REACTIVITY STUDIES OF 1-Benzoyl-3-(2,4,6-tri-*tert*-butylphenyl)thiourea AND RELATED LIGANDS

A dissertation presented in partial fulfilment of the requirements for
the degree of

Master of Philosophy
in
Chemistry

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New Zealand.

I. K. G. Indira Chandrasena

2001

Dedication

To my dearest father… though you are far away across the Pacific you gave me strength and courage through your mind.

&

To my dearest mother… though you are not in this world to see this piece of work, your love and support lead me through to this stage.

Errata

P111 line 10 should read " .....two types of complex, one with a CT band in the 300 nm region and the other in the 350 nm region."

P113 line 3 from the bottom Method (b) not Method (a)

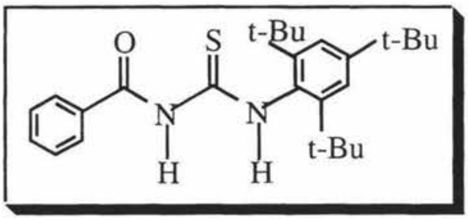
P115 line 11 from the bottom should read "......derives from the instability of the compound in CHCl3/pentane."

P 150 In Table 5.2 the spectra were recorded at room temperature.

P47 reference 22 Weinhiem should be Weinheim.

Abstract

This thesis aims to investigate the coordination modes, reactivity, spectroscopy and structures of bulky 1-benzoyl-3-(aryl)thioureas, with metals and non-metals. The bulky ligand, 1-benzoyl-3-(2,4,6-tri-*tert*-butylphenyl)thiourea (Bz^{t}BPtuH) and the related ligands, 1-benzoyl-3-(2,4,6-triphenylphenyl)thiourea (BzPPtuH), 1-benzoyl-3-(2,6-diisopropylphenyl)thiourea (Bz^{i}PPtuH), 1-benzoyl-3-(4-fluorophenyl)thiourea (BzFPtuH), and 1-benzoyl-3-phenylthiourea (BzPtuH) are the focus of the research in this thesis.



Bz^{t}BPtuH

Chapter One gives a brief review of the chemistry of thiourea and modified thiourea ligands.

In Chapter Two, the preparation, characterization and structure of Bz^{t}BPtuH are described and compounds of the type [M(L)$_2$] (M = Cu, L = Bz^{t}BPtu or Bz^{i}PPtu), [M(LH)$_2$X$_2$] (M = Cu(II) or Co(II), LH = Bz^{t}BPtuH or Bz^{i}PPtuH, X = Cl; M = Ni(II), LH = Bz^{t}BPtuH, X = I), [M(LH)$_2$Cl] (M = Cu(I), LH = Bz^{t}BPtuH, BzPPtuH, Bz^{i}PPtuH or BzFPtuH), [Cu(BzPtuH)$_3$Cl] and [M(LH)$_4$]PF$_6$ (M = Cu(I) or Ag(I), LH = Bz^{t}BPtuH or Bz^{i}PPtuH) have been synthesized. The deprotonated ligands, Bz^{t}BPtu and Bz^{i}PPtu, in the complexes [Cu(Bz^{t}BPtu)$_2$] and [Cu(Bz^{i}PPtu)$_2$] coordinate through the O and S atoms resulting in six-membered chelate rings from the anionic ligands. The electronic spectra give support for thiocarbonyl S being bound to the metal. This, combined with ESR spectra suggests square planar structures for [M(L)$_2$] (L = Bz^{t}BPtu or Bz^{i}PPtu). For [Cu(Bz^{t}BPtuH)$_2$Cl$_2$], the ligand remains neutral and binds through the S atom to form a distorted tetrahedral complex. The X-ray crystal structure of [Cu(Bz^{t}BPtuH-κ^1-*S*)$_2$Cl] shows the ligand is bound through S and the complex has a

trigonal planar structure. The X-ray structure of [Co(Bz^{t}BPtuH)$_2$Cl$_2$] shows it to be distorted tetrahedral with cobalt having an S_2Cl_2 donor set. The complexes [M(LH)$_4$]PF$_6$ (M = Cu(I) or Ag(I), LH = Bz^{t}BPtuH or Bz^{i}PPtuH) probably have tetrahedral structures.

In Chapter Three, $HgCl_2$ compounds of the type [Hg(LH)$_2$Cl$_2$] (LH = Bz^{t}BPtuH, Bz^{i}PPtuH or BzFPtuH) are reported as well as [Hg(BzPtuH)Cl$_2$]. With Hg(Ac)$_2$, the ligands (in alcoholic solvents) are converted to [C_6H_5CON=C(OX)NHR] (R = 2,4,6-tri-*tert*-butylphenyl, 2,4,6-tri-phenylphenyl, 2,6-diisopropylphenyl, *p*-fluorophenyl or phenyl, X = C_2H_5; and R = 2,4,6-tri-*tert*-butylphenyl, X = CH_3, or $CH_2C_6H_5$) while in CH_2Cl_2 [C_6H_5CON(COCH$_3$)C(O)NHR] (R = 2,6-diisopropylphenyl) or NHCN-(2,4,6-tri-*tert*-butyl)phenyl are obtained. With sodium ethoxide in alcohol and water NH$_2$-C(S)NH-(2,4,6-tri-*tert*-butyl)phenyl was isolated. For [Hg(LH)$_2$Cl$_2$] (LH = Bz^{t}BPtuH, Bz^{i}PPtuH or BzFPtuH) the ligand remains neutral and binds through the S atom to form a monomeric distorted tetrahedral complex. The structure of [Hg(Bz^{t}BPtuH-$\kappa^1 S$)$_2$Cl$_2$] was determined crystallographically. The complex Hg(BzPtuH)Cl$_2$ is possibly a polymer containing Cl and S bridges. The intermediate mercury complex formed with Hg(Ac)$_2$ in alcohol reaction was unstable, and it decomposed to form HgS and a new compound [C_6H_5CON=C(OX)NHR]. The X-ray crystal structure and spectroscopic data confirm the final product. Cd(Ac)$_2$ reacted with Bz^{t}BPtuH in ethanol to give some CdS, unreacted starting material and a little BzE^{t}BPA. No reaction was observed with Zn^{2+} or UO_2^{2+} acetate.

Chapter Four investigates the coordination chemistry and reactivity of Bz^{t}BPtuH and related ligands with halogens (I_2 and Br_2). The I_2 adducts of the type [(LH)I$_2$] (LH = Bz^{t}BPtuH, BzPPtuH, Bz^{i}PPtuH, BzFPtuH or BzPtuH) were obtained in 1:1 molar ratio as well as the metastable Br_2 adduct [(Bz^{i}PPtuH)Br$_2$]. The X-ray crystal structure of [(Bz^{t}BPtuH-$\kappa^1 S$)I$_2$] shows a I–I bond distance of 2.8537(4) Å. The X-ray crystal structure of [(Bz^{i}PPtuH-$\kappa^1 S$)Br$_2$], shows a Br–Br bond distance of 2.6118(4) Å. The Br_2 adduct that initially formed in ice-cooled conditions with Bz^{t}BPtuH was converted to a novel heterocyclic ring compound, 2-benzamido-5,7-di-*tert*-butylbenzothiazole hydrobromide (B^{t}BBTH) at room temperature. This compound is ionic with Br^- anions and benzothiazole cations.

In Chapter Five, the complexes [Rh(COD)(LH)Cl] (LH = Bz^{t}BPtuH, BzPPtuH, Bz^{i}PPtuH, BzFPtuH or BzPtuH; COD = 1,5-cyclooctadiene) are prepared from the reaction of $[Rh(COD)Cl]_2$ with the appropriate LH, and the complexes $[Pt(LH)_2Cl_2]$ (LH = Bz^{t}BPtuH or Bz^{i}PPtuH) by reacting $K_2[PtCl_4]$ with the appropriate LH. The X-ray structure of [Rh(COD)(BzPPtuH-$\kappa^1 S$)Cl] shows a square planar arrangement of the ligands about Rh, with LH binding through the sulfur atom. One of the π-bonds of COD is bound to Rh and is *trans* to the Cl group while the other π-bond is bound to Rh but is *trans* to the S atom. The two equivalent protons associated with the olefinic bonds *trans* to the Cl group have a different chemical shift from the two protons on the olefin arm *trans* to the S atom at low temperature (–20 to –40 °C), but coalesce into one broad band at higher temperature (20 to 40 °C). A preliminary X-ray structure on [Pt(Bz^{t}BPtuH-$\kappa^1 S$)$_2$Cl$_2$] shows the complex has a *cis* structure.

Acknowledgements

I take this opportunity to gratefully acknowledge the contribution from the following people, without which much of this work would not be possible.

It is with deep sense of gratitude and appreciation I thank my supervisors, Associate Professor Eric Ainscough and Professor Andrew Brodie for their excellent guidance, assistance, encouragement, valuable comments and giving their time, knowledge and experience freely from the beginning of my research project until the final review of the manuscript.

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I would also like to take this opportunity to thank all the academic staff and other members of the department for their help during the course of my Masterate and who with their team effort make the place run.

Finally I would like to thank my husband, Dhamsiri and my two daughters Nadeeka and Kanchana for their continuous support, patience and encouragement until the completion of my thesis.

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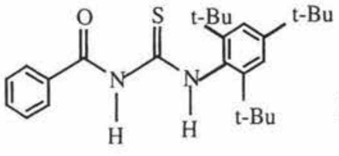
List of Schemes

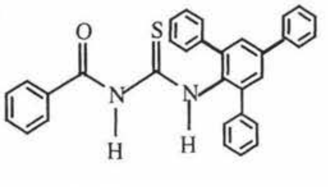
Abbreviations

ABz^{i}PPu	1-acetyl-1-benzoyl-3-(2,6-diisopropylphenyl)urea
Ac	acetate
Anal.	Analyses
B.M.	bohr magneton
bp	boiling point
B^{t}BBTH	2-benzamido-5,7-di-*tert*-butylbenzothiazole hydrobromide
Bu	butyl
BzEFPA	1-benzoyl-2-[ethoxyl-3-(4-fluorophenyl)amino]aldimine
BzE^{i}PPA	1-benzoyl-[2-ethoxyl-3-(2,6-diisopropylphenyl)amino]aldimine
BzEPA	1-benzoyl-2-[ethoxyl-3-(phenyl)amino]aldimine
BzEPPA	1-benzoyl-2-[ethoxyl-3-(2,4,6-tri-phenylphenyl)amino]aldimine
BzE^{t}BPA	1-benzoyl-2-[ethoxyl-3-(2,4,6-tri-*tert*-butylphenyl)amino]aldimine
BzFPtuH	1-benzoyl-3-(4-fluorophenyl)thiourea
Bz^{i}PPtuH	1-benzoyl-3-(2,6-diisopropylphenyl)thiourea
BzM^{t}BPA	1-benzoyl-2-[methoxyl-3-(2,4,6-tri-*tert*-butylphenyl)amino]aldimine
BzPM^{t}BPA	1-benzoyl-2-[phenylmethoxyl-3-(2,4,6-tri-*tert*-butylphenyl)amino]aldimine
BzPPtuH	1-benzoyl-3-(2,4,6-triphenylphenyl)thiourea
BzPtuH	1-benzoyl-3-phenylthiourea
Bz^{t}BPtuH	1-benzoyl-3-(2,4,6-tri-*tert*-butylphenyl)thiourea
$CDCl_3$	deuterated chloroform
COD	1,5-cyclooctadiene
CT	charge transfer
ESR	electron spin resonance
Et	ethyl
IR	Infrared
L	ligand
M	central metal atom in compound
m.p.	melting point
m/z	mass to charge ratio
M^{+}	molecular ion

Me	methyl
MS	mass spectra
MT	mull transmittance
NMR	nuclear magnetic resonance
ORTEP	the computer program used for crystal illustrations
Ph	phenyl
ppm	parts per million
Pr	propyl
R	organic group
rel. int.	relative intensity
^{t}BPc	2,4,6-tri-tert-butylphenylcyanamide
^{t}BPtu	2,4,6-tri-tert-butylphenylthiourea
TMS	tetramethylsilane
tu	thiourea
UV-vis	ultraviolet-visible
δ	chemical shift in ppm
ν(XY)	stretching frequency of X-Y bond (cm^{-1})
μ_{eff}	effective magnetic moment
2D	two dimensional



Bz^{t}BPtuH



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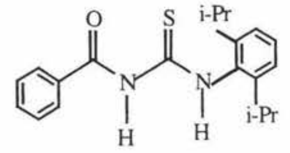

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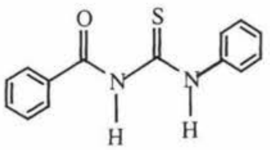

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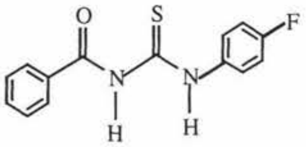

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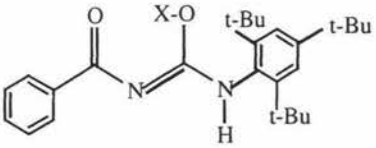
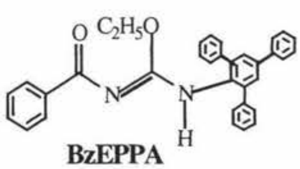
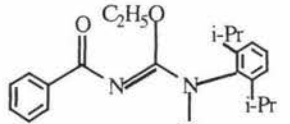




BzEPPA

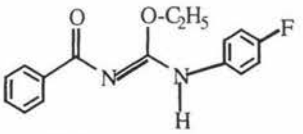


BzE^{i}PPA

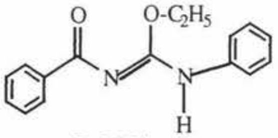
X = C_2H_5, 1-benzoyl-2-[ethoxyl-3-(2,4,6-tri-*tert*-butylphenyl)amino]aldimine (**BzE^{t}BPA**)

= CH_3, 1-benzoyl-2-[methoxyl-3-(2,4,6-tri-*tert*-butylphenyl)amino]aldimine (**BzM^{t}BPA**)

= $CH_2C_6H_5$ 1-benzoyl-2-[phenylmethoxyl-3-(2,4,6-tri-*tert*-butylphenyl)amino]aldimine (**BzPM^{t}BPA**)



BzEFPA



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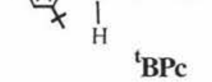
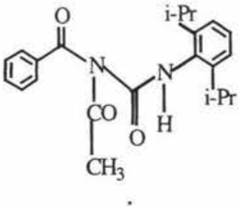


^{t}BPc



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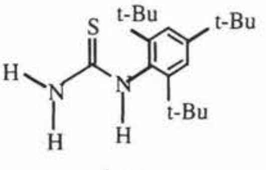
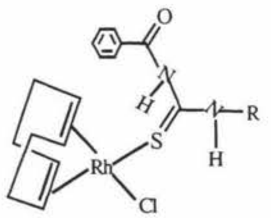


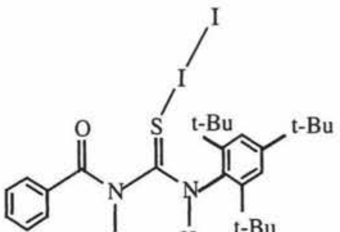
^{t}BPtu



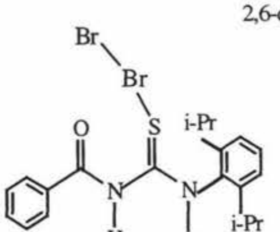
Rh(COD)(LH)Cl

LH = ^{t}BPtuH, BzPPtuH, Bz^{i}PPtuH, BzFPtuH or BzPtuH

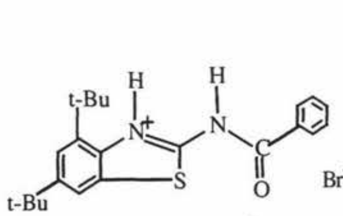
R = 2,4,6-tri-*tert*-butylphenyl, 2,4,6-tri-phenylphenyl,
2,6-diisopropylphenyl, *p*-fluorophenyl or phenyl



(Bz^{t}BPtuH)I_2



(Bz^{i}PPtuH)Br_2



B^{t}BBTH

The structures and abbreviations of the molecules used in this thesis

CHAPTER ONE

Thiourea Complexes Containing Nitrogen, Sulfur and Oxygen-Donor Ligands

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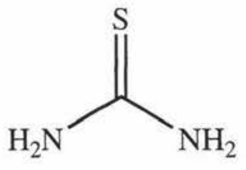
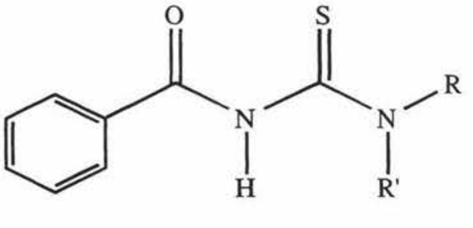
1.0 INTRODUCTION

The coordination chemistry of thiourea has been extensively studied and its complexes show a variety of structures with most transition metals. The parent thiourea ligand possesses potentially S and N donor atoms.

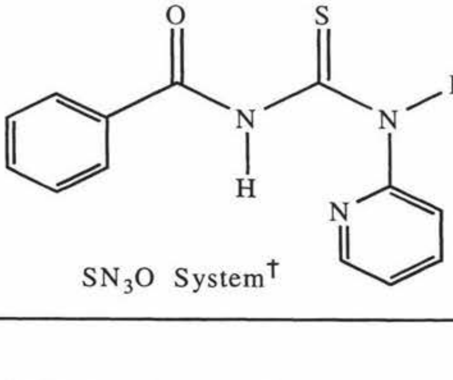


Thiourea (SN_2)

By adding appropriate moieties, the parent thiourea may be extended to systems containing SN_2O or SN_3O atoms as shown.



SN_2O System†



SN_3O System†

† This is not meant to imply that all these atoms will bind at the same time.

This study aims to investigate the coordination chemistry of bulky thioureas of the type SN_2O where e.g. R' is bulky. As the chemistry of all these systems is expected to be dominated by the S donor ability, a summary of some of the known properties of S acting as a ligand will be undertaken first.

1.1 Properties Associated with Sulfur Donors

The particular features of sulfur as a donor atom have been discussed in some detail in an earlier review[1] and these do not appear to have been updated in a more recent review. Since they are relevant to this study, they are summarized here as follows.

(i) Whereas the permanent dipole moment and the coordinating ability decrease in the order: $H_2O > ROH > R_2O$, the reverse order holds for sulfur, viz. $H_2S < RSH < R_2S$.

(ii) From a consideration of both electrostatic and covalent models the strength of bonding to a metal ion is in the order: $RO^- > RS^-$ and $R_2O > R_2S$. However, sulfur has vacant d (and σ^*) orbitals, which can be used for d_π-d_π (or d_π-σ^*) bonding such as can occur with the later transition metals and with the early transition metals in unusually low oxidation states. Consequently, if π-bonding occurs, it can cause a reversal of the order to $RS^- > RO^-$ and $R_2S > R_2O$.

(iii) The polarizabilities of sulfur donors decrease in the order $S^{2-} > RS^- > R_2S$; furthermore, the number of lone pairs decreases in the same order. Consequently, thiolato ligands are more polarizable but not as effective π- electron acceptors as thioethers.

(iv) Sulfur donors bind more strongly to soft metals than do oxygen donors. Soft metals form a triangular area in the centre of the Periodic Table. The oxidation state of the metal affects the degree of soft character, which is strongest for transition metals in low oxidation states; i.e. metals having non-bonding d electrons and thus capable of forming d_π-d_π or d_π-σ^* bonds by donating a pair of electrons to the ligand.

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[1] S.E. Livingstone, *Quart. Rev., Chem. Soc.,* 1965, **19**, 386.

(v) The spectrochemical series of ligands is arranged according to the spectroscopic splitting parameter Δ or 10Dq. Although some sulfur donors, including S-bonded SCN^-, $(RO)_2PS_2^-$, and S^{2-}, have a low position in the series near Cl^-, R_2S falls in the middle of series, probably between H_2O and N-bonded SCN^-, while S-bonded SO_3^{2-} has a later position near NO_2^-. The position of RS^- has not been established.

(vi) Sulfur ligands occupy a late position in the nephelauxetic series, which is, in effect, a measure of the degree of covalent bonding between metal and ligand. The series of donor atoms (arranged according to decreasing values of $1-\beta$) is roughly: $F < O < N < Cl < Br < S \approx I < Se$.

1.1.1 Some Additional General Observations

Sulfur atoms in heterocyclic rings have poor coordinating ability due to the pseudo-aromatic nature of the ring, which has the twofold effect of causing the lone pair on the sulfur atom to be less available for donation and the π-orbital to be less capable of accepting electrons from the metal. Towards soft and borderline metals, the coordinating ability of the various types of sulfur donors is:

$$RS^- > R_2S > RC{=}S \gg \text{ring sulfur}^1.$$

Some data are available on the nucleophilic reactivity of sulfur ligands[2]. The methylmercury cation CH_3Hg^+ has been used as a reference for bases L, since it acts as a Lewis acid as follows:

$$CH_3Hg^+ + L \rightarrow [CH_3HgL]^+$$

The values for $pK(CH_3Hg^+)$ are: S^{2-}, 21.3; RS^- in cysteine, 15.9; $S_2O_3^{2-}$, 10.95; SO_3^{2-}, 8.16; suggesting S^{2-} forms the strongest adduct.

1.1.2 Acid Dissociation Constants

Thiourea and its substituted analogs behave as monoacidic bases toward acids[3].

$$RH^+ \rightleftharpoons R + H^+$$

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[2] F. Basolo and R.G. Pearson, *Mechanisms of Inorganic Reactions*, 2nd edn., John Wiley, New York, 1967, pp. 138, 396.

[3] J.L. Walter, J.A. Ryan and T.J. Lane, *J. Am. Chem. Soc.*, 1956, **78**, 5560,

It follows that

$$K_a = [H^+][R]/[RH^+]$$

Where K_a = acid dissociation constant of the protonated reagent RH^+

R = neutral reagent

The pK_a values obtained for thiourea and its analogs are given in **Table 1.1**. Thiourea (pK_a = 2.03) was found to be more basic than the corresponding urea (pK_a = 1.40). Because of the inductive and hyperconjugative effects exhibited by alkyl substituents on thiourea, the basicity increases in the order of H < ethyl < methyl < diethyl. The order of increasing basicity for the aromatic substituted thiourea compounds is *m*-tolyl ≤ *p*-tolyl < *o*-tolyl < phenyl < diphenyl. However, it would be expected that the *ortho*- and *para*-tolyl groups would contribute more to the basicity of thiourea than a phenyl group[6].

Table 1.1 Acid dissociation constants of thiourea analogs in 50% by volume dioxane at 25 °C

	pK_a		pK_a
1. Thiourea	2.03	5. Phenylthiourea	2.80
2. Urea	1.40	6. *o*-Tolylthiourea	2.78
3. Ethylthiourea	2.85	7. *m*-Tolylthiourea	2.70
4. Methylthiourea	2.90	8. *p*-Tolylthiourea	2.72

1.1.3 Mean Metal-Sulfur Coordinate Bond Energies and Formation Constants

A small amount of quantitative information on the strengths of the metal-ligand bond of thiourea complexes has been reported. An earlier thermochemical study[4] on the octahedral $[M(II)tu_4Cl_2]$ complexes of the first transition series metals showed that the mean metal-sulfur bond energy is comparable with the M-O and M-N bonds in

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[4] S.J. Ashcroft, *J. Chem. Soc. A*, 1970, 1020.

H_2O and NH_3 complexes. Similar observations were also reported[5] for complexes of substituted thioureas.

The standard enthalpies of formation of crystalline complexes of thiourea (tu) with metal chlorides of the type [M(II)tu_2Cl_2] [M(II) = Co, Zn, Cd, Hg] and [M(I)tu_2Cl] [M(I) = Ag] were measured by reaction calorimetry at 298.15 K. The mean metal-sulfur coordinate bond dissociation energies range from 179kJ/mole for the Co complex to 104kJ/mol for the Hg complex[6].

Table 1.2 summarises the mean coordinate bond dissociation energies for cobalt, zinc, cadmium, silver and mercury thiourea complexes[6].

The mercury complex displays considerably weaker bonding. Direct comparison is probably unwise, however, owing to the uncertainty in the value of the enthalpy of sublimation (±20% for $\Delta_{cr}^{g}H$) and to the unusual structure of the complex. A consistent result for the enthalpy of sublimation could not be obtained for [Hg(II)tu_2Cl_2], presumably due to decomposition[6].

Table 1.2 Mean Coordinate Bond Energies, D (M-tu) at 298.15 K

complex	D(M-tu) kJ/mol	complex	D(M-tu) kJ/mol
[$Cotu_2Cl_2$]	179	[$Agtu_2Cl$]	148
[$Zntu_2Cl_2$]	148	[$Hgtu_2Cl_2$]	104
[$Cdtu_2Cl_2$]	142		

The X-ray structures indicate similar tetrahedral structures for [Zn(II)tu_2Cl_2][7] and for [Cd(II)tu_2Cl_2][8]. The structure of the complex [Hg(II)tu_2Cl_2] shows it to be [Hg(II)$tu_2Cl]^+Cl^-$ in which the chlorobis(thiourea) mercury ion is

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[5] S.J. Ashcroft, *J. Chem. Thermodyn.*, 1971, **3**, 853.

[6] J. Ashcroft, *J.Chem. Eng. Data,* 1988, **33**, 73.

[7] N.R. Kunchur, and M.R. Truter, *J. Chem. Soc.*, 1958, 3478.

[8] M. Nardelli, L. Cavalca and A. Braibanti, *Gazz. Chim. Ital.*, 1957, **87**, 137.

trigonal planar. This structure was confirmed by Brotherton *et al.*[9]. [Ag^Itu_2Cl] was shown to consist of infinite spiraling chains of -Ag-S-Ag-S-, each silver atom being surrounded by a distorted tetrahedron of ligands[10].

Toropova and Kirillova[11] have used a potentiometric method to measure the temperature dependence of the equilibrium between either Hg(II) or Ag(I) ions, in aqueous solution containing 0.8M $NaNO_3$, and thiourea. The derived thermodynamic data are shown in **Table 1.3**.

Table 1.3 Thermodynamic data for the reaction between Hg(II), Ag(I) and thiourea (tu), in 0.8M $NaNO_3$ at 25 °C[14]

	$[AgL_3]^+$			$[HgL_4]^{2+}$		
	ΔH^o (KJ mol^{-1})	ΔG^o (KJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	ΔH^o (KJ mol^{-1})	ΔG^o (KJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})
L = tu	−84.00	−74.76	−29.4	−184.8	−150.36	−117.6

The enthalpy of formation of the silver thiourea complex [Ag(I) $(thiourea)_3]^+$, $\Delta H^o = -84.0 \pm 8.4$ kJ/mole, is much less negative than that of −126 kJ/mole found by direct calorimetric measurements by Yatsimirskii and Astasheva[12]. The data in **Table 1.3** show that $\Delta H^o/4$ for the Hg^{2+} complex is greater than $\Delta H^o/3$ for the Ag^+ complex implying that the former interaction is stronger. In both complexes the central atom is bonded to the ligand only through the sulfur atom[1].

Stability Constants of metal-ion complexes[13] are given in **Table 1.4**.

Table 1.4 Overall Stability Constants of Thiourea Complexes

Metal	Medium	β_2
Ag^+	0.5M KNO_3	9.83±0.11
Hg^{2+}	0.1M CH_3CN	21.3

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[9] P.D. Brotherton, P.C. Healy, C.L. Raston and A.H. White, *J. Chem. Soc., Dalton Trans.,* 1973, 334.

[10] E.A. Vizzini and E.L. Amma, *J. Am. Chem. Soc.,* 1966, **88**, 2872.

[11] V.F. Toropova and L.S. Kirillova, *Russ. J. Inorg. Chem.,* 1960, **5**, 176.

[12] K.B. Yatsimirskii and A.A. Astasheva, *Zh. Fiz. Khim.,*1953, **27**, 1539.

[13] Stability Constants of Metal-ion Complexes: Part B, *Organic Ligands,* Pergamon Press, Oxford, 1979, p.16.

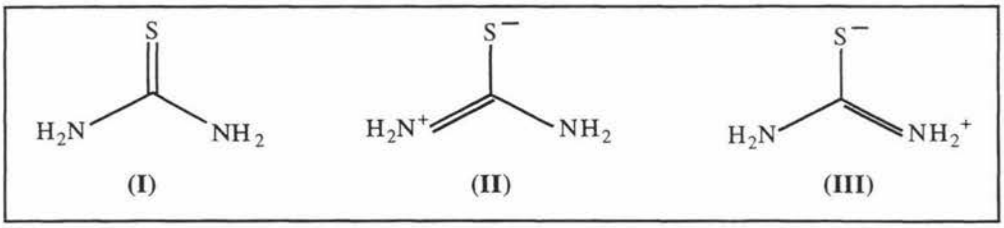
The above β_2 data indicates that the Hg^{2+} complex is more stable than the Ag^{+} complex. But in an apparent paradox, in **Table 1.2,** the mean coordinate bond energy is lower for [$Hgtu_2Cl_2$]. The reliability of the Hg-tu mean bond energy must remain in doubt and further attempts to measure it are needed.

1.2 Thiourea Complexes

Sulfur is considered to be a 'soft' atom in contrast to oxygen, which is a 'hard' atom, while the nitrogen atom ranges from 'borderline' to 'hard' [14]. Therefore, N and O donors are best suitable for higher oxidation state metal ions, and S is generally considered to be suitable for lower oxidation states.

Thiourea has been extensively studied over the last 60-70 years and a brief review of its chemistry will now be given.

The planar structure of thiourea can be represented by the three resonance structures:



Complexation with sulfur as the donor site would enhance (II) and (III). The formation of S → M bounds is expected to increase the contribution of the highly polar structure to the thourea molecule, resulting in a greater double bond character for the nitrogen-to-carbon bond and a greater single bond character for the carbon-to-sulfur bond.

Thiourea $(H_2N)_2C{=}S$ (tu), acts as a unidentate ligand forming strong complexes with soft metal ions, in particular Cu(I), Au(I) and Hg(II). It reduces Cu(II) to Cu(I), Au(III) to Au(I), Pt(IV) to Pt(II) and Te(IV) to Te(II), forming complexes with the metal in the lower oxidation state[1]. The only metal reported to be N-bond is Ti(IV),

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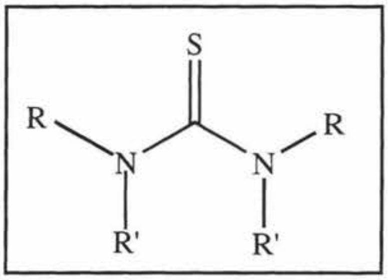
[14] R.G. Pearson, *Chemical Hardness*, 1997, Wiley-VCH, Weinhiem.

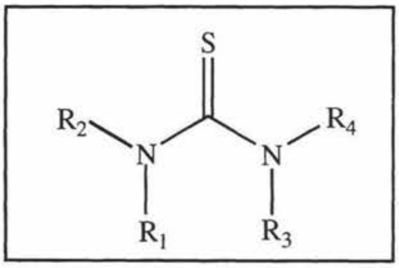
all others being S-bonded with ν(M-S) occurring at 300-200 cm^{-1} [15]. Thiourea, like other S-donor ligands, has a high *trans* effect [16,17].

Thiourea is remarkable for the number and variety of the addition compounds, which it forms, with salts of many metals. Its alkyl derivatives also share this property. Many of the interactions may serve as sensitive colour tests for the metal ions. Many addition compounds in solution have been detected by physical measurements. The relative stabilities of some metal complexes of thiourea and substituted thioureas have been investigated by means of a potentiometric procedure. Thiourea forms large complex metal cations, which can be precipitated by large anions [18].



Complexes of N,N'-substituted thioureas, R = alkyl or aryl, R' = alkyl, aryl or H, have also been extensively studied[1].

1.3 Modified Thiourea Ligands



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[15] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 2^{nd} edn., Wiley-InterScience, New York, 1970, p. 210.

[16] J.V. Quagliano and L. Schubert, *Chem. Rev.*, 1952, **50**, 201.

[17] F. Basolo and R.G. Pearson, *Mechanisms of Inorganic Reactions,* Wiley, New York, 1958, p.172.

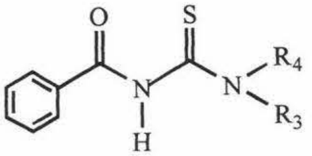
[18] E. Emmet Reid, *Organic Chemistry of Bivalent Sulfur*, Chemical Publishing Co., Inc., New York, 1963, **5**, 20.

The addition of appropriate moieties, R_1, R_2, R_3 and R_4, to thiourea (above) can modify the thiourea ligand. Interest in these systems commenced about 25 years ago and is continuing today.

1.3.1 1-Benzoyl-3,3-Dialkyl Thioureas and Related Ligands

One of the earliest studies[19] was done on a series of 1-benzoyl-3,3-dialkyl thioureas. The variety of R_3 and R_4 groups used are given in **Table 1.5** along with the complexes formed. In all cases the ligands act as monoanions[19].

Table 1.5 The ligands 1-benzoyl-3,3-disubstituted thioureas (HL) and their complexes with copper(II), nickel(II), palladium(II) and cobalt(III)

Structure	R_3R_4N	Complexes Formed
1-benzoyl-3,3-disubstituted thiourea 	$(CH_3)_2N$	NiL_2 CuL_2 CoL_3
	$(C_2H_5)_2N$	NiL_2 CuL_2 PdL_2 CoL_3
	$(n\text{-}C_3H_7)_2N$	NiL_2 CuL_2 PdL_2 CoL_3
	$(i\text{-}C_4H_9)_2N$	NiL_2 CuL_2 PdL_2 CoL_3
	Morpholino 	NiL_2 CuL_2 PdL_2 CoL_3
	Piperidino 	NiL_2 CuL_2 PdL_2 CoL_3
	Pyrrolidino 	NiL_2 CuL_2 PdL_2 CoL_3

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[19] L. Beyer, E. Hoyer, H. Hennig, R. Kirmse, H. Hartmann and J. Liebscher, *J. Prakt. Chem.,* 1975, **317**, 829.

ESR parameters and magnetic moment measurements have shown that 1-benzoyl-3,3-dialkyl thiourea complexes form chelates with transition metals which leads to square planar ML_2 (M = Ni, Cu, Pd) and octahedral CoL_3 compounds as shown below (**Fig. 1.1**). The ligand loses a proton and behaves as a bidentate anion.

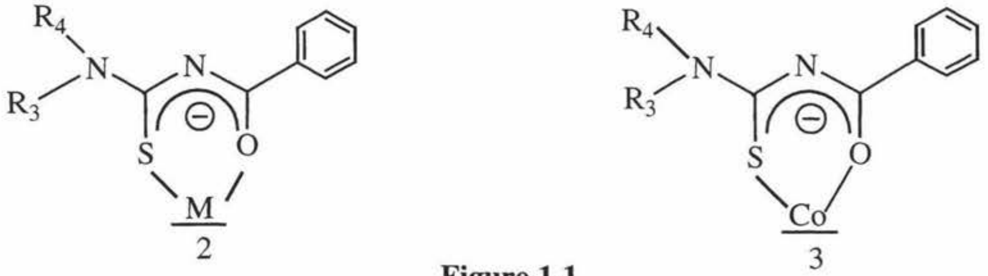
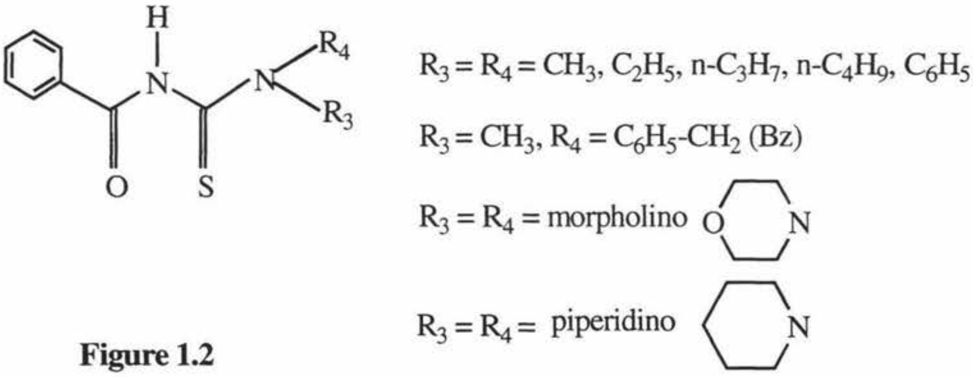


Figure 1.1

This work was followed up by Mohamadou *et al.*[20] nineteen years later and they claimed that the CoL_3 compounds were not very pure and the magnetic moments for the CoL_3 and NiL_2 compounds were abnormal because of purity problems. The ligands used in this study are given below (**Fig 1.2**).



$R_3 = R_4 = CH_3, C_2H_5$, n-C_3H_7, n-C_4H_9, C_6H_5

$R_3 = CH_3, R_4 = C_6H_5\text{-}CH_2$ (Bz)

$R_3 = R_4 =$ morpholino

$R_3 = R_4 =$ piperidino

Figure 1.2

Square planar complexes ML_2 (M = Cu, Ni) and *fac*-CoL_3 were formed, NiL_2 and CoL_3 were now diamagnetic indicating the ligand is a strong chelating agent. The CoL_3 complexes gave analytical compositions a little lower than expected. The authors extended their work to include NMR spectral and electrochemical studies. Reduction of

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[20] A. Mohamadou, I. Déchamps-Oliver and J.P. Barbier, *Polyhedron,* 1994, **13**, 1363.

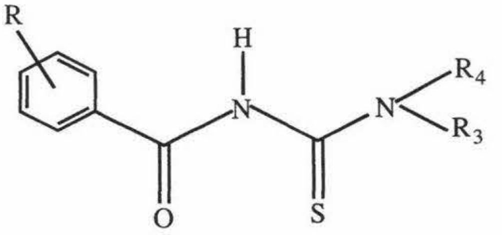
CuL_2 into CuL_2^- has been studied by cyclic voltammetry. **Table 1.6** shows the electrochemical data found for the irreversible Cu(II)/Cu(I) redox systems.

Table 1.6 Electrochemical data for copper compounds

R_3,R_4N-	E° (V)
$(CH_3)_2N-$	-0.18
$(C_2H_5)_2N-$	-0.25
$(n\text{-}C_3H_7)_2N-$	-0.30
$(n\text{-}C_4H_9)_2N-$	-0.33
$(C_6H_5)_2N-$	-0.15
$CH_3,BzN-$	-0.18
	-0.16
	-0.22

From the above data it seems that the nature of the R_3 and R_4 substituent groups has a weak influence on the electrochemical properties of these complexes; even the aromatic or cyclic substituents have the same effect.

Mohamadou *et al.*[21] have extended their studies to 1-substituted benzoyl-3,3-diethyl or 3-morpholine thioureas as below (**Fig. 1.3**).



R = Cl, Br, OCH_3 or NO_2 in *ortho, meta and para* positions

Et_2RbtuH, $R_3 = R_4 = C_2H_5$.

morphRbtuH, R_3, R_4 =

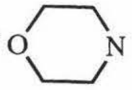


Figure 1.3

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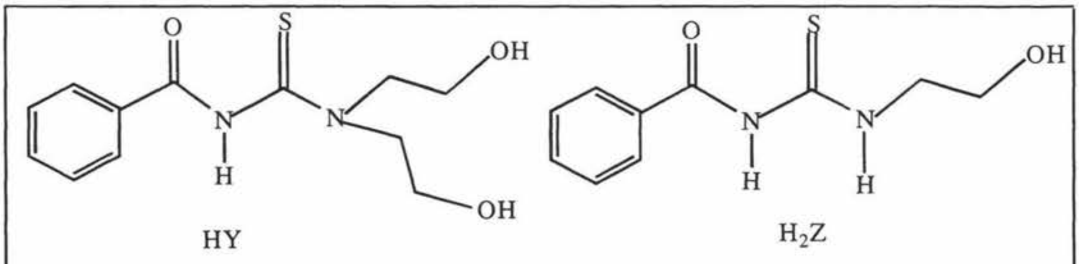
[21] A. Mohamadou, I. Déchamps-Olivier and J.P. Barbier, *Polyhedron*, 1994, **13**, 3277.

As before, complexes with copper were of the type CuL_2. Cyclic voltammetry for the irreversible copper(II)/copper(I) redox systems showed that the E^o values for a particular substituent are not influenced by the *ortho, meta* or *para* substituents, but were slightly influenced by the nature of the substituent. The E^o values for the quasi-reversible copper(III)/(II) redox systems are not influenced by the benzoyl substituents.

$$\text{copper(III) complexes} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} \text{copper(II) complexes} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} \text{copper(I) complexes.}$$

Déchamps-Olivier *et al.*[22] followed up this work and found the same ligands with Co and Ni, gave the square planar compounds NiL_2 and *fac*-CoL_3. Proton NMR and electronic spectral studies were used to characterize these compounds. The analytical compositions for the CoL_3 complexes were a little lower than expected as found before[20]. They explain that this may be due to the difficulty of drying these complexes. Also morpholine and *ortho* substituents on the benzoyl group gave no complexes with Co(III) and this may be due to the generation of strong steric hindrance by these groups.

Koch *et al.*[23] studied the coordinating properties of 1-benzoyl-3-(2-hydroxyethyl) (H_2Z) and 3,3-di(2-hydroxyethyl) thiourea (HY) ligands (**Fig. 1.4**) with platinum group metals such as, Pt(II), Pd(II) and Ni(II).



HY

H_2Z

Figure 1.4

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[22] I. Déchamps-Olivier, E. Guillon, A. Mohamadou and J. P. Barbier, *Polyhedron,* 1996, **15**, 3617.

[23] K.R. Koch, C. Sacht and S. Bourne, *Inorg. Chim. Acta*, 1995, **232**, 109.

[24] S. S. S. Raj, K. Puviarasan, D. Velmurugan, G. Jayanthi and H.K. Fun, *Acta Cryst.*, 1999, **C55**, 1318.

The ligands HY and H_2Z show remarkably different coordination chemistry to Pt(II), Pd(II) and Ni(II). This behavior is due to H-bonding which makes the H_2Z ligand behave more like a monodentate thiourea ligand since the carbonyl atom is prevented from coordination by an intramolecular hydrogen bond. A mixture of *cis* and *trans* complexes of $[Pt(H_2Z)_2Cl_2]$ with Pt(II) is obtained, whereas the HY ligand coordinates in a bidentate manner forming neutral complexes of the type *cis*-$[M(Y)_2]$ (M = Pt(II), Pd(II) and Ni(II))[23].

Possible intramolecular hydrogen bonding in the H_2Z ligand is depicted below (**Fig. 1.5**)[23] giving a 6-membered ring. This structure is based on a recently published crystal structure of 1-benzoyl-3-(3,4-dimethylphenyl)thiourea[24].

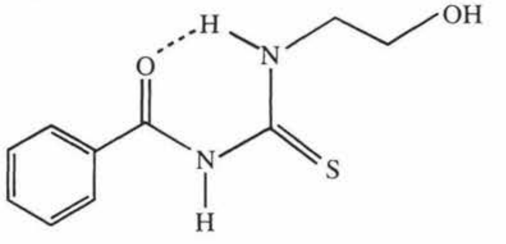

Figure 1.5

The coordination chemistry of this ligand (H_2Z) is strongly influenced by the intramolecular hydrogen bond between the carbonyl atom of the aroyl moiety and the thiourea N-H group on position 3. This favours coordination through the S atom only since O is *trans* to S [25].

In contrast, the free ligand, HY, does not possess a similar thiourea N-H group, but it does contain an intramolecular hydrogen bond between the thiourea N-H group on position 1 and the oxygen atom of one of the hydroxyethyl moieties, forming a 7-membered ring as shown in **Fig 1.6**. The O and S atoms are now *cis* to each other.

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[25] K.R. Koch and S. Bourne, *J. Chem. Soc., Dalton Trans.*, 1993, 2071.

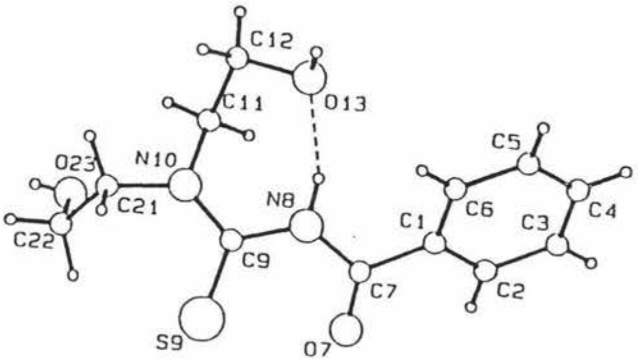

Figure 1.6 Molecular structure of 1-benzoyl-3,3-di(2-hydroxyethyl)thiourea (HY)

Therefore HY is geared up to bind through S and O atoms as a bidentate anion, *via* a loss of an N-H proton.

Koch *et al.*[26] also studied the coordination chemistry of similar ligands based on 1-benzoyl-3-alkyl and 3,3-dialkyl thioureas with the platinum group metals.

Koch *et al.*[27] and Fitzl et al.[28] studied the Pt(II) and Pd(II) complexes of 1-benzoyl-3-propyl thiourea (H_2L) and were able to obtain a crystal structure of *trans*-[Pd(H_2L)$_2$Br$_2$] where H_2L binds through S. They have previously shown that the coordination of the 1-benzoyl-3,3-dialkyl thioureas usually leads to very stable bidentate-S,O coordination to Pd(II)[28], Pt(II)[29] and Rh(III)[30].

1.3.2 1-Ethoxycarbonyl- 3-Disubstituted Thiourea

Guillon *et al.*[31] have synthesized the ligands, such as 1-ethoxycarbonyl-3-disubstituted thioureas (**Fig. 1.7**), to study the influence of the substitution of a strong

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[26] K.R. Koch, C. Sacht, T. Grimmbacher and S. Bourne, *S. Afr. J. Chem.,* 1995, **48**, 71.

[27] K.R. Koch, Y. Wang and A. Coetzee, *J. Chem. Soc., Dalton Trans.,* 1999, 1013.

[28] G. Fitzl, L. Beyer, R. Sieler, R. Richter, J. Kaiser and E. Hoyer, *Z. Anorg. Allg. Chem.,* 1977, **433**, 237.

[29] K.R. Koch, A. Irving and M. Matoetoe, *Inorg. Chim. Acta,* 1993, **206**, 193.

[30] W. Bensch and M. Schuster, *Z. Anorg. Allg. Chem.,* 1992, **615**, 93.

[31] E. Guillon, A. Mohamadou, I. Déchamps-Olivier and J.P. Barbier, *Polyhedron,* 1996, **15**, 947.

donor group such as ethoxy for the phenyl ring on the properties of copper, nickel and cobalt complexes.

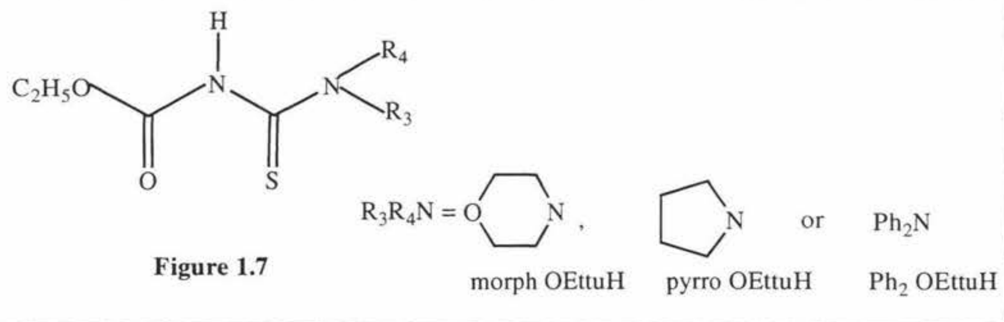
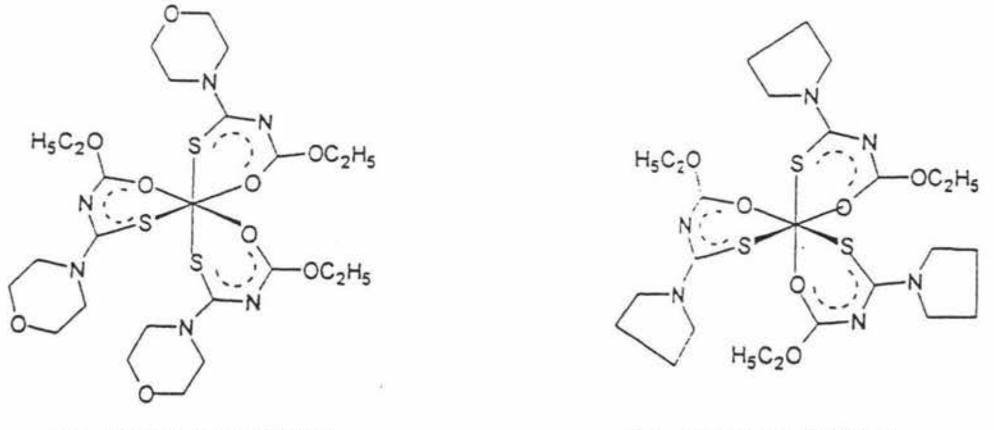


Figure 1.7

NMR spectra and magnetic data support the assignment of a square planar structure for NiL_2 and *fac or mer* structures for CoL_3 compounds. For unsymmetrical bidentate ligands, a single set of ethoxy group resonances for the ^1H NMR spectra is indicative of *fac*-Co(pyrro OEttu)$_3$, while two sets of resonances (intensity ratio 1:2) is obtained for *mer*-CoL_3 (L = morph OEttu or Ph_2 OEttu) as shown in **Fig. 1.8**[20,31]. These studies were confirmed by ^{13}C NMR data.



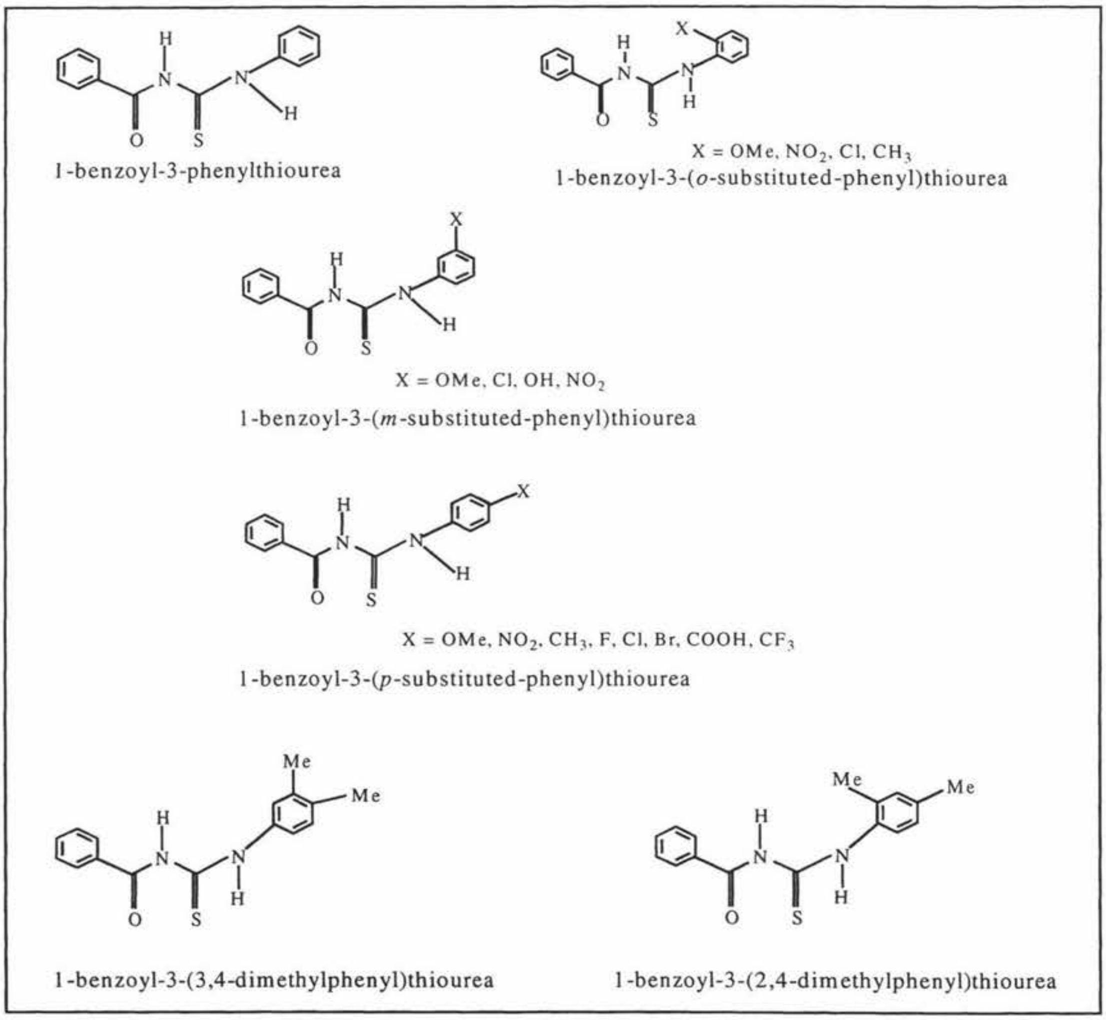
mer-Co(morph OEttu)$_3$ *fac*-Co(pyrro OEttu)$_3$

Figure 1.8

The electronic spectra of the metal complexes are similar to those obtained with 1-benzoyl-3,3-disubstituted thioureas [20]. The existence of copper(III), copper(II) and copper(II), copper(I) redox systems has been chemically and electrochemically determined in solution [31].

1.3.3 1-Benzoyl-3-Substituted Phenyl Thioureas

The previous studies relate to the coordination properties of 1-benzoyl or 1-ethoxy or 1-ethoxycarbonyl moieties with 3-mono or 3,3-disubstituted (aliphatic) thioureas. Recent studies are based on 1-benzoyl-3-unsubstituted[32] or *o-*, *m-* or *p-*substituted-phenyl thiocarbamides[33, 34,35]. **Figure 1.9** summarises the overall structures of some of the latter ligands. Important aspects of their limited coordination chemistry will be reviewed in Chapters 2 and 3.



1-benzoyl-3-phenylthiourea

X = OMe, NO_2, Cl, CH_3
1-benzoyl-3-(*o*-substituted-phenyl)thiourea

X = OMe, Cl, OH, NO_2
1-benzoyl-3-(*m*-substituted-phenyl)thiourea

X = OMe, NO_2, CH_3, F, Cl, Br, COOH, CF_3
1-benzoyl-3-(*p*-substituted-phenyl)thiourea

1-benzoyl-3-(3,4-dimethylphenyl)thiourea

1-benzoyl-3-(2,4-dimethylphenyl)thiourea

Figure 1.9 1-benzoyl-3-unsubstituted or *o, m* or *p*-substituted-phenyl thiocarbamides.

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[32] F. Kurzer, *J. Chem. Soc.,* 1949, 3034-3048; R.L. Frank and P.V. Smith, *Org. Synth.,* 1955, Coll. Vol. **3**, 735-736.

[33] K.C. Satpathy and H.P. Mishra, *Indian J. Chem.,* 1981, **20**A, 1035.

[34] J.R. A. Cornejo, M. Valko, G. Ondrejovic and D. Valigura, *Conf. Coord. Chem.,* 1993, 14th (Contributions to Development of Coordination Chemistry), 107.

[35] D. Negoiu, V. Circu, T. Rosu and N. Badicu, *Rev. Chim. (Bucharest),* 1999, **50**, 88.