^{195}Pt–^{13}C) = 46 Hz, (d) *cis*-$[PtL_2]$ plus 1 drop HBr, (e) authentic *cis*-$[Pt(LH)_2]I_2$ and *cis*-$[Pt(LH)L]I$.

tured, tight ion-pair formation between the halide ion and the mono- or di-protonated complex cation. It is not unreasonable to imagine that the halide ions occupy positions orthogonal to the square plane of the $[Pt(LH)L]^+$ and $[Pt(LH)_2]^{2+}$ cations. Although it is likely that primarily electrostatic forces are involved in the formation of such an ion pair, a degree of covalent interaction is likely to be present, analogous to that recently described for the $Tl_2Pt(CN)_4$ complex. In the $Tl_2Pt(CN)_4$ complex the net covalent contribution to the Tl–Pt bonding has been estimated to be about 15% of the total stabilization energy [21].

Given the current theoretical understanding of the diamagnetic and paramagnetic contributions to the shielding of the ^{195}Pt nucleus in terms of the Ramsey formulation [19, 20], the significant effect of the anion on the ^{195}Pt chemical shifts of *cis*-$[Pt(LH)_2]X_2$ may at least qualitatively be understood to result from a non-negligible covalent interaction between the *cis*-$[Pt(LH)_2]^{2+}$ cation and the anions Cl^-, Br^- and I^-. It is usually observed for halides coordinated to platinum, that the average excitation energy (ΔE) reflecting the energy difference between the HOMO and the LUMO of the Pt complex decreases in the order $I > Br > Cl$ [20]. Since the paramagnetic contribution to the ^{195}Pt shielding is inversely proportional to ΔE, the relative magnitude of this contribution should be largest for the Cl^- ion and smallest for the I^- ion, in qualitative agreement with the shielding trends observed in this work. In the absence of a more detailed theoretical study, however, further comments in this regard must remain speculative.

Molecular structure of cis-[PtL₂]

The molecular structure of the complex **I** is given in Fig. 3, the fractional atomic coordinates in

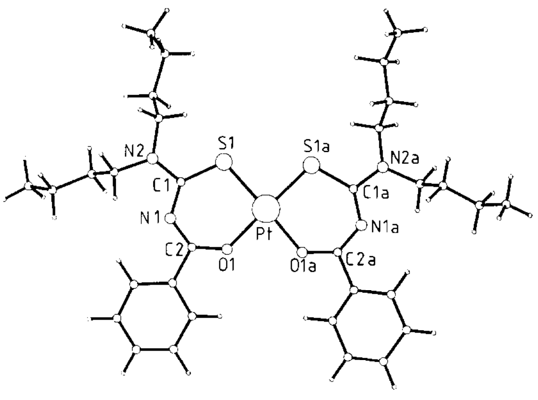


Fig. 3. The molecular structure of *cis*-$[PtL_2]$.

TABLE 2. (a) Fractional atomic coordinates for non-hydrogen atoms ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$)

	x/a	*y/b*	*z/c*	U_{eq}
Pt	2262(1)	10455(1)	2526(1)	57(1)
Sl	4292(1)	9452(1)	2926(1)	75(1)
Cl	5020(6)	10269(5)	3577(4)	63(2)
N1	4688(5)	11455(4)	3677(3)	63(2)
C2	3616(5)	12205(5)	3372(3)	58(2)
O1	2601(4)	11984(4)	2984(3)	85(2)
C3	3567(6)	13492(5)	3513(3)	62(2)
C4	2413(7)	14323(6)	3317(5)	86(3)
C5	2418(11)	15561(7)	3400(6)	116(4)
C6	3541(10)	15971(7)	3681(6)	104(4)
C7	4625(10)	15171(8)	3904(7)	117(4)
C8	4696(7)	13940(7)	3811(5)	93(3)
N2	6106(5)	9686(5)	4064(3)	75(2)
C9	6852(7)	10311(7)	4617(4)	85(3)
C10	7902(7)	11058(8)	4152(5)	87(3)
C11	8596(10)	11721(10)	4762(6)	116(4)
C12	9796(14)	12301(16)	4315(8)	177(8)
C13	6607(7)	8324(7)	4092(5)	92(3)
C14	7644(9)	8177(9)	3440(6)	105(4)
C15	8036(13)	6760(10)	3360(9)	145(6)
C16	8446(15)	5907(12)	4026(9)	171(7)
S1a	1811(2)	8826(1)	1969(1)	77(6)
C1a	293(5)	9246(5)	1416(3)	55(2)
N1a	−669(4)	10165(4)	1480(3)	50(1)
C2a	−566(5)	11116(4)	1841(3)	51(1)
O1a	435(4)	11431(4)	2202(3)	79(2)
C3a	−1783(5)	12028(5)	1798(3)	51(2)
C4a	−1701(6)	13181(5)	1973(4)	67(2)
C5a	−2861(7)	14051(6)	1944(5)	81(3)
C6a	−4055(7)	13758(7)	1746(5)	85(3)
C7a	−4174(6)	12566(7)	1560(4)	83(3)
C8a	−3033(5)	11719(6)	1592(4)	68(2)
N2a	10(4)	8525(4)	865(3)	64(2)
C9a	−1283(5)	8755(5)	391(3)	61(2)
C10a	−2420(6)	8115(6)	858(4)	68(2)
C11a	−3707(7)	8465(8)	368(5)	93(3)
C12a	−4884(12)	7729(11)	752(7)	153(3)
C13a	1027(6)	7580(6)	587(4)	81(3)
C14a	894(8)	6286(6)	1010(6)	93(3)
C15a	2001(11)	5414(9)	660(7)	128(4)
C16a	1905(15)	4171(13)	878(10)	183(8)

(b) Fractional atomic coordinates for hydrogen atoms ($\times 10^3$)

	x/a	*y/b*	*z/c*
H4	1576(7)	14033(6)	3115(5)
H5	1585(11)	16157(7)	3251(6)
H6	3546(10)	16870(7)	3718(6)
H7	5424(10)	15467(8)	4150(7)
H8	5552(7)	13373(7)	3956(5)
H91	6196(7)	10888(7)	4867(4)
H92	7308(7)	9659(7)	5089(4)
H101	8589(7)	10484(8)	3922(5)
H102	7463(7)	11697(8)	3666(5)
H111	8915(10)	11101(10)	5292(6)
H112	7945(10)	12391(10)	4921(6)
H121	10209(14)	12855(16)	4647(8)
H122	9478(14)	12798(16)	3741(8)
H123	10483(14)	11601(16)	4239(8)
H131	5826(7)	7871(7)	3984(5)
H132	7007(7)	7950(7)	4673(5)
H141	7289(9)	8664(9)	2870(6)
H142	8475(9)	8522(9)	3600(6)
H151	8773(13)	6767(10)	2932(9)
H152	7217(13)	6478(10)	3127(9)
H161	8411(15)	5090(12)	3844(9)
H162	7844(15)	5943(12)	4526(9)
H163	9393(15)	5987(12)	4195(9)
H4a	−805(6)	13419(5)	2124(4)
H5a	−2776(7)	14894(6)	2075(5)
H6a	−4872(7)	14376(7)	1729(5)
H7a	−5073(6)	12337(7)	1405(4)
H8a	−3115(5)	10873(6)	1466(4)
H9a1	−1558(5)	9678(5)	263(3)
H9a2	−1145(5)	8455(5)	−159(3)
H10a	−2529(6)	8364(6)	1427(4)
H10b	−2190(6)	7187(6)	947(4)
H11a	−3980(7)	9376(8)	342(5)
H11b	−3553(7)	8315(8)	−226(5)
H12a	−5605(12)	8009(11)	299(7)
H12b	−5246(12)	7864(11)	1316(7)
H12c	−4584(12)	6820(11)	792(7)
H13a	1949(6)	7781(6)	718(4)
H13b	916(6)	7651(6)	−46(4)
H14a	1019(8)	6190(6)	1644(6)
H14b	−20(8)	6062(6)	883(6)
H15a	2894(11)	5570(9)	876(7)
H15b	1964(11)	5654(9)	20(7)
H16a	2807(15)	3820(13)	706(10)
H16b	1179(15)	3833(13)	589(10)
H16c	1820(15)	3927(13)	1514(10)

TABLE 3. Some important bond lengths (Å) for **I**

Pt–S(1)	2.230(2)	N(1a)–C(1a)	1.336(7)
Pt–S(1a)	2.233(2)	N(1)–C(2)	1.309(7)
Pt–O(1)	2.017(5)	N(1a)–C(2a)	1.301(7)
Pt–O(1a)	2.026(4)	O(1)–C(2)	1.256(7)
S(1)–C(1)	1.708(7)	O(1a)–C(2a)	1.266(7)
S(1a)–C(1a)	1.726(5)	N(2)–C(1)	1.358(7)
N(1)–C(1)	1.349(7)	N(2a)–C(1a)	1.342(8)

Table 2, while the most important bond lengths are given in Table 3.

The overall structure of **I** is remarkably similar to that of bis(*N*,*N*-diethyl-N′-benzoylthioureato)palladium(II) [6]. By comparison with the structure of the uncomplexed ligand [22], the average C=S and C=O bond lengths in the complex are significantly longer (1.717 and 1.261 Å) than those in the ligand (1.672 and 1.207 Å). Furthermore the corresponding two contiguous C–N bond lengths (N(1)–C(1), N(1)–C(2), N(1a)–C(1a) and N(1a)–C(2a)) of the chelate ring are on average shorter in complex **I** at 1.343 and 1.305 Å, as compared to the ligand with 1.408 and 1.391 Å. Clearly the bond orders of the thiocarbonyl and carbonyl bonds decrease upon complexation, which together with the slight increase in the two average C–N bond lengths, confirms extensive electron delocalization within the chelate ring of complex **I**, supported by the IR and ^{13}C NMR data above. It is noteworthy that in the case of the bis(*N*,*N*-diethyl-*N*′-benzoylthioureato)-palladium(II) complex, the two Pd–S as well as the two Pd–O bond lengths differ significantly [6]. In the case of **I** a similar difference in comparable bond lengths is evident although less pronounced, since the two Pt–S bond lengths hardly differ from one another (Table 3). Furthermore there are small differences in related C–S and C–O bond lengths. All other bond lengths fall within the expected range, with the possible exception of the C(1)–N(2) and C(1a)–N(2a) bonds, which are somewhat longer in complex **I** (1.358 and 1.342 Å) compared to the ligand (1.323 Å) [22]. This is indicative of slightly less double bond character in this bond once the ligand is coordinated to Pt; nevertheless as is obvious from the non-equivalence of the ^{1}H resonances of the butyl fragments of **I** at 25 °C in chloroform-d solution (see 'Experimental'), a degree of double bond character of these C–N linkages persists in the complex.

From a packing diagram of **I** it is evident that there are no significant intermolecular contacts between the discrete molecules of **I** in the crystal.

Conclusions

Our studies have shown that *N*,*N*-dialkyl-*N*′-benzoylthiourea preferentially forms neutral *cis*-$[PtL_2]$ type complexes, although these are readily protonated to yield the complex cations *cis*-$[Pt(LH)L]^+$ and *cis*-$[Pt(LH)_2]^{2+}$. It appears that the halide anions play a role in stabilizing these cations by tight ion-pair formation in solvents such as chloroform as is evident from the large effect the anion has on the ^{195}Pt shifts of the species in solution. In contrast to $PtCl_4^{2-}$ and $PtBr_4^{2-}$, the PtI_4^{2-} complex reacts with LH to give predominantly the protonated *cis*-$[Pt(LH)_2]I_2$ complex. Numerous attempts to find evidence of corresponding *trans* complexes proved fruitless. The normal phase chromatographic separation of platinum complexes with these ligands can best be understood in terms of the ready protonation of **I**, which are more strongly retained on silica gel phases.

Acknowledgements

We are grateful to the University of Cape Town and the FRD for financial assistance, and to Johnson Matthey for the loan of platinum salts.

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