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# SYNTHESIS, CHARACTERIZATION AND POTENTIAL CHROMATOGRAPHIC SEPARATION OF PALLADIUM AND PLATINUM COMPLEXES OF N,N-DIALKYL-N'-BENZOYLTHIOUREAS

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by
'M'ANGAKA CLARA MATOETOE MONA

Department of Analytical Science
University of Cape Town
Rondebosch 7700
South Africa

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# ABSTRACT

A series of para-phenyl substituted N,N-dialkyl-N′-benzoylthioureas where para-phenyl substituents are H, Cl, Br, I, $NO_2$ and $OCH_3$ and alkyl chains are $-CH_2CH_3$, $-(CH_2)_3CH_3$ and $-CH_2C_6H_5$ as well as their corresponding neutral bis complexes of type cis $[ML_2]$ where M = Pd(II) and Pt(II) have been prepared and characterized. The structures of these compounds has been studied using high resolution nuclear magnetic resonance technique.

Studies were also carried out to investigate possible use of these N,N-dialkyl-N-benzoylthioureas as ligands suitable for the chromatographic separation of Pt(II), Pd(II), Ni(II) and Cu(II). To this end the possible selective extraction of these complexes from acidic aqueous phases was examined. This layer normal phase chromatography has been mainly used, using a variety of organic phases as eluent. A preliminary investigation of the suitability of using normal phase HPLC for the separation of the platinum and palladium complexes was undertaken.

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# CHAPTER 1

# INTRODUCTION

The interaction of organic compounds with noble metals has become well known as a result of their formation of stable neutral complexes [1,2,3]. Many of the complexes so produced are widely used in platinum group metal analysis, mostly in chromatographic analysis [4-6]. Such systems have now become nearly indispensable in trace analysis of platinum group metals. There is extensive literature concerning chromatography of metal chelates [7,8], and the whole subject has recently been reviewed.

The main advantages of chromatographic separations of metal chelates is the possibility of multi-element analysis due to the combination of liquid-liquid extraction with subsequent chromatographic separation and determination of metal complexes (figure 1.1). The above combination increases sensitivity as a result of preconcentration of the elements at trace level. Furthermore, interferences and contaminants can be eliminated due to differences in the extractability of elements such as base metals. In addition, these methods are often simple, cheap, non-destructive and adaptable to accurate quantitative methods.

Liquid solid chromatography, especially the normal and reverse phase techniques, are the most used in metal chelates analysis because most chelates usually cannot be directly volatized, hence only few gas chromatographic methods are available. Liquid chromatography includes thin layer chromatography (TLC) and column chromatography being now represented in general as high performance liquid chromatography (HPLC). The advantages of TLC are convenience, technical simplicity, economy, rather high productivity and ability to detect chelates of low mobility [10]. HPLC combines in itself the rapid and highly effective separation of mixtures of chelates with a high sensitivity for component determination. Detection limits of 0.1ng metal may be obtained [10].

SAMPLING

SAMPLE PREPARATION
(i) Fusion/dissolution process (if necessary)
(ii) Extraction from aqueous solutions with chelating agents

CHROMATOGRAPHIC SEPARATION
Separation of various metal chelates
of the excess chelating agent
of interfering organic Matrix

DETECTION

CALCULATION

Figure 1.1 chromatographic analysis of metals adapted from Steinbrech [14]

The use of liquid chromatography for the determination of metal chelates has been reviewed [9-11]. In these publications it is shown that Pt-group metal complexes usually have good chromatographic behaviour because they form stable neutral chelates. Good separations are obtained with silica gel, alumina and their derivatives as stationary phases. As mobile phases various pure and binary solvents have been used [12,13].

In addition to the versatility of chromatographic methods of separation and their scope, numerous publications [14,19] also show some difficulties resulting in unsuccessful chromatographic analysis. The difficulties result from the instability of some metal chelates, formation of mixtures of complexes with one element and incomplete separations due to similar chromatographic behaviour of metal chelates to be separated. It is known [14] that there is a close relationship between the chromatographic behaviour and the chemical properties of the metal chelates. The differing nature of metal complexes may be expected to significantly influence the type and strength of interaction with stationary phase and hence their chromatographic behaviour.

Interest in chromatographic analysis of platinum group metals recently increased due to toxic effects of platinum anti-cancer drug which has prompted an intense research in trace analysis of platinum [20-23]. Moreover, due to the soft acid nature of the platinum group metals, these tend to form stable neutral complexes with large numbers of sulphur containing chelating agents, which are soft bases (Pearson's principle) [24]. The sulphur donor chelating agents have been found to be well suited for chromatographic separations [14]. These chelating agents form stable neutral complexes which are not altered during chromatographic analysis; chelates with metal-sulphur-bondings, which are comparatively less polar than metal-oxygen-bondings, show better chromatographic behaviour [14].

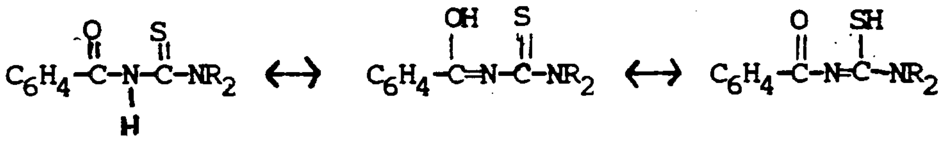
## 1.1 N,N'-DIALKYL-N'-BENZOYLTHIOUREAS

Alkylthioureas and N'N-disubstituted alkylthioureas have been known since about 1870 [25,26]. Several well established methods of preparation are available [27]. The most important standard preparation of thioureas is based on the reaction of alkyl and aryl isothiocynates with ammonia or primary and secondary amines [27]. By this reaction, (equation 1), a large variety of thioureas may be synthesized on the basis of the relative participation of aliphatic, aromatic, open-chain and cyclic amines as well as of amine derivatives. Douglas and Dains [28] first prepared N,N-dialkyl-N'-benzoylthioureas by reacting on appropriate secondary amine with acyl isothiocynates (equation 2).

$$R^1NCS + R^2R^3NH \longrightarrow R^1NHC(S)NR^2R^3 \qquad (R^2,R^3=H,\text{ alkyl, aryl etc}) \qquad (1)$$

$$C_6H_4C(O)NCS + R_2NH \longrightarrow C_6H_4C(O)NHC(S)NR_2 \qquad (R = \text{alkyl}) \quad (2)$$

N,N-dialkyl-N'-benzoylthioureas like other thioureas can exhibit isomerism. This gives rise to the hypothesis that the N,N-dialkyl-N'-benzoylthiourea can exist in the following Toutomeric forms:

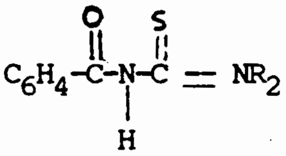


$$C_6H_4-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-\overset{S}{\overset{\|}{C}}-NR_2 \longleftrightarrow C_6H_4-\overset{OH}{\overset{|}{C}}=N-\overset{S}{\overset{\|}{C}}-NR_2 \longleftrightarrow C_6H_4-\overset{O}{\overset{\|}{C}}-N=\overset{SH}{\overset{|}{C}}-NR_2$$

(Ia) (Ib) (Ic)

(Ib) and (Ic) can have two isomers E and Z.

Relatively elaborate studies on the physical and chemical properties of N,N-dialkyl-N'-benzoylthioureas have been undertaken by Bayer et al [29]. In these studies it was found that under normal conditions the thiourea derivatives exist in the N-H (Ia) isomer. However, the above structures Ia, Ib, Ic failed to explain the NMR results of the N,N-dialkyl-N'-benzoylthioureas studied [29], which strongly indicates presence of restricted rotation at $C(S) - NR_2$ bond (s). The restricted rotation can only be explained by a highly polarized structure with partial double $C = S$ and partially double $C(S) = NR_2$ bond(s) Id.



$C_6H_4-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-\overset{\overset{S}{\|}}{C} = NR_2$

(Id)

N,N-dialkyl-N'-benzoylthioureas were mentioned as complexing agents in 1962 [30]. Complex formation of N,N-dialkyl-N'-benzoylthioureas show great similarities to that of monothio-diketones [31]. Both compounds have oxygen and sulphur as co-ordination sites, and also form intensely coloured chelates with a great number of metals.

As potential analytical reagents N,N-dialkyl-N'-benzoylthioureas have several advantages. In general they are well defined crystalline compounds of high stability, insoluble in water but highly soluble in a range of organic solvents. They are easily accesible by a relatively simple synthetic procedure. Moreover, they have exceptional oxidation resistance (precipitation can be done from aqueous nitric acid. [32]. Furthermore, they are easily derivatized, hence reactivity can be improved for any analytical task at hand.

N,N-dialkyl-N'-benzoylthioureas are known to form metal complexes which are almost insoluble in water, but highly soluble in polar organic solvents [32], with the result that these complexes may be expected to be greatly suited for liquid-liquid extraction. When a solution of a N,N-dialkyl-N'-benzoylthiourea in an immiscible organic liquid is shaken with an aqueous solution of a metal ion, the intensively coloured complexes may be extracted into the immiscible organic phase. In principle it may be expected that the neutral extraction process may be summarized by:

$$M^{2+} + 2LH_{org} \xrightarrow{K_{ex}} ML_{2org} + 2H^{+}_{aq}$$

The position of the equilibrium may be described by the extraction constant ($K_{ex}$) which is a constant under specific conditions.

$$K_{ex} = \frac{[ML_2]_{org} \quad [H^{+}]^{2}_{aq}}{[M^{2+}]_{aq} \quad [LH]^{2}_{org}}$$

From the expression of $K_{ex}$ it is evident that an increase in the acid concentration may be expected to shift the reaction to the left resulting in a decrease in $[ML_2]$ with subsequent decrease in the metal complex extraction.

Konig et al [32] have examined the ability of N,N-dialkyl-N'-benzoylthioureas to extract metals from acid aqueous solutions and they have shown that the extent of metal extraction depends on the temperature, the acidity (or pH) of the aqueous phase as well as on the nature of the alkyl substituents. These factors can be utilized to selectively extract the Pt-group metals from important base metals such as Cu, Fe or Ni.

The effect of temperature on the extraction of some members of the Pt-group metals may be explained on the basis of the kinetic inertness of Pt-chloro complexes [33]. On the other hand $PdCl_4^{2-}$ is generally much more labile so that substitution reaction takes place at room temperature, whereas $PtCl_4^{2-}$ requires the use of heat or catalyst for the formation of labile complexes so that substitution reactions can take place rapidly.

In general, the extent of extraction increases with increase in alkyl chain [32]. It is probable that the reason for this observation is because the shorter alkyl chain $(-N(Me)_2)$, (N-Pyrrol) or $(N-(ethyl)_2)$ complexes are slightly more soluble in water than the longer chain complexes $(N-(butyl)_2)$.

In general the N,N-dialkyl-N'-benzoylthiourea chelates have a number of characteristics that make their application to chromatographic separation of metal chelates rather interesting. These include their intense colour (exhibit high UV- extinction coefficient), their high stability, and their insolubility in water but high solubility in a range of organic solvents. Also the N,N-dialkyl-N'-benzoylthiourea chelates structure is similar to that of monothio-diketone chelates which have been used successfully in chromatographic separations [33]. In view of intense colour of these complexes, there is the possibility of an accurate determination using a spectrophotometric detector, which is commonly used in HPLC instruments.

TLC studies of only the N-Pyrrolidino-, N,N-dimethyl-, N,N-diethyl-, N,N-di-n-propyl-, N,N-di-n-butyl-, N,N-di-iso-butyl-, N,N-di-n-hexyl-, and N-methyl-N-stearyl- N'-benzoylthioureas complexes of Pt-group metals, Co, Cu and Hg have previously been undertaken [34]. In these studies silica gel was found to be best qualified as stationary phase. Silica gel separations depends on the relative humidity of the stationary phase. In these studies [34] optimum separations were obtained using HPTLC plates pre-conditioned for 2 hours in 40-70% relative humidity. Using chloroform, benzene or m-xylene as mobile phase, some of the chelates showed low mobility. In some cases no mobility was observed (Rh, Os, Ir and Rh). Excellent chromatographic behaviour was observed with Pt(II), Pd(II), Co(III), Hg(II) and Cu(II) metals which mostly showed moderate $R_f$ values and were separate from the excess ligands. These complexes form highly stable complexes, whereas the separation of Ni(II) complexes was complicated due to dissociation during elution and was therefore not further studied.

These studies showed that the chromatographic behaviour was influenced by the length of the alkyl substituents [34], thus increasing the alkyl chain length of the alkyl group from methyl to butyl, the $R_f$-values of the complexes increased strongly with simultaneous decrease in $R_f$-value-differences between the different metal complexes. This effect can be explained by the fact that longer chain substituents are more soluble in organic solvents and are probably less polar. Consequently, they favour the mobile phase more than the stationary phase, while shorter alkyl chain substituted complexes may be more polar which results in them being strongly retained by the stationary phase.

For TLC-separations of these chelates the N,N-diethyl-N-pyrrolidino-, N,N-diethyl- and N,N-di-n-propyl-N-benzoylthiourea were the best qualified ligands. With ligands mentioned above, Pt metals including Ru(II) and Os(II) were detected sensitively after chromatography using HPTLC plates following migration of 3 to 4cm and by UV-emission measurements at 280nm [34]. The detection limits of the metals were 0.5ng Pd and 2ng Pt and Cu [34].

### 1.1.2 Structure of N,N-dialkyl-N'-benzoylthioureas Metal Complexes

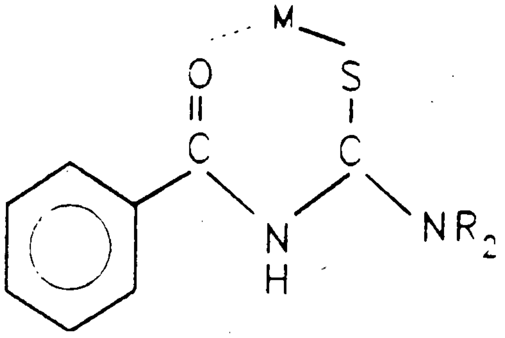
In principle the $d^8$ metal complexes (Pt(II), Pd(II), Cu(II) and Ni(II) ) could assume tetrahedral and square planar geometry [24]. In case of square planar complexes, the possibility of *cis* and *trans* complexes may be expected for bidentate co-ordination. In practise however, square planar geometry is preferred in the case of Pt(II) and Pd(II) [35].

The X-ray structure of N,N-dialkyl-N'-benzoylthiourea complexes of Pd [36], Pt [37], Ni [38] and Cu [39] as well as Pb [40] have been undertaken. In each case the N,N-dialkyl-N'-benzoylthioureas reacts as a bidentate chelating agents co-ordinating through a sulphur and benzoyl oxygen atom to give a 6-membered ring structure. In addition these studies showed that the length of C(S) - $NR_2$ bond(s) is shorter than normal C - N single bond(s). Furthermore, it has been found that these square planar complexes have only the *cis* configuration (Pd(II), Pt(II) and Pb(II)). Cu(II) and Ni(II) may form tetrahedral, square planar or a mixture consisting of planar and tetrahedral structure units in the ratio of 2:1 [38, 39]. Different modes of co-ordination of N,N-dialkyl-N′- benzoylthiourea are shown in figure 1.2.

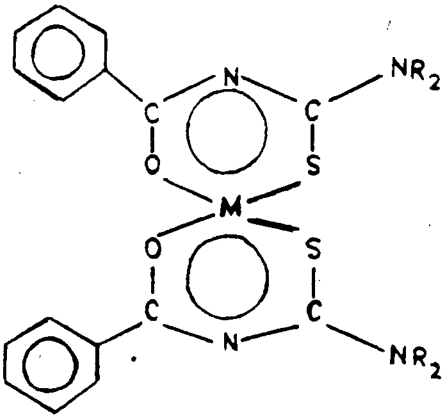
Depending on the nature of the metal, N,N-dialkyl-N-benzoylthioureas form trichelates, bichelates as well as monochelates (see figure 1.2) with metals like Co(III), Fe(III), Cu(III), Pd(II), Pt(II), Cu(II), Ni(II), Pb(II) and Tl(I).

The NMR studies showed presence of restricted rotation at C(S) - $NR_2$ bond(s) like in uncomplexed N,N-dialkyl-N-benzoylthioureas. The extent of restricted rotation about C(S) - $NR_2$ bond(s) increases in metal complexes with the exception of Tl(I) complexes which has shown a decrease in the restricted rotation [40].

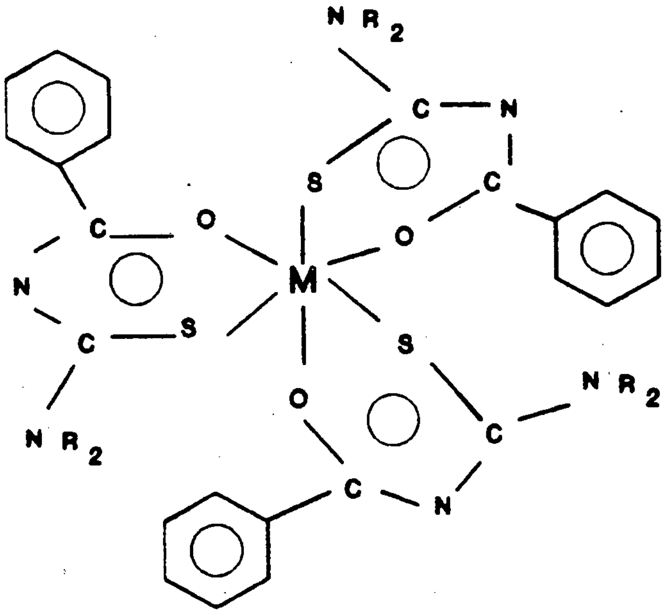
The synthesized metal complexes are capable of adduct formation with pyridine. In acetone and chloroform solutions, the light green bis pyridine adduct of metal complexes (Pd, Ni, Co, Cu) were isolated, yields increasing with the addition of pyridine [29]. The pyridine is loosely bound, and on standing in air, a brown-violet colour develops with time. On washing the complexes with methanol or chloroform, the solution takes on the colour of the starting complexes [29].



Monochelates M = TL(I)



Bichelates M = Pt(II), Pd(II), Cu(II) Ni(II) and Hg(II)
Square planar (cis and trans) or tetrahedral.



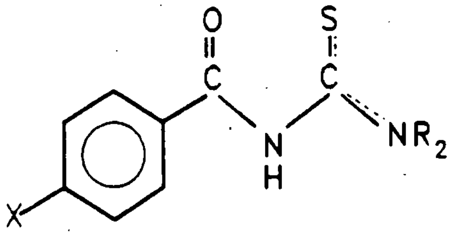
Trichelates M = Co(III), Cu(II) and Fe(III).

Figure 1.2 Some modes of co-ordination of N,N-dialkyl-N-benzoylthiourea

## 1.2 OBJECTIVES

In the literature it is evident that the N,N-dialkyl-N-benzoylthiourea reactivity as ligand is influenced by the alkyl chains [32,34]. From equation (2) there is a possibility of influencing the nature of the N,N-dialkyl-N-benzoylthiourea metal complexes by substitution in the benzene ring. The question arises whether any substituent effects are evident in both the chromatographic behaviour as well as the structure of neutral complexes of general type $[ML_2]$ where M = Pt(II), Pd(II), Ni(II) and Cu(II). The overall objectives of this work can be stated as follows:

(1) Preparation and characterization of a series of substituted N,N-dialkyl-N-benzoylthioureas derivatives



R = $CH_3CH_2$- , $CH_3(CH_2)_3$- , $C_6H_4CH_2$-

X = H, Cl, Br, I, $OCH_3$, $NO_2$

(2) Preparation and characterization of neutral binary metal complexes of Pt(II), Pd(II), Cu(II) and Ni(II)

(3) An investigation of the potential separation of the above binary metal complexes using normal phase thin layer chromotography

(4) Preliminary separation of the binary metal complexes using normal phase HPLC

# CHAPTER 2

# EXPERIMENTAL

## 2.1 GENERAL

To ensure that no impurities could result in contamination of the samples, during the study, analytically pure reagents and solvents as well as especially clean glassware were used. Where necessary, purification especially for solvents was undertaken.

### 2.1.1 Solvents and Chemicals

Glass-distilled water was used for all aqueous solutions. All reagents and solvents were analytically pure (ANALAR) from various suppliers. $K_2PtCl_4$ and $K_2PdCl_4$ were obtained from Johnson Matthey Chemicals, Herfordshire, $Cu(NO_3)_2.3H_2O$ was from Merck, Damstadt. Diethylamine, dibuthylamine and $Ni(CH_3COO)_2$ were supplied by BDH Chemical, England. All halogen derivatives of benzoyl chloride, 4-nitrobenzoyl chloride and P-anisoyl chloride were purchased from Aldrich Chemicals, while potassium thiocynate and benzoyl chloride were obtained from RSA.

### 2.1.2 Drying of Solvents and Purification

DRYING OF ACETONE

Acetone (ANALAR) was dried by heating under reflux over anhydrous $CuSO_4$ for a few hours followed by distillation. The dry acetone was stored in a clean, dry bottle containing some 4 Å molecular sieves (Merck).

## DRYING OF METHANOL

Methanol absorbs water from the atmosphere, hence it was necessary to dry it prior to use. Either one of the following methods were used:

a) by passing absolute methanol through Linde 4 Å molecular sieves, or

b) by the Lung and Bjerrum method [54]. Typically this involves warming dry, clean magnessium turning (5g) and iodine (0,5g) with about 50-70mls absolute methanol until the iodine disappeared and all the magnesium was converted to the methoxide. About 1$dm^3$ methanol was added and the mixture boiled under reflux for 2-3 hours. The distilled methanol was stored in a clean bottle containing some 4 Å molecular sieves.

## DRYING OF CHLOROFORM

Commercial chloroform often contains 0,1% ethanol which is commonly used as a stabilizer. The chloroform (CHROMAR) was washed with water to remove ethanol, followed by heating under reflux over $K_2CO_3$ or $CaCl_2$ and then distilled. Finally the distilled chloroform was passed through 4 Å molecular sieves and stored in a dark bottle containing some 4 Å molecular sieves.

PURIFICATION OF DIETHYLAMINE

Inpure diethylamine (black) was heated under reflux over KOH pellets for 2-3 hours and then distilled. The colourless diethylamine was stored in a clean dark bottle.

### 2.1.3 Glassware

All glassware used was cleaned by soaking for 24 hours in 10% contrad detergent. The glassware was then rinsed with distilled water and soaked in 10% $HNO_3$ solution overnight, followed by rinsing with deionized and distilled water and finally air dried in a dust free environment.

### 2.1.4 Instruments

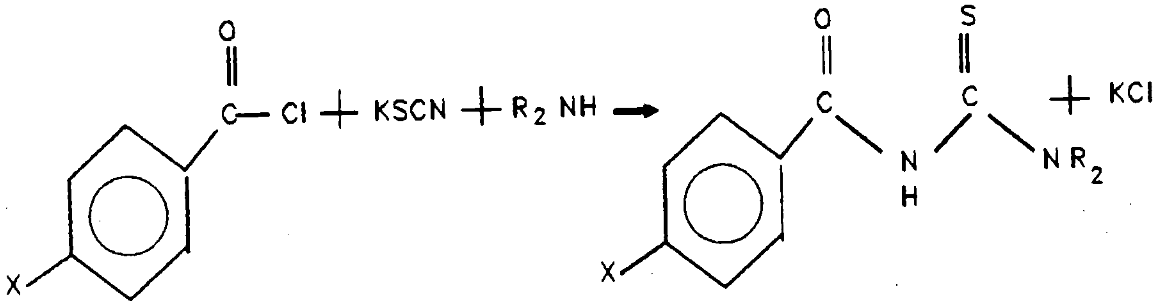
Melting points of all compounds were determined using a Reichart Thermovar melting point apparatus.

Elemental analysis were performed on a Heraus Universal Combustion analyser, model CHN - Micro by Mr P. Bennincassa, Department of Chemistry, University of Cape Town.

Mass spectra of all N,N'-dialkyl-N'-benzolythioureas and their para-substituted analogues were run using VQ Micromass Mass Spectrometer 16F by Ms H. Van Der Straaten, University of Cape Town.

## 2.2 PREPARATION OF N,N'-DIALKYL-N'-BENZOYLTHIOUREAS

In general the N,N'-dialkyl-N'-benzoylthioureas and the para-substituted analogues were prepared by the same overall method [28]. The method is particularly simple and readily gives high yields of the desired compounds.



The reaction involves two steps: In the first place the nucleophilic displacement of the chloride atom by the thiocynate ion occurs. The acid thiocynate isomerises in dry acetone to form acid isothiocynate. Secondly, the secondary amine is slowly added to the solution of acid isothiocynate to yield the desired product. Subsequently the N,N'-dialkyl--N'-benzoylthiourea is easily isolated by precipitation with 5M HCL solution, and purified by recrystallisation from an ethanol-water mixture.

### 2.2.1 Procedure

A 0.1 mol quantity of benzoyl chloride (or the corresponding para-substituted analogue with substituents Cl, Br, I, $NO_2$ and $OCH_3$) was heated under reflux for 20 minutes in 100 $cm^3$ dry acetone to which 0,1 mol KSCN (9,72g) had been added. Subsequently 0,12 moles of the appropriate secondary amine (diethylamine, dibutylamine or dibenzylamine) was added dropwise. The mixture was heated under reflux for another 20 minutes. When cool, the mixture was poured into 200 $cm^3$ of cold 5M HCL and allowed to stand overnight in a refrigerator for precipitation of the product. Most of the dibutylamine derivatives initially form oils which take more than one day to solidify. The crude product collected by filtration and recrystallized from ethanol-water mixture. The white to yellow crystals were dried overnight under vacuum. Yields of between 70-90% were obtained. For some compounds more than one recrystallization was necessary.

## 2.3 PREPARATION OF METAL COMPLEXES

The compunds prepared in Section 2.2 easily form neutral bis chelates with divalent metal ions in water/alcohol solutions. For the precipitation, the proportion of metal to complex former is determined in such a way that the metal is present in slight stoichiometric excess. In general, 1.01 mmoles of metal salt solution in 25 $cm^3$ $H_2O$ warmed to 70°C, was added dropwise to a hot solution of 2.0 m moles ligand (N,N'-dialkyl-N'-benzoylthiourea derivative) in 40 $cm^3$ of ethanol-water mixture (the composition of the solvent varied depending on the solubility of the ligand). The mixture was mechanically stirred for one hour, and allowed to cool in a refrigerator. The precipitate collected by centrifugation and recrystallized from ethanol-chloroform mixture. The brightly coloured (depending on the metal used) complexes were dried overnight under vacuum. Yields of between 65-99% were obtained. The compounds were characterized by elemental analysis. (See Chapter 3).

### 2.3.1 Preparation of Bis (N,N'-Dialkyl-N'-Benzoylthiourea) Platinum (II)

A warm solution of 1,01 mmol $K_2PtCl_4$ in 25 $cm^3$ $H_2O$ was added dropwise to a hot solution of 2,0 m moles ligand in 40 $cm^3$ water-ethanol mixture. The mixture was mechanically stirred for one hour, and allowed to cool in a refrigerator. The crude product collected by centrifugation and recrystallized from ethanol-chloroform mixture. The yellow to brown crystals were dried overnight under vacuum.

### 2.3.2 Preparation of Bis (N,N'-Dialkyl-N'-Benzoylthiourea) Palladium (II)

To a hot solution of 2,0 mmoles ligand in 40 $cm^3$ ethanol-water mixture a warm solution of 1,01 mmoles $K_2PdCl_4$ in 25 $cm^3$ $H_2O$ was added dropwise. Subsequently the mixture was mechanically stirred for one hour. The mixture was cooled in a refrigerator. The crude product was collected by centrifugation and recrystallized from the ethanol-chloroform mixture. The yellow to brown crystals were dried overnight under vacuum.

### 2.3.3 Preparation of Bis (N,N'-Dialkyl-N'-Benzoylthiourea) Nickel (II)

The Nickel (II) complexes were prepared by adding a warm solution containing 1.01 mmol $Ni(CH_3COO)_2$ in 25 $cm^3$ 50% (V/V) ethanol-water to a hot solution containing 2.0 m moles ligand in 40 $cm^3$ ethanol-water mixture. The mixture was mechanically stirred for one hour and allowed to cool in a refrigerator. The crude product was collected by centrifugation and recrystallized from ethanol-chloroform mixture. The red to violet crystals were dried overnight under vacuum. Yields of 70-85% were obtained.

### 2.3.4 Preparation of Bis (N,N'-Dialkyl-N'-Benzoylthiourea) Copper (II)

To a hot solution of 2.0 mmoles ligand in 40 $cm^3$ ethanol-water mixture, a warm solution of 1.01 mmoles $Cu(NO_3)_2.3H_2O$ dissolved in 25 $cm^3$ of water was added dropwise. Subsequently the mixture was mechanically stirred for one hour and allowed to cool in a refrigerator. The crude product was collected by centrifugation and recrystallized from ethanol-chloroform mixture. The green crystals were dried overnight under vacuum. Yields of 70-85% were obtained.

## 2.4 NMR EXPERIMENTS

All NMR spectra were measured using a Varian VXR-200 FT NMR Spectometer. In general $CDCl_3$ proved to be the best solvent for all ligands and complexes.

### $^1$H AND $^{13}$C NMR SPECTRA

All $^1$H and $^{13}$C NMR Spectra were measured at 25°C at 200.06 and 50.30 MHz respectively

### $^{195}$Pt NMR SPECTRA

$^{195}$Pt NMR Spectra wre recorded at 30° using 45.925MHz and a 80° pulse (90° pulse equals about 14$\mu$sec) with a 1.5 sec pulse delay. Depending on the concentration of the sample, between 2000 and 25000 transients were required. Shifts are quoted relative to the widely used external reference compound, $H_2PtCl_6$ in $D_2O$ at same temperature ( $\delta\ ^{195}Pt = 0$)

## 2.5 EXTRACTION EXPERIMENTS

### 2.5.1 Preparation of Solutions

Platinum and palladium stock solutions of 1000ppm were prepared by dissolving appropriate amounts of $K_2PtCl_4$ and $K_2PdCl_4$ respectively in 1M HCL.

The 1% aqueous stock solutions of copper and nickel were prepared from $Cu(NO_3)_2.3H_2O$ and $Ni(CH_3COO)_2$ respectively.

Tin(II)chloride stock solutions of appropriate concentratins were made by dissolving the solid $SnCl_2.2H_2O$ in concentrated HCL purged with dinitrogen to remove oxygen. The mixture was allowed to stand in a tightly stoppered flask, immersed into a beaker containing hot water until the cloudiness disappeared. The solution was then allowed to cool and diluted to the required volume with distilled water. The concentration of the tin(II) was checked before use by titration with $KIO_3$ [1].

### 2.5.2 Extraction Procedures

Equal volumes of organic and aqueous phases were used in the extraction. The proportion of metal to ligand was determined in such a way that the ligand was present in slight stoichiometric excess. Where tin(II)chloride was to be used, all solutions were purged with dinitrogen to remove oxygen as much as possible.

Generally the required volumes of metal solutions were dispensed by means of piston burettes into an extraction tube. Where necessary $SnCl_2$ solution (depending on the required Sn:Pt ratio) as well as water were added to make 5 $cm^3$ solution. In the latter case, an equilibration time of 15 minutes was allowed before adding 5 $cm^3$ of 0.1% ligand in chloroform. The tubes were then sealed with tightly fitting rubber stoppers, and the mixture shaken using a mechanical shaker for a fixed period of time. After phase separation had occurred, the organic phase was used for chromatographic experiments. A portion of the aqueous phase was removed with a pipette and prepared for atomic absorption measurements.

## 2.6 ATOMIC ABSORPTION SPECTROSCOPY

The palladium, platinum and tin(II) chloride solutions were prepared as described in Section 2.5.1. A stock solution of 500ppm Lanthanium was prepared by dissolving $La(NO_3)_3 \cdot 6H_2O$ in 1M HCL.

Sets of standard solutions were prepared for platinum and palladium as well as standards containing both platinum and palladium (desired ratios). The acid concentrations and tin concentrations were made to match the sample matrix as closely as possible. $La(NO_3)_3$ solutions were added in standards and samples in such a way that the final solutions contained about 0.2% La. Only Pt and Pd were determined by means of flame atomic absorption.

All measurements were undertaken using either a Varian Tectron (Pt) or a Perkin Elmer Spectrometer (Pd). Strongly oxidizing air-acetylene flames and the following settings were used:

| | | Pd | Pt |
|---|---|---|---|
| Lamp current | (mA) | 12 | 10 |
| Wavelength | (nm) | 247.6 | 265.9 |
| Slit width | (nm) | 0.2 | 0.2 |

## 2.7 THIN LAYER CHROMATOGRAPHY

### STATIONARY PHASE

Aluminium sheets, silica gel $60F_{254}$ (20 x 20 cm) pre-coated plates were used. Thin layer chromatography (TLC) Plates of 0.2mm layer thickness and high performance thin layer plates (HPTC) supplied by E. Merck. The 20 x 20 cm plates were cut into strips of 3 x 7 cm or 10 x 10 cm which were preconditioned before use.

## PRECONDITIONING OF STATIONARY PHASE

The plates were preconditioned using any of the following methods:

(i) Allowed to stand overnight in a dessicator with a beaker of 42% $H_2SO_4$ - $H_2O$ mixture. (Corresponds to 50% relative humidity).

(ii) Heated in an oven to 60°C for 2-3 hours, cooled in the dessicator containing silica and then used immediately (dry plate).

(iii) When investigating effects of dryness, humidities of about 30% were investigated by preparation of appropriate $H_2SO_4$ - $H_2O$ mixture.

### 2.7.1 Chromatographic Procedure

The starting line was drawn in pencil on the preconditioned strips about 1cm from the bottom edge. Several spots of the sample dissolved in chloroform were applied to the plate using the fine portion of the pipette (pipette was heated in a small flame until soft, then when removing it from the flame, the ends were pulled gently apart to produce two fine pipettes). The samples were applied in the form of a small spot about 4mm from one side of the plate and 5mm apart. Ascending elution was carried out in a screw cap jar (3 x 7 cm) or tank, covered with glass plate (10 x 10 cm). The mobile phases were always about 0.4mm below starting line of samples. Complete saturation of the tank was ensured before development, and facilitated during development by placing a peice of filter paper in the developing container. In general, it required 7 to 10 minutes for the plates to develop, that is until the solvent front had reached about 6 or 9 cm. The plates were removed and the solvent front marked and dried. The dry plates spots were then visualized.

### 2.7.2 Spot Visualization

The spots were detected visually (coloured compounds) or visualized using either of the following methods:

(i) Putting the plates in a container that contained a few crystals of iodine for a few minutes. Spots marked with pencil immediately after removing the plates from the container.

(ii) Ultra-violet lamp, with a wavelength of < 260mm. Spots marked with a pencil. $R_f$ values recorded, where $R_f$ is defined by:

$$R_f = \frac{\text{distance of spot}}{\text{distance of Solvent front}}$$

the $R_f$ value is estimated to ± 0.05 units.

Various mobile phases were investigated as pure solvents as well as binary mixtures of chloroform, methanol, tetrahydrofuran and benzene.

## 2.8 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

All HPLC chromatograms were measured using Beckman high performance liquid chromatography instrument, which consists of constant volume pumps, valve injector and UV-visible photometric detector. Haber pre-packed Licrosorb Si 60 (5$\mu$m) 250mm stainless steel column was used.

Numerous binary chloroform solutions as well as chloroform were investigated as mobile phase. In general the mobile phases were dried and degassed (using an ultrasonic bath) prior to use. The column was pre-conditioned by washing with chloroform for 3 hours followed by methanol for 2 hours, and chloroform again for 2 hours. The pre-conditioned column was then washed with the mobile phase to be used for 1½ hours before injection of sample. Samples were injected with a glass syringe.

# CHAPTER 3

# CHARACTERIZATION OF N,N-DIALKYL-N-BENZOYLTHIOUREAS AND THE CORRESPONDING BIS-METAL COMPLEXES OF Pt, Pd, Ni AND Cu

## 3.1 PREPARATION OF N,N-DIALKYL-N'-BENZOYLTHIOUREAS

The N,N-dialkyl-N'-benzoylthioureas and their para-substituted analogues were prepared by the method of Douglas and Dains [28]. The method involved formation of alkyl isothiocynates by direct thionation of benzoyl chloride in the presence of dry acetone. The benzoyl isothiocynates reacted with secondary amines to form N,N-dialkyl-N'-benzoylthioureas.

The reaction can be represented as follows:

$$XC_6H_4C(O)Cl + KSCN \rightleftharpoons XC_6H_4C(O)SCN + KCl$$

$$XC_6H_4C(O)SCN \xrightarrow[\text{acetone}]{\text{dry}} XC_6H_4C(O)NCS$$

$$XC_6H_4C(O)NCS + R_2NH \rightleftharpoons XC_6H_4C(O)NHC(S)NR_2$$

---

$$XC_6H_4C(O)Cl + KSCN + R_2NH \xrightarrow[\text{acetone}]{\text{dry}} XC_6H_4C(O)N(H)C(S)NR_2 + KCl$$

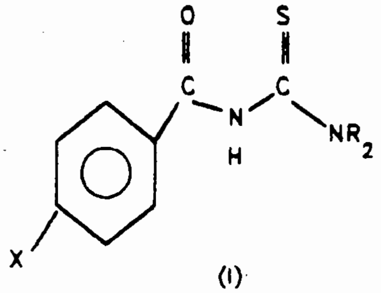
where $X = H, Cl, Br, I, OCH_3$ and $NO_2$

$R = -CH_2CH_3, -(CH_2)_3CH_3$ and $-CH_2C_6H_5$

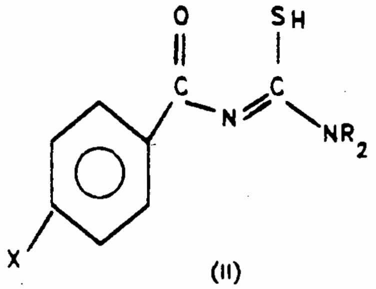
By the above reaction, a series of N,N-dialkyl-N'-benzoylthioureas were prepared. Details of the actual experimental procedure is given in Chapter 2, section 2.3.

## 3.2 CHARACTERIZATION OF N,N-DIALKYL-N'-BENZOYLTHIOUREAS

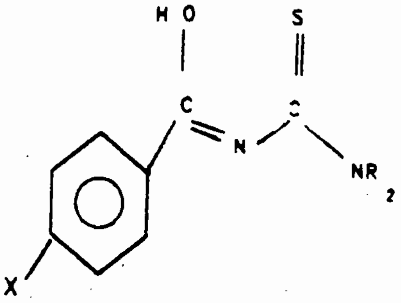
According to the literature [35] thioureas are commonly represented by the structure (I). However, N,N-disubstituted thioureas may be expected to exhibit isomerism and tautomerism, so that potential structures like (II) and (III) are commonly used to explain some of the properties of N,N-disubstituted thioureas [35]. Therefore N,N-dialkyl-N'-benzoylthioureas are best represented by all three forms I, II, and III. The extent to which any one form dominates probably depends on the nature of the X and R groups.



(I)



(II)



(III)

However, X-ray crystallographic investigations and NMR studies [27] disclosed bonding characteristics which are best interpreted in terms of highly polarized structure with partial double C═S (1.731A) and partially double C(S) ═ N (1.332A) bonds [27].

The N,N-dialkyl-N'-benzoylthioureas prepared are white to yellow crystalline solids. The thioureas were found to be almost insoluble in water but highly soluble in a range of organic solvents like methanol and chloroform forming colourless to yellow solutions.

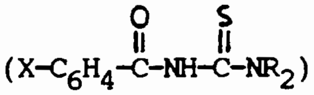
### 3.2.1 Melting Points and Elemental Analysis

To confirm the nature of and to test the purity of the N,N-dialkyl-N'-benzoylthioureas prepared, elemental analysis and melting points were determined. (See Chapter 2 for details).

A summary of elemental analysis data is given in Table 3.1 as well as corresponding melting points. The relatively high melting points (>90°C) of these compounds is in accordance with the high polarity of the thiourea structure as observed by Duus [27].

From the data in Table 3.1 it is evident that percent composition calculated and those observed show no significant difference, therefore the compounds prepared were relatively pure.

TABLE 3.1 Elemental analysis [a] and Melting points data for N,N-dialkyl-N'-benzoylthioureas



$X\text{-}C_6H_4\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}\overset{S}{\overset{\|}{C}}\text{-}NR_2$

| Compound | | Molecular formula | Elemental | Analysis | % |
|---|---|---|---|---|---|
| X | R | MP°C | C | H | N |
| H | $CH_3CH_2$ | $C_{12}H_{16}N_2SO$ | 60.9 | 6.6 | 11.9 |
| | (Lit 98°C) Ref. 32 | 101 | (61.0) | (6.8) | (11.9) |
| | $CH_3(CH_2)_3$ | $C_{16}H_{24}N_2SO$ | 65.9 | 8.4 | 9.8 |
| | (Lit 93°C) Ref. 32 | 93 | (65.7) | (8.3) | (9.6) |
| | $C_6H_5CH_2$ | $C_{22}H_{19}N_2SO$ | 72.7 | 5.7 | 7.9 |
| | | 123-141 | (73.0) | (5.6) | (7.8) |
| Cl | $CH_3CH_2$ | $C_{12}H_{15}N_2OCl$ | 53.2 | 5.4 | 10.1 |
| | | 146 | (53.2) | (5.6) | (10.3) |
| | $CH_3(CH_2)_3$ | $C_{16}H_{23}N_2SOCl$ | 58.7 | 6.8 | 8.5 |
| | | 84 | (58.8) | (7.1) | (8.6) |
| Br | $CH_3CH_2$ | $C_{12}H_{15}N_2SOBr$ | 45.7 | 4.4 | 8.4 |
| | | 110-124 | (45.2) | (4.7) | (8.8) |
| | $CH_3(CH_2)_3$ | $C_{16}H_{23}N_2SOBr$ | 50.9 | 6.2 | 7.3 |
| | | 94 | (51.3) | (6.2) | (7.5) |
| I | $CH_3CH_2$ | $C_{12}H_{15}N_2SOI$ | 39.2 | 4.0 | 6.8 |
| | | 155 | (39.8) | (4.2) | (7.7) |
| | $CH_3(CH_2)_3$ | $C_{16}H_{23}N_2SOI$ | 44.5 | 5.2 | 5.9 |
| | | 190-194 | (44.9) | (5.5) | (6.7) |
| $NO_2$ | $CH_3CH_2$ | $C_{12}H_{15}N_3SO_3$ | 51.2 | 5.4 | 15.0 |
| | | 171-174 | (51.2) | (5.37) | (14.9) |
| | $CH_3(CH_2)_3$ | $C_{16}H_{24}N_3SO_3$ | 49.8 | 6.1 | 10.7 |
| | | Impure Oil | (57.0) | (6.9) | (12.5) |
| $OCH_3$ | $CH_3CH_2$ | $C_{13}H_{18}N_2SO$ | 58.7 | 6.4 | 10.5 |
| | | 135 | (58.6) | (6.8) | (10.5) |

a - Calculated percentages in brackets

### 3.2.2 Mass Spectroscopy

Mass spectroscopy is extremely useful for the identification of compunds. The spectrometer converts the sample into ions, the masses of which may be resolved according to their mass to charge ratio (m/e). Valuable structural information is obtained from the molecular ion ($m^+$) and fragmentation patterns, which are characteristics of the compound. Under favourable conditions molecular ions are observed at a mass corresponding to the molecular weight of the original neutral molecules, thus determining the molecular weight of the compound to the nearest whole number [41].

A mass spectrum of N,N-dibutyl-N'-benzoylthiourea is illustrated in figure 3.1 and showed typical fragmentation pattern characteristic of N,N-dialkyl-N'-benzoylthioureas, the fragmentation pattern itself giving useful information. Analogous diethyl and dibutyl dirivatives have common m/e peaks due to the similar portion of the compounds, ($X-C_6H_4-C(O)-NH-C(S)-N^+$). The m/e = 72 and m/e = 128 were found in diethyl and dibutyl dirivatives respectively, which may be ascribed to the intact amine fragment, $(CH_3CH_2)_2N+$ and $(CH_3(CH_2)_3)_2N+$ respectively. The above fragments together with molecular ions can be used in identification of these compounds. In addition to several characteristic fragmentations, low intensity molecular ions were detected (Table 3.2). It is obvious that the desired compounds are obtained since the molecular ions agree with the calculated molecular weights within the experimental limits (±2).

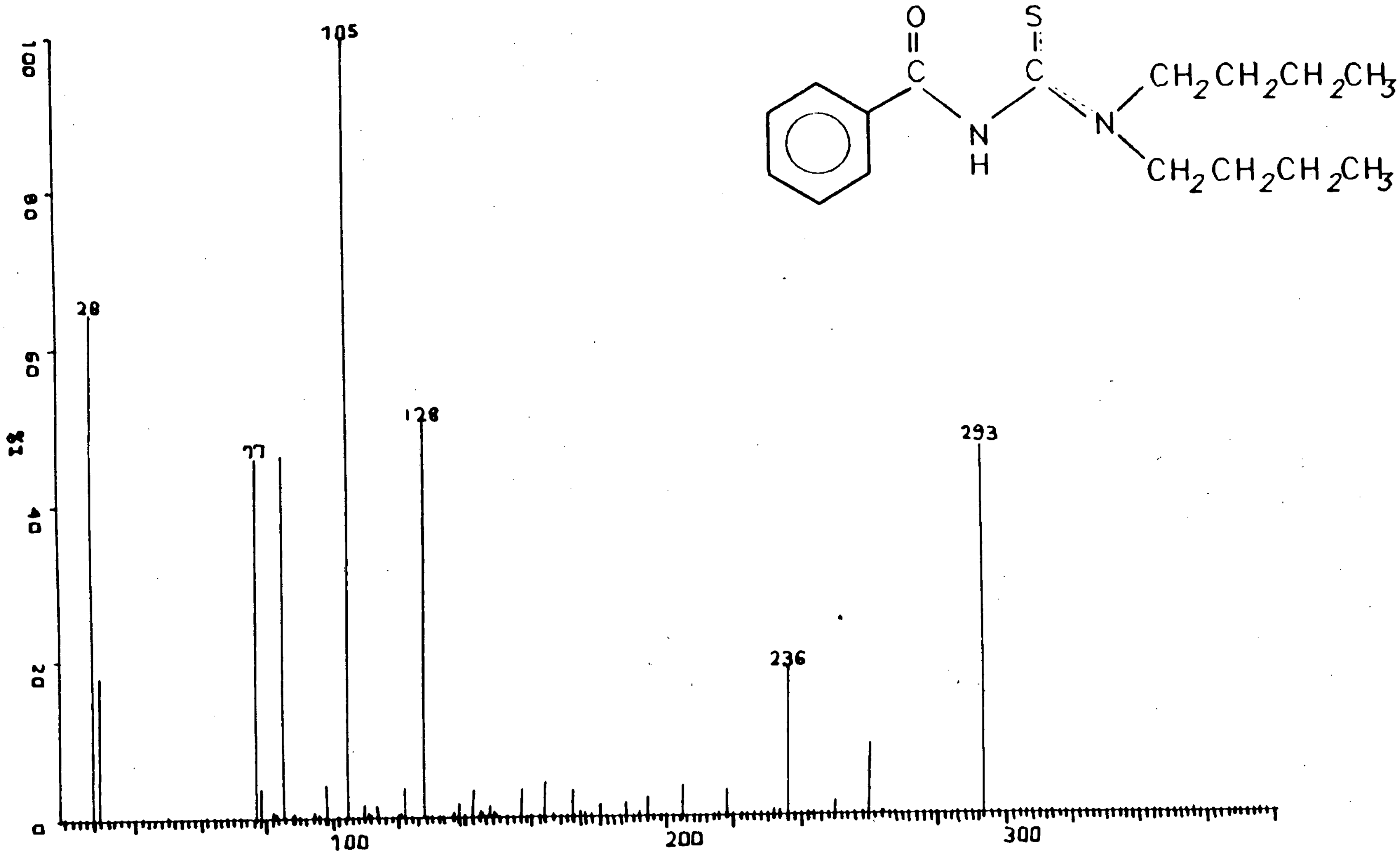
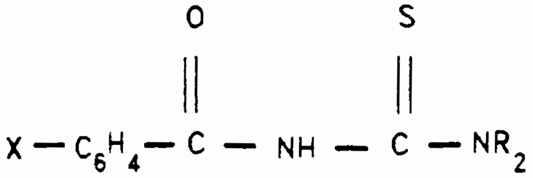


Figure 3.1 Mass spectrum of N,N-dibutyl-N-benzoylthiourea

TABLE 3.2 Mass spectra data for N,N′-dialkylbenzoylthioureas



$X-C_6H_4-C(=O)-NH-C(=S)-NR_2$

| Compound X | R | Molecular Weight | Molecular ion (m/e) | Principal ion (m/e) | Important Ions (m/e) |
|---|---|---|---|---|---|
| LH | $CH_3CH_2$ | 236.3 | 237 | 72 | 105, 77, 44 |
| | $C_6H_5CH_2$ | 292.4 | 293 | 105 | 128, 77, 44 |
| Cl | $CH_3CH_2$ | 270.8 | 271 | 72 | 139, 111, 44 |
| | $CH_3(CH_2)_3$ | 326.9 | 328/327 | 139 | 128, 105, 86, 111 |
| Br | $CH_3CH_2$ | 318.6 | 316/318 | 184 | 72, 156 |
| | $CH_3(CH_2)_3$ | 371.6 | 372/374 | 184 | 129, 157 |
| I | $CH_3CH_2$ | 362.2 | 364 | 76 | 72, 204, 104 |
| | $CH_3(CH_2)_3$ | 418.3 | 418 | 231 | 128, 203, 104 |
| $NO_2$ | $CH_3CH_2$ | 281.3 | 281 | 150 | 72, 104, 120 |
| $OCH_3$ | $CH_3CH_2$ | 266.4 | 267 | 135 | 72, 107, 194 |
| | $CH_3(CH_2)_2$ | 360.5 | 360 | 90 | 104, 111, 77 |

### 3.2.3 Nuclear Magnetic Resonance of N,N-dialkyl-N′-benzoylthioureas

Nuclear Magnetic Resonances (NMR) is commonly used in structure investigation of organic and organometallic compounds. The NMR is based upon the measurement of absorption electromagnetic radiation in the radio frequency region. The absorption involves the nuclei of atoms having nuclear spin and magnetic moments. A number of books [42-44] discuss the principles, theory and practise of NMR. Valuable structural information may be obtained from spectra in terms of characteristic chemical shifts and spin-spin coupling constants.

In this study use was made of $^{1}H$ and $^{13}C$ NMR. Physical properties relating to $^{1}H$ and $^{13}C$ spectra are listed in Table 3.3. Experimental details of the measurements are described in Chapter 2, section 2.4.

TABLE 3.3 Physical properties relating to $^{1}H$ and $^{13}C$ spectra

| | $^{1}H$ | $^{13}C$ |
|---|---|---|
| Rel. Abundance % | 99.95 | 1.11 |
| Spin I | ½ | ½ |
| Magnetic moment (u) (in multiples of nuclear magneton) | 2.7927 | 0.70216 |
| Lamor frequency $\sqrt{}$ (at 23.4KG) | 100 MHZ | 25.5 MHZ |
| Rel. Sensitivity for equal no. of nuclei | 1 | $^{1}/_{64}$ |
| Rel. Sensivity of natural abundances | 1 | $^{1}/_{5800}$ |

## BACKGROUND THEORY

### CHEMICAL SHIFTS

Chemical shifts arise from the secondary magnetic fields produced by the circulation of electrons in the molecules. Thus when a nucleus is observed in the same external magentic field but in different chemical environments, then the displacement of the resonance line is observed. The NMR spectrum of compounds arises from chemical shifts resonances patterns of the groups present. The groups experience slightly different magnetic fields and hence resonate at slightly different values of radio frequency values at magnetic field.

It is evident that the chemical shift is a relative term. As a result its measurement requires an arbitrary chosen standard. In $^{1}H$ and $^{13}C$ NMR tetramethylsitane (TMS) is the conventional standard. Chemical shifts are commonly measured as follows:

$$\delta = \frac{\nu \text{ substance} - \nu \text{ reference}}{\nu_0 \text{ (MHz)}}$$

$\nu_0$ is the operating frequency of the spectrometer employed [43]. Studies [44] revealed that chemical shifts are influenced by substituents in the molecule and that they can also be expressed by an empirical relationship

$$\delta = A + \sum B_i N_i k$$

where $A$ - appropriate compound (unsubstituted)

$B_i$ - i substituted effect

$N_i k$ - no. of substituents of type i relative to k

Charts of substituent effects are found in several books [42,43]. These charts are used in calculation of expected chemical shifts which helps in peak assignment.

## SPIN - SPIN COUPLING

In practise many $^1$H spectra appear to have multiplicity of the NMR signals. The resonances may appear as triplets or quartets due to spin-spin coupling of neighbouring protons. Spin-spin coupling is the result of magnetic interaction between non-equivalent protons by the network of bonding electrons through which the protons are directly connected. The appearance of these multiplets is very characteristic and contains much information additional to that gained from the chemical shifts. First order splitting due to n equivalent spin $I = \frac{1}{2}$ nuclei is n + 1. The intensities of the lines are given by the binomial coefficients $(a+1)^n$ [45].

In most spectra the line intensities and the number of the multiplets are not exactly as predicted by simple first order theory above. These distortions occur when the difference in the chemical shifts for a set of non-equivalent nuclei are small compared to the coupling constants. A further complication can arise due to resonances overlap resulting in spectra of complex appearance. These effects are often termed "second-order effects" and are common in $^1$H NMR.

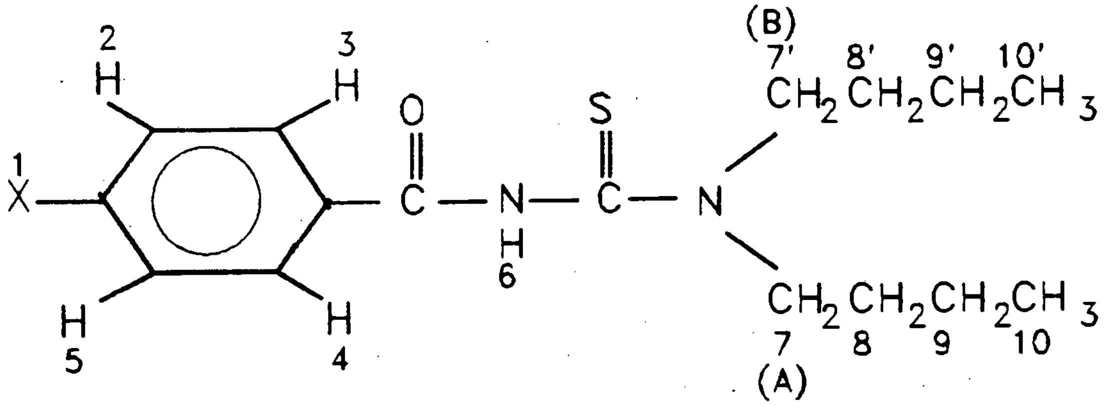
Spin-spin coupling between different neigbouring nuclei in a molecule occcurs when two nuclei are able to sense each others magnetic field. These spin couplings (J), like that between similar nuclei, depends upon the number and order of the bonds intervening between the two nuclei. Generally couplings are transmitted more effectively through multiple bonds than through single bonded systems. The interaction is not usually observed over more than five or six bonds and tend to be attenuated as the number of bonds increases. Nevertheless many cases are known where coupling over two bonds is less than coupling over three bonds ($^2J<^3J$).

The magnitude of the interaction is measured in Hz and is affected by the magnetic moments of the two nuclei, the valence S electron density at the nucleus, basicity and polarizability of the two nuclei.

## RESULTS AND DISCUSSION

### $^1$H NMR SPECTRA

For convenience, the disubstituted benzoyl-thiourea is represented by the following structure for which also the numbering of $^1$H atoms is given.



The $^1$H NMR spectra were expected to consist of a singlet due to H(6) at low field, two doublets due to two sets of aromatic protons. The high field resonance pattern of triplet, quartet, triplet for dibutyl or quartet, triplet for diethyl derivatives due to the alkyl chains.

A $^1$H spectrum of N,N-dibutyl-N'-p-bromobenzoylthiourea (figure 3.2) shows a $^1$H resonance AB pattern characteristic of N,N-dialkyl-N'-benzoylthioureas. The spectra of para substituted N,N-dialkyl-N'-benzoylthioureas consisted of a singlet at low field in the range $\delta$=8.4 - 10.8 ppm, two doublets, symmetrically spaced with weak, strong, strong, weak intensity relation at $\delta$=7.5 - 8.3 ppm, characteristic of para substituted benzene. Unsubstituted analogues have an additional doublet at $\delta$ 7.91 ppm. The high field resonance pattern of two triplets, two multiplets (two partially resolved quartets), quartet (two partially resolved triplets) for dibutyl or two triplets, quartet (two partially resolved triplets) for diethyl derivatives.

Table 3.4 summarises the $^1$H NMR data. Assignment of these resonances was based on the type of multiplets and their resonance intergral values. H(2,5) and H(3,4) were assigned on the basis of calculated chemical shifts (See $^{13}$C NMR spectra section). Assignment of N,N-dibenzoyl-N'-benzoylthioureas was not possible due to resonance overlap.

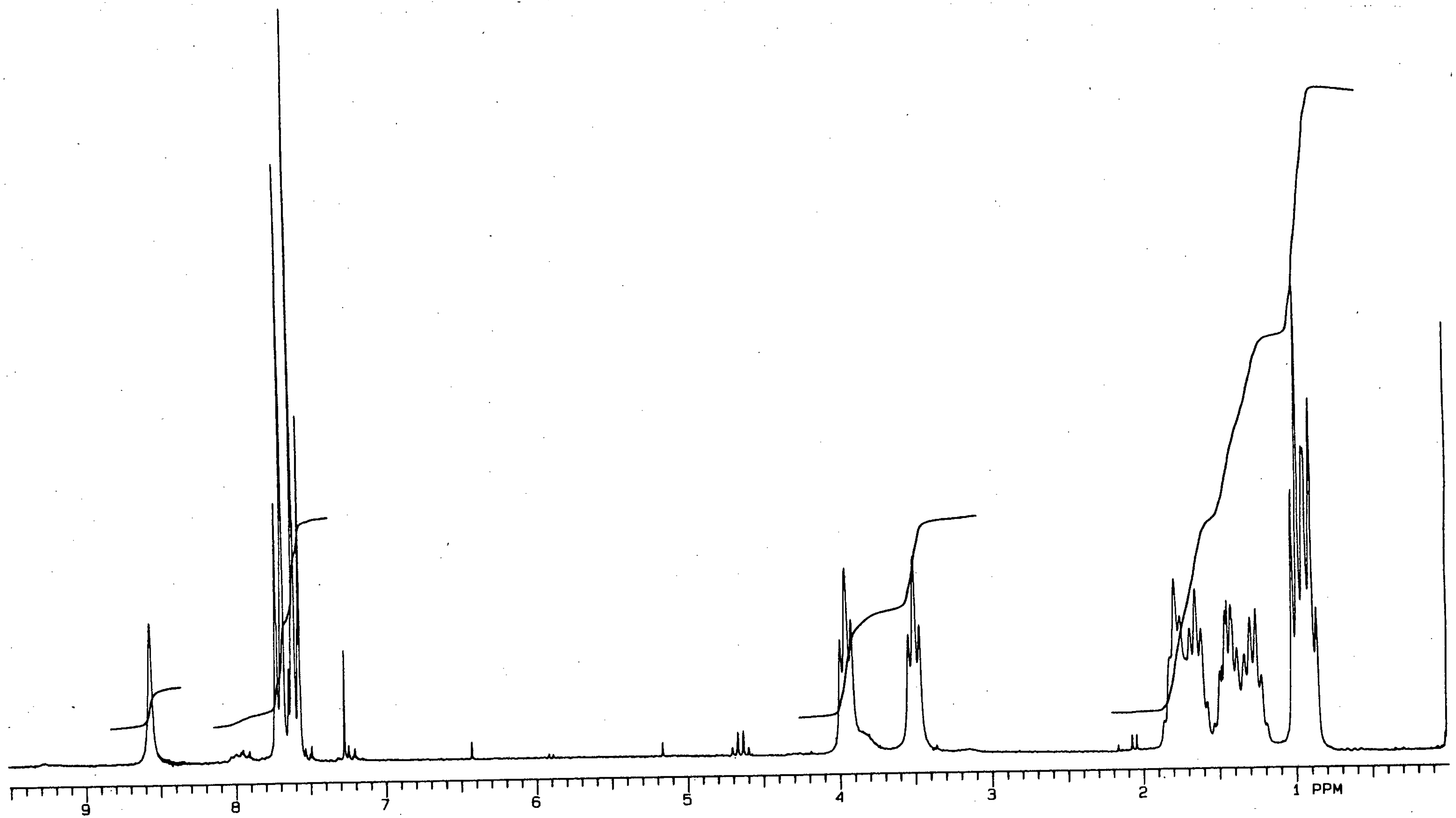
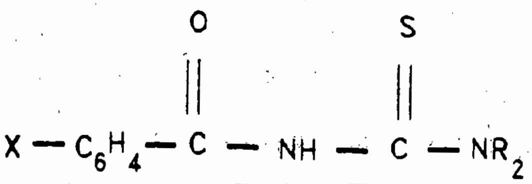


Figure 3:2 $^{1}H$ NMR spectrum of N,N-dibutyl-N-p-bromobenzoylthiourea

TABLE 3.4 $^1H$ NMR data of N,N-dialkyl-N'-benzoylthiourea



$$X-C_6H_4-\overset{O}{\overset{\|}{C}}-NH-\overset{S}{\overset{\|}{C}}-NR_2$$

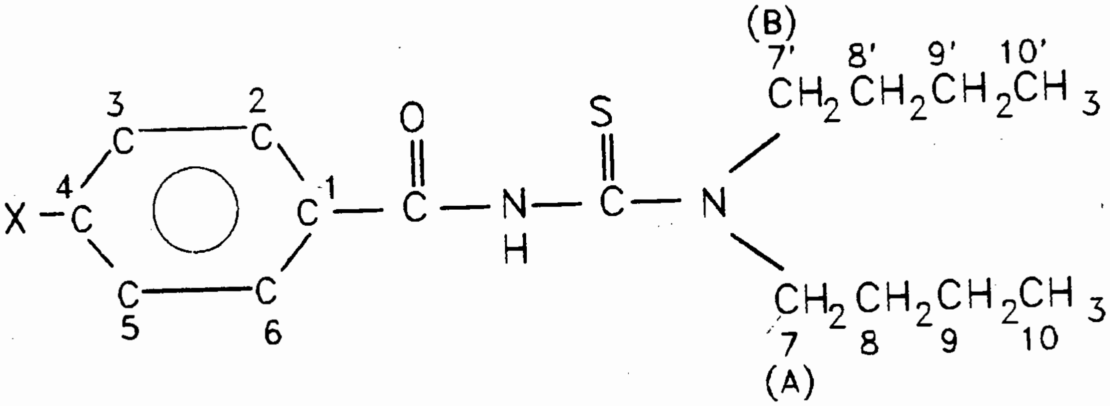
| Compound | | b | b | b | a | c | c | f | d | e |
|---|---|---|---|---|---|---|---|---|---|---|
| X | R | H(1) | H(2,5) | H(3,4) | H(6) | H(7) | H(7') | H(8,8') | H(9,9') | H(10,10') |
| H | Ethyl | 7.91 | 7,49 | 7.52 | 8.55 | 4.00 | 3.60 | 1.31 | | |
| | Butyl | 7.91 | 7.50 | 7.50 | 10.58 | 3.45 | 3.39 | 1.65 | 1.35 | 0.93 |
| Cl | Ethyl | - | 7.80 | 7.45 | 8.65 | 4.00 | 3.59 | 1.32 | | |
| | Butyl | - | 7.89 | 7.70 | 8.60 | 3.95 | 3.50 | 1.70 | 1.35 | 0.92 |
| Br | Ethyl | - | 7.72 | 7.60 | 8.65 | 4.00 | 3.60 | 1.31 | | |
| | Butyl | - | 7.70 | 7.60 | 8.60 | 3.95 | 3.49 | 1.70 | 1.35 | 0.92 |
| I | Ethyl | - | 7.80 | 7.54 | 8.45 | 3.99 | 3.59 | 1.29 | | |
| | Butyl | - | 7.78 | 7.53 | 8.35 | 3.93 | 3.48 | 1.70 | 1.35 | 0.92 |
| $NO_2$ | Ethyl | - | 8.27 | 8.21 | 10.81 | 4.00 | 3.57 | 1.31 | | |
| $OCH_3$ | Ethyl | - | 7.95 | 7.90 | 8.33 | 4.00 | 3.60 | 1.30 | | |

a - singlet
b - doublet
c - triplet
d - two partially resolved quartets
e - two partially resolved triplets
f - two partially resolved quartets (butyl) or two partially resolved triplets (ethyl)

An inspection of Table 3.4 shows that the different alkyl substituents induce slight chemical shift differences (0.0 - 2.1ppm) in analogous compounds. The chemical shift of H(6) being the most affected when compared to the other hydrogen atoms. Para-substituents also induce slight chemical shift differences (0.0 - 2.4ppm H(6) and H(2,5) being the most affected.

## $^{13}$C NMR spectra

The di-substituted-benzoylthioureas are in common practice represented by the following structure, which also shows the numbering of $^{13}$C atoms.



The $^{13}$C spectra were expected to consist of two low field resonances due to C = O (157 - 179 ppm) and C = S (180 - 195 ppm) [44], four resonances due to benzene moiety. In view of the presence of restricted rotation the high field resonances, due to alkyl chains, were expected to be eight (dibutyl) or four (diethyl).

N,N-dibutyl-N-p-bromobenzoylthiourea $^{13}$C spectrum (figure 3.3) shows a typical $^{13}$C spectra observed for the N,N-dialkyl-N'-benzoylthioureas studied. The spectra showed fourteen (dibutyl) or ten (diethyl) resonances which consisted of two low internsity signal carbon centred at $\delta$ 179.07 - 180.98 ppm and $\delta$ 167.58 - 163.89 ppm assigned to C = S and C = O respectively (assignment discussed later). Four resonances due to benzene moiety are characteristic of a para-substituted benzene. The high field part of the spectrum consisted of eight (dibutyl) or four (diethyl) resonances, further confirming presence of restricted rotation at C(S)-N bond(s) and highly indicating the (IV) structure. The spectra clearly show presence of one isomer.

Assignment of C = O and C = S resonances was based on the following arguments:

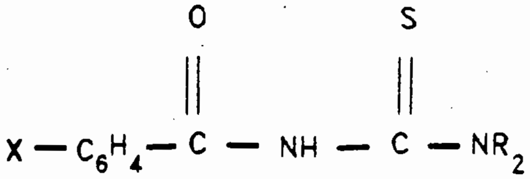
i) The chemical shift range of the C = S carbons $\delta$ 180 - 195 ppm while range for the N - C = O group is $\delta$ 152 - 179 ppm [44].

ii) Findings by Koch [53], that in case of the thiosemicarbazide, the C = S resonances appear at $\delta$ 179.6ppm.

iii) By comparison of substituents effect on the alkyl and para-substituents on 180 ppm and 163 ppm resonances.

Since the number of bonds between C = O and para-substituents is smaller compared to that between C = S and para-substituents, para-substituents may be expected to affect the C = S carbon atom more than that of C = O group. The reverse argument applies to the effect of alkyl substituents. Alkyl substituents were found to induce a variation of 0.3 - 1.6 ppm ( $\delta$ = 180 ppm) and 0.0 - 0.3 ppm ( $\delta$ = 163 ppm), while para-substituents induce 0.2 - 0.5 ppm ( $\delta$=180 ppm) and 0.9 - 1.30 ppm ( $\delta$ = 163 ppm).

TABLE 3.5 $^{13}C$ NMR data[a] for N,N-dialkyl-N'-benzoylthioureas in chloroform



$X-C_6H_4-\overset{\overset{O}{\|}}{C}-NH-\overset{\overset{S}{\|}}{C}-NR_2$

| X | R | Carbon number[c]<br>$C_1$ | $C_{2,6}$ | $C_{3,5}$ | $C_4$ | C=O | C=S | $C_{7/7'}$ | $C_{8/8'}$ | $C_{9/9'}$ | $C_{10/10}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| H | Ethyl | 132.7 | 128.8 | 132.9 | 127.4 | 163.9 | 179.4 | 47.9<br>(47.8) | 13.3<br>(11.5) | | |
| | Butyl | 133.0 | 128.0 | 128.0 | 132.2 | 163.9 | 180.9 | 51.69 | 28.8<br>(27.9) | 19.5<br>(20.0) | 13.8<br>(13.5) |
| Cl | Ethyl | 131.0 | 129.0 | 129.4 | 139.2 | 163.0 | 179.2 | 47.7 | 13.3<br>(11.5) | | |
| | Butyl | 131.0 | 129.3 | 129.1 | 139.4 | 162.8 | 179.6 | 53.3<br>(53.0) | 30.2<br>(28.4) | 20.1<br>(20.3) | 13.9<br>(13.7) |
| Br | Ethyl | 131.5 | 129.3 | 132.0 | 127.8 | 163.1 | 179.1 | 47.7<br>(47.3) | 13.3<br>(11.5) | | |
| | Butyl | 131.5 | 129.4 | 132.1 | 127.8 | 162.9 | 179.5 | 53.0 | 30.1<br>(28.4) | 20.0 | 13.9<br>(13.7) |
| I | Ethyl | 130.4 | 129.3 | 138.0 | 100.4 | 163.3 | 179.0 | 47.8<br>(47.7) | 13.3<br>(11.5) | | |
| | Butyl | 132.1 | 129.2 | 138.1 | 100.4 | 163.0 | 179.4 | 53.3<br>(53.0) | 30.1<br>(28.4) | 20.0 | 13.8<br>(13.7) |
| $NO_2$ | Ethyl | 138.6 | 129.5 | 123.2 | 149.6 | 162.6 | 179.9 | 47.5<br>(46.8) | 13.4<br>(11.1) | | |
| $OCH_3$ | Ethyl | 131.2 | 130.0 | 114.0 | 124.8 | 163.3 | 179.9 | 47.8<br>(47.7) | 13.2<br>(11.6) | 55.5[b] | |

a - carbon of B chain in brackets
b - $OCH_3$ carbon
c - carbon numbering shown in the text

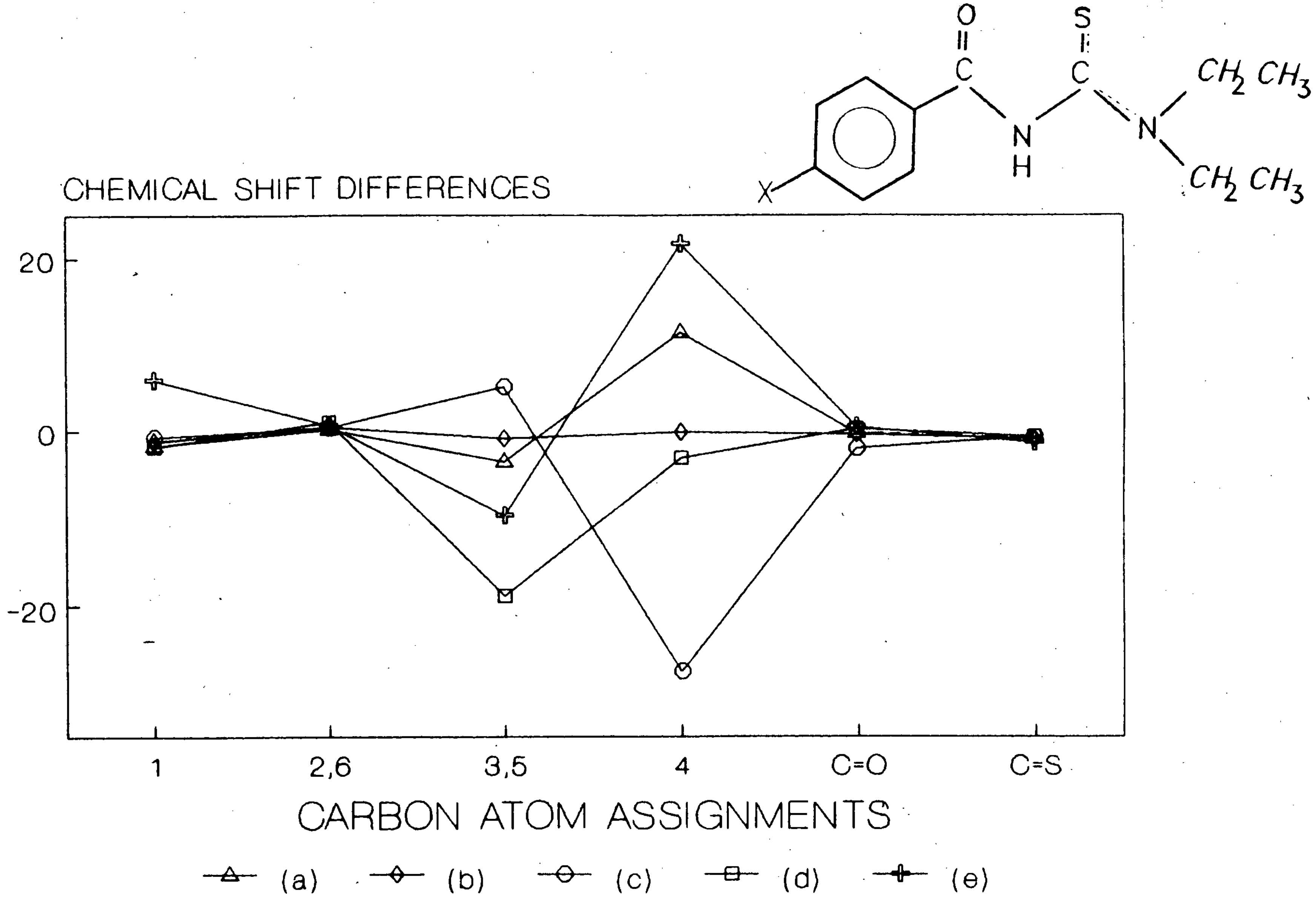


**Figure 3.4** The effect of para-phenyl substituents (X) of N,N-diethyl-N-benzoylthioureas on the chemical shifts of carbon atoms, where (X) = (A) Cl, (B) Br, (C) I, (D) $OCH_3$ and (E) $NO_2$

(149.6 > 139.2 > 127.9 > 127.8 > 124.84 > 100.36). These observations are consistent with calculated chemical shifts of para-substituted benzoyl chloride [X - $C_6H_4COCl$] where X = $NO_2$, Cl, Br, $OCH_3$ and I, which yield calculated chemical shift of $C_4$ of 155.5, 135.5, 141.7, 130.0, 103.5 respectively. Furthermore, the data indicates that para-substituent effects decrease with an increase in number of bonds between the substituent and the carbon of interest. Hence, $C_4$ and $C_{3/5}$ are most affected.

## 3.3 PREPARATION OF BIS (N,N'-DIALKYL-N'-BENZOYLTHIOUREAS) METAL COMPLEXES

Bayer et al [29] noted that N,N-dialkyl-N'-benzoylthioureas form neutral bis chelates with divalent metal ions. Precipitation is usually effected in water-alcohol solutions. Owing to low the solubility of N,N-dialkyl-N'-benzoylthioureas in water, addition of aqueous solutions of the metal ions to ethanolic solutions containing the ligand in the appropriate molar ratio was preferred to minimize possible ligand precipitation. A slight excess of metal solution was used so as to ensure that the complexation reaction proceeds to the completion. The reaction is assumed to proceed in two steps, formation of a charged $Pt(LH_2)^{2+}$ cationic complex which, by a loss of $2H^+$ ions, yields a neutral $PtL_2$ complex. Overall reaction can be summarised by the following equations using Pt (II) metal.

$$\begin{array}{l} \mathrm{PtCl_4}^{2-} + 2\ \mathrm{LH} \longrightarrow \mathrm{Pt}\ (\mathrm{LH_2})^{2+} + 4\mathrm{Cl}- \\ \mathrm{Pt}\ (\mathrm{LH_2})^{2+} \quad \xrightarrow{\underline{\text{Rapid}}} \quad \mathrm{Pt(L)_2} + 2\mathrm{H}^{+} \\ \hline \mathrm{PtCl_4}^{2-} + 2\mathrm{LH} \longrightarrow \mathrm{Pt(L)_2} + 4\mathrm{Cl}^{-} + 2\mathrm{H}^{+} \end{array}$$

The N,N-dialkyl-N'-benzoylthioureas and para-substituted analogues of the metal complexes of Pt(II), Pd(II), Cu(II) and Ni(II) were thus prepared. Experimental details are discussed in Chapter 2, section 2.3. This method gives relatively high yields of pure complexes. The metal chelates produced in this study are brightly coloured; colour depending on metal Pt(II) yellow, Pd(II) yellow to brown, Ni(II) red to violet and Cu(II) green. All the metal chelates are insoluble in water but highly soluble in chloroform.

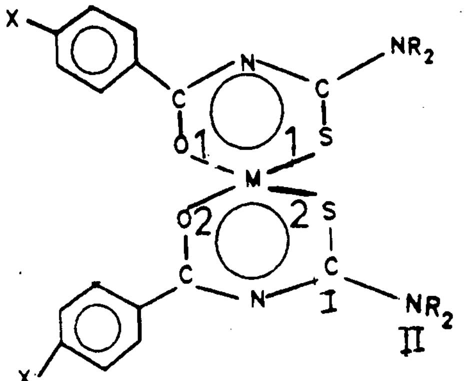
## 3.4 CHARACTERIZATION OF BIS (N,N'-DIALKYL-N'-BENZOYLTHIOUREAS) METAL COMPLEXES

The structure of several bis (N,N-dialkyl-N'-benzoylthioureas) metal complexes has been established by several workers using X-ray crystallography, infra-red spectroscopy and ESR spectroscopy [38-40].

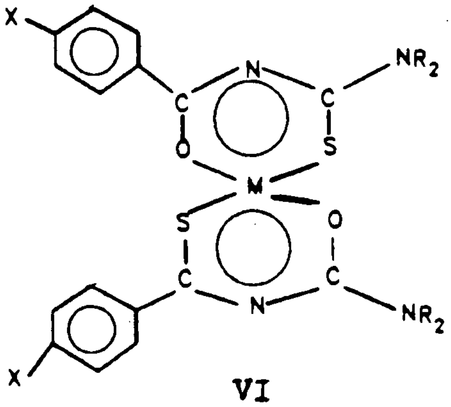
These studies involved several N,N-dialkyl-N′-benzoylthiourea complexes of Pd(II), Ni(II) and Cu(II). These studies showed that there is no significant difference between the M-S(1) (2.123 Å) and M-S(2) (2.144 Å) bonds and that M-O(I) (1.863 Å) and M-O(2) (1.856 Å) are equal within error limits [39]. (See (V).) In addition these studies showed that in general the oxygen and sulphur atoms are co-ordinated to the metal atom and that C(I) - N(II) bond is shorter than single C - N bond [29].

In majority of bis complexes with Pd(II), Ni(II) and Cu(II), square planar geometry is preferred [35]. In case of square planar complexes *cis* (V) and *trans* (VI) isomes may be expected. To date however, a survey of the literature [38-40] shows that only *cis*(V) complexes have been characterised.

Irving and Koch [46] determined the structure of Pt(II) and Pd(II) complexes of N,N-dibutyl-N′-benzoylthiourea by X-ray crystal structure and they found these complexes to be the *cis* isomers. On the basis of the literature [38-40, 46], the Pt, Pd, Cu and Ni complexes prepared are assumed to be *cis* and square planar.



V



VI

### 3.4.1 Elemental analysis and melting points

Elemental analysis and melting points of the metal complexes prepared were determined, to test the purity as well as to confirm the stoichiometry of the complexes prepared. Elemental analysis data as well as corresponding melting points are given in Table 3.6 for Cu(II) and Ni(II), Table 3.7 for Pd(II) and Table 3.8 for Pt(II) complexes. Examination of these tables showed that these complexes have relatively high melting points (>90°C).

The calculated and observed percentages of C,H and N are equivalent within experimental error. This observation clearly indicates that the method gives the desired compounds in relatively pure form. (All complexes were recrystallized from chloroform/methanol mixture.)

TABLE 3.6 Elemental analysis [a] and melting points data of bis (N,N-dialkyl-N'-benzoylthiourea) Cu (II) and Ni (II) complexes

| | | Molecular formula | Elemental | Analysis | % |
|---|---|---|---|---|---|
| X | Metal | MP °C | C | H | N |
| H | Cu | $C_{24}H_{30}N_4O_2S_2Cu$ | 51.7 | 5.6 | 10.3 |
| | | 117-119 | (53.96) | (5.7) | (10.5) |
| | Ni | $C_{24}H_{30}N_4O_2S_2Ni$ | 54.6 | 5.7 | 10.6 |
| | | 138-139 | (54.5) | (5.7) | (10.6) |
| $NO_2$ | Cu | $C_{24}H_{30}N_6O_6S_2Cu$ | 45.8 | 4.4 | 13.3 |
| | | 210-212 | (46.2) | (4.5) | (13.5) |
| | Ni | $C_{24}H_{30}N_6O_6S_2Ni$ | 46.8 | 4.7 | 13.8 |
| | | 279-281 | (46.5) | (4.6) | (13.6) |
| $OCH_3$ | Cu | $C_{26}H_{34}N_4O_2S_2Cu$ | 52.9 | 6.0 | 9.5 |
| | | 122-124 | (52.6) | (5.8) | (9.4) |
| | Ni | $C_{26}H_{34}N_4O_2S_2Ni$ | 53.0 | 5.9 | 9.5 |
| | | 170-171 | (53.0) | (5.8) | (9.5) |

a - calculated percentage in brackets
R = $CH_3CH_2$

TABLE 3.7 Elemental analysis [a] and melting points data for bis (N,N-dialkyl-N′-benzoylthiourea) Pd(II) complex.

| Compound | | Molecular formular | Elemental | Analysis | % |
|---|---|---|---|---|---|
| X | R | MP °C | C | H | N |
| H | $CH_3CH_2$ | $C_{24}H_{30}N_4O_2S_2Pd$ | 50.0 | 5.4 | 9.1 |
| | | 140-141 | (50.0) | (5.2) | (9.7) |
| | | (139-146)[29] | | | |
| | $CH_3(CH_2)_3$ | $C_{32}H_{46}N_4O_2S_2Pd$ | 55.9 | 6.7 | 8.1 |
| | | 144-145 | (55.8) | (6.7) | (8.1) |
| | $C_6H_5CH_2$ | $C_{44}H_{36}N_4O_2S_2Pd$ | 64.8 | 4.7 | 6.4 |
| | | 207-209 | 64.2 | 4.42 | 6.81 |
| Br | $CH_3CH_2$ | $C_{24}H_{28}N_4O_2S_2BrPd$ | 38.9 | 3.7 | 7.4 |
| | | 170-171 | (38.9) | (3.8) | (7.6) |
| | $CH_3(CH_2)_3$ | $C_{32}H_{44}N_4O_2S_2BrPd$ | 45.2 | 5.3 | 6.6 |
| | | 150-151 | (45.4) | (5.2) | (6.6) |
| I | $CH_3CH_2$ | $C_{24}H_{28}N_4O_2S_2IPd$ | 34.5 | 3.4 | 6.7 |
| | | 214-216 | (34.8) | (3.4) | (6.8) |
| | $CH_3(CH_2)_3$ | $C_{32}H_{44}N_4O_2S_2IPd$ | 40.5 | 4.6 | 5.9 |
| | | 171-172 | (40.8) | (4.7) | (6.0) |
| Cl | $CH_3CH_2$ | $C_{24}H_{28}N_4O_2S_2ClPd$ | 44.5 | 4.5 | 8.6 |
| | | 180-181 | (44.6) | (4.4) | (8.7) |
| | $CH_3(CH_2)_3$ | $C_{32}H_{44}N_4O_2S_2ClPd$ | 50.6 | 5.8 | 7.4 |
| | | 138-140 | (50.7) | (5.9) | (7.4) |
| $NO_2$ | $CH_3CH_2$ | $C_{24}H_{28}N_6O_6S_2Pd$ | 43.2 | 4.00 | 12.7 |
| | | 262-264 | (43.2) | (4.2) | (12.6) |
| | $CH_3(CH_2)_3$ | $C_{32}H_{44}N_6O_6S_2Pd$ | 48.2 | 5.2 | 10.6 |
| | | 190-191 | (49.3) | (5.7) | (10.8) |
| $OCH_3$ | $CH_3CH_2$ | $C_{26}H_{34}N_4O_4S_2Pd$ | 49.0 | 5.3 | 8.8 |
| | | 180-183 | (49.0) | (5.7) | (8.8) |

a - calculated percentage in brackets

TABLE 3.8 Elemental analysis [a] and melting points data for bis (N,N-dialkyl-N'-benzoylthiourea) Pt(II) complex.

| Compound | | Molecular formula | Elemental | Analysis | % |
|---|---|---|---|---|---|
| X | R | M.P°C | C | H | N |
| H | $CH_3CH_2$ | $C_{24}H_{30}N_4S_2O_2Pt$ | 43.1 | 4.6 | 8.3 |
| | | 125-130 | (43.3) | (4.5) | (8.4) |
| | $CH_3(CH_2)_3$ | $C_{32}H_{46}N_4S_2O_2Pt$ | 48.9 | 5.9 | 6.9 |
| | | 164-166 | (49.4) | 6.0 | (7.2) |
| | $C_6H_5CH_2$ | $C_{44}H_{36}N_4S_2O_2Pt$ | 57.2 | 4.4 | 6.1 |
| | | | (57.8) | 4.2 | (6.1) |
| Cl | $CH_3CH_2$ | $C_{24}H_{28}N_4S_2O_2ClPt$ | 39.3 | 3.9 | 7.6 |
| | | 214-218 | (39.2) | 3.8 | (7.6) |
| | $CH_3(CH_2)_3$ | $C_{32}H_{44}N_4S_2O_2ClPt$ | 44.8 | 5.1 | 6.6 |
| | | 160-166 | (45.4) | 5.2 | (6.6) |
| Br | $CH_3CH_2$ | $C_{24}H_{28}N_4S_2O_2BrPt$ | 34.7 | 3.4 | 6.8 |
| | | 220-223 | (34.7) | (3.4) | (6.8) |
| | $CH_3(CH_2)_3$ | $C_{32}H_{44}N_4S_2O_2BrPt$ | 41.0 | 4.6 | 5.9 |
| | | 170-174 | (41.1) | (4.7) | (6.0) |
| I | $CH_3CH_2$ | $C_{24}H_{28}N_4S_2O_2IPt$ | 31.3 | 3.0 | 6.1 |
| | | 213-216 | (31.4) | (3.1) | (6.1) |
| | $CH_3(CH_2)_3$ | $C_{32}H_{44}N_4S_2O_2IPt$ | 37.1 | 4.2 | 5.2 |
| | | 216-220 | (37.3) | (4.3) | (5.4) |
| $NO_2$ | $CH_3CH_2$ | $C_{24}H_{28}N_6O_6S_2Pt$ | 38.0 | 3.7 | 11.3 |
| | | 200-205 | (38.1) | (3.7) | (11.1) |
| | $CH_3(CH_2)_3$ | $C_{32}H_{44}N_6O_6S_2Pt$ | 44.1 | 5.1 | 9.7 |
| | | >300 | (44.3) | (5.1) | (9.7) |
| $OCH_3$ | $CH_3CH_2$ | $C_{26}H_{34}N_4O_4S_2Pt$ | 42.9 | 4.8 | 7.6 |
| | | 135-148 | (43.0) | (5.0) | (7.7) |

a - calculated percentage in brackets.

### 3.4.2 Nuclear magnetic resonances of bis (N,N-dialkyl-N'-benzoylthioureas) metal complexes

The Pt(II) and Pd(II) complexes are diamagnetic and thus readily examined by $^{1}H$, $^{13}C$ and $^{195}Pt$ NMR. Not so for Ni(II) and Cu(II) complexes as these complexes are paramagnetic which results in very broad $^{1}H$ and $^{13}C$ NMR resonances, therefore not readily examinable by NMR.

The NMR spectra of Pt(II) and Pd(II) complexes arise from the complexed ligand structure through chemical shifts and coupling constants which are slightly different from those of the free ligand [44]. The $^{1}H$, $^{13}C$ and $^{195}Pt$ NMR were measured and experimental details are discussed in Chapter 2, section 2.4.

The $^{195}Pt$ isotope natural abundances 33.7% has nuclear spin I = ½, has been used successfully since 1977 [47] due to the introduction of pulsed NMR. Direct measurement of $^{195}Pt$ resonances in some Pt complexes by Pidcock et al [48] and Zelewsky [49] showed that $^{195}Pt$ chemical shifts, cover a wide range, are sensitive to ligands present in the co-ordination sphere and even their arrangement. The $^{195}Pt$ chemical shifts are affected by temperature and solvent. Solvents effects of up to 400 ppm has been observed on going from $H_2O$ to DMSO, with the latter appearing at higher field [47]. Temperature effects are small (< 1.0 ppm per 6°C) but a change of 100°C could result in 40-50 ppm shift [47]. As a consequence $^{195}Pt$ spectra were always measured at the same temperature (30°C) relative to the same reference (500mg $H_2PtCl_6$ in HCl containing 30% $D_2O$ V/V) and in the same solvent $CDCl_3$.

# RESULTS AND DISCUSSION

## $^1$H NMR spectra

The fact that the two ligands around the metal (Pd(II), Pt(II)) are equivalent, results in relatively simple spectra. The $^1$H NMR spectra of bis(N,N-dialkyl-N′-benzoylthiourea) Pd(II) and Pt(II) complexes are expected to be quite similar to $^1$H spectra of analogous N,N-dialkyl-N′-benzoylthioureas, although slight chemical shift differences were expected. One major difference of the $^1$H spectra of complexes and that of free ligands expected is the missing of ′N-H proton in the $^1$H spectra of these complexes. The expectations are based on the elemental analysis, which confirms formation of neutral complexes and on the literature [38-40,46] where all results showed absence of ′N-H in complexes. The similarity of free ligands and complexes $^1$H spectra make the numbering and assignment of $^1$H atoms given in section 3.2.3 valid for $^1$H atoms of complexes.

The $^1$H NMR spectra of Pd(II) and Pt(II) bis (N,N-dibutyl-N′-p-bromobenzoylthiourea) complexes are displayed by figure 3.5 and 3.6 respectively, and they show a resonance pattern characteristics of $^1$H NMR spectrum of bis(N,N-dialkyl-N′-benzoylthiourea) metal complexes studied.

Observation of these $^1H$ NMR spectra (Pd(II), Pt(II) complexes) showed that the multiplets, due to the butyl or ethyl groups still show presence of restricted rotation as observed in the free ligand spectra (figure 3.2). The H(7') and H(7) are partially resolved, unlike in free ligands where they are completely resolved triplets. This indicates some change in the degree of restricted rotation due to the presence of metal. As expected, the H(6) resonance is missing.

A summary of $^1H$ data is given in Table 3.8 Pd(II) and Table 3.9 Pt(II). The $^1H$ data of Pd(II) complexes is similar to that of analogous Pt(II) complexes, with only slight chemical shift differences (< 0.2 ppm). Except for the complete absence of H(6) in complexes, comparison of $^1H$ data of complexes with that of analogous free ligands showed slight chemical shift difference (< 0.5 ppm). The chemical shift differences between complexes (Pd(II), Pt(II)) and analogous free ligands is not affected by the alkyl and para-substituents.

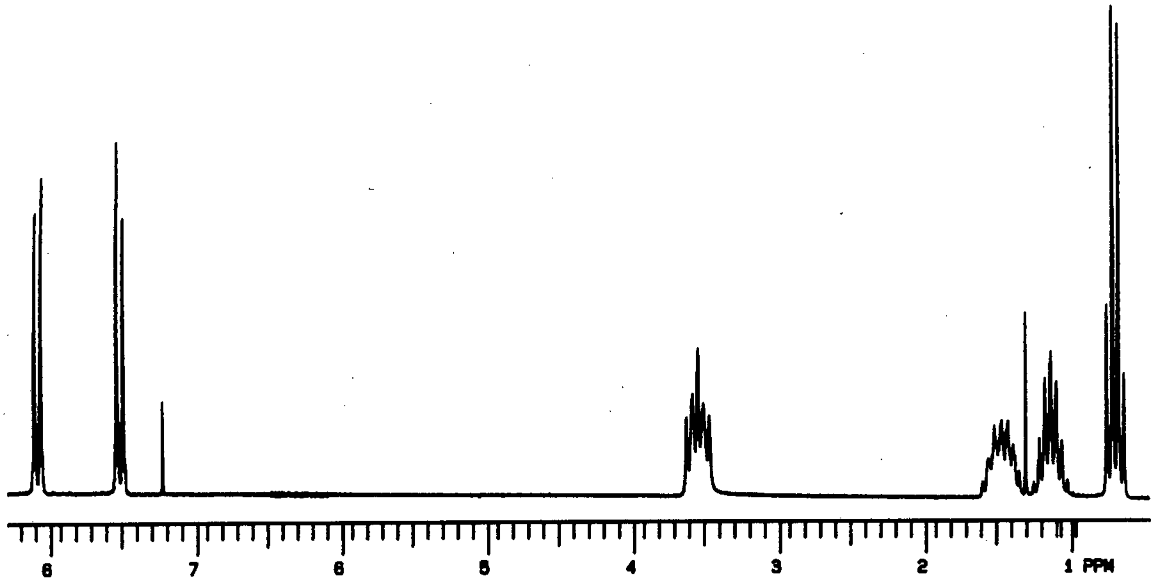


Figure 3.6 $^1$H NMR spectrum of (N,N-dibutyl-N-p-bromobenzoylthiourea) Pt(II) complex

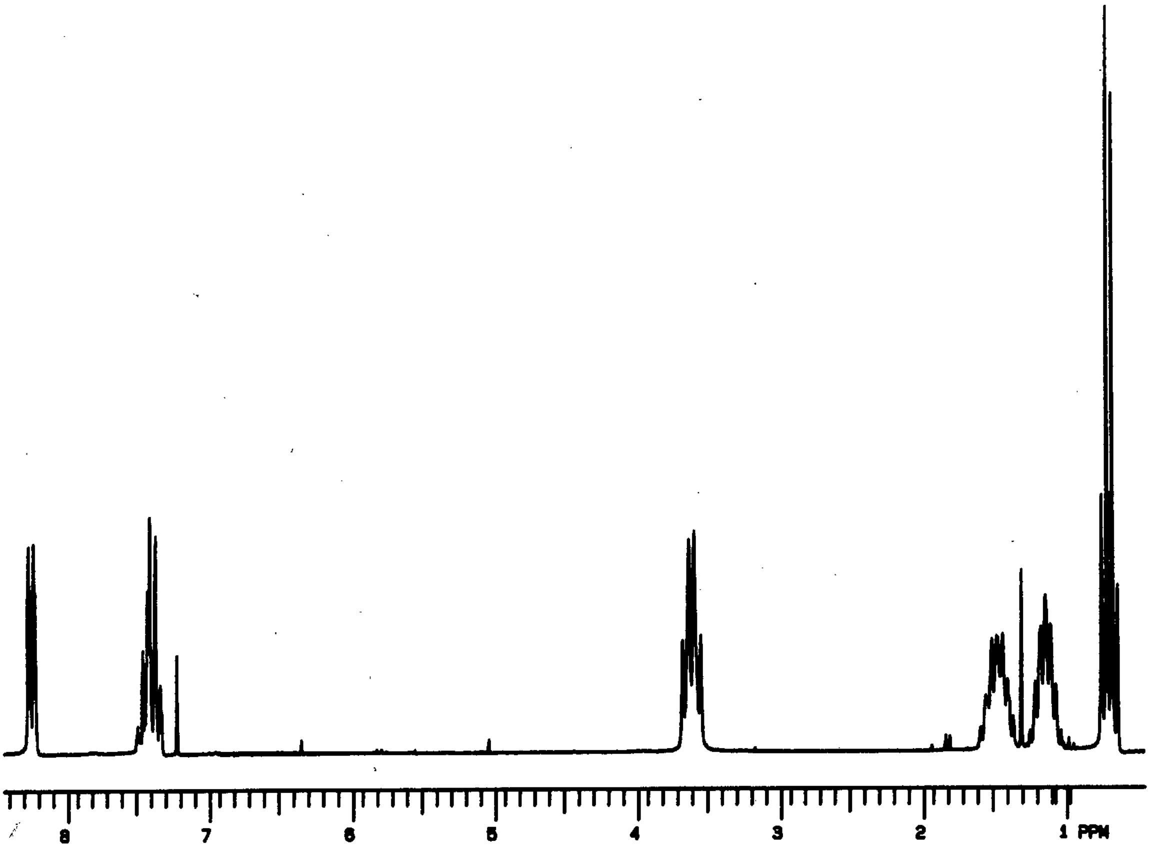
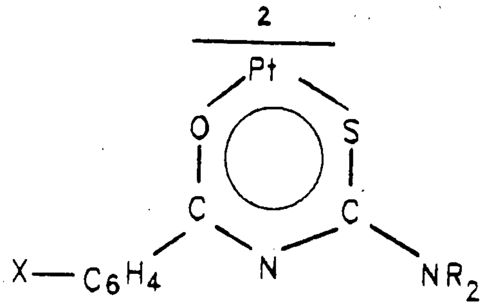


Figure 3.5 $^1$H NMR spectrum of (N,N-dibutyl-N-p-bromobenzoylthiourea) Pd complex

TABLE 3.9 $^1H$ NMR data of bis(N,N-dialkyl-N′-benzoylthiourea) Pt(II) in $CDCl_3$



| Compound X | R | H(1)[a] | H(2,5)[a] | H3,4[a] | H(7,7′)[c] | H(8,8′)[c] | H(9,9′)[c] | H(10,10′)[d] |
|---|---|---|---|---|---|---|---|---|
| H | Ethyl | 8.26 | 7.43 | 7.45 | 3.82 | 1.30[d] | | |
| | Butyl | 8.24 | 7.44 | 7.40 | 3.74 | 1.72 | 1.39 | 0.97 |
| Cl | Ethyl | | 8.13 | 7.39 | 3.78 | 1.29[d] | | |
| | Butyl | | 8.15 | 7.40 | 3.72 | 1.68 | 1.39 | 0.98 |
| Br | Ethyl | | 8.06 | 7.56 | 3.78 | 1.29[d] | | |
| | Butyl | | 8.10 | 7.60 | 3.79 | 1.40 | 0.89 | |
| I | Ethyl | | 7.92 | 7.78 | 3.78 | 1.36[d] | | |
| | Butyl | | 7.98 | 7.76 | 3.85 | 1.71 | 1.39 | 0.82 |
| $NO_2$ | Ethyl | | 8.38 | 8.27 | 3.75 | 1.74[d] | | |
| | Butyl | | 8.35 | 8.30 | 3.83 | 1.34 | 1.40 | 0.96 |
| $OCH_3$ | Ethyl | 3.86[e] | 8.22 | 6.96 | 3.80 | 1.27[d] | | |

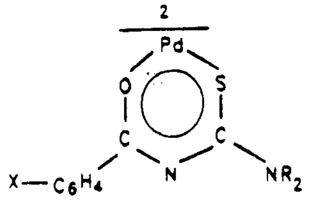
a - doublet b - two doublets

c - two partially resolved quartets

d - two partially resolved triplets

e - singlet due to $OCH_3$

TABLE 3.10 $^{1}H$ NMR data of bis (N,N-dialkyl-N'-benzoylthiourea) Pd(II) in $CDCl_3$



| | | b | b | b | c | c | c | d |
|---|---|---|---|---|---|---|---|---|
| X | | H(1) | H(2,6) | H(3,4) | H(7,7') | H(8,8') | H(9,9') | H(10,10') |
| X | Ethyl | 8.20 | 7.44 | 7.39 | 3.84 | 1.30$^{d}$ | | |
| | Butyl | 8.23 | 7.45 | 7.4 | 3.79 | 1.73 | 1.40 | 0.90 |
| Cl | Ethyl | | 8.15 | 7.40 | 3.83 | 1.31$^{d}$ | | |
| | Butyl | | 8.19 | 7.40 | 3.76 | 1.71 | 1.38 | 0.95 |
| Br | Ethyl | | 8.05 | 7.55 | 3.84 | 1.32$^{d}$ | | |
| | Butyl | | 8.09 | 7.56 | 3.77 | 1.71 | 1.39 | 0.98 |
| I | Ethyl | | 8.89 | 7.89 | 3.83 | 1.30$^{d}$ | | |
| | Butyl | | 7.89 | 7.78 | 3.76 | 1.72 | 1.39 | 0.96 |
| $NO_2$ | Ethyl | | 8.34 | 8.29 | 3.88 | 1.34 | | |
| | Butyl | | 8.33 | 8.28 | 3.86 | 1.72 | 1.42 | 0.90 |
| $OCH_3$ | Ethyl | 3.90$^{e}$ | 8.70 | 6.89 | 3.80 | 1.33$^{d}$ | | |

b - doublet c - two partially resolved quartets

d - two partially resolved triplets e - singlet

In general there is no $^{195}Pt$ - $^{1}H$ coupling visible and the similarity of ligand and complex spectra (except for the differences already mentioned) do not allow one to deduce whether the *cis* and *trans* isomer is formed. However, the proton spectra suggest only one isomer. To date however, literature [38-40, 46] showed that only *cis* complexes have been characterised. Hence it can be deduced that the proton spectra are probably due to the *cis* isomer.

### $^{13}C$ NMR spectra

The $^{13}C$ NMR spectra of Pd(II) and Pt(II) complexes are expected to show quite substantial similaritites to the $^{13}C$ NMR spectra of analogous free ligands. Thus the numbering and assignment of $^{13}C$ atoms discussed in Section 3.2.3 still holds in complexes. (Additional help in assignment is discussed later.)

The $^{13}C$ NMR spectra of Pt(II) (figure 3.7) and Pd(II) (figure 3.8) show typical resonance pattern characteristic of $^{13}C$ NMR spectra of bis (N,N-dialkyl-N'-benzoylthiourea) metal complexes in this study. The spectra show quite substantial similarities. They all consist of two low field resonances due to C = S and C = O, four aromatic resonances, eight (dibutyl) or four (diethyl) resonances in the high field. The $^{13}C$ NMR spectra of Pt(II) complexes showed $^{195}Pt$ - $^{13}C$ coupling as expected (discussed later).

The spectra of the complexes clearly show that the carbonyl carbon and the thiocarbonyl carbon atoms are not easily distinguished as compared to the free ligand spectra. The C = S moves upfield and the C = O moves downfield so that in complexes these carbon atoms have similar chemical shifts (170 - 172 ppm for Pd(II) and 167 - 170ppm for Pt(II)). These suggest that on average the thiocarbonyl and carbonyl carbon nuclei find themselves in the same electronic environment, since $^{13}C$ NMR shifts are approximately proportional to the effective electron density [44].

The change of electronic environment of these two resonances may be explained as follows:

i) The electrons of the unsaturated C = S bond are involved in the S- metal bond, so that the C = S bond order is reduced resulting in high field shift.

ii) The C = O due to the lone pairs on the oxygen has mesomeric effect, which may result in delocalization of the negative charge from the -N- with simultaneous increase in C = O bond order and low field shift.

In addition the complexes spectra showed that the restricted rotation at $C(S)-NR_2$ bond(s) is retained. The effect was not investigated, but it has been found in the literature [40] that different metals have different effects on the $C(S)-NR_2$ bond. Bayer et al [40] found that in N,N-diethyl-N'-benzoylthiourea metal complexes, restricted rotation increases in the following order: Ni(II) > Pb(II) > Co(III) and Tl(I) showed a decrease in restricted rotation.

The $^{13}C$ NMR data for the complexes is summarised in table 3.10 Pd(II) and table 3.11 Pt(II). The $^{13}C$ NMR data of Pd(II) is quite similar to that of Pt(II) complexes with slight chemical shifts differences (< 4 ppm). The thiocarbyl and carbonyl carbons resonances being the most different. Except for the thiocarbonyl carbon resonances with 12.5 ppm chemical shift differences, carbonyl and C(1) carbon resonances with 5.5 ppm chemical shift differences, the $^{13}C$ NMR data for complexes is similar to that of analogous ligands with chemical shift differences < 2.5 ppm.

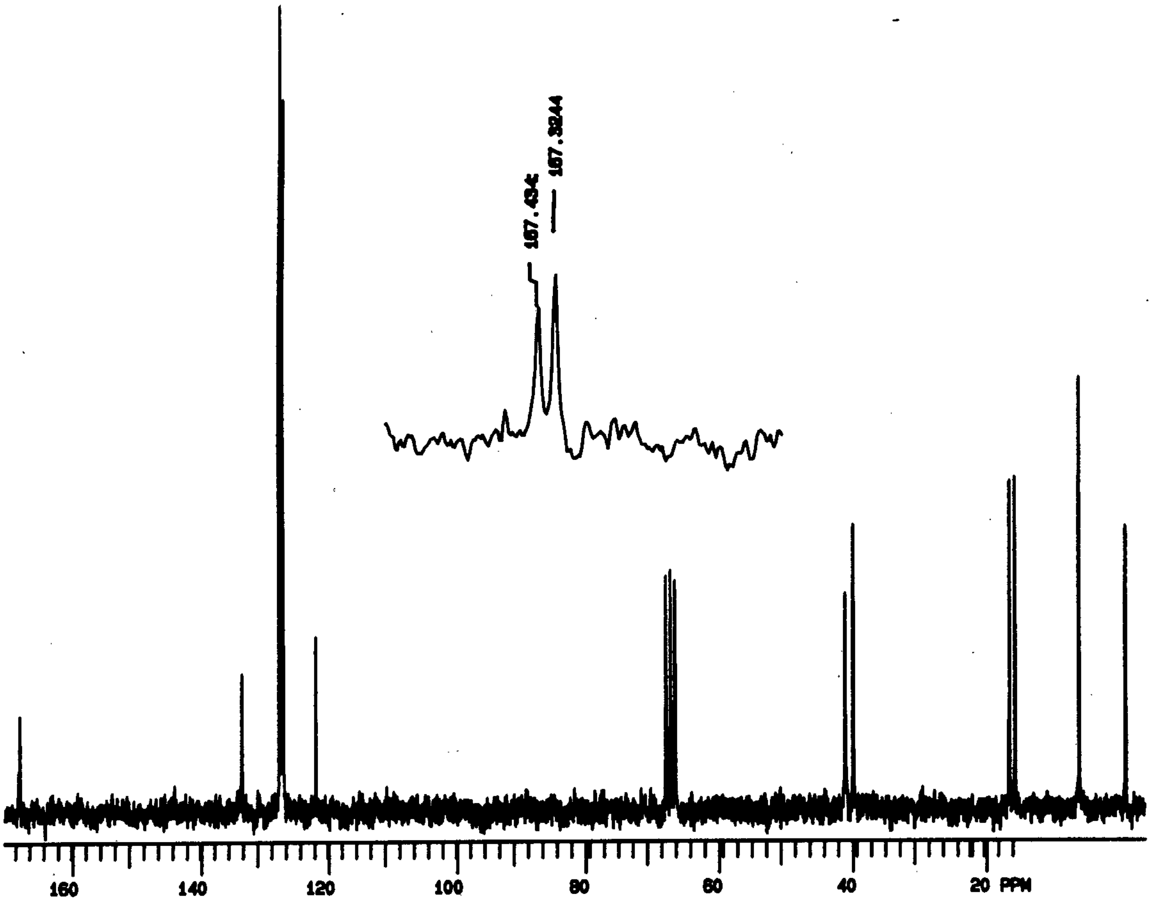


Figure 3.7 $^{13}C$ NMR spectrum of (N,N-dibutyl-N-p-bromobenzoylthiourea) Pt(II) complex

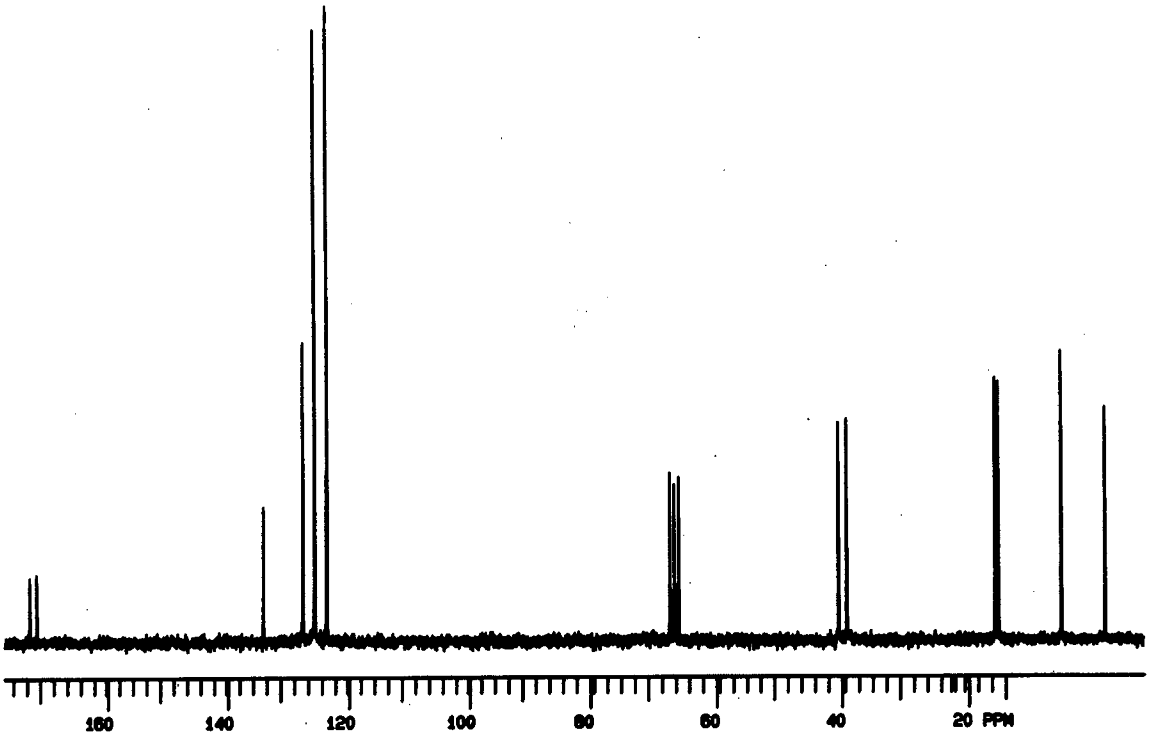
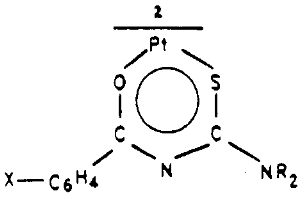


Figure 3.8 $^{13}C$ NMR spectrum of (N,N-dibutyl-N-p-bromobenzoylthiourea) Pd(II) complex

TABLE 3.11 $^{13}C$ NMR data[b] of bis (N,N-dialkyl-N′-benzoylthiourea) Pt(II) in $CDCl_3$

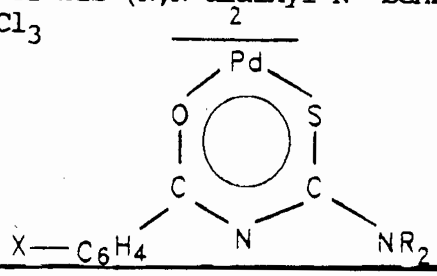


| Compound<br>X | R | $C_1$ | $C_{2,6}$ | $C_{3,5}$ | $C_4$ | C=O | C=S | $C_{7/7'}$ | $C_{8/8'}$ | $C_{9/9'}$ | $C_1$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| H | Ethyl | 137.6 | 129.3 | 128.0 | 131.3 | 168.4 | 167.0 | 47.0<br>(45.9) | 13.0<br>(12.4) | | |
| | Butyl | 137.6 | 129.2 | 128.0 | 131.3 | 168.2 | 167.3 | 52.6<br>(51.5) | 30.0<br>(29.3) | 20.3<br>(20.3) | 1<br>(1 |
| Cl | Ethyl | 137.6 | 130.7 | 128.4 | 136.1 | 167.4 | 167.1 | 47.1<br>(46.0) | 13.1<br>(12.4) | | |
| | Butyl | 137.1 | 130.7 | 128.3 | 137.6 | 167.5 | 167.3 | 52.7<br>(51.6) | 30.0<br>(29.2) | 20.3<br>(20.3) | 1<br>(1 |
| Br | Ethyl | 136.5 | 131.3 | 130.8 | 126.3 | 167.5 | 167.1 | 47.1<br>(46.0) | 13.1<br>(12.4) | | |
| | Butyl | 136.6 | 131.3 | 130.8 | 126.2 | 167.4 | 167.3 | 52.7<br>(52.6) | 29.9<br>(29.2) | 20.3<br>(20.3) | 1<br>(1 |
| I | Ethyl | 137.3 | 137.4 | 130.9 | 98.9 | 167.8 | 167.0 | 47.1<br>(46.0) | 13.1<br>(12.4) | | |
| | Butyl | 137.2 | 137.3 | 130.9 | 98.8 | 167.5 | 167.4 | 52.7<br>(51.6) | 29.9<br>(29.2) | 20.3<br>(20.3) | 13<br>(13 |
| $NO_2$ | Ethyl | 143.4 | 130.1 | 123.4 | 149.5 | 167.5 | 166.1 | 47.4<br>(46.3) | 13.1<br>(12.3) | | |
| | Butyl | 143.5 | 130.0 | 123.3 | 149.5 | 167.8 | 165.9 | 53.0<br>(51.9) | 20.0<br>(29.1) | 20.3<br>(20.3) | 1<br>(1 |
| $OCH_3$ | Ethyl | 162.1 | 131.3 | 113.3 | 130.1 | 168.2 | 166.6 | 46.8<br>(45.7) | 13.1<br>(12.1) | 55.3[a] | |

a - carbon of $OCH_3$

b - carbons of alkyl chain A are in brackets

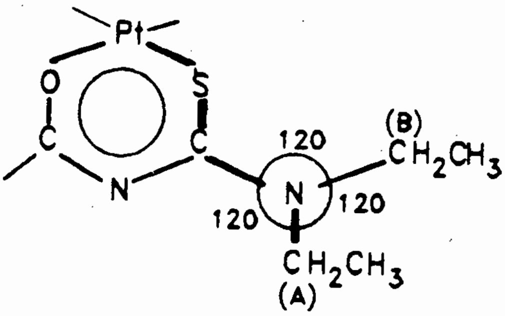
TABLE 3.12 $^{13}$C NMR data$^{b}$ of bis (N,N-dialkyl-N'-benzoylthioureas) Pd(II) in CDCl$_3$



| Compound X | R | $C_1$ | $C_{2,6}$ | $C_{3,5}$ | $C_4$ | C=O | C=S | $C_{7/7'}$ | $C_{8/8'}$ | $C_{9/9'}$ | $C_1$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| H | Ethyl | 131.4 | 129.6 | 127.9 | 137.1 | 171.1 | 170.6 | 47.2<br>(46.0) | 13.1<br>(12.6) | | |
| | Butyl | 131.4 | 129.6 | 127.9 | 137.1 | 171.5 | 170.4 | 52.8<br>(51.6) | 30.0<br>(29.5) | 20.3<br>(20.2) | 1<br>(1 |
| Cl | Ethyl | 137.7 | 131.0 | 128.2 | 135.6 | 171.3 | 169.6 | 47.3<br>(46.2) | 13.1<br>(12.6) | | |
| | Butyl | 137.7 | 130.9 | 128.2 | 135.6 | 171.6 | 169.3 | 52.9<br>(51.7) | 30.0<br>(29.5) | 20.3<br>(20.2) | 1<br>(1 |
| Br | Ethyl | 136.1 | 131.7 | 131.2 | 126.4 | 171.3 | 170.4 | 47.3<br>(46.1) | 13.10<br>(12.61) | | |
| | Butyl | 136.1 | 131.2 | 131.2 | 126.4 | 171.7 | 169.5 | 53.0<br>(51.8) | 30.0<br>(29.5) | 20.3<br>(20.3) | 1<br>(1 |
| I | Ethyl | 136.7 | 137.2 | 131.2 | 99.0 | 171.2 | 169.9 | 47.3<br>(46.2) | 13.1<br>(12.6) | | |
| | Butyl | 136.7 | 137.2 | 131.2 | 98.9 | 171.6 | 169.7 | 53.0<br>(51.8) | 30.0<br>(29.5) | 20.3<br>(20.3) | 1<br>(1 |
| $NO_2$ | Ethyl | 142.9 | 130.4 | 123.2 | 149.6 | 171.7 | 168.3 | 47.6<br>(46.5) | 13.1<br>(12.5) | | |
| | Butyl | 142.9 | 130.4 | 123.2 | 149.6 | 172.0 | 168.7 | 53.2<br>(52.0) | 30.1<br>(29.3) | 20.3<br>(20.3) | 1<br>(1 |
| $OCH_3$ | Ethyl | 129.7 | 131.6 | 113.2 | 162.4 | 170.6 | 170.4 | 47.1<br>(45.9) | 13.1<br>(12.7) | | 55.4$^{a}$ |

b) A carbons in brackets a - carbon of $OCH_3$

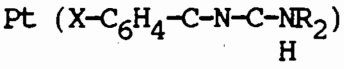
As expected $^{13}C$ NMR of Pt(II) complexes showed $^{195}Pt - ^{13}C$ coupling. In the literature [47, 51] the values of $J(^{195}Pt - ^{13}C)$ has been reviewed. The reports on carbonyl complexes [47] emphasises the trans influence while pointing out that $J(^{195}Pt - ^{13}C)$ depends on the carbon hybridization. Because of the presence of restricted rotation, long range $J(^{195}Pt - ^{13}C)$ coupling for carbon A and not for B is expected due to "W" configuration of the coupling groups which results in transmitting of the four bond coupling effects [50]. In aromatic ring attached to the C=O group "W" configuration cannot be achieved because of free rotation, which results in C(2) and C(6) experiencing the same coupling interaction from $^{195}Pt$ nucleus (See table 3.13).



In $^{13}C$ NMR spectra of the Pt(II) complexes studied coupling over four bonds were observed for carbon A and not B, which allows for the assignment of the chemical shifts of the high field resonances. Furthermore, in all the Pt(II) $^{13}C$ spectra, not all the expected J $^{195}Pt - ^{13}C$ coupling constant were observed. The $^{2}J(^{195}Pt - ^{13}C)$ coupling was Observed in only one of the low field resonances, because it is not easy to distinguish between C=O and C=S in complexes spectra. As a result, we cannot say which of the two carbons (C=O or C=S) show coupling. Similar observations have been reported in the literature [51], where studies on trans- $[PtCl_2\ (^{15}NH_2\ (CH_2)_5CH_3)\ (PBu^n{}_3)]$ showed coupling constants over two and three bonds whereas $[Pt(CN)_6{}^{2+}]$ and $[Pt(CN)_3{}^{4+}]$ showed no $^{195}Pt$ - $^{13}C$ coupling when $^{13}C$ nucleus is one atom removed from Pt(II).

Table 3.12 summarises the $^{195}Pt$ - $^{13}C$ observed for diethyl derivatives. Similar coupling constants are observed for dibutyl derivatives. Spin-spin coupling theory points out that the magnitude of spin-spin coupling decreases with increase in number of bonds ($^1J >> {}^2J > {}^3J > {}^4J$) for single bonds, while such effects are transmitted most favourably in double bonds with some minor exceptions. In this study spin-spin coupling was formed to decrease in the following order $^2J > {}^4J > {}^3J$. $^4J$ (in carbon C(7)) was found to be more than $^3J$ (in carbon C(1) as a result of "W" configuration in these bonds which is absent in C(1).

TABLE 3.13 $^{n}J$ ($^{195}Pt-^{13}C$) NMR data of bis (N,N-dialkyl-N'-benzoylthiourea) Pt(II)

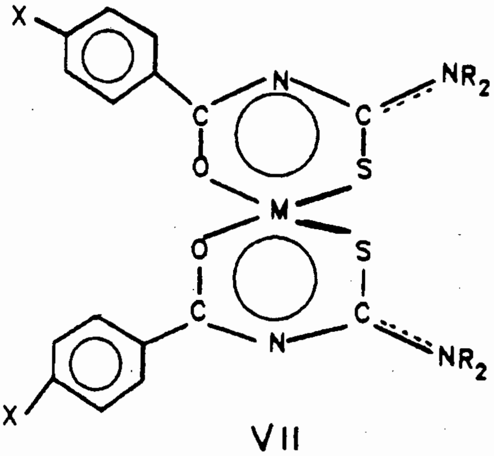


$Pt\ (X\text{-}C_6H_4\text{-}C\text{-}N\text{-}C\text{-}\underset{H}{N}R_2)$

$^{3}J$ ($^{195}Pt-^{13}C$) (Hz)

| X | R | $^{2}J$ ($^{195}Pt-^{13}C$) | $^{3}J$ ($^{195}Pt-^{13}C$) | $^{4}J$ ($^{195}Pt-^{13}C$) |
|---|---|---|---|---|
| H | $CH_3CH_2$ | 46 | 26 | 27 |
| Cl | " | — | 28 | 28 |
| Br | " | 44 | 24 | 25 |
| I | " | — | — | 28 |
| $OCH_3$ | " | 45 | 24 | 27 |
| $NO_2$ | " | — | — | 27 |

Hence in chloroform solution, at room temperature the best presentation of bis (N,N-dialkyl-N'-benzoylthiourea) metal complexes prepared is shown by (VII). This is also based on the literature results that complexes studied are always *cis* [38-40, 46].



VII

## $^{195}$Pt NMR spectra

The $^{195}$Pt NMR spectra of bis (N,N-dialkyl-N′-benzoylthioureas) Pt(II) complexes are expected to have two resonances if they are composed of mixture of *cis* and *trans* isomers. Studies on $[PtX_2L_3]$ where X = Cl and L = $PR_3$ or $ASR_2$ showed that the $^{195}$Pt resonance of the *cis* complex is upfield to the *trans* analogue by 400-500 ppm. Where X and L are not markedly different, the effect disappears, for example, *cis* and *trans* of $[PtBr_2(SMe_2)_2]$ have $\delta$ = -3879 and $\delta$ = -3899 respectively [47]. This results in difficulty to distinguish *cis* from trans isomers.

The $^{195}$Pt of the NMR spectrum (N,N-dibutyl-N-p-bromobenzoylthiourea) Pt(II) complex (figure 3.7) is characteristic of spectra observed for all bis(N,N-dialkyl- N′-benzoylthiourea)Pt(II) complexes. The spectra showed only one resonance, indicating presence of one isomer. As stated above, sometimes it is very difficult to identify *cis* and *trans* resonances, as a result we cannot say whether we have *cis* or *trans* based on $^{195}$Pt resonances. In the view of the literature [38-40, 46], where only the form was produced, we can assume that in our studies only the *cis* form was produced.

The $^{195}$Pt NMR data is summarised in Table 3.14. From the data it is obvious that different alkyl substituents induce slight chemical shift difference (0.2 - 18 ppm) in analogous compounds. This observation is consistent with the literature [47] in that for *trans* - $[PtCl_2$(nitrogen ligand)$C_2H_4]$ and $[PtCl_2L_2]$ complexes where L = tertiary phorphine, tertiary arsine, and dialkyl sulphide, when ligand atoms substituents are replaced by a substituent such as $CH_3$ for H, or by a longer alkyl chain, this results in relatively small (< 100 ppm) variation of the shifts of the $^{195}$Pt resonance.

TABLE 3.14 $^{195}$Pt NMR data of bis (N,N-dialkyl-N′-benzoylthioureas) Pt(II)

| Compound | Chemical Shift (ppm) |
|---|---|
| $C_{24}H_{30}N_4S_2O_2Pt$ | - 2723.4 |
| $C_{32}H_{46}N_4S_2O_2Pt$ | - 2723.2 |
| $C_{24}H_{28}N_4S_2O_2ClPt$ | - 2718.4 |
| $C_{32}H_{44}N_4S_2O_2ClPt$ | - 2719.8 |
| $C_{24}H_{28}N_4S_2O_2BrPt$ | - 2716.4 |
| $C_{32}H_{44}N_4S_2O_2BrPt$ | - 2718.2 |
| $C_{24}H_{28}N_4S_2O_2IPt$ | - 2715.6 |
| $C_{32}H_{44}N_4S_2O_2IPt$ | - 2716.1 |
| $C_{24}H_{28}N_6S_2O_6Pt$ | - 2688.8 |
| $C_{32}H_{44}N_4S_2O_2Pt$ | - 2688.1 |
| $C_{26}H_{34}N_4O_4S_2Pt$ | - 2738.7 |
| $C_{44}H_{36}N_4S_2O_2Pt$ | - 2725.5 |

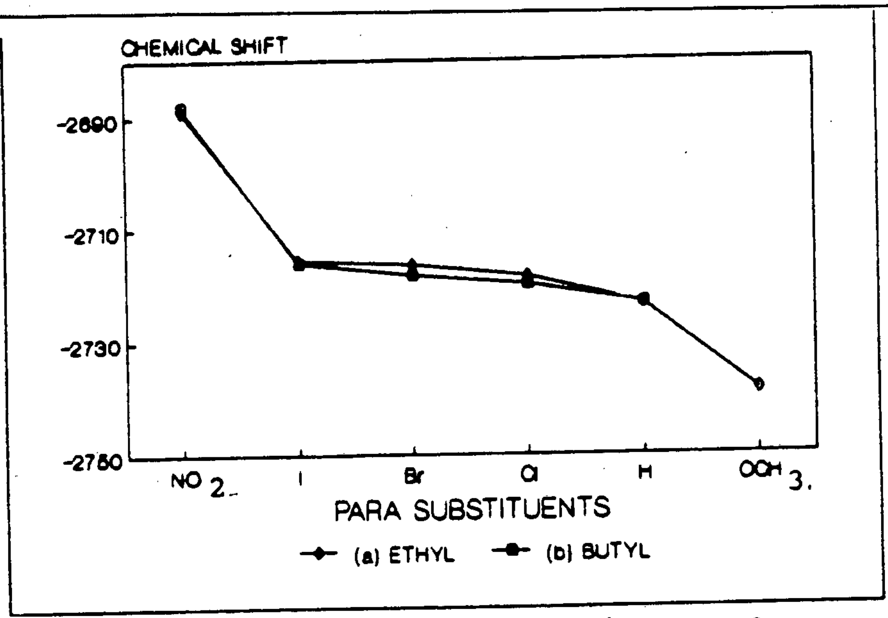


Figure 3.8 The effect of para-phenyl substituents of N,N-diethyl-N-benzoylthioureas on the $^{195}$Pt NMR spectra.

In this work the data shows that there is a dependence of $^{195}Pt$ on the para-substitution of the ligand (figure 3.8). By substitution of halogen (Cl, Br or I) for H results in relatively small variations of between 3-8 ppm. Substitution of $OCH_3$ or $NO_2$ for H however, results in variations of 15 ppm and 35 ppm respectively. A general tendency of upfield shift in the order $OCH_3>H>Cl>Br>I>NO_2$ was observed. This order is consistent with empirical generalizations drawn by Pregosin [47] that as one moves down a group, there is often (but not always) an upfield shift and parallels to electron donating parameters order as well as electron density order [52] which is as follows: $OCH_3 > H > Cl > Br > I > NO_2$.

# CHAPTER 4

# THE POTENTIAL SEPARATION OF PLATINUM AND PALLADIUM BY SOLVENT EXTRACTION AND THIN LAYER CHROMATOGRAPHY

Thin layer chromatography (TLC) of metal chelates is based on the differences in the extent to which metal chelates are partitioned between the mobile and stationary phase, which is applied as a thin layer on an inert support material. This differential partition depends upon the equilibrium distribution of each metal chelate between stationary and mobile phase and is the basis of the separation phenomenon. The distribution is characteristic of a metal chelate and is reflected by the differential immigration of different chelates which in turn is measured by the $R_f$ value. $R_f \text{ value} = \frac{\text{distance travelled by solute}}{\text{distance travelled by solvent}}$

The separation factor , $\alpha = R_f(y)/R_f(x)$ and the resolution of the two metal chelates are governed by the principle of adsorption and partition systems. Resolution is calculates as follows: $R_s = \frac{2\ (R_f(x) - R_f(y))}{W_x + W_y}$

$W_x$ and $W_y$ are the spot widths.

Resolution and separation factor can be changed by varying composition of stationary phase and mobile phase.

In anticipation of using solvent extraction followed by TLC, as has been done by several workers [55-58], preliminary investigation of the solvent extraction was undertaken. Solvent extraction prior to TLC has the advantage of achieving preconcentration and possible elimination of contamination, and interferences.

## 4.1 PRELIMINARY SOLVENT EXTRACTION

According to reports in the literature [33], most platinum group metals are slowly extracted due to the relatively slow ligand substitution reactions of their chlorocomplexes. The the extractable species of Pd(II) are produced rapidly, even in room temperature, whereas extractable Pt(II) complexes form slowly and often heating, or use of catalyst is required. Konig et al [32] found that this also applies in the solvent extraction of Pt-group metals using N,N-dialkyl-N-benzoylthioureas. In their studies these authors increased the rate of most Pt-group metal extraction by heating the solution to at least 60°C.

In the realm of liquid-liquid extraction studies, the interaction of tin(II) chloride with the platinum group metals has been usefully exploited. Several investigations of the use of tin(II)chloride in platinum extraction have been reported [59-61]. In general, tin(II)chloride is reported to exert a favourable kinetic effect on the rate of ligand substitution of the $PtCl_4^{2-}$ ion in aqueous acidic solutions. In these studies, it was found that several independent equilibria exist simultaneously in solutions containing tin(II)chloride and $[PtCl_4]^{2-}$ resulting in the formation of more labile $[Pt(SnCl_3)_5]^{3-}$ complex. The following equilibria are probably involved.

$$SnCl_2 + Cl^- \rightleftharpoons SnCl_3^-$$

$$[PtCl_4]^{2-} + SnCl_3^- \rightleftharpoons [PtCl_3(SnCl_3)]^{2-} + Cl^-$$

$$[PtCl_3(SnCl_3)]^{2-} + SnCl_3^- \rightleftharpoons \textit{trans}\ [PtCl_2(SnCl_3)_2]^{2-} + Cl^-$$

$$\textit{trans}\ [PtCl_2(SnCl_3)_2]^{2-} \rightleftharpoons \textit{cis}\ [PtCl_2(SnCl_3)_2]^{2-}$$

$$\textit{trans / cis}\ [PtCl_2(SnCl_3)_2]^{2-} + 3SnCl_2^- \rightleftharpoons [Pt(SnCl_3)_5]^{3-} + 2Cl^-$$

Such processes were found to reach equilibrium in 10-20 minutes, depending on concentration of acid used [62]. An equilibration time of at least 15 minutes is thus recommended.

The labile $[Pt(SnCl_3)_5]^{3-}$ so produced rapidly form extractable species of Pt(II) at room temperature. Some workers found out that $SnCl_2$ is co-extracted at first and then back extracted with time, and this may be happening in the present work, since when water was used to wash the organic extract, the presence of $SnCl_2$ was detected in the aqueous phase.

From the above observations, the extraction of Pt(II) using N,N-dialkyl-N-benzoylthioureas (LH) may be described as shown by the following reactions

$[Pt(SnCl_3)_5]^{3-} + LH \rightleftharpoons [Pt(LH)(SnCl_3)_2]_{org} + 3SnCl_3^-$

$[Pt(LH)(SnCl_3)_2] + LH \rightleftharpoons [Pt(LH)_2]^{2+}_{org} + 2SnCl_2 + 2Cl^-$

$[Pt(LH)_2]^{2+}_{org} + 2Cl^- \rightleftharpoons [Pt(L)_2]_{org} + 2HCl$

In order to determine the amount of metal extracted, accurate measurement of the concentration of these metals, was required. Systematic experimental studies [62] have been carried out to establish suitable analytical methods for determination of tin, platinum and palladium in the presence of each other. In these studies atomic absorption spectroscopy was found to be best suited and addition of 0.2% La as 'releasing' agent was recommended.

In the present work, preliminary extraction study of palladium and platinum from acid solutions, containing tin(II) chloride using N,N-dibutyl-N-benzoylthioureas in chloroform was undertaken. The N,N-dialkyl-N-benzoylthiourea ligand was found to be one of the best suited for liquid-liquid extraction in the literature [32]. Solvent extraction experiments were carried out as described in Chapter 2, section 2.5

### 4.1.1. Effect of time

In view of the kinetic inertness of the $PtCl_4^{2-}$ ion to substitution reactions, it was necessary to undertake a study of the effect of time on the extraction efficiency with and without tin(II)chloride being present. Experiments were carried out by shaking the Pt(II) and Pd(II) metal solution in 1M HCl for various fixed times with equal volumes of chloroform containing 0.1% (W/V) ligand. The percentage Pt and Pd extracted was determined by monitoring the amount of the metal remaining in the aqueous phase by means of atomic absorption measurements (see Chapter 2 section 2.6), and comparison with a blank. The percentage metal extracted was then calculated from

$$\%E = \frac{([Pt]_B-[Pt]_S)}{[Pt]_B} \times 100$$

where $[Pt]_B$ = concentration of platinum in blank; and $[Pt]_S$ = concentration of platinum in the sample. The blank was identical to the sample except that the chloroform contained no ligand.

Figure 4.1 illustrates the percentage metal extracted with time for Pt(II) and Pd(II). From the graph it is clear that Pt(II) and Pd(II) extraction is time dependent and generally the %E[Pt] and %E[Pd] increases with time. Complete extraction was achieved after two hours for Pd(II), while for Pt(II) even after six hours only 85% Pt was extracted. In the presence of tin(II)chloride however, complete extraction was obtained within 30 minutes. It was then decided to investigate possibilities of improving rate of extraction using tin(II) chloride as catalyst.

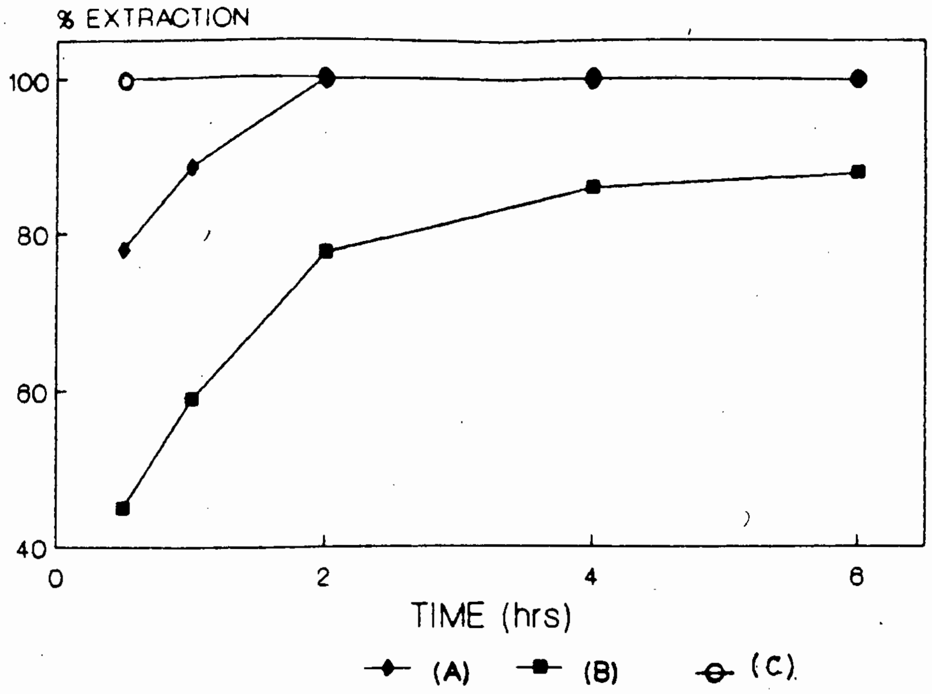


Figure 4.1 The variation of percentage extraction of (A) Palladium (B) Platinum without tin(II) chloride (C) Platinum with tin(II) chloride, with time in 1M HCl.

### 4.1.2 Effect of acid concentrations

Before tin(II)chloride experiments were undertaken, it was necessary to first investigate the effect of acid concentrations, since the use of tin(II)chloride requires an acid concentration greater than 0.5M HCl. Experiments were carried out by shaking Pd(II) solutions in various acid concentrations for thirty minutes with equal volumes of chloroform containing 0.5% (W/V) ligand. Percentage Pd(II) extracted was determined by atomic absorption measurements of aqueous phases and comparison with blank. The Pd(II) extraction was used as a model for Pt(II) extraction, because Pt(II) extraction is time consuming.

Percentage Pd extracted in different acid concentrations and using different Pd(II) concentrations is displayed by figure 4.2. Complete Pd extraction was only achieved with 0.01M HCl for all Pd concentrations studied. Since an increase in HCl concentration results in a decrease in percentage Pd extraction and $SnCl_2$ hydrolyses to Sn(OH)Cl type species in HCl concentrations less than 0.5M, 1M HCl concentration was chosen as the best compromise for the platinum case.

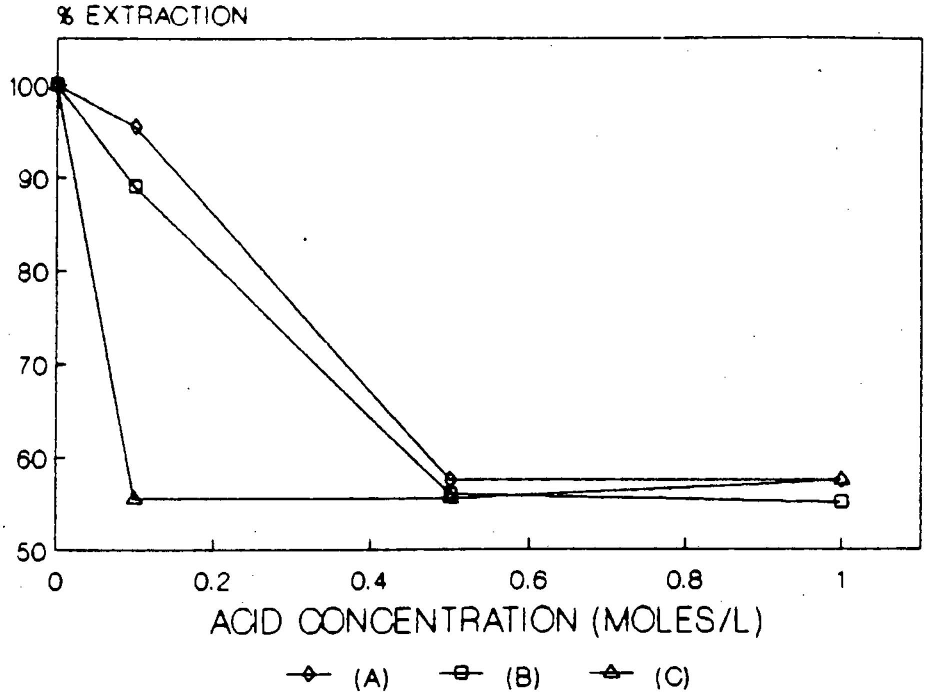


Figure 4.2 The variation of percentage extraction of Palladium with acid concentration. Palladium concentration of :
(A) 4 ppm (B) 10 ppm (C) 20 ppm

### 4.1.3 Effect of tin (II) chloride

To investigate the effect of tin(II)chloride on the extraction of Pt(II), a study of the Sn:Pt the ratio on the Pt(II) extraction was undertaken. Solutions of different mole ratios of Sn:Pt were equilibrated for 15 minutes, followed by shaking with an equal volume of chloroform containing 0.1% ligand for 30 minutes. The percentage Pt(II) extracted was then again determined in the aqueous phase using atomic absorption measurements.

The amount of Pt(II) extracted as a function of Sn:Pt ratio (figure 4.3) clearly shows an increase in the %E(Pt) with increasing Sn:Pt ratio. Hence the presence of tin(II) chloride increases the rate of Pt(II) extraction as expected, but complete extraction was only achieved with a Sn:Pt ratio of 10:1.

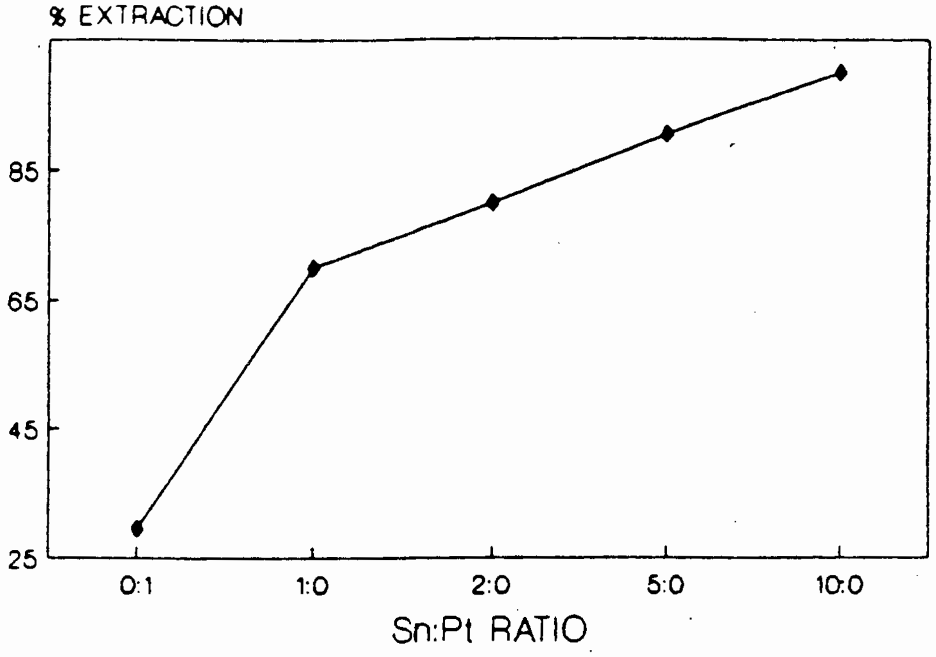


Figure 4.3 The variation of Platinum extraction with Sn:Pt ratio.

The above experiments were repeated in the presence of Pd(II) solutions. Solutions of various Sn:Pt ratios were equilibrated to 15 minutes then desired concentrations of Pd(II) solutions added. The solutions immediately shaken with chloroform containing varying concentrations of ligands for 30 minutes, after which the amount of Pd(II) and Pt(II) extracted were determined as before. Table 4.1 summarises the percentage extraction data of Pd(II) and Pt(II).

Inspection of table 4.1 indicates that tin(II) chloride increases the rate of extraction for both Pt(II) and Pd(II). In addition it is obvious that percentage extracted for Pt(II) and Pd(II) depends on the metal (Pd+Pt): ligand as well as Pt:Pd ratios. Complete extraction was obtained for both metals with metal:ligand ratios > 1:12, where total metal concentrations were < 40 ppm.

On the basis of the above results, it may be concluded that $SnCl_2$ strongly influences the percentage metal extracted, particularly in the case of Pt(II). On the other hand, it is necessary to use higher HCl concentrations which tends to result in a decrease in overall Pt or Pd extracted, which is a disadvantage. To obtain optimum extraction conditions as well as to investigate the nature of intermediate reactions, further studies are required.

TABLE 4.1 The effect of $SnCl_2$ on the extraction of Pd(II) and Pt(II) using N,N-dibutyl-N-benzoylthiourea in chloroform

| Concentration (ppm) | | Ratio | | | %E | |
|---|---|---|---|---|---|---|
| Pt | Pd | Pt:Pd | Pt:Sn | M:L[a] | Pd | Pt |
| 40 | 40 | 1 : 1 | 1 : 10 | 1 : 6 | 100 | 43 |
| 10 | 50 | 1 : 5 | 1 : 30 | 1 : 7 | 100 | 100 |
| 50 | 10 | 5 : 1 | 1 : 6 | 1 : 10 | 100 | 24 |
| 20 | 20 | 1 : 1 | 1 : 20 | 1 : 12 | 100 | 100 |
| 5 | 25 | 1 : 5 | 1 : 61 | 1 : 13 | 100 | 100 |
| 25 | 5 | 5 : 1 | 1 : 12 | 1 : 20 | 100 | 100 |
| 20 | 0 | 1 : 0 | 1 : 6 | 1 : 33 | - | 100 |
| 20 | 20 | 1 : 1 | 1 : 0 | 1 : 12 | 86 | 5.5 |
| 20 | 0 | 1 : 0 | 1 : 0 | 1 : 33 | - | 0.0 |
| 0 | 20 | 0 : 1 | 0 : 0 | 1 : 18 | 86 | - |

a) M = total metal (Pt+Pd), L = ligand

## 4.2 THIN LAYER CHROMATOGRAPHY (TLC)

Intensive studies [7,14] on the TLC of neutral metal chelates has shown that best chromatographic separations in terms of separation and compact spots are obtained with silica gel and alumina as stationary phase. In the present work silica gel 60 was chosen on the basis of the work of Konig et al [33]. In the latter studies of the chromatography of N,N-dialkyl-N-benzoyl-thioureas, it was found that aluminium and silianised silica gels showed worse separation properties than silica gel 60. As mobile phase various systems were investigated.

### 4.2.1 Thin layer chromatography of ligands

Since it was found previously that a ligand:metal ratio of 12:1 was necessary for effective extraction of the Pt and Pd, it is obvious that excess ligand would be expected in the $CHCl_3$ phase. Thus if these extracts were to be used, the TLC would only be successful if the ligand and complexes $R_f$ values do not coincide. Hence it was necessary to study the TLC of ligands. The elution properties were examined using silica gel and numerous systems of mobile phases were investigated.

In general ligands formed broad spots (streaking) with low $R_f$ values except when methanol was used as mobile phase. Table 4.2 summarises the TLC of ligands. From the table it is obvious that alkyl and para-substituents affects the $R_f$ values of these substances. TLC of dibutyl derivatives show higher $R_f$ values than diethyl derivatives in general. Furthermore, the $R_f$ values tend to decrease in the order I > Br > Cl > $NO_2$ > $OCH_3$ for both diethyl and dibutyl derivatives.

TABLE 4.2 $R_f$ values of N,N-dialkyl-N-benzoylthioureas on silica gel 60
$XC_6H_4C(O)N(H)C(S)NR_2$

| Compound | | Mobile Phase | | |
|---|---|---|---|---|
| X | R | $CHCl_3$ | $CH_3OH$ | Benzene |
| H | Ethyl | 0.24 | 0.76 | 0.40 |
| | Butyl | 0.48 | 0.71 | 0.28 |
| Cl | Ethyl | 0.36 | 0.79 | 0.20 |
| | Butyl | 0.51 | 0.77 | 0.12 |
| Br | Ethyl | 0.45 | 0.83 | 0.21 |
| | Butyl | 0.57 | 0.80 | 0.28 |
| I | Ethyl | 0.33 | 0.80 | 0.18 |
| | Butyl | 0.57 | 0.73 | 0.38 |
| $NO_2$ | Ethyl | 0.20 | 0.19 | 0.11 |
| | Butyl | Impure (oil) | impure | impure |
| $OCH_3$ | Ethyl | 0.17 | 0.17 | 0.08 |

The above observations can be explained by the fact that the ligands have an acidic hydrogen (-N-H) which strongly interacts with the active sites of silica gel resulting in low $R_f$ values. The acidity probably depends on the nature of para-phenyl substituent and the alkyl group, which in turn affects the $R_f$ values in a complicated way. Furthermore, the solubility of these compounds is poor in non-polar and moderately polar solvents, but very high in polar solvents, which could explain the high $R_f$ values in methanol. The $R_f$ values of these substituted N,N-dialkyl-N-benzoylthioureas decrease in the following order of mobile phases methanol > chloroform > benzene. This order approximately parallels the decreasing order of polarity and eluent strength of the mobile phases [63].

### 4.2.2 Thin layer chromatography of organic phase of extraction

The organic extracts of the Pt and Pd extraction experiments described in section 4.1 were passed through ETRELUT (E Merck)to absorb water, then applied on silica gel TLC plates. Elution was carried out with various mobile phases. Generally, the chromatograms obtained showed three spots, except for organic extracts where the aqueous phase was not acidified, which showed only two spots. The spots were established to be due to excess of ligand and Pt and Pd complexes which was formed during extraction. The ligand spot was identified by comparison with pure ligand TLC. The spots due to the metal complexes one at starting line (which is not present for aqueous phases contains no acid) and the other at $R_f$ values of 0.5 - 0.8 depending on the mobile phases used. These were obtained with Pt(II) and Pd(II) extractions alone as well as with mixtures of both.

The two spots observed due to complexes strongly suggest that during extraction, more than one complex is formed with one metal in the presence of acid. In particular, it is possible that a charged complex of type $[M(LH)L]^+$ or $[M(LH)_2]^{2+}$ could have been co-extracted. The charged complex is strongly retained by the silica gel suggesting the spot at the starting line. Further evidence that the charged complex is the one accountable for the starting line spot, is obtained from the absence of these spots in non acidic extractions. The spot at $R_f$ values of between 0.5 - 0.8 is ascribable to the neutral complex $[M(L)_2]$.

The protonated complex is not unexpected in view of the nature of the initial complex formation. This may be summarised by the following reactions:

$$MCl_4{}^{2-} + 2LH \rightleftharpoons [M(LH)_2]^{2+} + 4Cl^- \tag{1}$$

$$[M(LH)_2]^{2+} \rightleftharpoons [M(LH)L]^- + H^+ \tag{2}$$

$$[M(LH)L]^- \rightleftharpoons M(L)_2] + H^+ \tag{3}$$

In presence of acid, reactions 2 and 3 may be expected to shift to the left resulting in less production of $[M(L)_2]$ and consequently a mixture of complexes $[M(L)_2]$, $[M(LH)L]^+$ and $[M(LH)_2]^{2+}$. The two charged complexes are likely to have similar chromatographic properties which will result in one spot, i.e. they are strongly retained by silica gel and thus remain immobile on the plate.

From the above observations it is clear that use of tin(II)chloride and acidduring the extraction of Pt and Pd, results in complex chromatograms. Consequently it does not appear to be an acceptable strategy to undertake the extraction of Pd and Pt, followed by TLC. On the other hand, extraction without acid results in formation of only neutral $M(L)_2$ complexes, but the rate of extraction is very slow, particularly for $PtCl_4{}^{2-}$, making this approach also not practical. In addition the complexes of Pd and Pt appear to have similar chromatographic properties, making separation with conditions investigated difficult. Due to these problems extraction of Pt(II) and Pd(II) metals with N,N-dialkyl-N-benzoylthioureas followed by TLC is not an acceptable procedure for Pt and Pd analysis. Further TLC studies were then undertaken using chloroform solutions of chelates which were precipitated from aqueous solutions.

### 4.2.3 Thin layer chromatography of metal complexes

The elution properties of N,N-dialkyl-N-benzoylthiourea chelates of Pt(II) and Pd(II) were investigated on silica gel with variants of the mobile phase systems. Experimental details are given in Chapter 2, section 2.7.

The Pd(II) and Pt(II) chelates formed compact, single clear spots with moderate $R_f$ values depending on the elution solvent polarity such as chloroform, as well as binary mixtures with tetrahydrofuran, benzene, methanol and carbon tetrachloride. When polar solvents such as methanol are used the spots due to the metal chelates tended to display streaking and in most cases two spots with low $R_f$ values resulted. Acetonitrite also showed very poor chromatograms as the spots displayed a significant degree of streaking (see figure 4.4).

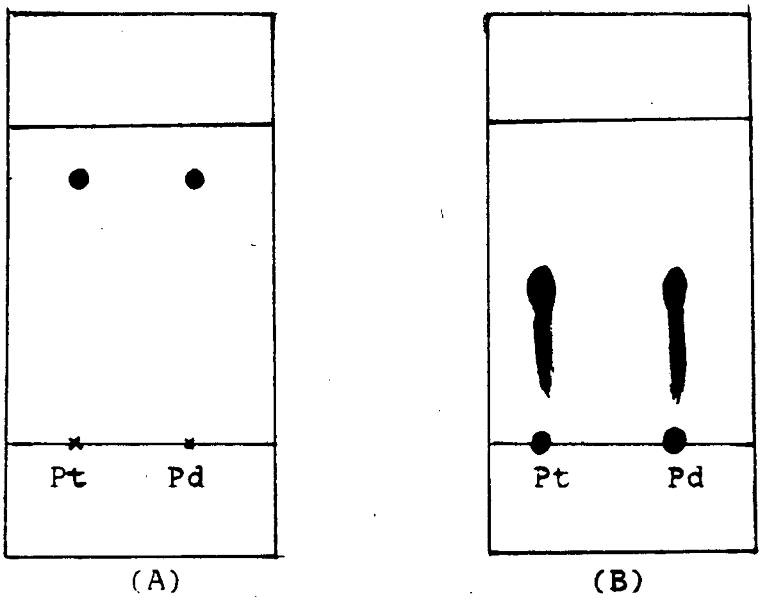


Figure 4.4 Thin layer chromatography of N,N-dibutyl-N-benzoylthiourea Pd(II) and Pt(II) complexes in (A)
(A) Chloroform (B) Methanol

Since the chelates may undergo protonation as suggested in the extraction section it may be that in methanol some protonation occur.

$$M(L)_2 + H^+ \ (CH_3OH \text{ or } H_2O) \qquad [M(LH)L]^+ + CH_3O^- \text{ or } OH^-$$

This may acount for the additional spot observed when using methanol as well as streaking. Furthermore. the neutral $M(L)_2$ metal complexes poor solubility in methanol and acetonitrite leads to an effective supersaturation of the mobile phases and hence non-equilibrium distribution of the chelates between stationary and mobile phases. This may be considered to be the cause of streaking and low $R_f$ values of the chelates in these solvents.

The Pd(II) and Pt(II) N,N-dialkyl-N-benzoylthiourea chelates were most extensively studied. Table 4.3 summarises the $R_f$ values of N,N'-dibutyl-N'-benzoylthioureas chelates in different mobile phases. From this data it is obvious that Pd(II) and Pt(II) chelates have very similar chromatographic properties. Thus to investigate separation conditions for these compounds optimum chromatographic conditions had to be found. This was undertaken by studying the effect of humidity and mobile phases in chromatographic analysis of these chelates.

TABLE 4.3 $R_f$ values of Pd(II) and Pt(II) N,N-dibutyl-N-benzoylthiourea chelates in various mobile phases

| Mobile phase | $R_f$ values<br>Pd | <br>Pt |
|---|---|---|
| $CHCl_3$ | 0.81 | 0.81 |
| $CH_3OH$ | 0.57 | 0.58 |
| Tetrahydrofuran (THF) | 0.74 | 0.74 |
| 10% THF in $CHCl_3$ | 0.81 | 0.81 |
| THF: $CHCl_3$: $CH_2Cl_2$(95:2:3) | 0.80 | 0.81 |
| THF: $CHCl_3$: $CH_2Cl_2$(78:2:20) | 0.83 | 0.80 |
| Benzene | 0.71 | 0.72 |
| Acetonitrite | Very bad chromatograms (streaking) | |
| 0.1% $N[ETH]_3$ in $CH_3OH$* | 0.56 | 0.57 |
| 0.1% $N[ETH]_3$ in $CHCl_3$* | 0.72 | 0.73 |

* $N[ETH]_3 = N(CH_2CH_3)_3$

## EFFECT OF HUMIDITY

The chromatographic activity of silica gel is known to be strongly influenced by the amount of residual water that remains in the stationary phase [33]. To establish optimum chromatographic activity of the stationary phase for the separation of the Pt(II) and Pd(II) complexes, thin layer chromatograms of these chelates was run using plates pre-conditioned in various conditions prior to use.

The effect of humidity on $R_f$ values of Pt(II) anmd Pd(II) complexes of N,N-dibutyl-N-benzoylthioureas in chloroform and methanol is displayed by figure 4.5. From figure 4.5 it is obvious that the $R_f$ values for both complexes decrease with increasing humidity. The shape of the spot was also found to be affected by pre-conditioning of the TLC plates. Compact clear spots were always obtained with chloroform but with methanol, as the humidity increases, the spot tends to streaking. At 50% relative humidity two spots were observed, again suggesting formation of charged complexes in the presence of $H_2O$ and $CH_3OH$.

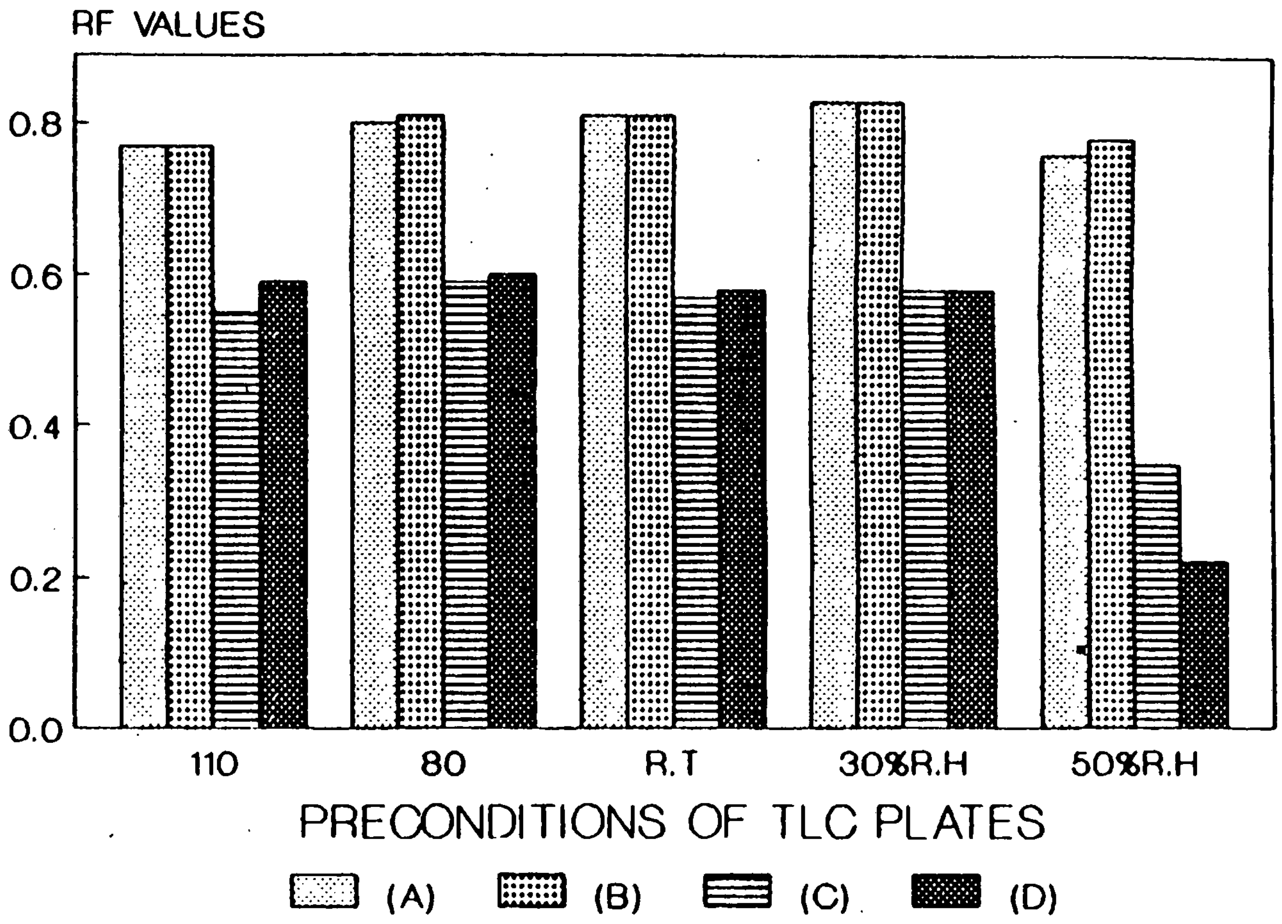


Figure 4.5 Variation of $R_f$ values of Pd(II) and Pt(II) N,N-dibutyl-N' benzoylthiourea complexes with preconditions of TLC plates. Preconditions of TLC plates: dried by heating for 3 hours in 110°C and 80°C temperature, left to stand for 3 hours at room temperature (R.T) and kept overnight in 50% and 30% relative humidity (R.H). In various mobile phases: (A) Pd($CHCl_3$) (B) Pt($CHCl_3$) (C) Pd($CH_3OH$) (D) Pt($CH_3OH$)

The decrease in $R_f$ values as the water content of the silica gel increases is consistent with the idea that leads to a decrease in concentration of active sites of the absorbent. Water is thought to bind with the active centre of silica gel through electron donor acceptor interactions, or simply hydrogen bonding. Streaking on the other hand may be due to two factors, poor solubility of solute in mobile phase (thus chromatographic overload) and the presence of very polar forms of solute (protonated complexes $[M(LH)L]^{+}$ or $[M(LH)_2]^{2+}$) which may be expected to interact strongly with the silica gel.

On the basis of $R_f$ value differences and the compact spots, good separations can be obtained with plates pre-conditioned overnight in 50% relative humidity, using chloroform. These results are consistent with literature results [33]. Where relative humidities between 40% - 70% were found to be the best suited for good separations.

## SUBSTITUENT EFFECTS

In the literature [33], it was found that alkyl substituents significantly influence the chromatographic behaviour of the N,N'-dialkyl-N-' benzoylthiourea complexes. In these studies it was found that for increasing chain length of the alkyl group the $R_f$ values of the complexes increased. To investigate the para-phenyl substituent effects, thin layer chromatography of mixtures of dibutyl and diethyl derivatives of all para-substituted analogues of Pt(II) complexes was undertaken using chloroform as eluent (figure 4.6).

From figure 4.6 it is clear that different alkyl and para-phenyl substitution influence the chromatographic behaviour of the chelates. With increasing alkyl chain (from ethyl to butyl) the $R_f$ values increased. This observation could parallel order of solubility, although the latter was not studied in detail. The observation could also be explained by the fact that an increase of the bulk of the alkyl chain (fron ethyl to butyl) results in differences in overall polarity as well as the nature of the complex. Hence it might be expected that longer, somewhat more hydrophobic butyl substituents, would result in differences in the distribution of the complexes between the very polar silica gel phase and the comparitively non-polar $CHCl_3$ phase.

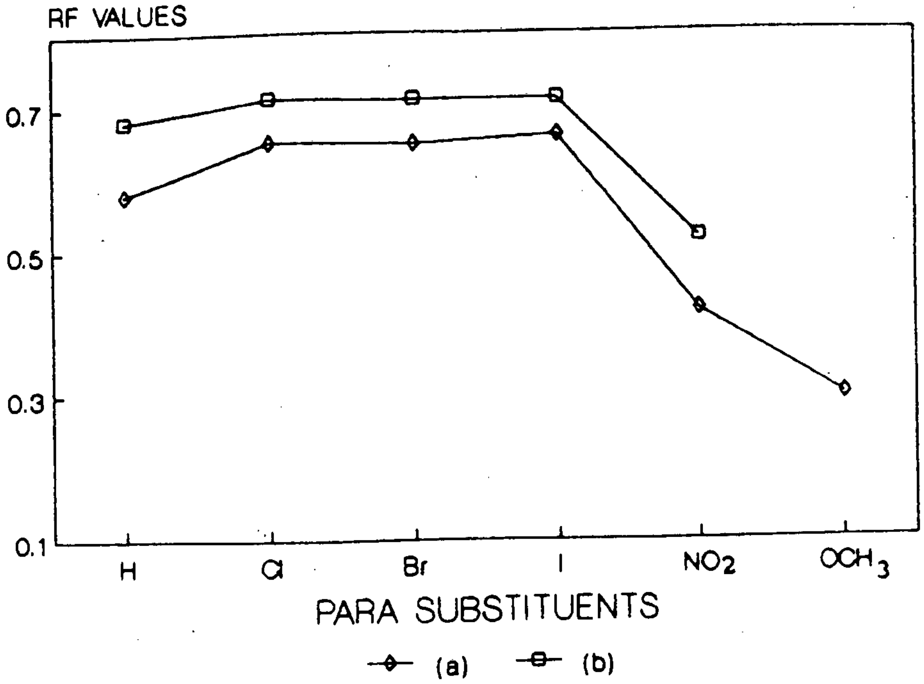


Figure 4.6 Variation of $R_f$ values with alkyl and para-phenyl substituents. (A) diethyl (B) dibutyl

The effect of para-phenyl substituents on the $R_f$ values shows that the $R_f$ decreases in this order I $\geqslant$ Br $\geqslant$ Cl > H > $NO_2$ > $OCH_3$. The order of the para-substituent $R_f$ values may parallel the order of basicity of the nitrogen (C(O) - N - C) in that the different para-phenyl substituents may result in small differences in electron density availability at the nitrogen atom, which results in different basicity of the complex.

The. halogen substituents are weakly electron donating, and their electron donating capacity varies slightly. They could slightly increase the electron density on the nitrogen making it slightly less basic and less polar, resulting in higher $R_f$ values. The substituents $NO_2$ and $OCH_3$ on the other hand have two effects. They result in mesomeric effects due to lone electron pair delocalization of the attachment atoms N and O into the phenyl ring respectively. They are strongly electron donating ($OCH_3$) and strongly electron withdrawing ($NO_2$). The overall effect of the two substituents is that they can be thought to make the complex more polar and thus these substances are more strongly retained by the active sites of silica gel, resulting in low $R_f$ values. The $R_f$ value of the $NO_2$ substituted complex may be decreased further by poor solubility of the complex in chloroform. However, this speculation should be supported by further experimental evidence before the order of $R_f$ values as a function of para-phenyl substituents can be fully explained.

## SEPARATION OF METAL COMPLEXES

After optimum pretreatment conditions of the stationary phase were established, optimum mobile phase composition was determined by trial and error. Preliminary TLC separations investigations were undertaken using chelates of dibutyl derivatives and halogen para-phenyl substituted analogues because they had relatively large $R_f$ values in moderately polar solvents such as chloroform. Furthermore, since use of HPLC was anticipated, which works best with solutes of moderate $R_f$ values. In these TLC investigations no separations were achieved with Pt(II) and Pd(II) chelates using chloroform and binary mixtures listed in table 4.3. Thus investigations using complexes of relatively small $R_f$ values were undertaken. Further investigations were done using 'normal' TLC and high performance thin layer plates (HPTLC) which have a thinner layer of stationary phase with a more uniform and smaller particle size distribution. A variety of mobile phase systems were studied.

Thin layer chromatograms of mixtures of Pt(II), Pd(II), Cu(II) and Ni(II) complexes obtained with various mobile phases using TLC plates are illustrated in figure 4.7. Plates pre-conditioned overnight in 50% relative humidity as well as dry plates (heated for 3 hours in 80°C) were used. Similar results were observed when using HPTLC plates resulting in slight difference of separation.

It is clear from figure 4.7 that separation of non-precious metal from Pt-group metals as well as separation of Pt from Pd was possible with N,N-diethyl-N-anisoylthiourea and N,N-diethyl-N-benzoylthiourea using dry or 50% relative humidity pre-conditioned plates. For mobile phases chloroform, 5% benzene in chloroform and 5% hexane in chloroform were used. In the case of N,N-diethyl-N-p-nitrobenzoylthiourea as ligand, only the Ni(II) chelate were separable from the mixture of Pd, Pt, Ni and Cu. As expected, separations were better when using HPTLC plates than using normal TLC plates. This is because HPTLC plates have a more uniform and smaller particle size distribution, so that the plates are more efficient. As a result, spot broading, due to stationary phase mass transfer, longitudinal diffusion and eddy diffusion is less pronounced, resulting in compact clear spots and better separation. There is a very slight difference in using dry plates and plates pre-conditioned in 50% relative humidity.

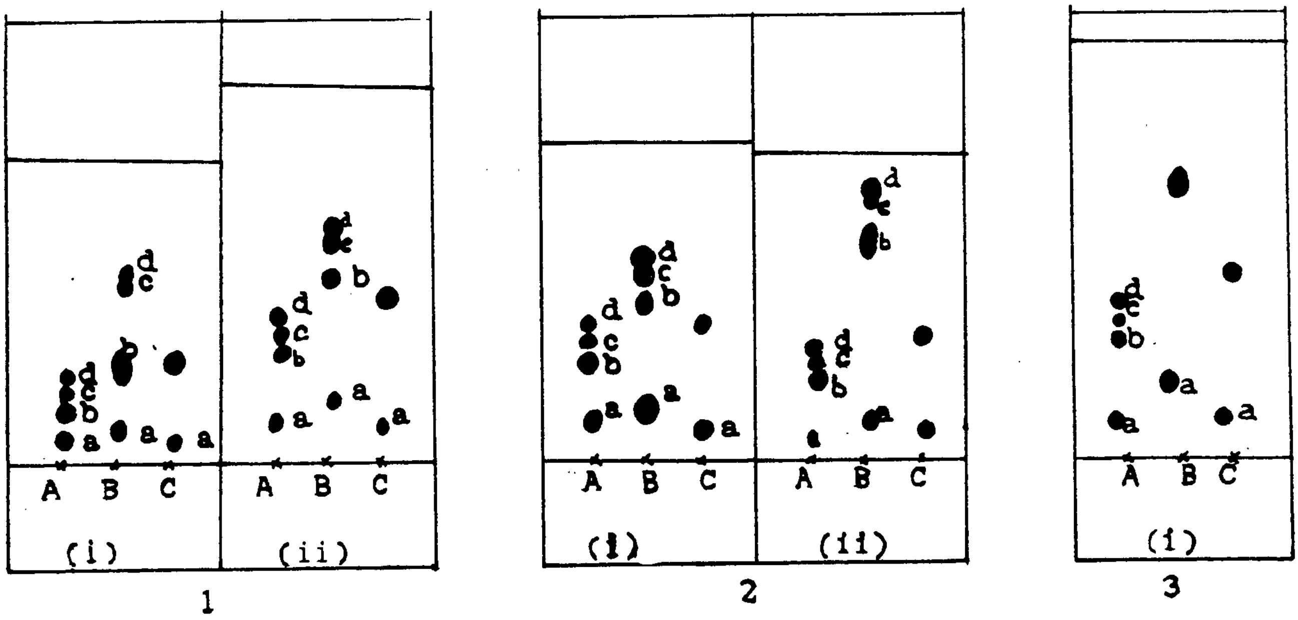


Figure 4.7 Thin layer chromatography separations of (a) Ni, (b) Cu, (c) Pd, (d) Pt complexes of (A) N,N-diethyl-N-anisoylthourea, (B) N,N-diethyl-N-benzoylthiourea and (C) N,N-diethyl-N-p-nitrobenzoylthiourea

Mobile phase : (1) 5% benzene in chloroform
(2) 5% hexane in chloroform
(3) Chloroform

Preconditions: (i) Dried by heating for 3 hours in 80°C
(ii) Kept overnight in 50% relative humidity

Detection : Iodine fumes

On the basis of these results, it is clear that butyl derivatives, halogen para-substituted analogues and the nitro-analogues are not suitable for chromatographic separations of the Pt and Pd chelates under the conditions studied. This may be due to the fact that butyl groups may be expected to dominate the overall polarity and chromatographic nature of the $M(L)_2$ chelates relative to the ethyl analogues. Since the butyl complexes are more soluble in $CHCl_3$, the differences in the distribution of the complex between the polar stationary phase and mobile phase is reduced for the metal complexes, hence similar $R_f$ values and no separation. The above agurments apply to the halogen substituted diethyl derivatives. On the other hand the $NO_2$ derivatives are only poorly soluble in chloroform, as well as most other common solvents, except DMSO and DMF. Hence the chromatographic behaviour of these complexes is complicated by streaking and the formation of broad spots, which overlap, making separation impossible.

The chromatographic observations were not totally unexpected. Since the structure of metal complexes may be expected to show a close relationship with chromatographic behaviour of the metal chelates [14], and the structure of these complexes is probably very similar as reported in literature [37-40] using X-ray structure analysis. Therefore similar chromatographic properties of these complexes were expected. However, the para-phenyl substituents might affect the electron distribution in the complex and hence affects the polarity of the complex. Results in Chapter 3 showed great similarities of the NMR spectra of the Pt(II) and Pd(II) complexes a well as the halogen para-substituted analogues. Therefore these compounds are expected to have similar chromatographic properties. NMR results in Chapter 3 showed that halogen substituents have only a small effect on the $^{13}C$ chemical shifts, while the $NO_2$ and $OCH_3$ had a significant effect, indicating a more significant substituent effect and thus suggesting different chromatographic behaviour on polar silica gel stationary phase. Similar results were obtained in TLC of the pure ligands. These factors together with solubilities of these complexes clearly explain observed chromatographic properties.

## ESTIMATED DETECTION LIMITS

Approximate detection limits for Pd(II) and Pt(II) complexes were determined using complexes of N,N-diethyl-N-anisoylthioureas. Solutions of known concentrations of Pd(II) and Pt(II) complexes were prepared. The solutions were diluted until the spot that was applied to the TLC plates was not visualized in the normal way (iodine fumes). Different amounts of the dilute solution were also applied to the TLC plates, their approximate concentration calculated. The TLC was then developed and visualized in the normal way. The detection limits are calculated by averaging the concentration where spots are first detected and where spots were no longer detectable. Table 4.5 summarises these observations.

TABLE 4.5 Observations

| Pd(II) |  | Pt(II) |  |
|---|---|---|---|
| Applied conc. (μg/ml) | Obs | Applied conc. (μg/ml) | Obs |
| 10.4 | N/D | 11.2 | N/D |
| 20.4 | D | 224.0 | N/D |
| 52.4 | D | 268.0 | N/D |
| 104.0 | D | 448.0 | D |

N/D - not detected D - detected

The approximate limits for Pd and Pt complexes were found to be 15.4 ug/ml and 358 ug/ml respectively. Lower detection limits of 2ng Pt and 0.5ng Pd were reported in the literature [33] using a better detection system (scanner Schimadzu CS910 with integrator on CRIA and 2 channel plotter V235) as well as using HPTLC plates which have thinner stationary surface, thus less concentrated samples can easily be detected resulting in lower detection limits.

## 4.3 PRELIMINARY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

High performance liquid chromatography (HPLC) possess a number of significant advantages over TLC both in separation ability and in analytical possibilities. The many advantages of HPLC include good control over flow rate, and composition of mobile phase. Furthermore, very efficient columns with a large number of theroretical plates are available. This fact explains the growing number of reports of the HPLC methods for the separation of metal chelates in recent years [63-65].

In general the techniques of HPLC and TLC share a common theoretical basis, although the physical application of the techniques is substantially different (see Chapter 2, section 2.7 and 2.8). In HPLC retention time ($T_R$), which is the time from injection of substance to the peak maximum leaving the column at constant flow rate is measured instead of $R_f$ value. The retention time ($T_R$), depends on partition of solute between the stationary phase and is characteristic for each substance. Separation of solutes is based on the differential partition of each solute. The separation and resolution of solutes can be calculated using equations discussed in the TLC section replacing $R_f$ with $T_R$ values.

In the present work, a Beckman high performance liquid chromatography instrument, which consists of constant volume pumps, sample valve injection, Haber pre-packed Licrosorb Si 60 (5µm) 250mm column and UV-visible photometric detector was used. Before running any experiments automatic selftest of the instrument was performed, which ascertains that the system was in good working condition.

### 4.5.1 Testing of column efficiency

The effectiveness of HPLC as a separation method is determined by the column efficiency and the sensitivity of the detector. Hence it was necessary to determine the efficiency as well as optimum working conditions of the columns. Test solution containing benzene (4.39mg/ml) and phenol (2.09mg/ml) in chloroform was used constantly to determine the efficiency of the column. When the instrument is in good working condition, the $T_R$ and peak height of benzene and phenol are as shown in table 4.4.

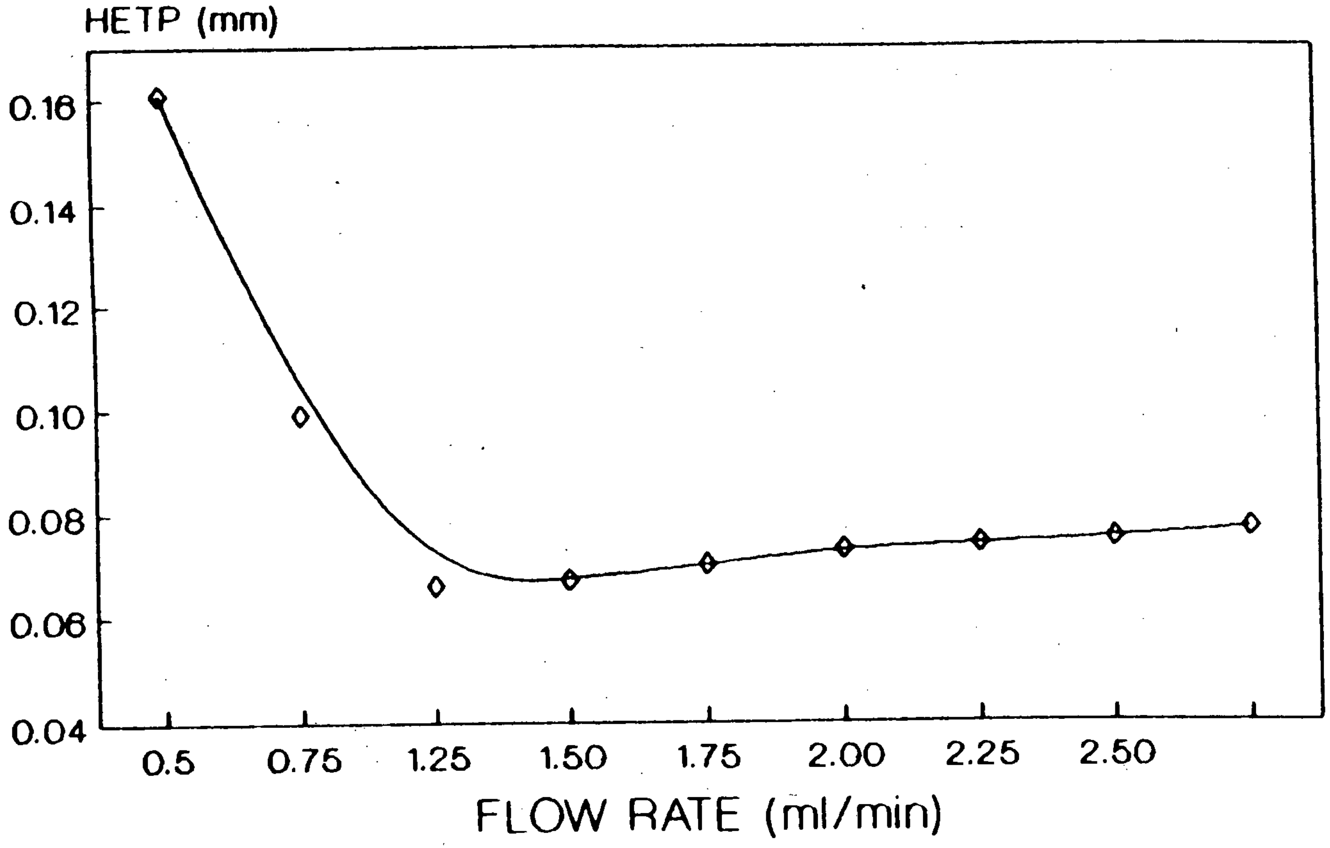


Figure 4.8 Variation of height equivalence of theoretical plates (HETP) with flow rate.

### 4.5.2 High performance liquid chromatography of metal chelates

After determination of optimum column conditiond for the test solution, a study of the potential separation of Pt and Pd metal chelates was undertaken. The optimum wavelength for setting of the detector was chosen as a compromise from the maximum wavelength of the UV-spectrum of the metal chelates and the UV cut off (245nm for chloroform) of the mobile phase. Wavelength $\lambda$ = 275nm was the best compromise for most mobile phases. Unless otherwise stated, this wavelength selection was used for all other experiments. Table 4.6 lists the maximum wavelength of Pt(II) and Pd(II) N,N-dibutyl-N'-benzoylthiourea chelates.

TABLE 4.6 Summary of UV-visible spectrum of N,N-dibutyl-N'-benzoylthiourea chelates

| Chelate | maximum (nm) |
|---|---|
| Pt | 245, 273 |
| Pd | 245, 273 |
| ligand | 244, 282 |

In anticipation of developing an analytical method for Pt and Pd, extraction of the Pt and Pd as chelates into $CHCl_3$ and then directly injecting this extract into HPLC system, seemed very convenient. The organic extracts of the N,N-dibutyl-N'-benzoylthiourea complexes were passed through EXTRELUT (E Merck) to absorb water before injection into the system.

The chromatograms of the organic extracts from acidic aqueous solutions showed three peaks, while organic extracts from non-acidic extracts showed only two peaks. The peaks were established to be due to excess ligand and complexes produced during extraction. The ligand peak was identified by comparison of $T_R$ values with the $T_R$ of the pure ligand. As explained in TLC of organic extracts, the peaks ascribed to the metal complexes may result from charged complexes $[M(LH)H)L]^+$ or $[M(LH)_2]^{2+}$ (higher $T_R$ value) and neutral complex $[M(L)_2]$. The peak with higher $T_R$ value (220 sec) is absent in non-acidic extracts and only peak of $T_R$ 163 sec and $T_R$ 168 sec are observed. (See chromatogram figure 4.9). This strongly suggests that peak of $T_R$ 220 sec is more likely due to charged complexes, which strongly interacts with stationary phase, thus being eluted last.

The organic extracts produced complicated chromatograms, especially in large excess of ligands, where the ligand peak becomes too broad and the complex peak appeared as a shoulder due to peak overlap. Furthermore, in acid extracts the charged complex peak complicates the chromatograms further. It was then decided to inject chloroform solutions of N,N-dibutyl-N'-benzoylthiourea Pt and/or Pd chelates, which were precipitated from the aqueous solutions.

The chromatograms of chloroform solutions of N,N-dibutyl-N′-benzoylthiourea Pd(II) and Pt(II) chelates showed a single peak, which is most likely due to neutral complex $[M(L)_2]$. However, the peak areas were not reproducible. The peak area decreases with every repeated injection with consequent peak broading. Eventually three peaks were observed after repeated sample injections.

The above observation suggests that some reactions are taking place on the column during elution, which causes the decomposition of the complexes. This process may occur especially if the mobile phase is contaminated with traces of water. It is possible that on column reactions which involve dissociation, hydrolysis as well as ligand-exchange processes in the stationary and/or mobile phases, which causes the considerable retention resulting in a memory effect. Furthermore, there is a possibility that repeated injections may lead to overloading of the column as a result of the strongly retained complexes resulting in broad peaks.

Notwithstanding the above difficulties the Pt(II) and Pd(II) chelates proved to have such similar chromatographic properties (Table 4.7) that separation was not possible even after varying flow rate and mobile phase composition (chloroform binary solvents). When varying the mobile phase composition, there were slight changes in $T_R$ values except in cases where there was no detection. In the latter case the complexes were so strongly retained that no elution occurred at all. An irreversible absorbtion can also occur due to poor solubility of chelates in the mobile phase. Furthermore the $T_R$ for the complexes increases with a decrease in flow rate with a simultaneous increase in peak broadening, thus increasing peak overlap resulting in no separation.

TABLE 4.7 $T_R$ value of N,N-dibutyl-N'-benzoylthiourea complexes

| | $T_R$ (sec) | |
|---|---|---|
| Complex | $CHCl_3$ | $CH_3OH$ |
| Pt | 173 | 155 |
| Pd | 162 | 155 |
| ligand | 168 | 140 |

When separation failed with N,N-dibutyl-N'-benzoylthiourea chelates N,N-diethyl-N-anisoylthiourea chelates were investigated. The N,N-diethyl-N-anisoylthiourea chelates were chosen because reagents with substituents might be expected to influence the separability of the Pt and Pd complexes as was observed in the TLC separation. A mixture of Pd, Pt, Cu and Ni N,N-diethyl-N'-anisoylthiourea complexes were injected after pre-conditioning of the column and running of test solution using chloroform as mobile phase.

The N,N-diethyl-N′-anisoylthiourea complexes appear as one broad peak with large $T_R$. This happens because N,N-diethyl-N′-anisoylthiourea chelates strongly interacts with silica gel as observed in TLC (low $R_f$ values) so that as a result of the solute spends longer time in the stationary phase which results in increase in peak broadening and severe peak overlap. In addition there is a possibility that slow decomposition reactions occur, the longer the complexes are absorbed by the acidic silica gel. Further studies are needed to test those suggestions. In general though it was found that the HPLC separation of Pt and Pd complexes of N,N-dialkyl-N′-benzoylthiourea was not as successful as was hoped. In this respect TLC was found to be more successful and convenient.

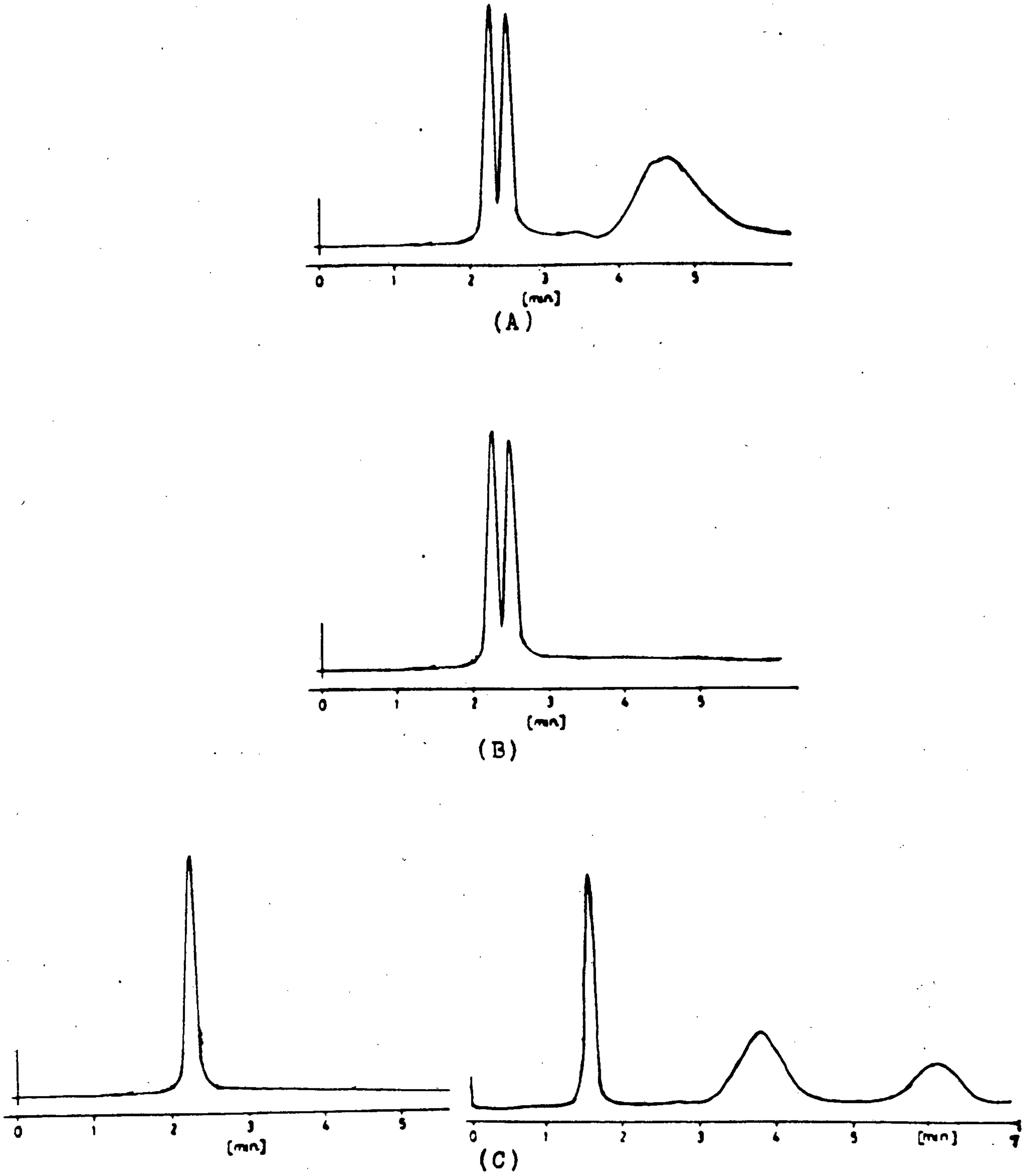


Figure 4.9 HPLC chromatograms (A) Acidic extract (B) Non-acidic extract (C) Precipitate after repeated injections.

# CHAPTER 5

# DISCUSSION AND CONCLUSION

Results obtained from our studies on a series of para-phenyl substituted N,N-dialkyl-N-benzoylthioureas have provided useful information regarding preparation, structure, as well as possibility of using compounds in normal phase chromatographic metal analysis. From the results it is clearly established that high yields of white crystalline and relatively pure potential ligands may be obtained by reaction of parra-phenyl substituted benzoyl chloride, potassium thiocynate and secondary amine in the presence of dry acetone. The preparation mechanism may be summarised as follows:

$$X - C_6H_4C(O)Cl \; + \; KSCN \; \rightleftharpoons \; XC_6H_4C(O)SCN \; + \; KCl$$

$$XC_6H_4C(O)SCN \; \underset{\text{acetone}}{\overset{\text{dry}}{\rightleftharpoons}} \; XC_6H_4C(O)NCS$$

$$XC_6H_4H(O)NCS \; + \; R_2NH \qquad\qquad XC_6H_4C(O)N(H)C(S) - NR_2$$

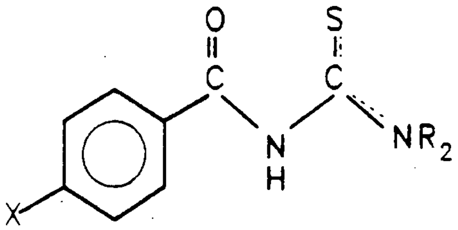
$$R = -CH_2CH_3, \quad -(CH_2)_3CH_3, \quad -CH_2C_6H_5$$

$$X = H, Cl, Br, I, NO_2, OCH_3$$

It is known that disubstituted benzoylthioureas can appear in various structural forms, However, the NMR studies of these compounds showed evidence of one isomer. The NMR studies further showed that $^1H$ and $^{13}C$ chemical shifts are slightly affected by para-phenyl and alkyl substituents in the expected way. Different para-phenyl substituents affected the H(6) and H(2,5) resonances mostly while in $^{13}C$ NMR spectra carbon atoms $C_4$ and $C_{3,5}$ were the most affected. The above observation can be explained by the fact that different substituents change the electronic environment of the nuclei in question, as reflected in the observed chemical shifts.

The NMR spectra of the ligands are slightly complicated by the non-equivalence of the alkyl chains which suggested presence of restricted rotation at C(S) - $NR_2$ bond(s). The restricted rotation is in harmony with a highly polarized thiourea structure with partially single C = S and partial double C(S) ---- $NR_2$ bond(s). These observations are further supported by the relatively high melting points of these compounds (93 - 195°C).

From the studies and literature reports [29], where the N-H form had been identified by infra-red spectroscopy, these compounds are probably best represented as follows:



The para-phenyl substituted N,N-dialkyl-N-benzoylthioureas formed coloured crystalline complexes of relatively high melting points (90-350°C) with bivalent metals Pt(II), Pd(II), Cu(II) and Ni(II). The $^1H$ and $^{13}C$ NMR spectra of these complexes Pt(II) and Pd(II) showed great similarities to free ligand spectra except for loss of H(6) resonance in $^1H$ NMR spectra and significant shifts of C = O and C = S $^{13}C$ resonances in complexes.

On the basis of the above observations and elemental analysis results, reasonable mechanism for complex formation cam be presented by the following equilibria:

$$PtCl_4^{2-} + 2LH \rightleftharpoons [Pt(LH)_2]^{2+} + 4Cl^- \qquad 1$$

$$[Pt(LH)_2]^{2+} \rightleftharpoons [Pt\ L\ (LH)]^+ + H^+ \qquad 2$$

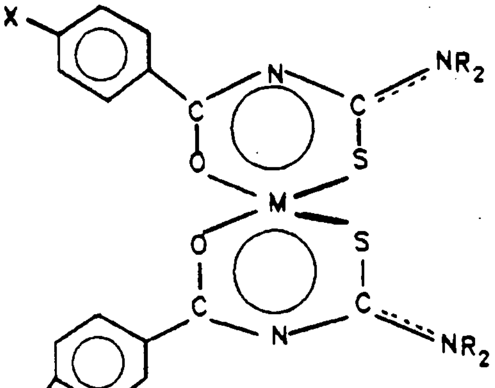
$$[Pt\ L\ (LH)]^+ \rightleftharpoons Pt(L_2) + H^+ \qquad 3$$

---

$$PtCl_4^{2-} + 2LH \rightleftharpoons Pt(L_2) + 2H^+ + 4Cl^-$$

On heating, the above reactions are relatively fast resulting in formation of complexes within ten minutes.

It is interesting to note that several workers [38-40, 46] have reported only the *cis* isomer of the square planar complexes of Pd and Pt. Therefore even though from our studies it was not possible to absolutely identify which isomer was produced, it was clear that a neutral complex was produced which we also assign to be the *cis* isomer as shown below.



VII

The complexes formed are almost insoluble in water but highly soluble in polar organic solvents such as $CHCl_3$ and DMSO. Thus these complexes may be expected to be suitable to liquid-liquid extraction. These complexes were found to be readily extractable into $CHCl_3$ although the extraction was affected by a number of factors. However, on the basis of final results we were able to propose reasonable mechanism for the extraction processes.

The variation of amount of Pt(II) and Pd(II) extracted with time confirmed the kinetic inertness of $PtCl_4^{2-}$ ions to substitution reactions. The presence of tin(II)chloride drastically affected the percentage Pt(II) and Pd(II) exctracted. It is thought that in presence of tin(II)chloride labile $[Pt(SnCl_3nCl_4-n]^{2-}$ complexes were formed which easily react with the N,N-dialkyl-N-benzoylthioureas to form the extractable species.

The variation of Pd extraction with HCl concentration provides further evidence of the complex formation mechanism proposed. The percentage Pd extracted decreased with an increase in acid concentration, which is expected from the equation (2) and (3) above.

The coloured metal complexes are very stable and ideal for chromatographic analysis. The chromatographic studies were found to be complicated and affected by a number of factors. However, it was possible to obtain some compounds from the series of substituted N,N-dialkyl-N-benzoylthioureas suitable for TLC analysis of metal complexes Pt(II), Pd(II), Cu(II) and Ni(II).

The $R_f$ values varied with increasing length of the alkyl chain (dibutyl > diethyl). The $R_f$ values of the complexes increased strongly with simultaneous decrease in $R_f$ differences between metal complexes. These observations may be explained by the higher solubility of longer alkyl chain complexes in mobile phases, which results in reduced differential distribution of the complexes between the polar stationary phase and mobile phases.

The variation of $R_f$ values with para-phenyl substituents confirmed that para-phenyl substituents affects the electronic environment of the complexes as seen in NMR studies. This affects the complexes interaction with stationary phase resulting in different $R_f$ values. The $R_f$ values decrease in this order: $I \geqslant Br \geqslant Cl > H > NO_2 > OCH_3$.

The chromatographic studies of organic solvent extracts were complicated by the existence of more than one spot on a TLC plate indicating presence of mixture of complexes (probably charged complexes $[M(LH)_2]^{2+}$ and $[ML(LH)]^+$ in the acidic extracts. Preliminary HPLC experiments were not encouraging in that it appears as if some on column reactions occur resulting in the formation of complex mixtures. Highly charged complexes would be strongly retained by the silica gel and the possibility of neutral complexes disproportionating on column cannot be ignored. Clearly, for the use of HPLC-system, further investigations to elucidate the reactions involved and to investigate necessary precautions on column reactions are required to obtain successful separation of these complexes.

On the basis of the studies we can conclude that the TLC properties of these compounds are influenced by the para-phenyl and alkyl substituents. For the TLC separation complexes derived from N,N-diethyl-N-benzoylthiourea and N,N-diethyl-N-anisoyl-thiourea were the best suited. The separation of Pt(II), Pd(II), Cu(II) and Ni(II) complexes was obtained using the above ligands, using both TLC and HPLC plates pre-conditioned overnight in 50% relative humidity. As mobile phases chloroform, 5% benzene in chloroform and 5% hexane in chloroform were used.

HPTLC plates (although not extensively used) showed that better separation can be obtained using these plates. Although further studies are needed to clarify certain points, it is clear that use of these compounds in chromatographic analysis of metals is a viable method.

# REFERENCES

1. VOGEL
Textbook of quantitive inorganic analysis
Longman Group Limited, 4th edition (1986).

2. SEKINE T., HASEGAWA Y.
Solvent extraction chemistry
Mercel Dekker (1977).

3. BEAMISH F.B.
The analytical chemistry of noble metals
Pergamon, Oxford (1966).

4. BEAMISH F.E., VAN LOON J.C.
Recent advances in the analytical chemistry of noble metals
Pergamon, Oxford (1972).

5. STEINBRECH G., SCHNEEWIES G., KONIG K.H.
Fresenius Z. Anal. Chem., (311), (1982), 499.

6. STAHL E.
Thin layer chromatography
Academic, New York, (1965).

7. SCHWEDT G.
Chromatographic methods in inorganic analysis
New York (1981).

8. SYNDER KIRKLAND
Introduction to modern liquid chromatography
Wiley-interscience (1974).

9. NICKLESS G.
Journal of chromatography, (313), (1985), 129.

10. TIMBERBRAEV A.R., PETRUCHKIN O.M., YU A.
Fresenius Z. Anal. Chem., 327, (1987), 87.

11. BENNEHR, WILLEFORD, HANS VEENIG
Journal of chromatography, 251, (1982), 61.

12. SURENDRA, SHARMA D, SMITI MISRA
Journal of liquid chromatography, 816, (1985), 2991.

13. RONALD L.S., DONALD J.P.
Anal. Chem., 56, (1984), 610.

14. STEINBRECH B.
Journal of liquid chromatography, 10(1), (1987), 1.

15. AL-BAZI S.J., CHOW A.
Talanta, 31 (10A), (1984), 815.

16. YOUNG-TZUNG STUL, PETER W. CARR
Analytica Chimica Acta, 142, (1982), 55.

17. JOEL KIRSCHBAUM
Journal of chromatographic science, 23, (1985), 483.

18. SCHIMIZU T., ABE S.
Chromatographica, 21 (12), (1986), 708.

19. MULLER B.J., LOVETT R.J.
Anal. Chem. 57, (1985), 2693.

20. BANNNISTER S.J., STERNSON L.A., REPTA J.
Journal of chromatography, 173, (1979), 333.

21. RILEY C.M., STERNSON L.A., REPTA A.J.
Journal of chromatography, 219, (1981), 235.

22. REECE P.A., MECALL J.T., POWIS G., RICHARDSON R.
Journal of chromatography, 306, (1984), 417.

23. MARSH G.K., STERNSON L.A., REPTA A.J.
Anal. Chem., 56, (1984), 491.

24. HUHEEY J.E.,
Inorganic chemistry principles of structure and reactivity
2nd edition (1978)

25. NECKI K.
Chem. Ber 6: 598 (1873)

26. PIKE W.H.
Chem. Ber 6: 755 (1873)

27. DUUS F.
Comprehensive organic chemsitry, 3,(1979),373

28. DOUGLAS I.B., DAINS F.B.
J. of Am. Chem. Soc., 56, (1934), 719.

29. BAYER L., HOYER E., HENNING H., KIRMSE R.
Journal of Pratt Chemie, 317 (5), (1975), 829.

30. BANERJEE S.N., SUKTHANAKAR A.C.
J. Indian chem. soc., 39, (1962), 197.

31. HONJO T., KIBA T.,
Bull. chem. soc. JPN, 46, (1978), 3678.

32. KONIG K.H., SCHUSTER M., STEINBRECH B., SCHNEEWIES G., SCHLODDER R.
Fresenius Z. Anal. Chem., 321, (1985), 457.

33. MULLER H., ROTHER R.
Analitica Chimica. Acta., 66, (1973), 49.

34. KONIG K.H., SCHUSTER M., SCHNEEWIES G., STREINBRECH B.
Fresenius Z. Anal. Chem., 319, (1984), 66.

35. COTTON AND WILKINSON
Wiley-interscience, New York, 4th edition (1980).

36. FITZL V.G., BAYER L., SIELER J., RICHTER, KAISER J., HOYER E.
Z. Anorg. Allg. Chem., 433, (1977), 237.

37. ENGELHARDT H.
High performance liquid chromatography
Translated from German by George Gufnikov, New York (1979).

38. KUUTLILA P., KUUTLILA H., HENNIG H., BAYER L.
Acta chemica scandinavica, 36, (1982), 541.

39. RICHTER V.R., BAYER L., KAISER J.
Z. Anorg. Allg. Chem., 461, (1980), 67.

40. BAYER L.V., BEHRENDT S., KLEINPETER E., BORSDORF R., HOYER E.
Z.Anorg. Allg. Chem. 437, (1977), 282.

41. MIDDIEDITCH B.S.
Practical mass spectrometry
Plenum, New York and London (1979).

42. WEHRI F.W., WIRTHLIN T.,
Interpretation of Carbon-13 NMR spectra
Hyden London (1978).

43. AKITT J.W.
NMR and chemistry, an introduction to the fourier transform multinuclear era
Chapman and Hall Ltd, London, New York (1983).

44. EDWIN D. BECKER
High resolution NMR, theory and chemical applications.
Academic, 2nd edition (1980).

45. STOOG D.A.
Principles of instrumental analysis.
HRW International, 3rd edition (1985).

46. KOCH K.R. AND IRVING H.
Unpublished results.

47. PREGOSIN P.S.
Co-ordination chemistry reviews, 44, (1982), 247.

48. PIDCOCK A., RICHARDS R.E., VENAZI L.M.
J. Chem Soc., A, (1970), 1068.

49. ZELEWSKY A.V.,
Helv. Chim. Acto., 51, (1968), 803.

50. JACKMAN L.M., STEMHELL S.
Applications of NMR spectroscopy in organic chemistry
2nd edition (1969).

51. MANN B.E.
Advances in organometallic chemistry Vol. 12
Academic, New York, (1974), 135.

52. SYKES P.
A guidebook to mechanism in organic chemistry, 3rd edition (1970).

53. KOCH K.R.
Inorganica chimica Acta., 147, (1988), 227.

54. LUNG AND BJERUM
bER, 64, (1931), 210.

55. FLIEGER A., PREZESZIA KOWSKI S.
Talanta, 32 (12), (1985), 1141.

56. SCHUSTER M.
Fresenius Z. Anal. Chem., 324, (1986), 127.

57. KONIG K.H., HESSLER I., SCHUSTER M., STEINBRECH B.
Fresenius Z. Anal. Chem., 33, (1985), 322.

58. EDWARD-INATIMI G.B., DALZIEL J.A.W.
Anal. Proc., (1980), 40.

59. MOJSKI M.
Talanta, 27, (1980), 7.

60. ZOLOTOV YU. A., PETRUKHIM O.M., SCHEVCHENKO V.N., DUNIMA V.V., RUKHADZE E.G.
Analytica Chemica Acta., 100, (1978), 613.

61. CRAMER R.D., LINDSEY R.V., PREWITT C.T., STOLBERG U.G.
J. Am. Chem. Soc., 87, (1965), 658.

62. KOCH K.R., YATES J.E.
Analytica Chimica Acta., 147, (1983), 235.