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New chemistry with old ligands: *N*-alkyl- and *N*,*N*-dialkyl-*N*′-acyl(aroyl)thioureas in co-ordination, analytical and process chemistry of the platinum group metals

Klaus R. Koch *

Department of Chemistry, University of Stellenbosch, P.B. X1, Matieland,
Stellenbosch 7602, South Africa

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Contents

Abstract

Recent developments in the fundamental co-ordination chemistry of *N*-alkyl-*N*′- (**H_2L**) and *N*,*N*-alkyl-*N*′-acyl(aroyl)thioureas (**HL**) of Pt(II), Pd(II) and Rh(III) are reviewed. These studies show that the mode of co-ordination of **H_2L** differs markedly from that of **HL**, the former ligand generally co-ordinating through the sulphur donor atom to Pt(II) and Pd(II), mimicking the co-ordination of simple thioureas, while **HL** tends to co-ordinate in a *cis* bidentate *S*,*O* manner to d^8 metal ions, with loss of a proton. A series of new, relatively

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* Tel.: + 27-21-808-3020; fax: + 27-21-808-3849.
E-mail address: krk@maties.sun.ac.za (K.R. Koch).

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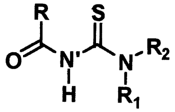
hydrophilic *N*-alkyl-*N'*- and *N*,*N*-alkyl-*N'*-acylthioureas have been prepared, and their co-ordination chemistry investigated. The new ligand, *N*-propyl-*N'*-butanoylthiourea (**H_2L^8**) shows an unprecedented *N'*,*S* mode of co-ordination of Pt(II) to yield *trans*-[Pt(HL^8-*N*,*S*)$_2$]. Moreover, the favourable physiochemical properties of Pt(II), Pd(II) and Rh(III) complexes makes these ligands useful for the reversed-phase HPLC determination of traces of these metal ions in real effluent streams, following complex formation in a homogeneous acetonitrile–hydrochloric acid phase and subsequent salt-induced phase separation. Complexes prepared in situ of Pt(II), Pd(II) and Rh(III) with *N*,*N*-di(2-hydroxylethyl)-*N'*-benzoylthiourea can quantitatively be pre-concentrated onto thin film C_{18}-modified glass-fibre disks, followed by quantification using laser ablation inductively coupled mass spectroscopy at trace levels. Preliminary results show this method to be applicable to untreated PGM refinery process effluents. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: *N*-alkyl-*N'*-acyl(aroyl)thiourea; *N*,*N*-alkyl-*N'*-acyl(aroyl)thiourea; Pt(II); Pd(II); Rh(III) complexes; RP-HPLC determination; Thin film pre-concentration; LA-ICP mass spectroscopy

1. Introduction

South Africa is the world's leading source of platinum, contributing more than three quarters of the world's annual supply, in addition to producing a large proportion of the associated platinum group metals (PGMs) Pd, Rh, Ru, Ir and Os [1]. Given the complex and diverse chemistry of these noble metals, the process of extraction, concentration, separation and ultimately refining to 99.99% pure metals, is a wonderful example of inorganic chemistry on a large scale. Despite the development of highly efficient processes for the separation and refinement of these metals [2], there is a trend to develop newer, more cost-effective methods of separation and refinement. Moreover, increased environmental awareness and stricter legislation for the control of industrial effluents present some interesting and challenging opportunities to the co-ordination chemist, concerned with the chemistry of the PGMs.

In this context, we have become interested in a class of deceptively simple ligands based on the *N*,*N*-alkyl-*N'*-acyl(aroyl)thiourea motif below. These ligands show a pronounced affinity for co-ordination to the PGMs, this tendency becoming more selective over other transition metal ions with increasing acid (particularly hydrochloric acid) concentration.[1]



R = aryl or alkyl
R_1 R_2 = alkyl; *N,N*-dialkyl-*N'*-(aroyl)acylthiourea **HL**
R_1 = alkyl, R_2 = H; *N*-alkyl-*N'*-(aroyl)acyl-thiourea **H_2L**

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[1] In the limited space available, a comprehensive review of the co-ordination chemistry of these ligands will not be attempted. However, aspects of the co-ordination chemistry of these ligands with Pt(II), Pd(II) and Rh(III), including practical applications, will be discussed.

Remarkably, the first example ($CH_3C(O)NHC(S)NH_2$) of this class of molecules reported by Neucki [3] has been known for more than a century; it was also reported what is likely to be the first platinum complex derived from this ligand, with a stoichiometry $CS(C_2H_3O)H_3N_2{\cdot}2HCl{\cdot}PtCl_4$. Since these ligands can be considered to be either acyl or aroyl substituted thioureas, their co-ordination chemistry might be expected to resemble (the long known) platinum complexes with simple unsubstituted thioureas, first reported by Kurnakow [4] in 1898.

As will become evident form the work described here, any resemblance of the co-ordination chemistry of *N*-alkyl-*N*′-acyl(aroyl)thiourea (**H_2L**) and in particular of *N*,*N*-alkyl-*N*′-acyl(aroyl)thioureas (**HL**) to that of simple, unsubstituted thioureas ($(NH_2)_2CS$) is limited. The co-ordination chemistry of the ligands **H_2L** and **HL** is much more varied than that of simple thioureas. Moreover, the physiochemical properties of their metal complexes are more favourable, resulting in a number of interesting potential technical and analytical applications. The co-ordination chemistry and potential applications of such ligands have only been explored to some extent in the last three decades, pioneered by the work of Hoyer and Beyer. These authors first reviewed the co-ordination chemistry of *N*′-acylthioureas, particularity their co-ordination with some first and second row transition metal ions such as Ni(II), C(II/I), Co(III), Zn(II), Pd(II), Ag(I), Cd(II), as well as Pb(II) and Hg(II) [5].

Of possible technical interest is the potential application of *N*-alkyl-*N*′-acyl(aroyl)thioureas for the liquid–liquid extraction and separation of several ‘soft’ transition metal ions, notably Cu(II), Hg(II) as well as Au(III) and Pd(II) [6]. Studies of *N*,*N*-dialkyl-*N*′-benzoylthioureas for the liquid–liquid extraction of the platinum group metals from hydrochloric acid solutions [7–10], further exemplify the potential utility of this class of ligands. The determination of traces of the PGMs by means of high-performance thin layer chromatography (HPTLC) after complexation with suitably modified fluorescent *N*-aroylthioureas is also of interest [11–14]. Recently an elegant application of the use of *N*,*N*-diethyl-*N*′-benzoylthiourea for the selective on-line pre-concentration and highly selective trace determination of Pd(II) (in up to 6.5% (v/v) nitric acid) by means of graphite furnace atomic absorption spectrometry has been published [15].

The above work, by no means comprehensive overview of potential applications of *N*,*N*-alkyl-*N*′-acyl(aroyl)thioureas, stimulated our interest in the fundamental co-ordination chemistry of this class of ligands with particular reference to possible technical applications to the chemistry of the PGMs in South Africa. A survey of the literature yielded relatively little detailed structural and solution co-ordination chemistry of particularly Pt(II/IV), Rh(III) and Pd(II), with this class of ligands.

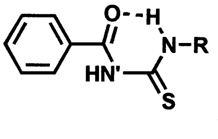
2. Ligand synthesis, structure and properties

Amongst the attractive features of these ligands is their facile synthesis from readily available and inexpensive starting materials [16,19], giving in the case of the

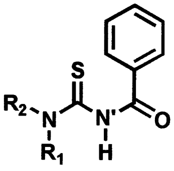
N′-benzoylthiourea derivatives, usually high yields of pure product in a two-step, 'one-pot' synthesis. In general, ligands of type **HL**, derived from benzoyl chloride are stable, relatively hydrophobic substances, with one dissociable proton on the weakly acidic amido –C(O)NHC(S)– moiety. For a series of hydrophilic *N*,*N*-dialkyl-*N*′-aroylthioureas, the acid dissociation constants, $pK_{a(NH)}$ have been found to range from 7.5 to 10.9 in water–dioxane mixtures [17]. No similar information is available for the corresponding ligands with two dissociable protons (**H₂L**), although as will be seen below, there exists at least one example in which the doubly de-protonated anion of *N*-phenyl-*N*′-benzoylthiourea is co-ordinated to two Rh(I) centres (see Fig. 2(c)). On the other hand, the mono- and di-protonation constants of *N*′-benzoylthioureas have also been estimated spectrophotometrically in aqueous sulphuric acid, with the observation that the sulphur atom is protonated first ($pK_{B1} = -4.55 \pm 0.02$) in 35–65% sulphuric acid, followed by a second protonation of the amidic moiety ($pK_{B2} = -4.68 \pm 0.06$) in 65–95% sulphuric acid [18].

With the exception of *N*,*N*-dialkyl substituted *N*′-ethoxycarbonylthioureas [20] as intermediates to the preparation of *N*,*N*-disubstituted-thioureas, and a study of some alkyl-alkanedioylbis(thioureas) [21], almost all previously reported ligands of this type were derived from *aromatic* acid chlorides, benzoyl chloride being the most widely used starting material. In this context we have re-examined the Douglass and Dains synthetic procedure [16], and found a means to synthesise, from certain *aliphatic* acid chlorides, a variety of new hydrophilic *N*,*N*-dialkyl-*N*′-acylthioureas in good yield [19].

The structure of the **HL** and **H₂L** ligands, as determined by X-ray diffraction, generally shows a significant influence of intramolecular hydrogen bonding, which results in substantial differences between the preferred conformation (and consequently co-ordination chemistry, vide infra) of the *N*,*N*-dialkyl-substituted molecules **HL**, compared to the *N*-alkyl-substituted analogue, **H₂L**. For **H₂L**, we [22] and Dago et al. [23] have found that an intramolecular hydrogen-bond between the thiourea –C(S)NHR moiety and the oxygen atom of the amidic group 'locks' the –C(O)NHC(S)NHR unit into a planar six-membered ring structure. In contrast, the corresponding *N*,*N*-dialkyl substituted **HL** ligand assumes a twisted conformation in the solid state, with the sulphur and oxygen atoms pointing approximately in opposite directions [22,24], as shown schematically below:



H₂L



HL

Another significant feature characteristic of these ligands is evident from the crystal structures of these ligands: the amidic (O)C–N′H and thioamide N′H–C(S) and (S)C–N(R/H) bonds are both shorter that a C–N single bond at 1.472(5) Å.

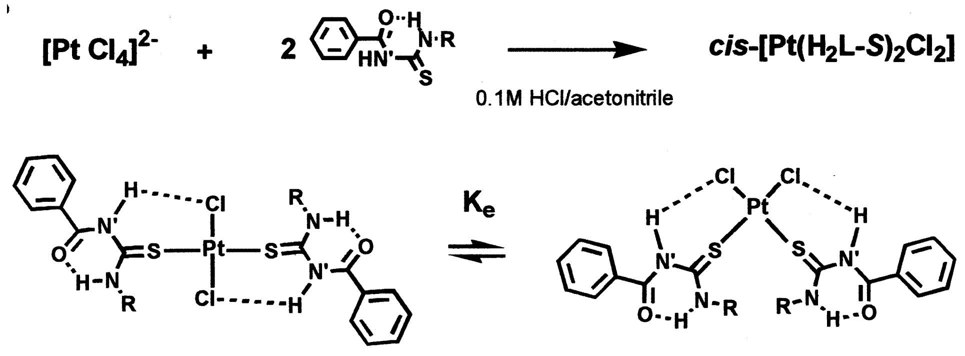
Moreover there is a definite trend in these average bond C–N distances [25], the lengths increasing in the order (S)C–N(R/H), 1.327(± 0.006) < (O)C–N′H, 1.374(± 0.011) < N′H–C(S), 1.409(± 0.016) Å. The partial double bond character of the (S)C–N(R/H) bond is reflected by the restricted rotation around this bond in solution on the NMR time scale, since separate ^{1}H and ^{13}C resonances are observed for the two methylene groups of the (S)CN(CH_2)$_2$– moiety in the ^{1}H- and ^{13}C-NMR spectra in $CHCl_3$-*d* at room temperature. This restricted rotation has the interesting consequence that for unsymmetrically *N*,*N*-dialkyl substituted **HL** molecules, *E*/*Z* configurational isomerism is observed in solution, something which is carried through into the complexes of these ligands [22]. In the case of $\mathbf{H_2L}$ ligands in solution this phenomenon is not observed, presumably as a result of the intramolecular H-bond 'locking' the $\mathbf{H_2L}$ molecules into a planar six-member ring structure. Nevertheless, the comparable bond lengths observed for the $\mathbf{H_2L}$ molecules are virtually indistinguishable from those of **HL** ligands.

In order to explore the fundamental nature of these ligands, we have recently carried out ab initio DFT [26] calculations of *N*-methyl-*N*′-benzoylthiourea to gain insight into the electron occupation of the frontier orbitals in these molecules. These calculations also show that the HOMO orbital is predominantly located on the sulphur atom, having essentially non-bonding σ-donor character. The LUMO orbitals are essentially of a π-acceptor anti-bonding nature, and are delocalised over the amidic and benzoyl moieties of the molecule. Table 1 shows the results of our model calculations, the good agreement between calculated and observed bond lengths and angles lending confidence to these DFT calculations.

Table 1
Calculated bond lengths (Å) and angles (°) for *N*-methyl-*N*′-benzoylthiourea using DFT methodology (B3LYP using the GAUSSIAN94 program) with varying basis sets (6-31G(d) and 3-21G), as compared with experimental data for related molecules

	Calc. (6-31G(d))	Calc. (3-21G)	X-ray $\mathbf{H_2L}$[a]	X-ray $\mathbf{H_2L}$[b]
Length (Å)				
C=O	1.233	1.255	1.226	1.226
(O)C–N	1.381	1.381	1.368	1.383
N–C(S)	1.407	1.411	1.386	1.393
C=S	1.678	1.731	1.676	1.678
(S)C–N(R)	1.336	1.334	1.317	1.332
Angle (°)				
O=C–N	122.5	122.1	–	122.2
(O)C–N–C(S)	128.9	127.6	–	127.9
N–C=S	118.3	116.7	–	118.5
N–C(S)–N	115.7	115.7	–	117.4

[a] *N*-propyl-*N*′-benzoylthiourea (Ref. [23]).
[b] *N*-(*n*-butyl)-*N*′-benzoylthiourea (Ref. [22]).



Scheme 1.

3. *N*,*N*-dialkyl- and *N*-alkyl-*N*′-acyl(aroyl)thiourea co-ordination chemistry

3.1. *N-alkyl-N′-aroylthioureas and N,N-dialkyl-N′-aroylthioureas*

The co-ordination of *N*,*N*-dialkyl-*N*′-benzoylthioureas (**HL**) to a number of first- and second-row transition metals has been reviewed by Beyer and co-workers [5,6]. These and other authors have also published several crystal structures of complexes of *cis*-[M(L-*S*,*O*)$_2$] for M = Pd(II) [27], Cu(II) [28] Ni(II) [5,29], as well as *fac*-[M(L-*S*,*O*)$_3$] complexes, for M = Rh(III) [30], Ru(III) [31] and Co(III) [32], to mention but some examples. From this literature it is clear that the predominant mode of co-ordination of **HL** ligands is the formation of bidentate chelates (usually with loss of a proton) of type *cis*-[M(L-*S*,*O*)$_2$] particularly with d^8 metal ions. The complete absence of any published studies concerning the co-ordination chemistry of the corresponding *N*-alkyl-*N*′-benzolythioureas (**H$_2$L**) is surprising, but might be explained by an assumption that the chemistry of **H$_2$L** closely resembles that of **HL** ligands.

Recent work in our laboratory has shown, however, that the mode of co-ordination of **HL** and **H$_2$L** is deceptively simple, and differs significantly for these ligands in some important aspects. For **H$_2$L**, the mode of co-ordination to Pt(II) and Pd(II) at least, is dominated by the intramolecular hydrogen bond between the thiourea –C(S)NHR moiety and the oxygen atom of the amidic moiety as shown in Scheme 1 below.

This intramolecular hydrogen bond results in the co-ordination chemistry of **H$_2$L** to resemble that of simple thioureas, which generally co-ordinate through the S donor atom to the metal ions in mono-dentate fashion [33]. Thus *N*-propyl-*N*′-benzoylthiourea readily forms *cis*/*trans*-[M(H$_2$L-*S*)$_2$X$_2$] complexes with M = Pt(II) and Pd(II), but forms no complex with Ni(II) under similar conditions. The *cis*-[Pt(H$_2$L-*S*)$_2$Cl$_2$] complex has been characterised by X-ray diffraction [34]. Moreover, in the preparation of Pt(II) complexes with **H$_2$L**, *only* the *cis*-[Pt(H$_2$L-*S*)$_2$Cl$_2$] complexes are initially obtained, while mixtures of *cis*- and *trans*-[Pt(H$_2$L-*S*)$_2$X$_2$] are formed when X = Br$^-$ and I$^-$ [35]. In contrast, for Pd(II) only mixtures of *cis*- and *trans*-[Pd(H_2L-*S*)$_2$$X_2$] with X = Cl^- and Br^- could be prepared, the *trans* isomers predominating in all attempted preparations [35].

We find that the *cis*-[Pt(H_2L-*S*)$_2$$Cl_2$] complex, however, readily undergoes spontaneous *cis*/*trans* isomerisation on dissolution in a variety of organic solvents. This isomerism can conveniently be monitored by means of ^{1}H-NMR spectroscopy, the rate of which falls fortuitously within the NMR time scale. In general, the rate of isomerisation follows a second-order rate law, being a function of the square of the initial concentration of the *cis*-[Pt(H_2L-*S*)$_2$$Cl_2$] complex, suggesting an auto-catalytic isomerisation process. Moreover, the equilibrium distribution of isomers at 25°C has been found to depend directly on the dipole moment of the solvent ($K_e = [trans]/[cis]$, and ranges from 0.16 in nitromethane-d_3 to 0.88 in benzene-d_6) [35]. Low-polarity solvents such as benzene favour the formation of the less polar *trans* complex, so that the spontaneous isomerism of our *cis*-[Pt(H_2L-*S*)$_2$$Cl_2$] complexes resembles the seminal, early work on the isomerisation of *cis*/*trans*-[Pt(PR_3)$_2$$Cl_2$] and *cis*/*trans*-[Pt($AsR_3$)$_2$$Cl_2$] complexes by Chatt and Wilkinson [36].

As mentioned above, the **HL** ligands overwhelmingly, but not exclusively, tend to form *cis*-[M(L-*S*,*O*)$_2$]-type complexes for Ni(II) [27], Pd(II) [28] and Pt(II) [37] and [M(L-*S*,*O*)$_3$] complexes for Rh(III) [30], Ru(III) [31] and Co(III) [32]. On the other hand, *N*,*N*-di(*n*-butyl)-*N*′-naphthoylthiourea (**HL^1**) reacts with $PtCl_4^{2-}$ to yield a mixture of *cis*- and *trans*-[Pt(L^1-*S*,*O*)$_2$] complexes, the latter being the *only* authenticated example of a *trans* complex as characterised by X-ray diffraction [38]. In this reaction the major component, *cis*-[Pt(L^1-*S*,*O*)$_2$], can readily be distinguished from the *trans*-[Pt(L^1-*S*,*O*)$_2$] isomer, by means of their respective ^{195}Pt-NMR chemical shifts[2] at −2708 and −3038 ppm in $CHCl_3$-*d* solution. The absence of any other example of a *trans*-[M(L-*S*,*O*)$_2$] complex derived from related ligands is striking, despite numerous attempts to prepare *trans* complexes. Recent work in our laboratory, however, shows that with *N*,*N*-di(*n*-butyl)-*N*′-(3,4,5-trimethoxy)-benzoylthiourea (**HL^2**) as well as *N*-morpholino-*N*′-(3,4,5-trimethoxy)-benzoylthiourea (**HL^3**), a mixture of *cis*- and *trans*-[Pt(L-*S*,*O*)$_2$] complexes is obtained, the *cis* isomer generally predominating [39]. Our assignments are based on ^{195}Pt- and ^{13}C-NMR spectroscopy, which must nevertheless await verification by X-ray diffraction studies, if these isomers can be separated by fractional crystallisation or chromatographic means. This observation does imply however that the *trans* Pt(II) complexes can only be isolated for bulky, electron-rich *N*′-aroylthiourea ligands, possibly because *electron releasing aroyl* groups enhance the relative ‘softness’ of the amidic oxygen donor atom, thus stabilizing a *trans* complex, although this is speculative at present.

For unsymmetrically *N*,*N*-dialkyl substituted **HL** ligands, the partial double bond character of the (S)C–NRR′ moiety in the **HL** is expected to result in configurational *E*/*Z* isomerism in the resultant metal complexes. This is indeed confirmed for *cis* Pt(II) complexes derived from *N*-methyl-*N*-(*n*-butyl)-*N*′-benzoylthiourea (**HL^4**), for which a mixture of *cis*-[Pt(*E*,*E*-L^4-*S*,*O*)$_2$], *cis*-[Pt(*E*,*Z*-L^4-*S*,*O*)$_2$] and *cis*-[Pt(*Z*,*Z*-L^4-*S*,*O*)$_2$] complexes is clearly evident from the ^{195}Pt-NMR spectrum which shows *three* signals (at −2722, −2719 and −2718 ppm, respec-

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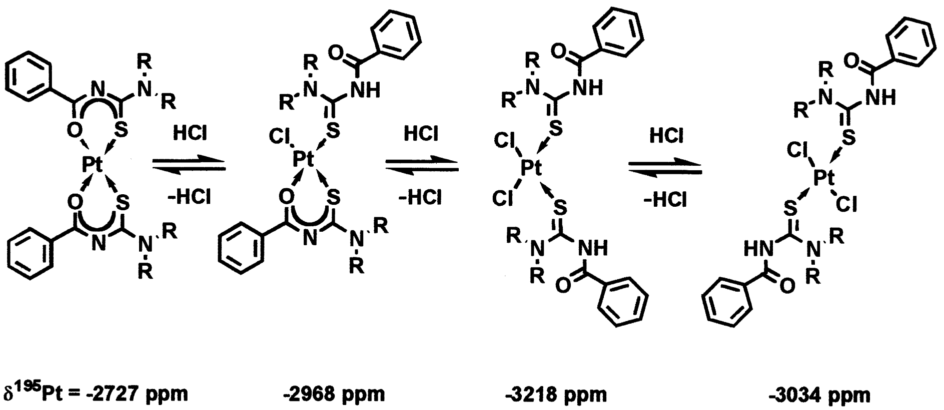
[2] Shifts at 30°C in $CHCl_3$-*d* solution relative to external H_2PtCl_6 in 1 M HCl at $\delta(^{195}Pt) = 0$ ppm.



Scheme 2.

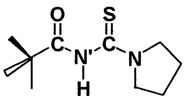
tively) in $CHCl_3$-*d*. The chemical shifts of these species have been assigned on the basis of semi-quantitative ^{13}C-NMR spectroscopy and the presence of an interesting $^4J(^{195}Pt-^{13}C)$ coupling in these complexes [22].

In summary, the deceptively simple co-ordination chemistry of HL toward Pt(II) is shown in Fig. 1.

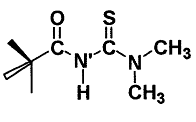
Despite the overwhelming tendency of **HL** ligands to form stable *cis*-[Pt(L-*S*,*O*)$_2$] chelates with d^8 metal ions, we have shown that under relatively acidic conditions in the presence of co-ordinating Cl^-, Br^- and I^- anions, the *cis*-[Pt(L-*S*,*O*)$_2$] complexes can become protonated to yield a variety of complex species in solution, including the *cis*-[Pt(L-*S*,*O*)(HL-*S*)Cl] complex, in which one ligand is bound to Pt through the S atom only, the amidic oxygen donor being pendant in solution as shown in Scheme 2 below. These complex species, as well as all the corresponding mixed halide (Cl^-/Br^-) complexes, have been identified from their ^{195}Pt-NMR signals under suitable conditions in solution [40]. Protonation of the *cis*-[Pt(L-*S*,*O*)$_2$] chelates in the presence of a co-ordinating anion can be exploited to prepare new complexes such as *trans*-[Pt(HL-*S*)$_2$I$_2$] which are readily obtained as exclusive product on treatment of pure *cis*-[Pt(L-*S*,*O*)$_2$] with HI in acetone solution [41]. The crystal structure of *trans*-[Pt(HL-*S*)$_2$I$_2$] also shows a example of the potentially bidentate ligand HL bound only to Pt(II) through the sulphur atoms.

3.2. N-alkyl-N′-acylthioureas and N,N-dialkyl-N′-acylthioureas

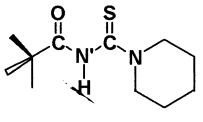
In an effort to study water soluble ligands, we recently prepared a series of *N*-alkyl- and *N*,*N*-dialkyl-*N*′-acylthioureas derived from aliphatic acid chlorides such as trimethylacetyl chloride and propyl chloride, examples of which are:



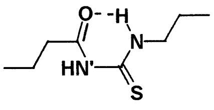
HL^5



HL^6



HL^7



H$_2$L^8

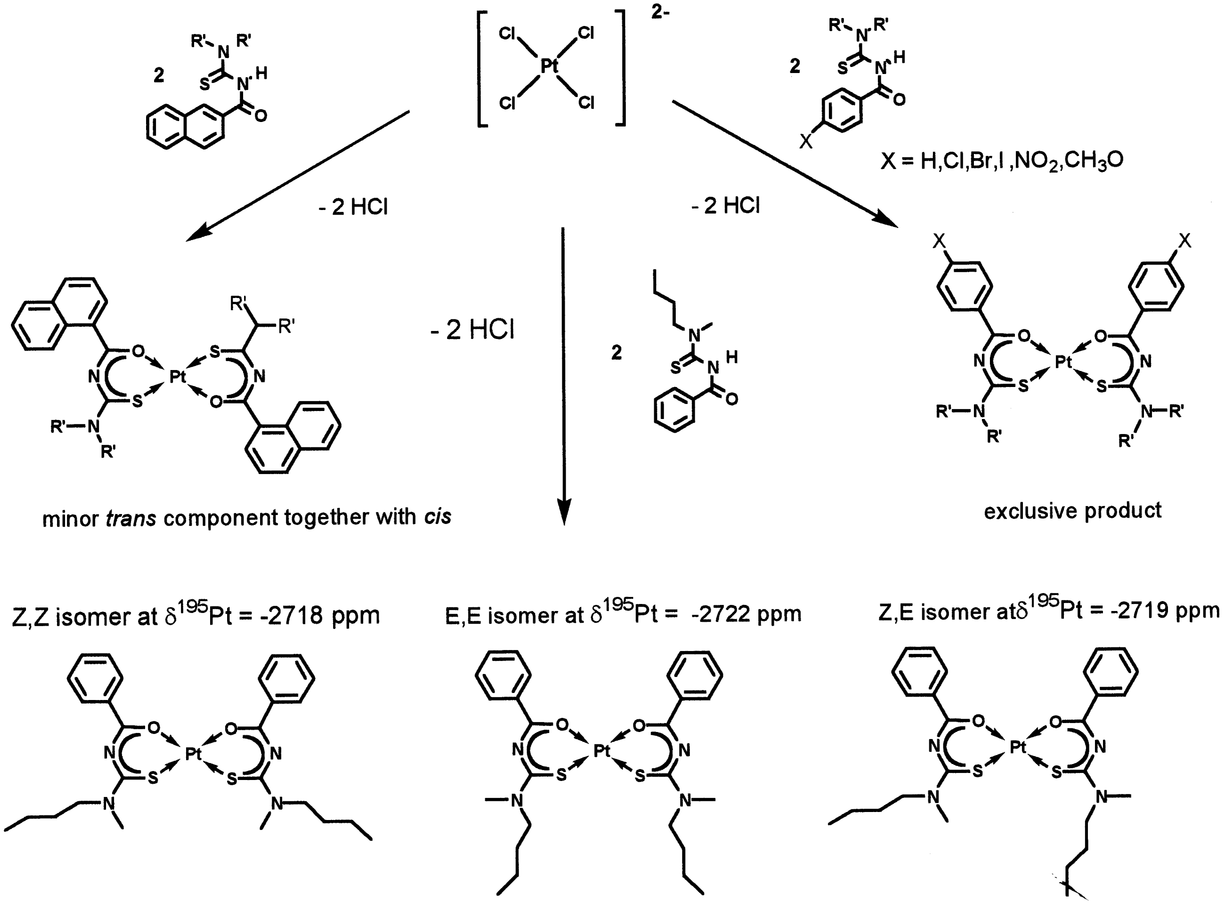
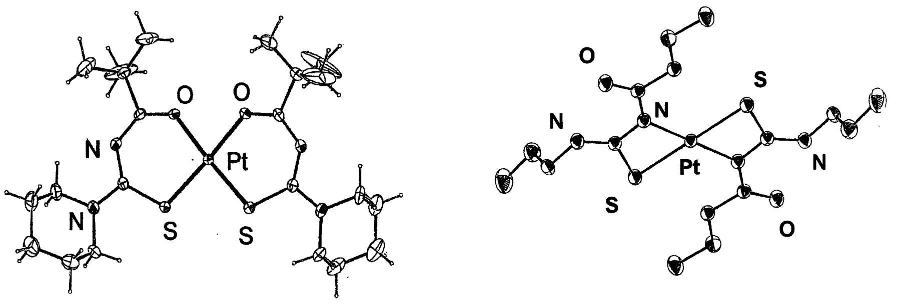


Fig. 1. Co-ordination chemistry *N*,*N*-alkyl-*N*′-aroylthioureas (**HL**) with $PtCl_4^{2-}$.


(a) ***cis*****-[Pt(L^7-*S,O*)$_2$]**

(b) ***cis*****-[Pt(L^8-*N′,S*)$_2$]**

(c) [(PPh$_3$)$_2$(CO)Rh(μ-L^9-κ*N′*: κO,S)Rh(PPh$_3$)(CO)]

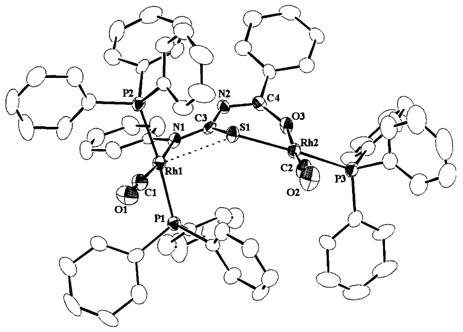


Fig. 2. Representative crystal structures showing various modes of co-ordination: (a) *S*,*O* chelation: *cis*-bis(*N*-piperidyl-*N′*-(2.2-dimethylpropanoyl)-thioureato)platinum(II); (b) *S*,*N′* chelation: *trans*-bis(*N*-propyl-*N′*-butanoylthiourea)-platinum(II); and (c) *S*,*N′*,*O* (bridging) mode: [(PPh$_3$)$_2$(CO)Rh(μ-L^9-κ*N′*:κ*O*,*S*)Rh(PPh$_3$)(CO)].

These *N*-acylthiourea ligands, and their corresponding metal complexes, are all reasonably water-soluble. To our knowledge, there are only few reports of metal complexes derived from related *N*-acylthiourea ligands in the chemical literature [3,20,21], although no structural data for any complexes are available. As might be anticipated, ligands **HL^5**, **HL^6** and **HL^7** readily form the expected *cis*-[M(L-*S*,*O*)$_2$] complexes, where M = Pt(II) and Pd(II) (see for example the crystal structure of *cis*-[Pt(L^7-*S*,*O*)$_2$] in Fig. 2(a)). Moreover, **HL^5** reacts with Rh(III) to form *fac*-[Rh(L-*S*,*O*)$_3$] as seen from the crystal structure of this complex [42].

Contrary to expectation, the co-ordination of **H$_2$L^8** to Pt(II) yields a very interesting result: in the presence sodium acetate, treatment of [PtCl$_4$]$^{2-}$ with two equivalents of **H$_2$L^8** results in a *mixture* of complexes, about a third of which is the unprecedented complex *trans*-[Pt(HL^8-*N*,*S*)$_2$], shown in Fig. 2(b) [39]. This mode of co-ordination has not previously been observed for any related *N*-acylthiourea ligands, thus providing more evidence of the important, though subtle, influence of the intramolecular H-bond between the amidic O atom and the HNRC(S)– moiety of this ligand, and whether one is dealing with alkyl or aroyl substituents in these molecules. Yet another unprecedented mode of *N*,*S*,*O* co-ordination of *N*-phenyl-*N′*-benzoylthiourea (**H_2L^9**) is exemplified by the crystal structure of $[(PPh_3)_2(CO)Rh(\mu\text{-}L^9\text{-}\kappa N'{:}\kappa O,S)Rh(PPh_3)(CO)]$, in which the doubly de-protonated anion $(\mathbf{L^9})^{2-}$, forms a bridging ligand between two Rh(I) centres (Fig. 2(c)) [43].

From the overview above, it should be clear that the fundamental co-ordination of the **HL**- and **H_2L**-type ligands of Pt(II), Rh(III) and Pd(II) is deceptively simple and certainly not entirely predictable. A thorough study of this co-ordination chemistry has yielded some interesting new results and has guided us in the design of a number of potentially useful ligands applicable to the analytical and process chemistry of the PGMs. Although much of this work is still in an early stage, several promising applications have emerged, which are illustrated in the following section.

4. Analytical and process chemistry applications of *N*,*N*-dialkyl-*N′*-acyl(aroyl)thioureas

4.1. Reversed-phase HPLC determination of Pt(II), Pd(II) and Rh(III)

Despite the demonstrated application of *N*,*N*-dialkyl-*N′*-benzoylthioureas in normal-phase (NP)-TLC separation of a series of transition metal ions, including Pt(II), Pd(II), Ir(III), Os(III) Rh(III) and Ru(III) [11–14], we have found the metal complexes derived from *N′*-benzoylthioureas show some disadvantages. Foremost amongst these is the relatively poor solubility and hydrophobicity of the *N′*-benzoylthioureas ligands and their corresponding complexes. This necessitates either the quantitative precipitation of uncharged metal complexes from the aqueous phase or a solvent extraction process using water-immiscible solvents, an approach advocated and successfully applied previously by Schuster et al. [11–14,44]. As has been shown by these authors, silica-gel (SG)-based NP-TLC and HPTLC gives good separations of the resultant *N′*-benzoylthiourea complexes of PGMs (with careful sample preparation). Moreover, the separated complexes can be successfully quantified at ultra-trace levels by means of a TLC scanner. Our attempts to transfer this methodology to conventional normal-phase high-performance liquid column chromatography with photometric detection (NP-HPLC) failed, however, due to ‘on-column’ complex decomposition and irreversible retention of metal complexes (the latter probably due to the inherent acidity of the SG column packing material). Furthermore, the notorious sensitivity of NP-HPLC with SG-based packing materials to traces of water is a considerable disadvantage resulting in poor control of retention behaviour for these complexes [42,45]. On an industrial scale, the separation and refining of the PGMs takes place in relatively concentrated hydrochloric acid solutions, and is based on their complex metal chloro-anion ($[MCl_4]^{2-}$/$[MCl_6]^{n-}$) chemistry [2]. Hence using NP-HPLC methodology, problems due to protonation and/or chloride ion binding to the uncharged $[M(L\text{-}S,O)_{2/3}]$ complexes of N'-benzoylthioureas to give highly polar species such as *cis*-$[Pt(H_2L\text{-}S)_2Cl_2]$ might be anticipated. Such species are likely to be irreversibly retained species on SG (confirmed by our experience), rendering NP-HPLC impractical for process solutions.

Wishing to exploit the remarkable selectivity of this class of ligands toward the PGMs over other transition metal ions, particularly in relatively concentrated hydrochloric acid solutions, we explored the application of the newly prepared hydrophilic *N*,*N*-dialkyl-N'-acylthioureas in combination with RP-HPLC, using predominantly aqueous eluents. We find that ligands $\mathbf{HL^5}$, $\mathbf{HL^6}$ and $\mathbf{HL^7}$, readily form stable hydrophilic *cis*-$[M(L\text{-}S,O)_2]$ ($M = Pt(II)$ and Pd(II)) and *fac*-$[Rh(L\text{-}S,O)_3]$ complexes under conditions which are well-suited for RP-HPLC separations using buffered water–acetonitrile eluents. A typical separation of the Pt(II), Pd(II) and Rh(III) complexes derived from the ligand $\mathbf{HL^5}$ is illustrated in Fig. 3 showing good resolution at relatively short retention times. Excellent linear calibration lines based on the optimised photometric detection of chromatographic peaks from solutions of pure complex are achievable, and the method shows a dynamic range of 2–3 orders of magnitude. Moreover, we have developed a simple and rapid sample preparation procedure, which allows the convenient mixing of a sample containing trace amounts of the $[PtCl_4]^{2-}$, $[PdCl_4]^{2-}$ and $[RhCl_5(H_2O)]^{2-}$ species in dilute HCl, with an aliquot of acetonitrile containing a slight excess of $\mathbf{HL^5}$. This homogeneous solution is allowed to stand for 5–10 min either at room temperature (for Pt(II)- and Pd(II)-containing samples only) or at 70–80°C (for solutions containing also Rh(III)), followed by a salt-induced (2 M NaCl) phase separation of the sample phase into an acetonitrile-rich phase containing the PGMs complexes of $\mathbf{HL^4}$ and a water-rich phase, which is discarded. The acetonitrile-rich phase is then directly injected into the RP-HPLC system for separation and quantification. The excess ligand present is only slightly retained under these conditions, typically eluting as a single peak within < 2.5 min. Using this procedure, the retention behaviour of the complexes is highly reproducible, and it is possible to achieve satisfactory quantification of Pt(II), Pd(II) and Rh(III) in dilute hydrochloric acid solutions. This RP-HPLC method, using $\mathbf{HL^4}$ as ligand, has a limit of detection to levels of ca 2 $\mu g\ ml^{-1}$ Pt, 0.1 $\mu g\ ml^{-1}$ Pd and 3 $\mu g\ ml^{-1}$ Rh, at optimised photometric detection, respectively. Details of this procedure will be published elsewhere [42].

4.2. Thin film pre-concentration of PGM complexes followed by laser ablation ICP-MS

In an attempt to achieve detection limits for Pt(II), Pd(II) and Rh(III) significantly lower than 1 $\mu g\ ml^{-1}$, particularly in solutions with complex matrices, we have explored the use of glass-fibre disks impregnated with C_{18}-modified silica. These are used to pre-concentrate onto a thin film, trace amounts of Pt(II), Pd(II) and Rh(III) complexes prepared in situ with the ligand *N*,*N*-di(2-hydroxylethyl)-N'-benzoyl-thiourea ($\mathbf{HL^{10}}$), according to a procedure shown schematically in Fig. 4.

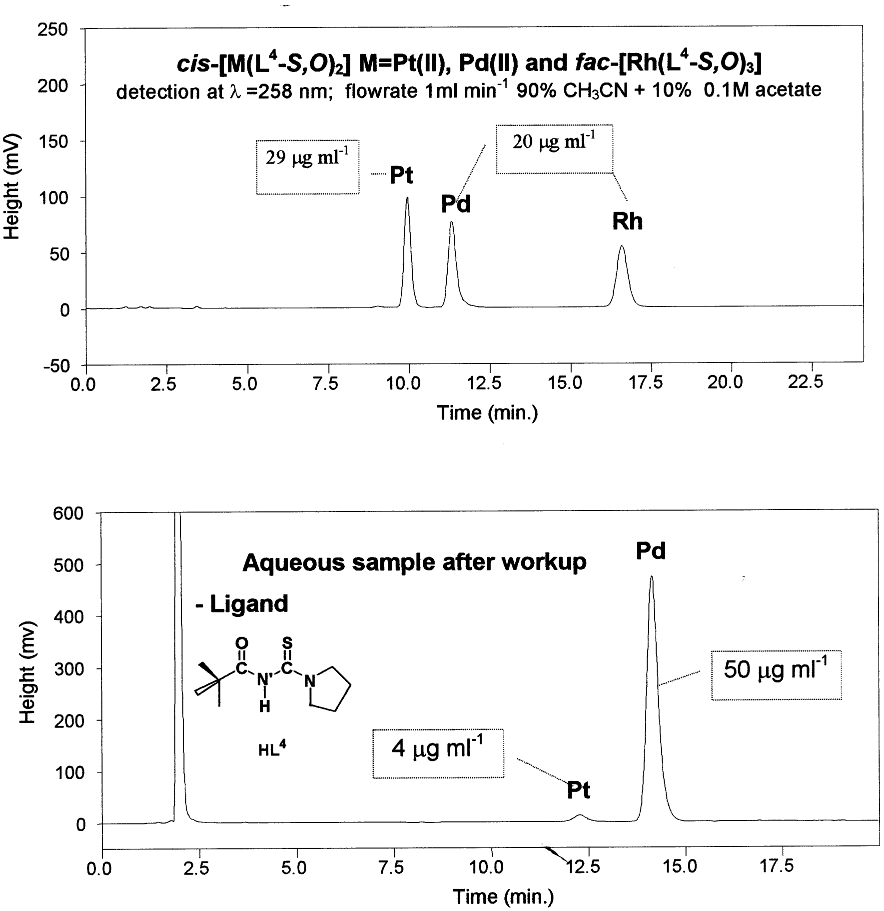


Fig. 3. Representative chromatograms of *cis*-[M(L-*S*,*O*)$_2$] (M = Pt(II) and Pd(II)) and *fac*-[Rh(L-*S*,*O*)$_3$] obtained on a LUNA C_{18} HPLC column (5 μm, 150 mm × 4.6 mm column; eluent 90:10 vol% acetonitrile:0.1 M sodium acetate, pH 6 flow rate 1 cm^3 min^{-1}, 20 μl sample injection); Pt, Pd and Rh standards and aqueous sample after workup.

Preliminary results are encouraging and confirm that Pt, Pd and Rh can readily be pre-concentrated and determined by means of this methodology. An aqueous sample in dilute hydrochloric acid is treated with a catalytic amount of stannous chloride and excess ligand, **HL^{10}**, followed by absorption on the thin C_{18}-modified silica glass-fibre disks. The loaded disks are presented for analysis by means of laser-ablation inductively coulped plasma mass spectroscopy (LA-ICP MS), for which remarkably linear response–concentration curves are obtained, as shown in Fig. 5. Recovery tests result in $>99\%$ recovery of the PGMs with this procedure, so that it is possible to detect and quantify levels of Pt, Pd and Rh to ca 10 ng ml^{-1}, with acceptable precision ($\pm$ 10% relative) for synthetic Pt(IV), Pd(II) and Rh(III) solutions in dilute hydrochloric acid.

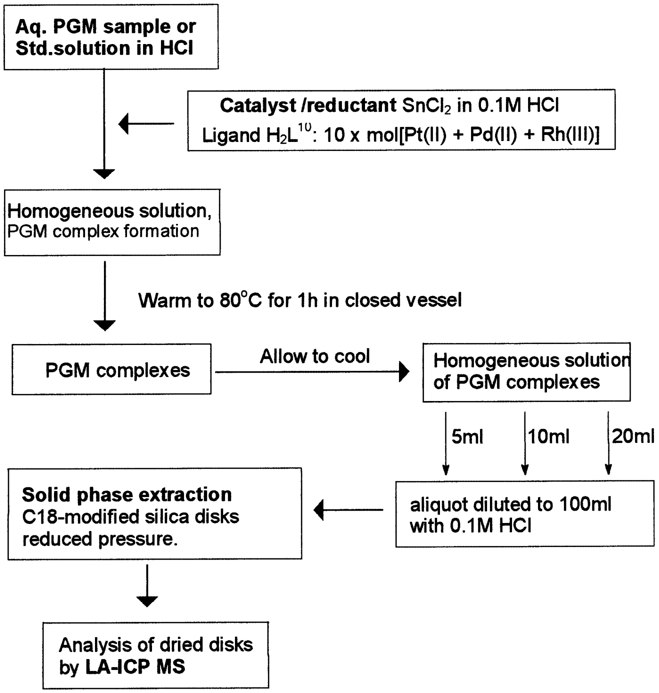


Fig. 4. Sample preparation procedure for pre-concentration on C_{18}-impregnated glass-fibre disks of Pt(II), Pd(II) and Rh(III) complexes with *N*,*N*-di(2-hydroxylethyl)-*N′*-benzoylthiourea, prior to LA-ICP mass spectroscopy determination.

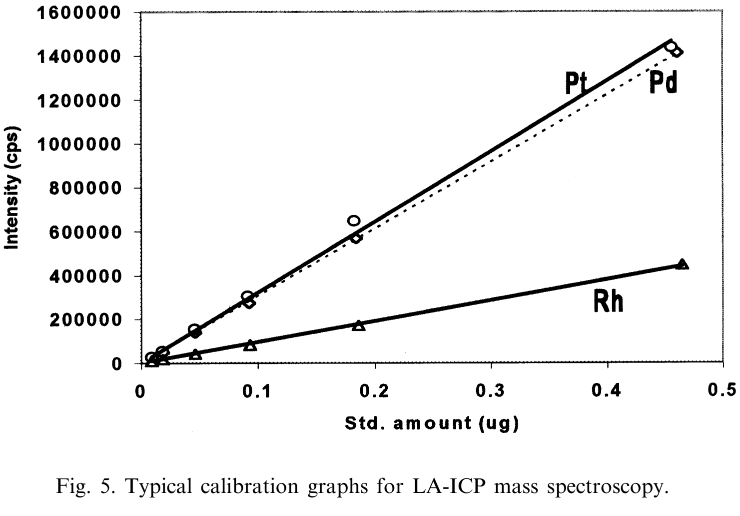


Fig. 5. Typical calibration graphs for LA-ICP mass spectroscopy.

This methodology has been tested on authentic, untreated plant effluent samples obtained from a local refining process for the PGMs, with encouraging results. Some typical concentrations of 164 ± 13 μg ml^{-1} Pt, 53 ± 5 μg ml^{-1} Pd and 55 ± 6 μg ml^{-1} Rh were found using the RP-HPLC procedure developed for these effluents, as compared to the independent analysis results of 167 ± 8 μg ml^{-1} Pt and 45 ± 3 μg ml^{-1} Pd (no result for Rh was available for this sample); the reasonably good concurrence of these metal concentrations in this effluent matrix confirms the accuracy of this pre-concentration methodology. Further work, with particular reference to potential interferences, to critically assess this methodology for the rapid trace determination of PGMs in process effluents and other complex matrices is in progress. Moreover, attention is being given to extend this method to the other members of the platinum group metals, notably Ru(IV/III), Ir(IV/III) and Os(IV/III).

In conclusion, we hope to have shown that these simple *N*,*N*-alkyl-*N*′-acyl-(aroyl)thiourea ligands, which have been known for more than a century, show some interesting and new co-ordination chemistry, particularly concerning the PGMs. With appropriately designed ligand systems based on this motif, some promising and useful analytical applications for monitoring industrial effluents from the PGM refining process have been developed. We are currently exploring larger scale process applications of these ligands, as well as the fundamental co-ordination chemistry of these ligands with Ir(IV/III), Ru(IV/III) and Os(IV/III).

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